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0. Primary
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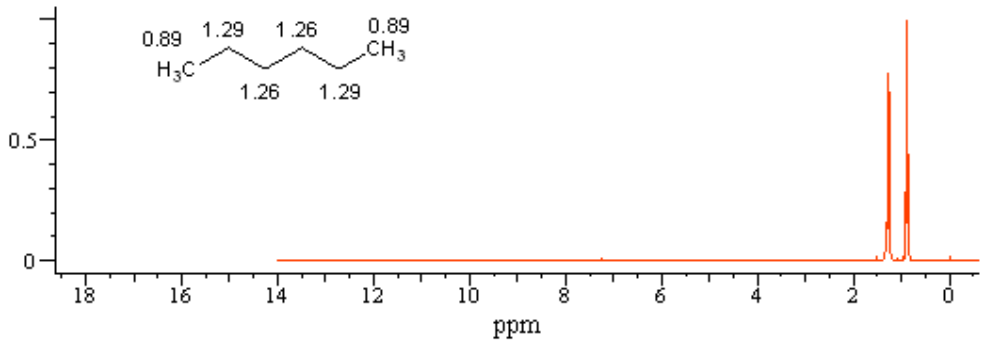
I. Hydrocarbons

A. Saturated Hydrocarbons

1. Normal Alkanes



The normal alkanes are an easily recognized group of compounds consisting of two higher order bands resonating in a narrow chemical shift range at high field.

Chemical Shifts

$(CH_2)_n$ near 1.3 ppm - a complex multiplet in the shorter (C_4, C_5, C_6) alkanes gradually becoming a broad, single peak as the number of carbons in the chain increases.

CH_3 near 0.9 ppm - a distorted triplet

Due to the higher order patterns which result from the very narrow chemical shift range, it is not possible to measure accurately the vicinal coupling constants (H-C-C-H). However, because the distorted triplet at 0.9 ppm is nearly identical to those observed for the substituted alkanes, it would appear that the coupling constants are similar to those of the substituted alkanes, i.e.

^{J}H-C-C-H = 6-8 Hz.

Solubility and Solvent Effects

The normal alkanes, as indeed all of the hydrocarbons, are most readily soluble in the halogenated solvents, CCl_4 and $CDCl_3$. Their solubility in even these liquids decreases markedly as the molecular weight (chain length) increases beyond molecular weight 200 (C_{12} to C_{15}). Allowing the sample-solvent slurry to stand overnight, agitation of the mixture and warming, are helpful in obtaining higher sample solution concentrations.

Impurities

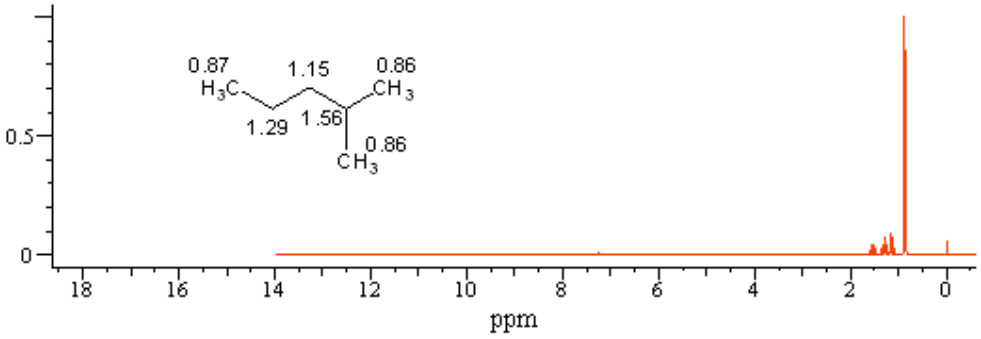
Because most commercially available alkanes are obtained from the fractional distillation of petroleum, impurities such as the cyclic alkanes, and simple aromatic hydrocarbons such as toluene, ethyl benzene and the xylenes, may be observed in their NMR spectra.

Characterization

Differentiating between the various alkanes is usually accomplished by careful measurement of the methyl and methylene integration values. Determinations accurate to within one carbon are routinely obtained with chain lengths up to about Triacontane (C_{30}).

Note: Other nuclei which possess a weak deshielding effect similar to that of hydrocarbon groups may produce spectra almost identical in appearance and chemical shift to those of the normal alkanes. Included in this group would be nuclei such as Phosphorus, Tin, Lead, Mercury, Boron and Silicon. Since many of these nuclei possess a spin greater than zero, their spectra may display isotope sidebands slightly above and/or below the primary chemical shift range of the sample. These isotope sidebands are helpful in determining that a high field pattern is not that of a normal alkane.

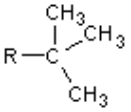
2 Branched Alkanes



The presence of one or more branching groups along the hydrocarbon chain increases the complexity and chemical shift ranges of the branched alkanes in comparison to those of the normal alkanes. As a consequence of the larger number of methyl groups that are present, the intensity of the bands at higher field is increased.

Chemical Shifts

The overall range of chemical shifts for the branched alkanes is 0.6-2.0 ppm, with the methyl (CH_3) resonances on the higher field side, the methylene (CH_2) resonances in the intermediate portion of the range and the methine (CH) groups resonating in the lower field area (1.3-2.0 ppm).

Methyl Groups	0.8-0.95 ppm
	distorted triplet
	broadened doublet
	sharp singlet

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Methylene and Methine Groups

The methylene and methine groups are almost always complex, higher order, overlapping multiplets that cannot be easily characterized by first order approximations.

Coupling and Coupling Constants

As with the normal alkanes, higher order effects prevent the direct measurement of coupling constants, however, the separation of the peaks of methyl doublets indicates that the ^{3}H-C-C-H (vicinal) coupling constants are of the order of 6-9 Hz.

Solubility and Solvent Effects

The branched alkanes are readily soluble in the halogenated hydrocarbons normally utilized as NMR solvents. The presence of branching groups makes the branched hydrocarbons more soluble than a normal hydrocarbon of comparable molecular weight.

Impurities

Branched hydrocarbons obtained from petroleum sources may display impurities arising from the cyclic alkanes and low molecular weight aromatic hydrocarbons.

Characterization

The branched alkanes are probably the most difficult compounds to identify without the aid of known reference spectra. These spectra do however produce unique "fingerprint" patterns which are well represented in the various collections of NMR reference spectra which are currently available.

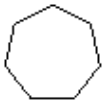
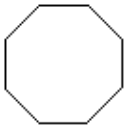
If the methyl, methylene and methine resonance bands are sufficiently well separated, a comparison of the integration values can be used to advantage in determining the relative number of the various types of carbon atoms present (methyl, methylene, methine).

3 Cyclic Alkanes

The cyclic alkanes produce both the simplest patterns (one single peak) for the unsubstituted parent rings, and the most complex, poorly resolved patterns, for the substituted derivatives. The three, four and five membered rings usually produce complex but relatively well resolved absorption patterns. The larger rings (C_6 and higher) due to the slow interchange in ring shape produce poorly resolved, broad bands often covering more than a full one ppm, arising from the hydrogens attached to the ring carbons.

Alicyclic Protons

ppm	Compound	Solvent
0.22		(lit.)
1.96		(lit.)
1.50		CCl_4
1.42		CCl_4

1.53		$CDCl_3$
1.52		CCl_4

Coupling and Coupling Constants

The spectral patterns of the cyclic alkanes are usually too complex or too poorly resolved to provide any useful measurements of the coupling constants.

Solubility and Solvent Effects

Most representatives of the cyclic alkanes are readily soluble in the halogenated hydrocarbon solvents.

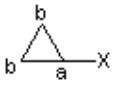
Characterization

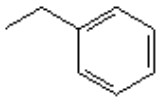
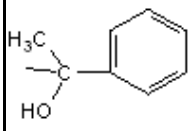
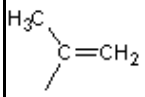
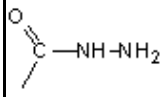
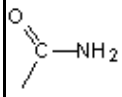
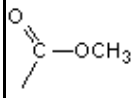
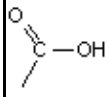
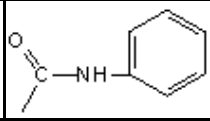
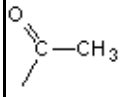
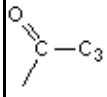
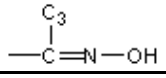
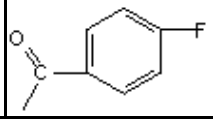
As with the branched alkanes, if the resonance bands are sufficiently well separated, then a comparison of the integration values may be useful. Generally, though, a comparison with known reference spectra will be found to be the most reliable method of identifying an unknown of this group.

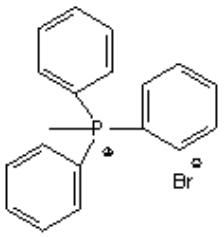
Alicyclic Derivatives

Substitution of the cyclic alkanes by a deshielding substituent leads to a characteristic chemical shift for the hydrogen attached to the alpha carbon depending upon the size of the ring and the deshielding effect of the substituting group as listed below.

Cyclopropane Derivatives (C_3-X)

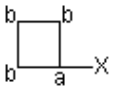


δ_b (ppm)	δ_a (ppm)	-X	Solvent
0.1-0.7	0.98		$CDCl_3$
0.1-0.6	1.05		CCl_4
0.2-0.9	1.10	$-CH_2-NH_2$ HCl	D_2O
0.3-0.8	1.29		CCl_4
0.5-1.1	1.36		$CDCl_3$
0.5-1.2	1.40		$CDCl_3$
0.6-1.1	1.50		CCl_4
0.7-1.3	1.53		CCl_4
0.6-1.2	1.79		Polysol
0.7-1.1	1.97		$CDCl_3$
0.4-1.2	2.00		CCl_4
0.9-1.5	2.07		CCl_4
0.2-0.7	2.31	$-NH_2$	$CDCl_3$
0.5-1.2	2.49		$CDCl_3$
0.7-1.4	2.61		$CDCl_3$

0.63,1.80	3.35		Polysol

With the exception of the last substituent on the list, the hydrogens bonded to the beta carbons produce a complex higher order pattern at thigh field.

Cyclobutane Derivatives (C_4-X)



δ_b (ppm)	δ_a (ppm)	-X	Solvent
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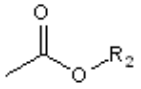
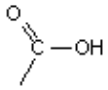
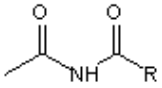
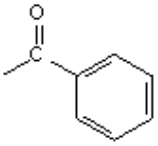
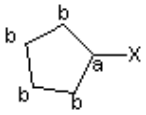
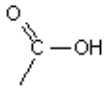
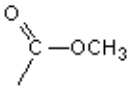
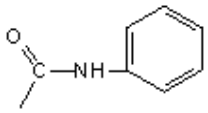
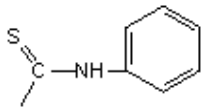
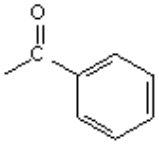
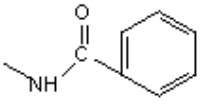
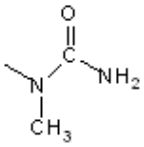
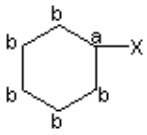
1.7-2.5	3.08		CCl_4
1.6-2.7	3.19		$CDCl_3$
1.7-2.6	3.45		$CDCl_3$
1.6-2.7	3.60		CCl_4
1.5-2.6	3.85	$-NH_2$ HCl	D_2O
1.6-2.7	3.95		CCl_4
1.1-2.5	4.16	-OH	$CDCl_3$

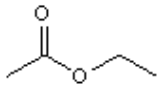
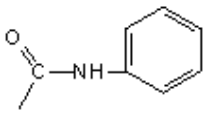
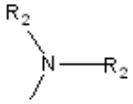
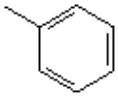
Cyclopentane Derivatives (C_5—X)

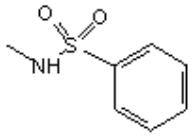
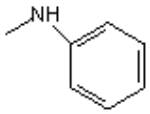
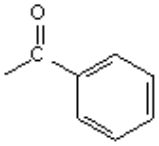
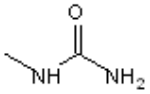
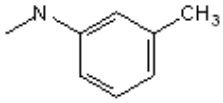
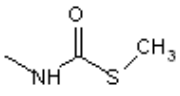
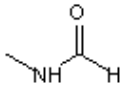
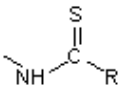


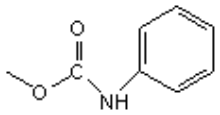
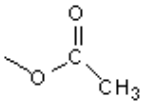
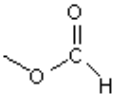
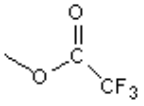
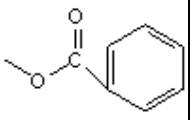
δ_b (ppm)	δ_a (ppm)	-X	Solvent
1.2-2.3	1.81	$-CH_2$	CCl_4
1.3-2.2	2.69		CCl_4
1.6-2.2	2.70		CCl_4
1.4-2.3	2.76		$CDCl_3$
1.3-2.2	2.90		$CDCl_3$
1.2-2.2	3.00	$-NH-CH_3$	$CDCl_3$
1.4-2.3	3.19		CCl_4
1.0-2.1	3.31	$-NH_2$	$CDCl_3$
1.3-2.2	3.65		CCl_4
1.1-2.2	4.19		$CDCl_3$
1.3-2.2	4.21	-OH	CCl_4
1.3-2.4	4.32	-I	CCl_4
1.4-2.3	4.35	-Cl	CCl_4
1.4-2.4	4.38	-Br	CCl_4
1.1-2.1	4.49		Polysol

Cyclohexane Derivatives (C_6-X)

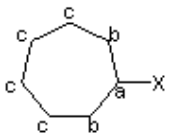


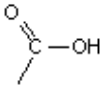
δ_b (ppm)	δ_a (ppm)	-X	Solvent
0.9-2.2	2.26		CCl_4
0.7-2.1	2.32	-NH-R_2	CCl_4
0.9-2.2	2.34		Polysol
0.6-2.1	2.35	-NH-CH_3	$CDCl_3$
0.8-2.1	2.39		CCl_4
0.8-2.2	2.40		$CDCl_3$
0.9-2.1	2.40		CCl_4
0.8-2.1	2.42		CCl_4
0.5-2.2	2.42		CCl_4
0.7-2.1	2.49		CCl_4
0.6-2.1	2.64	-NH_2	CCl_4
1.2-2.1	2.64	-C≡N	CCl_4
1.0-2.4	2.71		CCl_4
1.0-2.2	2.74	-SH	CCl_4
1.0-2.5	2.92	-SO_2-R	$CDCl_3$
0.7-2.2	3.00	-NH-SO_2-NH-C_6	Polysol

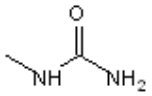
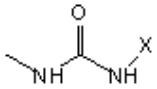
0.8-2.1	3.10		$CDCl_3$
0.7-2.2	3.17	-N=C=N-C_6	$CDCl_3$
0.6-2.3	3.21		$CDCl_3$
0.8-2.3	3.25		$CDCl_3$
0.7-2.2	3.27	-O-R	$CDCl_3$
0.6-2.2	3.36		Polysol
0.9-2.2	3.46		$CDCl_3$
1.0-2.2	3.48	-N=C=O	$CDCl_3$
0.8-2.1	3.49	-OH	CCl_4
1.0-2.2	3.60	-N≡C	$CDCl_3$
0.7-2.3	3.70		$CDCl_3$
0.8-2.2	3.79		$CDCl_3$
0.9-2.8	3.80	-NH-SO_2-OH	TFA
0.8-2.4	3.95	-Cl	CCl_4
0.7-2.3	4.03		$DMSO-d_6$

0.9-2.2	4.04	-OB(-O-C_6)$_2$	$CDCl_3$
1.1-2.5	4.13	-Br	CCl_4
1.0-2.5	4.29	-NO_2	CCl_4
0.9-2.5	4.36	-I	$CDCl_3$
0.9-2.2	4.71		CCl_4
1 .0-2. 1	4.76		$CDCl_3$
0.9-2.3	3.75, 4.83	-N(N=O)-C_6	$CDCl_3$
0.9-2.2	4.89		$CDCl_3$
1.0-2.2	4.95		CCl_4
1.1-2.4	5.16		$CDCl_3$

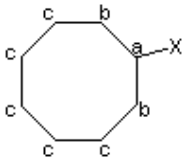
Cycloheptane Derivatives

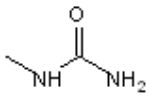
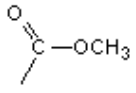
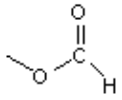


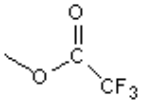
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
1.80	1.80	2.53		$CDCl_3$

1.3-2.3	1.3-2.3	2.78	-C≡N	CCl_4
1.0-2.2	1.0-2.2	2.92	$-NH_2$	$CDCl_3$
1.2-2.2	1.2-2.2	3.80	-OH	$CDCl_3$
ca 1 .66	2.10	3.85		TFA
1.2-1.8	1.90	3.86		$CDCl_3$
ca 1.61	2.00	4.10	-Cl	CCl_4
ca 1.53	2.17	4.33	-Br	$CDCl_3$

Cyclooctane Derivatives

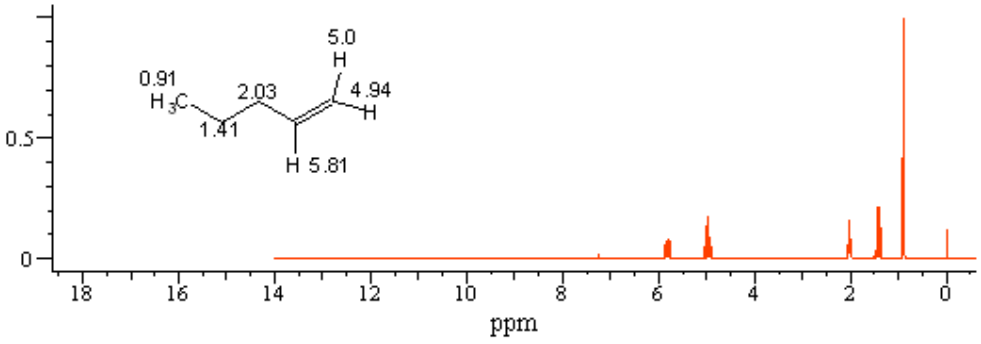


δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
1.2-2.0	1.2-2.0	2.53	$-NH-CH_3$	$CDCl_3$
1.1-2.1	1.1-2.1	2.90	$-NH_2$	CCl_4
1.2-2.1	1.2-2.1	3.72	-OH	CCl_4
1.4-2.2	1.4-2.2	3.88		TFA
ca 1.59	2.19	4.31	-Br	CCl_4
1.3-2.1	1.3-2.1	4.83		CCl_4
ca 1 .59	1.85	5.09		CCl_4

ca 1.59	1.85	5.15		CCl_4

B Unsaturated Hydrocarbons

1. Acyclic Alkenes

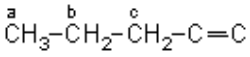


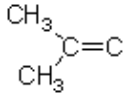
No other type of organic compound produces such a wide variety of multiplet types over such a large chemical shift range as the acyclic alkenes. Proton-proton coupling through four bonds is common. Many samples are found to contain both cis and trans isomers producing a spectrum more complex than might be expected from a proposed structure.

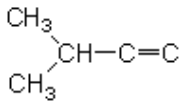
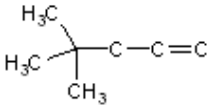
The olefinic double bond is a weak deshielder of both aliphatic and aromatic hydrogens often resulting in higher order, overlapping multiplets.

The aliphatic chemical shift ranges below were abstracted from a large number of representative compounds.

Aliphatic Protons (General ranges)



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
		1.6-2.0	$H_3C-C=C$	CCl_4, $CDCl_3$
		(1.6-1.8)		CCl_4, $CDCl_3$
	0.9-1.3	1.9-2.1	$CH_3-CH_2-C=C$	CCl_4, $CDCl_3$
0.9-1.0	1.3-1.7	1.9-2.2	$CH_3-CH_2-CH_2-C=C$	CCl_4, $CDCl_3$

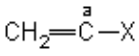
	(0.9-1.2)	1.9-2.7		CCl_4, $CDCl_3$
	(0.9-1.2)			CCl_4, $CDCl_3$

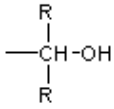
Coupling and Coupling Constants

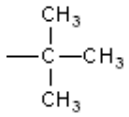
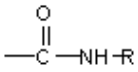
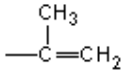
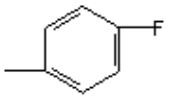
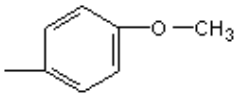
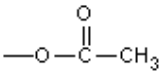
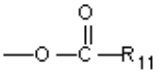
The wide variety of coupling constants observed in the spectra of the alkenes is quite helpful in determining the molecular arrangement of such structures and aid the analyst in differentiating the spectra of cis and trans isomers. The general coupling constant ranges provided below are the values observed for a large number of alkene compounds.

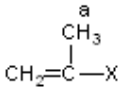
Compound		J value
CH=CH	trans	J = 13-17 Hz
CH=CH	cis	J = 6-14 Hz
C=CH−CH		J = 4-8 Hz
H_2C=C	geminal	J = 0-3 Hz
HC−C=CH		J = 0-2 Hz

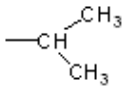
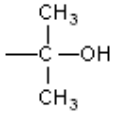
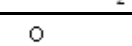
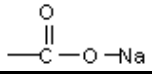
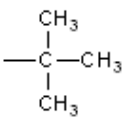
Vinyl Compounds

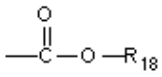
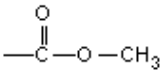
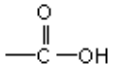
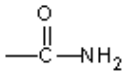
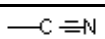
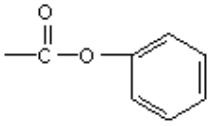
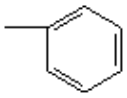


trans (ppm)	cis (ppm)	δ_a (ppm)	X	Solvent
5.10	5.01	5.79		CCl_4

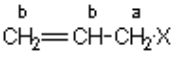
4.82	4.78	5.80		CCl_4
5.53	6.20	6.00		$CDCl_3$
5.02	5.10	6.34		CCl_4
5.12	5.53	6.60		$CDCl_3$
5.04	5.50	6.62		CCl_4
4.43	4.74	7.18		CCl_4
4.49	4.80	7.23		$CDCl_3$

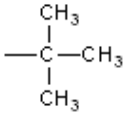
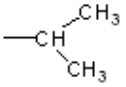
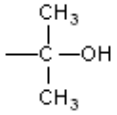
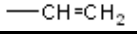


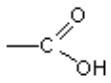
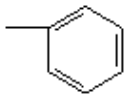
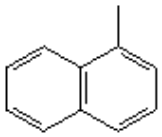
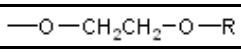
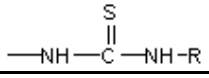
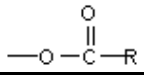
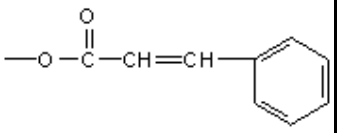
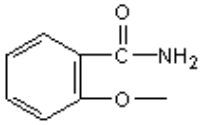
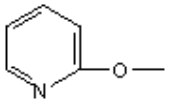
trans (ppm)	cis (ppm)	δ_a (ppm)	X	Solvent
4.60	4.60	1.62	C_3	CCl_4
4.60	4.60	1.68		CCl_4
4.70	4.89	1.70		CCl_4
4.93	4.93	1.82		CCl_4
5.39	5.71	1.89		D_2O
4.59	4.77	1.90		CCl_4

5.47	6.02	1.90		CCl_4
5.47	6.00	1.91		CCl_4
5.60	6.20	1.95		CCl_4
5.40	5.79	1.97		$CDCl_3$
ca 5.79		1.98		CCl_4
5.68	6.30	2.03		$CDCl_3$
5.01	5.31	2.10		CCl_4

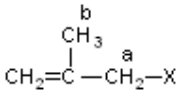
1-Propenes



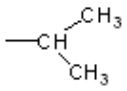
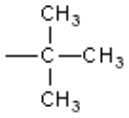
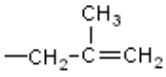
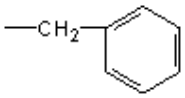
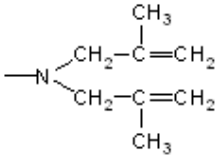
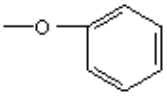
δ_b (ppm)	δ_a (ppm)	-X	Solvent
4.6-6.0	1.91		CCl_4
	1.93		CCl_4
	2.07		$CDCl_3$
	2.17		CCl_4
	2.79		$CDCl_3$
	3.10		CCl_4

	3.12		$CDCl_3$
	3.29	-S-S-R	CCl_4
	3.30	$-NH_2$	$CDCl_3$
	3.33		CCl_4
	3.63		CCl_4
	3.80	-I	CCl_4
	3.88	-Br	CCl_4
	3.99	-Cl	CCl_4
	4.02		$CDCl_3$
	4.05	-OH	CCl_4
	4.11		$CDCl_3$
	4.48		CCl_4
	4.60		CCl_4
	4.62		$CDCl_3$
	4.82		CCl_4

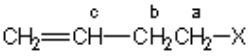
2-Methyl Propenes



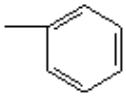
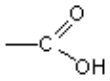
δ_b (ppm)	δ_a (ppm)	-X	Solvent

1.68	1.85		CCl_4
1.75	1.90		$CDCl_3$
1.69	1.98	$-R_2$	CCl_4
1.69	2.01	$-CH_3$	CCl_4
1.70	2.00	$-R_5$	CCl_4
1.62	2.11	$-CH_2-CH=CH_2$	$CDCl_3$
1.71	2.13		CCl_4
1.69	2.34	$-CH_2-OH$	$CDCl_3$
1.67	2.37		CCl_4
1.71	2.78		CCl_4
1.73	3.12	$-NH_2$	CCl_4
1.87	3.98	-Cl	CCl_4
1.79	4.36		CCl_4

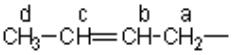
1-Butenes

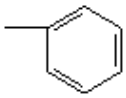


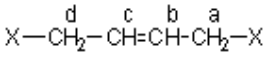
trans (ppm)	cis (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
4.88	4.92	5.68	1.99	1.32	$-CH_3$	CCl_4
4.89	4.86	5.69	2.00	1.45	$-R_{11}$	CCl_4
4.87	4.91	5.68	2.05	1.45	$-R_4$	CCl_4
4.91	4.96	5.70	2.11	2.11	$-CH=CH_2$	CCl_4

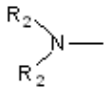
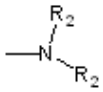
4.97	5.01	5.81	2.37	2.67		$CDCl_3$
5.10	5.14	5.80	2.37	3.65	-OH	$CDCl_3$
5.02	5.08	5.80	2.40	2.40		$CDCl_3$

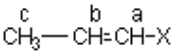
2-Butenes

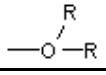


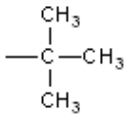
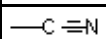
δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
1.59	5.33	5.33	1.96	$-R_2$	CCl_4
1.59	5.31	5.31	1.97	$-R_3$	CCl_4
1.60	5.34	5.34	1.98	$-CH_3$	CCl_4
1.68	5.47	5.47	3.27		CCl_4



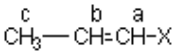
X-	δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
	3.07	5.63	5.63	3.07		$CDCl_3$
Br-	3.99	6.01	6.01	3.07	-Br	$CDCl_3$
HO-	4.18	5.72	5.72	4.18	-OH	D_2O

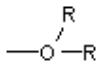
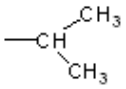
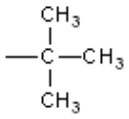
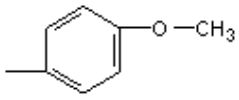
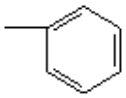
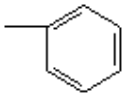
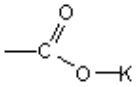
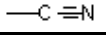
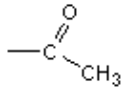


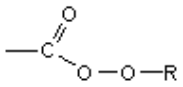
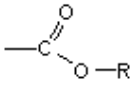
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
1.53	4.27	5.82		CCl_4

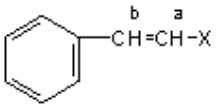
1.74	5.35	5.35		$CDCl_3$
2.03	6.62	5.38		$CDCl_3$

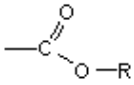
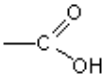
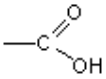
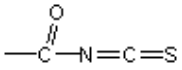
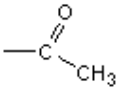
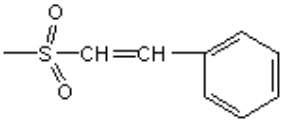
Olefinic Protons

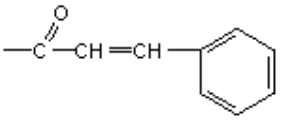


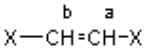
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X (all trans)	Solvent
1.53	4.68	6.12		CCl_4
1.61	5.32	5.32		CCl_4
1.63	5.40	5.40	$-R_4$	$CDCl_3$
1.63	5.58	5.58		$CDCl_3$
1.78	5.91	6.21		CCl_4
1.80	6.00	6.34		CCl_4
1.79	6.08	6.37		$CDCl_3$
1.81	6.59	5.84		D_2O
1.92	6.62	5.38		$CDCl_3$
1.89	6.70	6.00		CCl_4
2.00	6.80	6.04		CCl_4

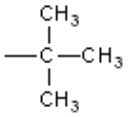
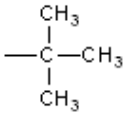
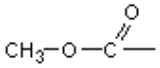
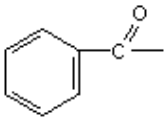
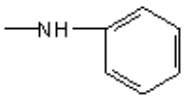
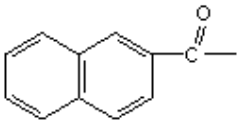
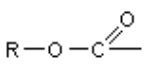
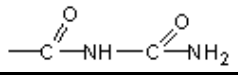
1.90	7.01	5.84		$CDCl_3$
1.93	7.10	5.91		CCl_4

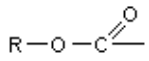
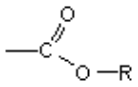
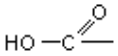
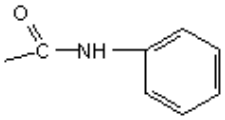
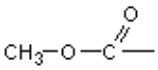
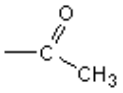
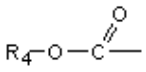
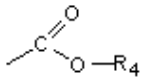


δ_b (ppm)	δ_a (ppm)	-X	cis/trans	Solvent
7.35	5.53	—C≡N	cis	$CDCl_3$
7.71	5.86	—C≡N	trans	$CDCl_3$
6.21	5.91	$-CH_3$	trans	CCl_4
6.48	6.11	-Cl	cis	CCl_4
6.73	6.42	-Cl	trans	CCl_4
6.57	6.31	$-CH_2-OH$	trans	$CDCl_3$
7.56	6.31		trans	CCl_4
7.60	6.38		trans	DMSO-d_6
7.80	6.43		trans	$CDCl_3$
7.71	6.45		trans	$CDCl_3$
7.02	6.61	-Br	trans	CCl_4
7.44	6.67		trans	CCl_4
7.52	6.67		trans	$CDCl_3$
7.60	6.82		trans	$CDCl_3$

7.79	6.91		trans	DMSO-d_6
7.70	7.02		trans	$CDCl_3$
7.79	7.29		trans	$CDCl_3$
7.97	7.45		trans	$CDCl_3$

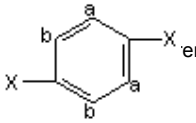


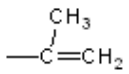
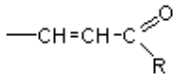
X-	δ_b (ppm)	δ_a (ppm)	-X	Solvent	cis/trans
CH_3-	5.32	5.32		$CDCl_3$	cis
R_7-	5.34	5.34	-R_7	CCl_4	
R_2-	5.37	5.37	-R_2	CCl_4	trans
CH_3-	5.45	5.45		$CDCl_3$	trans
	5.79	6.98	-R_4	$CDCl_3$	
	5.89	7.46		$CDCl_3$	cis
	6.00	7.64		$CDCl_3$	trans
	6.24	6.48		Polysol	cis

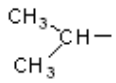
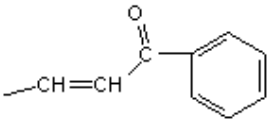
	6.25	6.25		CCl_4	cis
	6.32	6.82		$CDCl_3$	
	6.59 or	7.03		CDCl3	
Br-	6.64	6.64	-Br	CCl_4	cis
	6.83	6.83		$CDCl_3$	trans
Br-	7.04	7.04	-Br	CCl_4	trans

Aromatic Protons

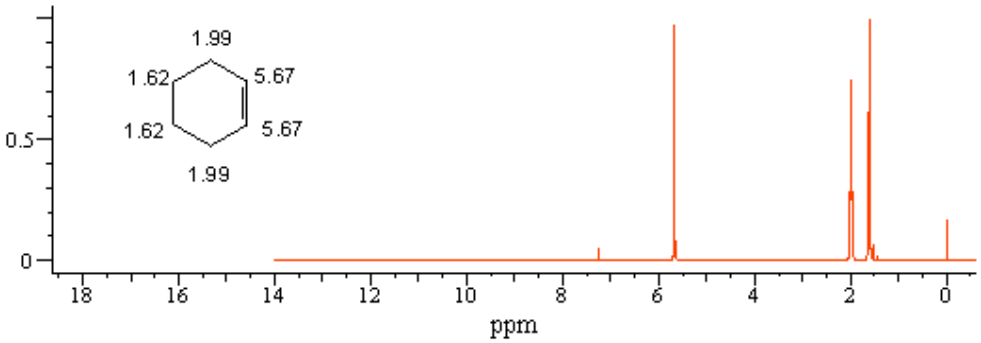
The aromatic patterns produced by the phenyl protons of alkene substituted benzenes are represented by a wide variety of chemical shifts and patterns depending on the site and type of substituents on the C=C moiety. A relatively sharp single peak may be observed as high as 7.13 ppm (Cl-CH=CH-, trans) or as low as 7.54 ppm (Cl-SO_2-CH=CH-). Generally, a complex band of overlapping multiplets is observed in the range from 7.1-7.6 ppm (CH_2=CH-, CH_2=C(CH_3)-, R-C(=O)-CH=CH-). In at least one case, the ortho aromatic hydrogens are strongly deshielded in relation to the meta and para hydrogens producing two sets of bands, one at 7.55 and a range from 7.1-7.4 ppm (Cl-CH=CH-, cis).

 ene derivatives

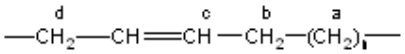
X	δ_b (ppm)	δ_a (ppm)	para -X	Solvent
CH_3-O-	6.65	7.08	-CH=CH-CH_3	CCl_4
F-	6.90	7.23	-CH=CH_2	$CDCl_3$
CH_3-O-	6.76	7.22	-CH=CH_2	CCl_4
Cl-	7.21	7.21	-CH=CH_2	CCl_4
Cl-	7.23	7.23		$CDCl_3$
Br-	7.34	7.12	-CH=CH_2	CCl_4
Cl-	7.32	7.47		$CDCl_3$

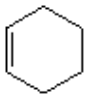
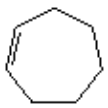
	7.28	7.68		Polysol
	8.07	7.49	-CH=CH-CH_2-OH	Polysol

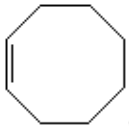
2 Cyclic Alkenes



The cyclic alkenes are usually a relatively simple group to identify from their HNMR spectra. The spectra display three sets of resonance bands with the olefinic protons resonating in the range from 5-6 ppm, the methylene groups adjacent to the double bonds deshielded to about 2.1 ppm and the remaining methylene groups forming a separate band at slightly higher field. In the spectra of the smaller rings, cyclopentene and cyclohexene, the coupling constant between the aliphatic and olefinic hydrogens (CH_2-CH=C) is quite small resulting in a single, slightly broadened peak for the olefinic hydrogens. As the ring sizes increase, this coupling constant increases in magnitude, to about 4 Hz for cycloheptene and about 5 Hz for cyclooctene.



δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
2.29	5.66	2.29	(1.85)		CCl_4
1.97	5.58	1.97	$(1.62)_2$		CCl_4
2.11	5.71	2.11	$(1.64)_3$		CCl_4

2.12 5.59		2.12	$(1.53)_4$	 (cis)	CCl_4

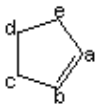
The deshielding effect of the olefinic bond on aliphatic groups bonded to it is similar to that observed for the acyclic alkenes, i.e. a weakly deshielding effect.

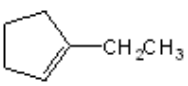
δ_b (ppm)	δ_a (ppm)	-X	Ring system	Solvent
		CH_3-		CCl_4
1.03	2.19	CH3-CH_2-		CCl_4
	1.60	CH_3-		CCl_4
0.96	1.95	CH3-CH_2-		CCl_4

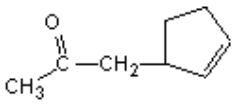
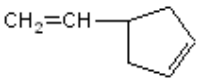
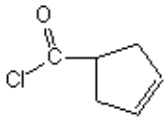
The chemical shift changes brought about by substituents bonded to the various positions of the cyclic alkenes are often dramatic, particularly on the position-2 olefinic hydrogen. A series of monosubstituted compounds is listed below.

Because of their smaller ring size, the cyclopentenes usually display two or three distinct bands at high field for the ring methylene groups depending on the position and deshielding effect of the substituent.

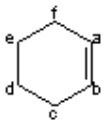
Cyclopentenes

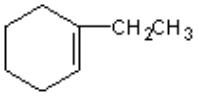
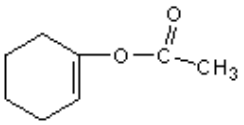
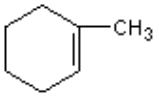
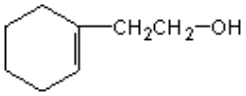
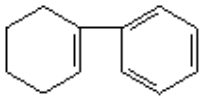
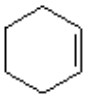
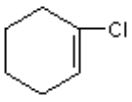


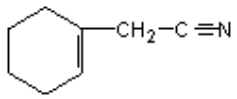
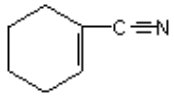
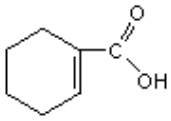
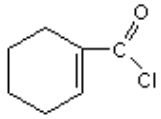
δ_e (ppm)	δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
2.29	1.85	2.29	5.66	5.66		CCl_4
	(1.5-2.5)		5.19			CCl_4

2.30	1.40	3.30	5.63	5.63		CCl_4
	(1.0-2.5)		5.61	5.61		CCl_4
2.00	2.98	2.00	5.61	5.61		CCl_4

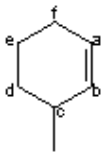
Cyclohexenes

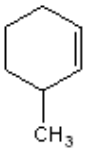
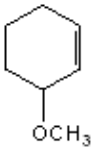
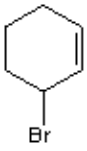


δ_f (ppm)	δ_e (ppm)	δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
1.89	1.57	1.57	1.89	5.23			CCl_4
2.09	1.72	1.72	2.09	5.27			CCl_4
1.88	1.60	1.60	1.88	5.30			CCl_4
1.98	1.65	1.65	1.98	5.46			CCl_4
2.15	1.69	1.69	2.15	5.49			CCl_4
1.97	1.62	1.62	1.97	5.58	5.58		CCl_4
2.00	1.60	1.60	2.00	5.71			CCl_4

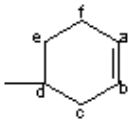
2.05	1.65	1.65	2.05	5.78			$CDCl_3$
2.22	1.68	1.68	2.22	6.58			CCl_4
2.28	1.68	1.68	2.28	7.11			CCl_4
2.32	1.69	1.69	2.32	7.39			CCl_4

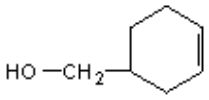
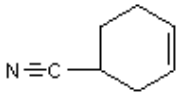
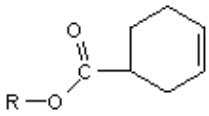
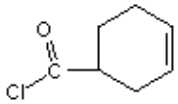
3-Substituted Cyclohexenes



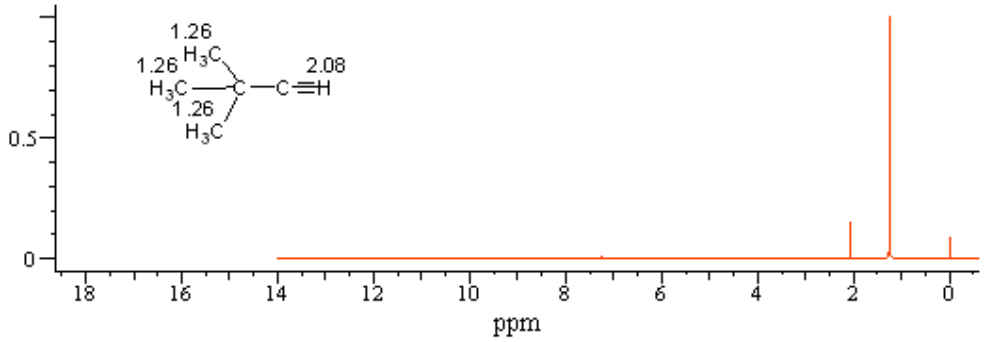
δ_f (ppm)	δ_e (ppm)	δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
	(1.1-2.5)			5.56	5.56		$CDCl_3$
1.95	(1.3-1.9)		3.61	5.74	5.74		CCl_4
2.11	(1.3-2 .1)		4.78	5.80	5.80		CCl_4

4-Substituted Cyclohexenes



δ_f (ppm)	δ_e (ppm)	δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		(1.0-2.4)		5.63	5.63		$CDCl_3$
(1.6-2.5)		2.71		5.65	5.65		CCl_4
		(1.6-2.8)		5.66	5.66		$CDCl_3$
(1.6-2.6)		3.00		5.79	5.79		CCl_4

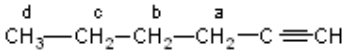
3 Alkynes

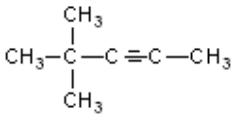
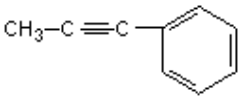
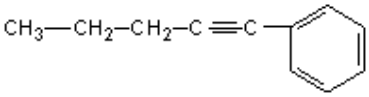


The monosubstituted acetylenes (H-C≡C-X) are usually easily characterized because the acetylenic hydrogen appears over a relatively limited chemical shift range (2.0—3.0 ppm in CCl_4) and displays coupling between non-equivalent proton groups on opposite sides of the triple bond linkage (J = 2.0-3.2 Hz). The absence of this hydrogen in the disubstituted acetylenes makes the identification of these compounds somewhat more difficult -although the coupling across the triple bond may still be observed.

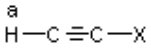
The deshielding effect of the C≡C linkage is similar to that of the C=C group, i.e., it is a weak deshielder of both aliphatic and aromatic protons.

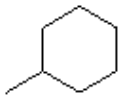
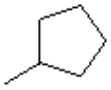
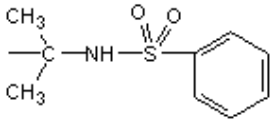
Aliphatic Protons

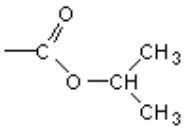
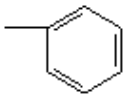
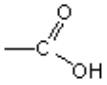
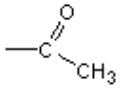
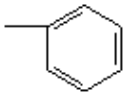


δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
			1.80	CH_3-C≡C-H	$CDCl_3$
	1.01	1.55	2.12	CH_3-CH_2-CH_2-C≡C-H	CCl_4
0.93	1.40	1.53	2.11	CH_3-CH_2-CH_2-CH_2-C≡C-H	CCl_4
			1.70		CCl_4
		(1.18)			CCl_4
			1.71		$CDCl_3$
	1.01	1.59	2.32		CCl_4

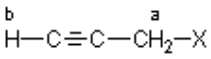
Monosubstituted ethynes

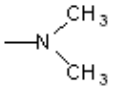
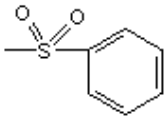
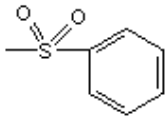


δ_a (ppm)	-X	Solvent
1.79	-R_3	CCl_4
1.80	-CH_3	$CDCl_3$
2.25	-C(-CH_3, -CH_3, -R_2)	CCl_4
2.29		$CDCl_3$
2.30	-C(-CH_3, -R_2, -OH)	CCl_4
2.33	-CH(-R_2)-OH	CCl_4
2.33	-CH(-R_3)-OH	CCl_4
2.37		CCl_4
2.71		Polysol

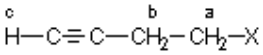
2.86		$CDCl_3$
3.04		$CDCl_3$
3.19		$CDCl_3$
3.40		$CDCl_3$
4.06		DMSO-d_6

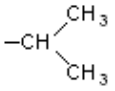
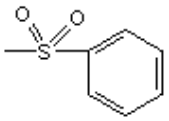
1-Propynes



δ_b (ppm)	δ_a (ppm)	-X	Solvent
2.23	3.29		$CDCl_3$
2.31	3.99	-O-CH_3	CCl_4
2.39	3.97		$CDCl_3$
2.41	3.83	-Br	CCl_4
2.42	4.06	-Cl	CCl_4
2.49	4.25		TFA
2.54	4.23	-OH	$CDCl_3$

1-Butynes



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
1.89	2.20	1.40		CCl_4
1.90	2.39	2.39	-C≡C-H	CCl_4
1.96	2.38	2.67	-OH	CCl_4
2.53	2.55	3.43		Polysol

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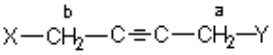
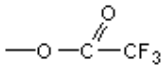
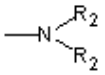
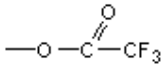
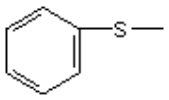
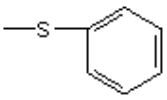
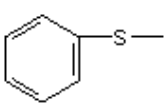
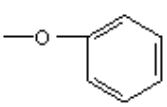
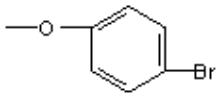
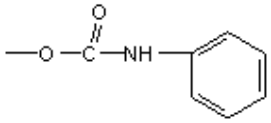
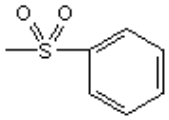
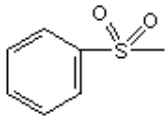
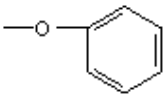
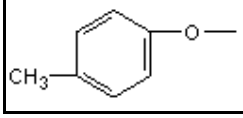
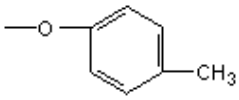
2-Butynes (1,4-disubstituted)

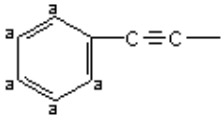


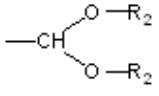
-X	δ_b (ppm)	δ_a (ppm)	-Y	Solvent
R_5-	2.20	4.19	-OH	CCl_4
R_4-	2.22	4.89		$CDCl_3$
CH_3-	2.23	4.17	-OH	CCl_4
R-	2.24	3.27		CCl_4
CH_3-	2.26	4.90		$CDCl_3$
	3.60	3.60		Polysol
	3.68	4.61		$CDCl_3$

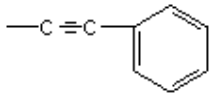
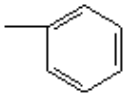
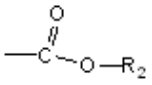
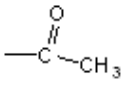
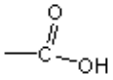
Br-	3.98	3.98	-Br	$CDCl_3$
Cl-	4.12	4.12	-Cl	CCl_4
Cl-	4.12	4.68		$CDCl_3$
Cl-	4.16	4.82		$CDCl_3$
Cl-	4.32 or	4.41		Polysol
	4.32	4.79		Polysol
	4.65	4.65		$CDCl_3$

Aromatic Protons

The placement of various substituents on the triple bond opposite a phenyl group has only a slight effect upon the chemical shift ranges observed for the resulting complex, higher order bands. The fact that the lower field limit of these ranges is only about 0.2 ppm downfield from the chemical shift of unsubstituted benzene (7.37 ppm) indicates that the C≡C group has only a slight deshielding effect on the ortho aromatic hydrogens.



δ_a (ppm)	-X	Solvent
7.00-7.65	-H	$CDCl_3$
7.05-7.50	$-R_7$	CCl_4
7.10-7.50	$-CH_3$	$CDCl_3$
7.15-7.60		$CDCl_3$

7.15-7.65		$CDCl_3$
7.15-7.65		CCl_4
7.20-7.65		CCl_4
7.20-7.70		$CDCl_3$
7.25-7.70		Polysol

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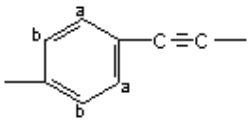
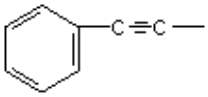
Para substituted compounds



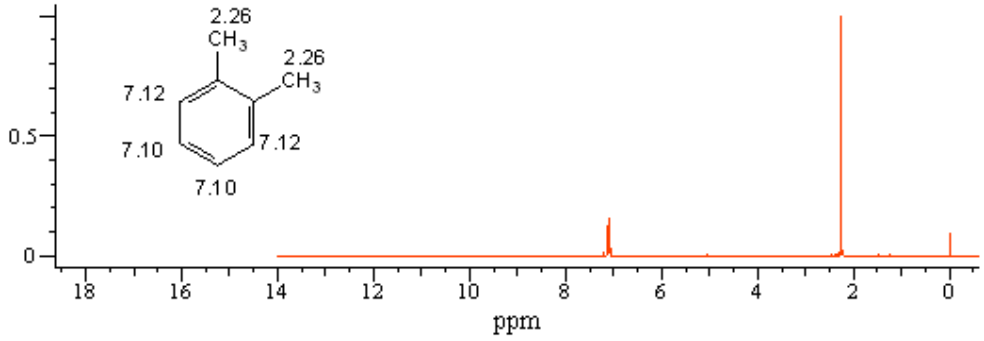
x	δ_a (ppm)	δ_b (ppm)	para	Solvent
	7.42	6.85	$-O-CH_3$	$CDCl_3$
H-C≡C	7.43 or	7.30	-Br	$CDCl_3$

Solubility and Solvent Effects

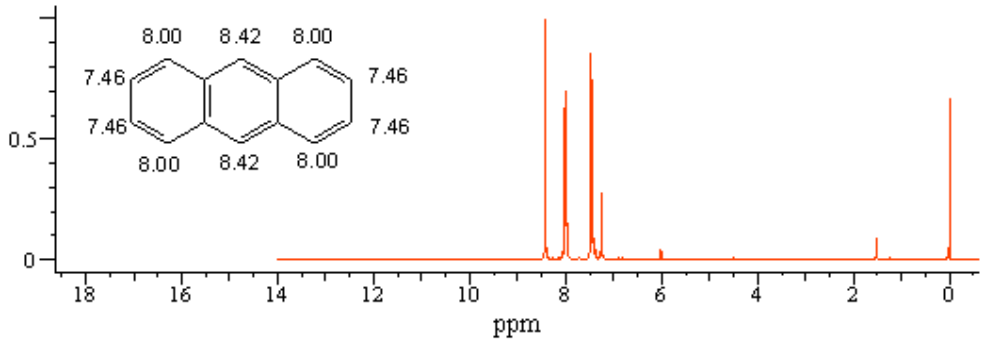
The low molecular weight alkynes are readily soluble in the halogenated solvents normally used for the preparation of NMR solutions. It has been noted that the hydrogen bonded directly to the triple bond carbon is strongly deshielded in the presence of DMSO-d_6 in comparison to CCl_4 and $CDCl_3$. For example, the acetylenic hydrogen of phenyl acetylene appears at about 3.0 ppm in $CDCl_3$ solution but at 4.1 ppm in DMSO-d_6.

C□ Aromatic Hydrocarbons

1. Monocyclic (Benzenes)



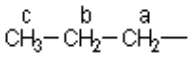
2 Polycyclic



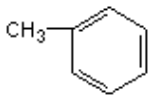
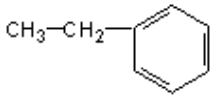
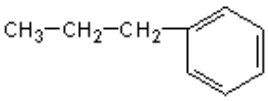
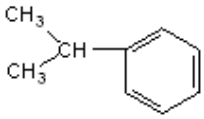
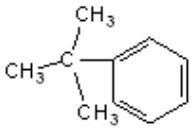
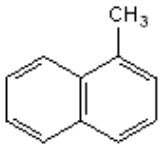
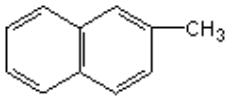
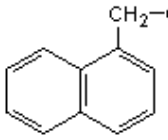
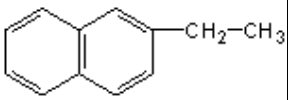
The aromatic protons of alkyl substituted benzene rings usually appear as a single broad peak near 7.1 ppm or a complex multiplet in the range from 6.9-7.5 ppm for highly branched chains such as the tert-butyl group. Aliphatic groups shield the ortho aromatic hydrogens by a factor of about 0.34 ppm, as evidenced by the aromatic resonance of mesitylene (1,3,5-trimethyl benzene) which appears at 6.69 ppm.

Compound	(ppm)	Solvent
Benzene	7.37	CCl_4
Toluene	7.04	CCl_4
p-Xylene	7.07	CCl_4
Mesitylene	6.69	CCl_4

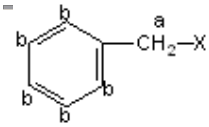
Aliphatic Protons



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent

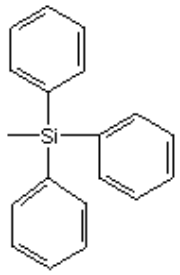
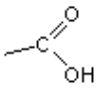
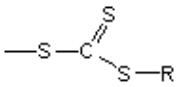
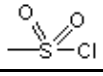
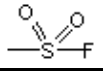
		2.29		CCl_4
	1.19	2.53		CCl_4
0.93	1.63	2.58		$CDCl_3$
	(1.22)	2.83		CCl_4
	(1.32)			CCl_4
		2.46		$CDCl_3$
		2.49		$CDCl_3$
	1.37	3.03		CCl_4
	1.30	2.77		$CDCl_3$

The alkyl protons of aliphatic groups bonded to the naphthalene ring system resonate at lower field than those bonded to benzene, in addition, the groups bonded to carbons 1,4,5,8 resonate at lower field than similar groups situated at positions 2,3,6,7. The aromatic resonances of naphthalene ring systems generally appear as a complex, higher order series of multiplets in the range from 7.0-8.0 ppm.



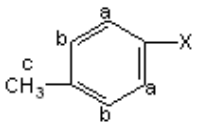
d toluenes

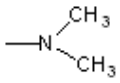
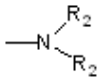
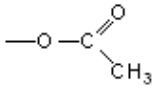
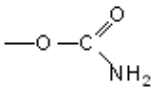
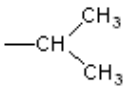
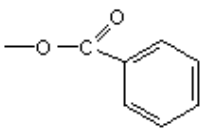
δ_b (ppm)	δ_a (ppm)	-X	Solvent
ca7.07	2.53	$-CH_3$	CCl_4

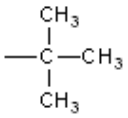
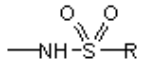
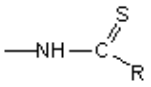
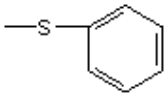
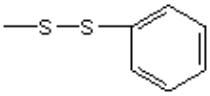
ca 7.24	2.53	$-C_3$	$CDCl_3$
ca 6.94	2.91		$CDCl_3$
ca7.14	3.33	$-CH=CH_2$	CCl_4
ca 7.27	3.61		$CDCl_3$
ca 7.27	3.62	-C≡N	CCl_4
ca 7.22	3.64	-SH	CCl_4
7.0-7.4	3.67		$CDCl_3$
ca 7.29	3.85		$CDCl_3$
ca 7.29	3.85	$-NH_2$	$CDCl_3$
ca7.59	4.27	$-NH_2$ (salt)	D_2O
ca 7.22	4.34	-Br	CCl_4
7.07-7.5	4.38	-I	$CDCl_3$
ca7.19	4.41	-OH	CCl_4
ca 7.28	4.48	-Cl	CCl_4
ca7.24	4.55		$CDCl_3$
ca7.33	4.59	-N≡C	$CDCl_3$
ca 7.29	4.59	-N=C=S	$CDCl_3$
ca 7.44	4.83		$CDCl_3$
ca 7.42	5.07		Polysol
ca 7.27	5.24	-F	CCl_4

Aromatic Protons

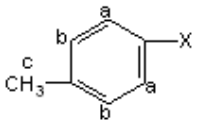
Para substituted toluenes (in increasing "meta" shift)

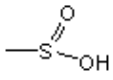
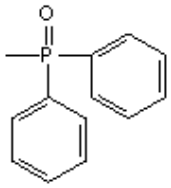


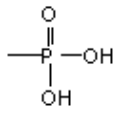
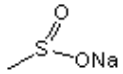
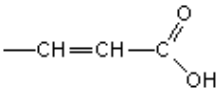
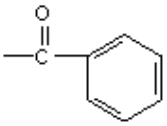
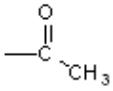
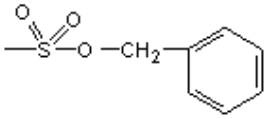
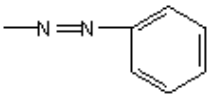
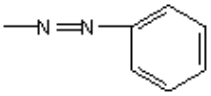
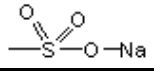
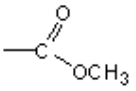
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
2.18	6.79	6.33	$-NH_2$	CCl_4
2..21	6.92	6.40	$-NH-CH_3$	$CDCl_3$
2.18	6.89	6.49		CCl_4
2..21	7.01	6.59		$CDCl_3$
2.22	6.93	6.62	$-O-R_{12}$	CCl_4
2.20	6.92	6.69	-OH	$CDCl_3$
2.28	7.09	6.79	$-O-CH_3$	$CDCl_3$
2.23	7.00	6.81	-F	CCl_4
2.28	7.01	6.82		CCl_4
2.27	6.90	6.90	$-CH_3$	CC_{l4}
2.27	7.14	6.92		DMSO-d_6
2.28	6.99	6.99		CCl_4
2.28	7.01	7.01	$-CH_2-OH$	CCl_4
2.30	7.04	7.04	$-CH_2-CH_3$	CCl_4
2.30	7.04	7.04	$-CH_2-NH_2$	CCl_4
2.28	7.05	7.05	$-S-CH_3$	CCl_4
2.29	7.05	7.05	$-CH_2-C\equiv N$	CCl_4
2.34	7.07	7.07		CCl_4
2.20	6.91	7.09	-SH	$CDC!_3$
2.30	7.09	7.09	$-CH_2-CH_2-NH_2$	$CDC!_3$

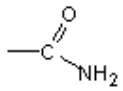
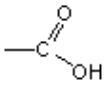
2.31	7.10	7.10	-CH_2-CH_2-OH	$CDCl_3$
2.29	6.98	7.12	-Cl	CCl_4
2.29	7.00	7.12		CCl_4
2.30	7.16	7.16		$CDCl_3$
2.29	6.99	7.18	-CH_2-Br	CCl_4
2.28	7.02	7.18	-CH_2-Cl	CCl_4
2.33	7.19	7.19		$CDCl_3$
2.30	7.07	7.21		$CDCl_3$
2.25	6.95	7.30	-Br	CCl_4
2.26	7.08	7.30	-Hg-Cl	DMSO-d_6
2.30	7.05	7.34		$CDCl_3$

Para substituted toluenes (in increasing “meta”shift)



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	para	Solvent
2.41	7.23	7.47	-C≡N	CCl_4
2.26	6.89	7.55	-I	$CDCl_3$
2.35	7.20	7.55		$CDCl_3$
2.36	7.22	7.55		$CDCl_3$

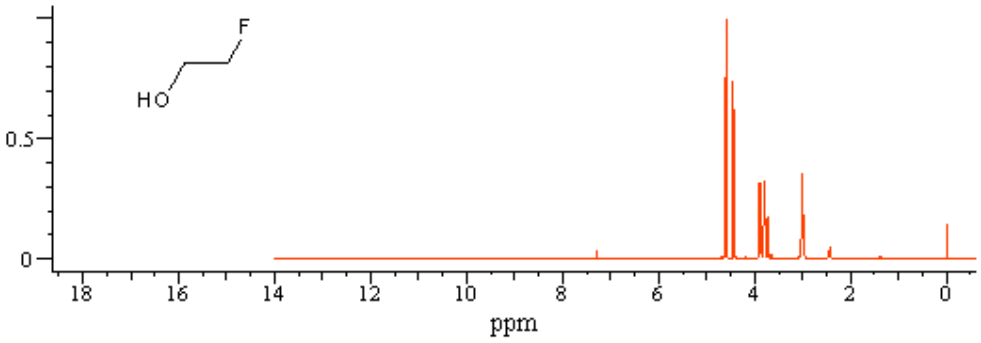
2.32	7.24	7.58		DMSO-d_6
2.36	7.35	7.58		D_2O
2.33	7.21	7.59		DMSO-d_6
2.30	7.21	7.61	-SO_2-OH (salt)	DMSO-d_6
2.39	7.22	7.65		$CDCl_3$
2.32	7.09	7.69		CCl_4
2.33	7.10	7.69	-N=S=O	CCl_4
2.33	7.12	7.70	-SO_2-OH (salt)	$CDCl_3$
2.43	7.32	7.71	-SO_2-O-CH_3	CCl_4
2.42	7.29	7.70	-SO_2-O-R_{10}	CCl_4
2.41	7.31	7.76		$CDCl_3$
2.43	7.37	7.79		$CDCl_3$
2.39	7.22	7.83		$CDCl_3$
2.46	7.37	7.84	-SO_2-NH_2	TFA
2.39	7.25	7.84		$CDCl_3$
2.29	7.26	7.88		D_2O
2.30	7.15	7.89		$CDCl_3$
2.50	7.41	7.90	-SO_2-F	$CDCl_3$
2.49	7.41	7.90	-SO_2-Cl	$CDCl_3$

2.49	7.43	7.92		TFA
2.44	7.24	7.96		CCl_4
2.47	7.30	8.02		TFA
2.45	7.30	8.10		$CDCl_3$

II. Halogenated Hydrocarbons

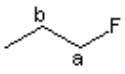
A. Fluorinated Hydrocarbons

1. Aliphatic



Fluorine containing compounds characteristically display coupling between the fluorine nuclei and nearby hydrogens. The multiplets which are produced are usually well resolved and the magnitude of the Fluorine-Hydrogen coupling constants is quite large in comparison to those produced by Hydrogen-Hydrogen and Phosphorus-Hydrogen coupling. Fluorine is a strong deshieider of aliphatic groups but has a moderately strong shielding effect upon the aromatic hydrogens that are ortho and para to it.

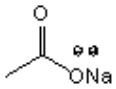
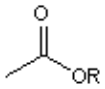
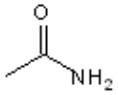
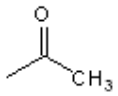
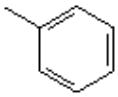
Aljphatic Protons



δ_b (ppm)	δ_a (ppm)	Compound	Solvent
3.72	4.37		$CDCl_3$

1.8-1.9	4.3-4.4		$CDCl_3$

Substituted Fluoromethanes

δ_a (ppm)	-X	Solvent
4.75		D_2O
4.88		$CDCl_3$
5.02		TFA
5.07		D_2O
5.11		$CDCl_3$
5.24		CCl_4

Coupling and Coupling Constants

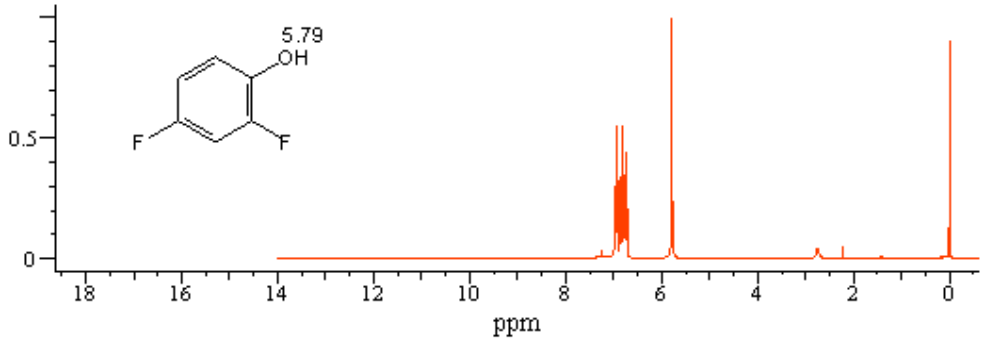
Aliphatic Protons

^{J}F-C-H = 46.7-51 .9 Hz

^{J}F-C-C-H = 20.0-30.0 Hz

$^{J}F_2$-C-C-H = 3.9-13.0 Hz

2 Aromatic

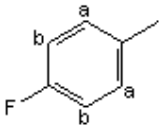


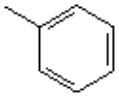
Fluorine containing compounds characteristically display coupling between the fluorine nuclei and nearby hydrogens. The multiplets which are produced are usually well resolved and the magnitude of the Fluorine-Hydrogen coupling constants is quite large in comparison to those produced by Hydrogen-Hydrogen and Phosphorus-Hydrogen coupling. Fluorine is a strong deshieider of aliphatic groups but has a moderately strong shielding effect upon the aromatic hydrogens that are ortho and para to it.

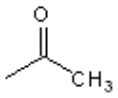
Aromatic Protons

Fluorine substituents on aromatic rings have a moderately strong shielding effect upon the ortho and para hydrogens and display coupling to the ortho, meta and para hydrogens.

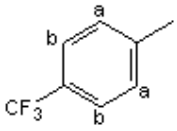
Para-substituted fluorobenzenes

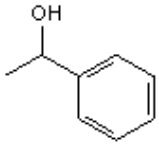
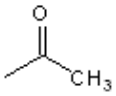
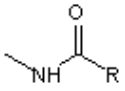
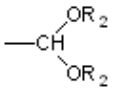
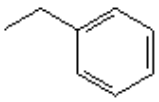


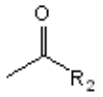
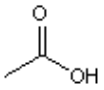
δ_b (ppm)	δ_a (ppm)	para-X	Solvent
6.81	7.00	$-CH_3$	CCl_4
6.89	7.09	-R	CCl_4
6.90	7.12	$-CH_2-OH$	$CDCl_3$
6.90	7.15	-N=C=S	CCl_4
6.90	7.23	$-CH=CH_2$	$CDCl_3$
6.91	7.19	-Cl	$CDCl_3$
6.92	7.29	$-CH_2-Br$	CCl_4
6.93	7.40		CCl_4

6.99	7.19	-CH_2-C≡N	CCl_4
7.00	6.81	-O-CH_3	$CDCl_3$
7.11	7.99		$CDCl_3$
7.15	8.01		$CDCl_3$
7.17	7.66	-C≡N	$CDCl_3$
7.20	8.20	-NO_2	$CDCl_3$

Para-substituted alpha,alpha,alpha-trifluorotoluenes



δ_b (ppm)	δ_a (ppm)	para-X	Solvent
7.46	6.91	-OH	$CDCl_3$
7.49	7.60	-Br	CCl_4
7.51	7.37		$CDCl_3$
7.51	8.08		$CDCl_3$
7.60	7.60		$CDCl_3$
7.60	7.60		$CDCl_3$
7.61	7.31		DMSO-d_6
7.64	7.13	-F	CCl_4

7.69	8.03		CCl_4
7.71	8.18		Polysol
7.73	8.20		$CDCl_3$
7.80	7.80	-C≡N	$CDCl_3$

Coupling and Coupling Constants

Aromatic Protons

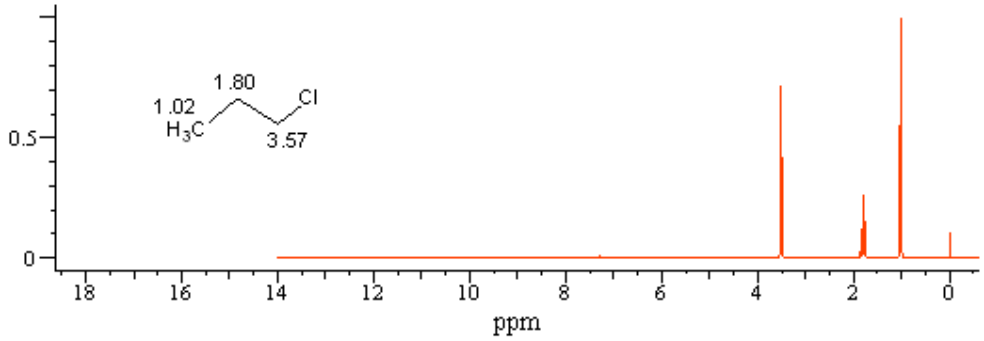
J_{F-H} (ortho) = 8.0-9.0 Hz

J_{F-H} (meta) = 5.0-6.0 Hz

J_{F-H} (para) = 2.0-3.0 Hz

B Chlorinated Hydrocarbons

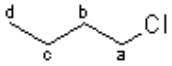
1. Aliphatic

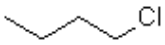


Because Chlorine does not possess a spin as Fluorine does, nor does it possess any exchangeable hydrogens, the identification of chlorine substituents via NMR must be based solely upon the observed chemical shifts.

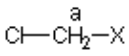
Fortunately, chlorine has a strong deshielding effect upon aliphatic hydrogens and thus the analysis of such materials is relatively straightforward. However, since it has only a very weak shielding/deshielding effect upon aromatic hydrogens, it becomes quite difficult to identify chlorine groups bonded to an aromatic ring without the use of alternate techniques.

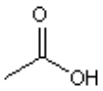
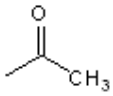
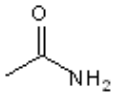
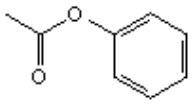
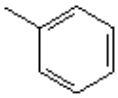
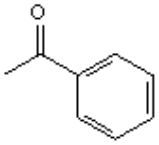
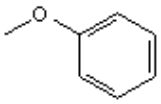
Aliphatic Protons



δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
			3.05		(lit.)
		1.33	3.47		(lit.)
	1.05	1.77	3.45		CCl_4
0.95	1.45	1.75	3.49		CCl_4
		(1.51)	4.11		CCl_4
		(1.61)			CCl_4

Substituted Chloromethanes



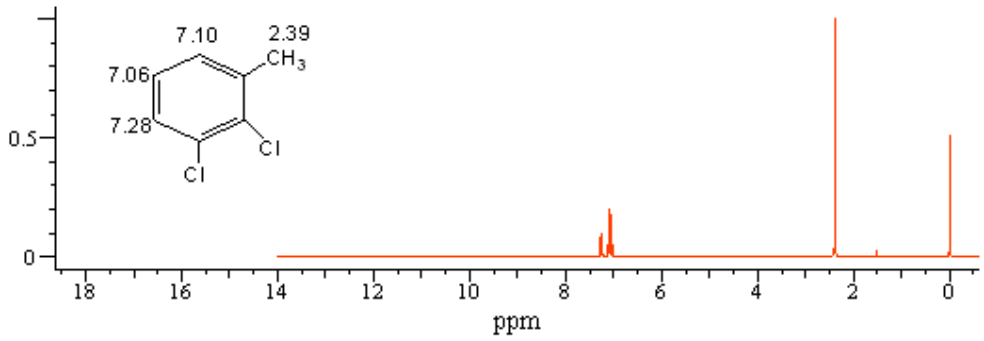
δ_a (ppm)	-X	Solvent
4.05		CCl_4
4.06	-C≡C-R	CCl_4
4.11	-C≡N	CCl_4
4.12		$CDCl_3$
4.18		D_2O
4.20		$CDCl_3$
4.33		$CDCl_3$
4.48		CCl_4
4.50		CCl_4
4.66		$CDCl_3$
5.73		CCl_4

Halogenated Hydrocarbons

A. Chlorinated Hydrocarbons
   1. Aliphatic
   2. Aromatic

Chlorinated Hydrocarbons

Aromatics



Because Chlorine does not possess a spin as Fluorine does, nor does it possess any exchangeable hydrogens, the identification of chlorine substituents via NMR must be based solely upon the observed chemical shifts.

Fortunately, chlorine has a strong deshielding effect upon aliphatic hydrogens and thus the analysis of such materials is relatively straightforward. However, since it has only a very weak shielding/de-shielding effect upon aromatic hydrogens, it becomes quite difficult to identify chlorine groups bonded to an aromatic ring without the use of alternate techniques.

Aromatic Protons

As noted previously, chlorine does not significantly alter the chemical shifts of aromatic hydrogens in comparison with the effects noted for other substituents. The NMR spectrum of chlorobenzene displays only a broad, single band at about 7.2 ppm.

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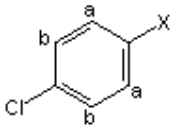
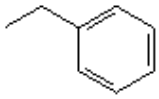
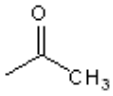
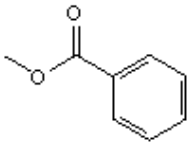
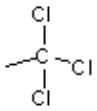
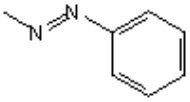
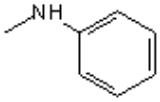
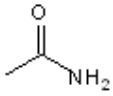
para-substituted Chlorobenzenes



δ_b (ppm)	δ_a (ppm)	-X	Solvent

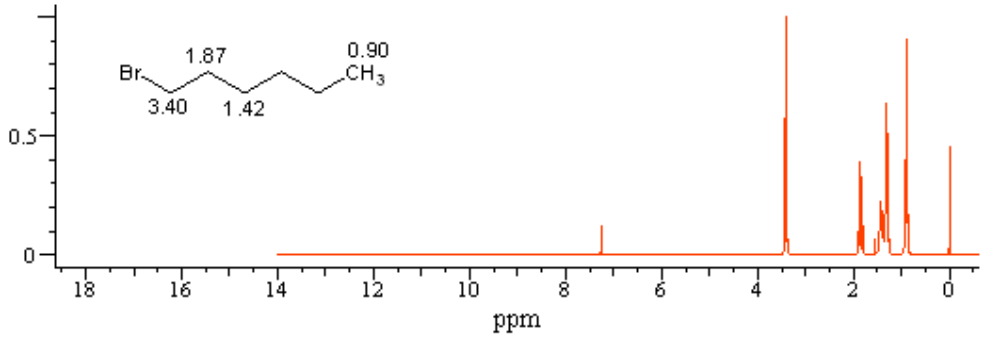
7.00	6.39	-NH-R	$CDCl_3$
7.09	7.61	-I	$CDCl_3$
7.12	6.91		$CDCl_3$
7.12	6.98	$-CH_3$	CCl_4
7.13	7.37	-Br	CCl_4
7.19	6.91	-F	$CDCl_3$
7.21	7.21	$-CH=CH_2$	CCl_4
7.22	6.85	-O-R	Polysol
7.23	7.23	-Cl	CCl_4
7.27	7.02	-N=S=O	$CDCl_3$
7.30	7.30	$-CH_2-Cl$	CCl_4
7.31	7.80		CCl_4
7.32	7.11		$CDCl_3$
7.36	7.84		CCl_4
7.40	7.81		$CDCl_3$
7.45	7.45		Polysol
7.46	8.02		$CDCl_3$
7.55	7.97		DMSO

A. Brominated Hydrocarbons

1. Aliphatic

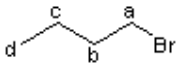
Brominated Hydrocarbons

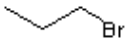
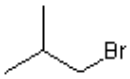
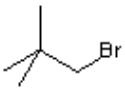
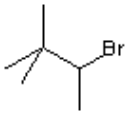
Aliphatics



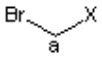
The Bromine nucleus is an intermediate deshielding group in relation to both aliphatic and aromatic hydrogens. It does not couple to nearby hydrogens and thus its presence in a molecule must be inferred from the observed chemical shifts.

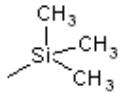
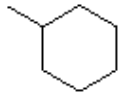
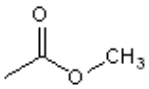
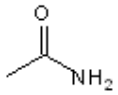
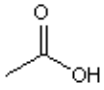
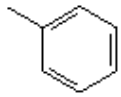
Aliphatic Protons



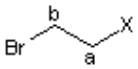
δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		1.66	3.34		CCl_4
	1.02	1.89	3.36		CCl_4
0.99	1.43	1.82	3.39		CCl_4
	(1.08)	1.93	3.24		CCl_4
	(1.02)		3.15		CCl_4
		(1.70)	4.21		CCl_4
		(1.77)			CCl_4

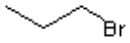
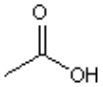
Substituted Bromoethanes



δ_a (ppm)	-X	Solvent
2.38		CCl_4
3.21		Polysol
3.77		CCl_4
3.83	-C≡C-H	CCl_4
3.88	$-CH=CH_2$	CCl_4
3.91		D_2O
3.92		$CDCl_3$
3.98	-C≡C-R	$CDCl_3$
4.38		CCl_4
4.34		CCl_4
4.40		CCl_4
4.94	-Br	CCl_4
5.18	-Cl	CCl_4

2-Substituted Bromoethanes

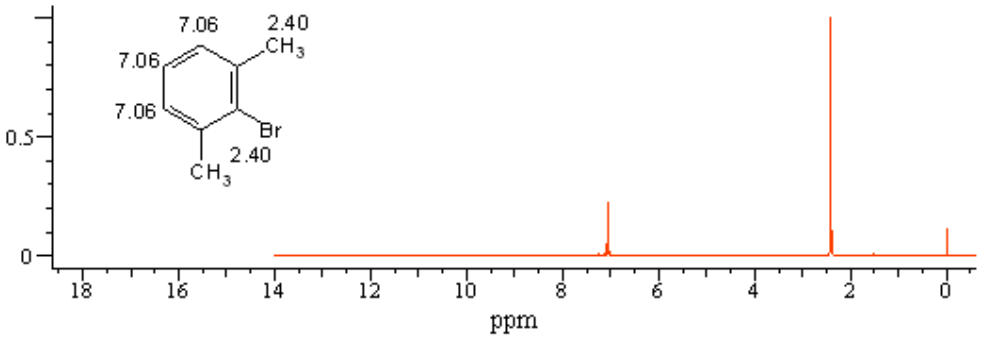


δ_b (ppm)	δ_a (ppm)	-X	Solvent
3.40	3.65	-O-CH_3	CCl_4
3.41	2.04		CCl_4
3.45	3.85	-OH	CCl_4
3.51	2.36		CCl_4
3.53	2.97	-C≡N	CCl_4
3.56	2.97		$CDCl_3$
3.56	3.70	-Cl	CCl_4
3.68	3.68	-Br	$CDCl_3$

Aromatic

Brominated Hydrocarbons

Aromatics

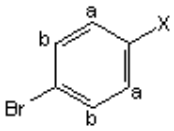


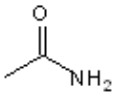
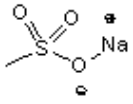
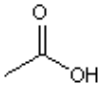
The Bromine nucleus is an intermediate deshielding group in relation to both aliphatic and aromatic hydrogens. It does not couple to nearby hydrogens and thus its presence in a molecule must be inferred from the observed chemical shifts.

Aromatic Protons

Bromine has a weakly deshielding effect upon the ortho aromatic hydrogens. The ortho hydrogens are deshielded to 7.41 ppm while the meta and para hydrogens appear as a complex higher order pattern centered to about 7.2 ppm.

para-substituted Bromobenzenes



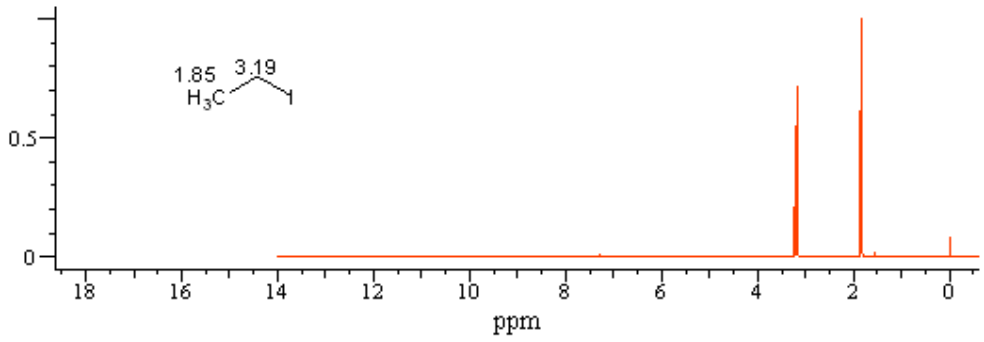
δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.18	7.50	-I	$CDCl_3$
7.20	6.49	-NH-R	$CDCl_3$
7.29	6.69	$-O-CH_3$	CCl_4
7.29	7.29	-Br	$CDCl_3$
7.30	6.92	$-CH_3$	CCl_4
7.30	7.07	-SH	$CDCl_3$
7.31	6.98	$-R_2$	$CDCl_3$
7.34	7.12	$-CH=CH_2$	CCl_4
7.37	7.13	-Cl	CCl_4
7.39	7.11	$-S-CH_3$	$CDCl_3$
7.40	6.90	-F	CCl_4
7.45	7.62	-C≡N	$CDCl_3$
7.49	7.60	$-CF_3$	CCl_4
7.61	7.87		DMSO-d_6
7.68	7.68		$CDCl_3$
7.68	7.79		D_2O
7.71	7.90		DMSO-d_6

A. Iodinated Hydrocarbons

1. Aliphatic

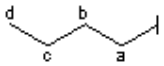
Iodinated Compounds

Aliphatics



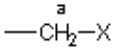
Of the halogens, Iodine has the weakest deshielding effect upon aliphatic hydrogens, but the strongest deshielding effect on the ortho aromatic hydrogens. It is observed to have an unusually strong deshielding effect upon the hydrogens bonded to beta aliphatic carbon atoms.

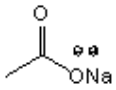
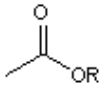
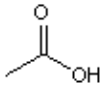
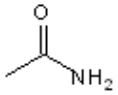
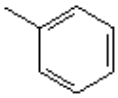
Aliphatic Protons



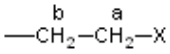
δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
			2.20		$CDCl_3$
		1.84	3.13		CCl_4
	1.00	1.85	3.15		CCl_4
0.99	1.40	1.80	3.19		CCl_4
	(1.01)	1.73	3.10		CCl_4
		(1.91)	4.29		CCl_4

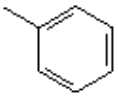
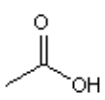
Substituted Iodomethanes



δ_a (ppm)	-X	Solvent
3.55	$-CF_2-CF_3$	$CDCl_3$
3.63		D_2O
3.69		CCl_4
3.71		$CDCl_3$
3.80	$-CH=CH_2$	CCl_4
3.88	-I	CCl_4
3.98		TFA
4.38		$CDCl_3$

2-Substituted Iodoethanes



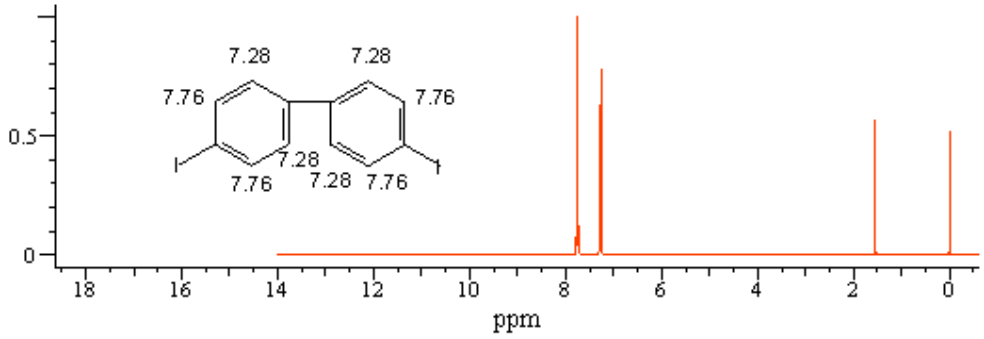
δ_b (ppm)	δ_a (ppm)	-X	Solvent
3.17	1.94	$-CH_2-CH_2-I$	CCl_4
3.19	3.08		$CDCl_3$
3.28	3.81	-OH	$CDCl_3$
3.30	3.09		$CDCl_3$

3.29	2.29	-CH_2-I	$CDCl_3$
3.70	3.70	-I	CCl_4

Aromatic

Iodinated Compounds

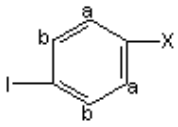
Aromatics



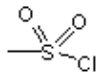
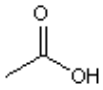
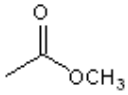
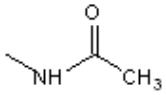
Of the halogens, Iodine has the weakest deshielding effect upon aliphatic hydrogens, but the strongest deshielding effect on the ortho aromatic hydrogens. It is observed to have an unusually strong deshielding effect upon the hydrogens bonded to beta aliphatic carbon atoms.

Aromatic Protons

Of the four halogens, iodine has the strongest deshielding effect on aromatic hydrogens, producing a shift of the ortho hydrogens to 7.65 ppm.



δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.40	7.40	-I	$CDCl_3$
7.50	7.18	-Br	$CDCl_3$
7.55	6.89	$-CH_3$	$CDCl_3$
7.55	7.95	-C≡N	Polyso l
7.58	6.78	-F	$CDCl_3$

7.61	7.09	-Cl	$CDCl_3$
7.61	7.88		$CDCl_3$
7.69	7.99		$CDCl_3$
7.71	7.90		DMSO-d_6
7.78	7.78		Polysol
7.70	7.09		TFA
7.79	7.30	-CF_3	$CDCl_3$

III. Nitrogen Containing Compounds

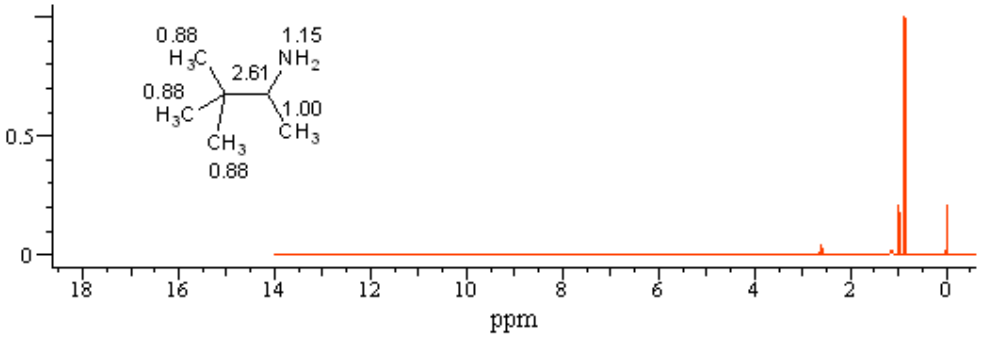
A. Amines

1. Primary

a. Aliphatic

Primary Amines

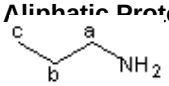
Aliphatics

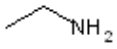
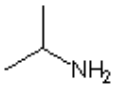
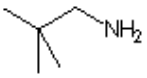


The primary amines are often relatively easy to characterize due to the presence of the -NH_2 group which appears as a broadened band at intermediate to high field (6.7-0.6 ppm).

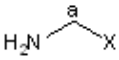
The primary amine group acts as a weak deshielding substituent on methyl, methylene and methine groups, but has a strong shielding effect upon the ortho and para aromatic hydrogens.

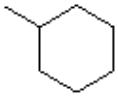
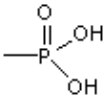
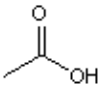
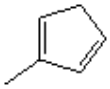
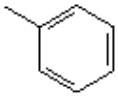
Aliphatic Protons

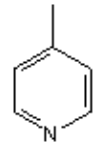


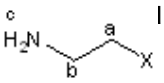
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
	1.05	2.61		D_2O
0.91	1.48	2.65		CCl_4
	(1.01)	3.04		D_2O
	(1.30)			$CDCl_3$

Substituted Methylamines

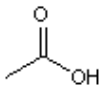
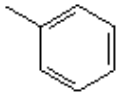


δ_a (ppm)	-X	Solvent
2.52		$CDCl_3$
3.12		D_2O
3.30	$-CH=CH_2$	$CDCl_3$
3.58		D_2O
3.76		D_2O
3.85		$CDCl_3$

3.86		$CDCl_3$



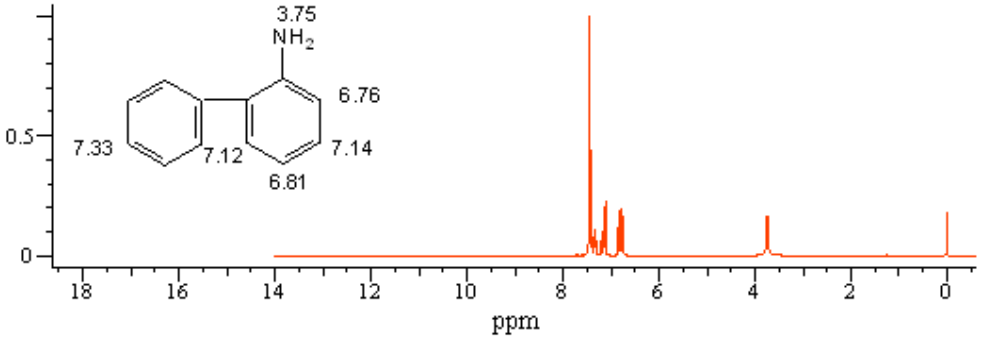
Ethylamines

δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
	2.65	1.48	$-CH_3$	CCl_4
1.55	2.99	2.49	-C≡N	D_2O
	3.18	2.53		D_2O
	2.86	2.59	-SH	D_2O
1.19	2.60	2.60	$-NH_2$	CCl_4
0.93	2.82	2.68		CCl_4

Aromatic

Primary Amines

Aromatics

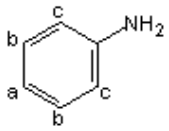


The primary amines are often relatively easy to characterize due to the presence of the $-NH_2$ group which appears as a broadened band at intermediate to high field (6.7-0.6 ppm).

The primary amine group acts as a weak deshielding substituent on methyl, methylene and methine groups, but has a strong shielding effect upon the ortho and para aromatic hydrogens.

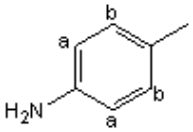
Aromatic Protons

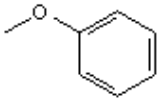
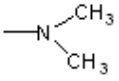
The strong shielding effect of the primary amine group on the hydrogens of benzene is evident from the chemical shifts of the parent compound, aniline.

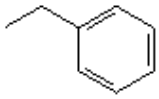
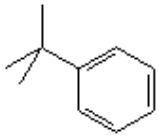
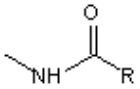
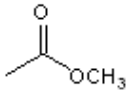
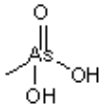
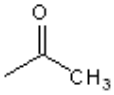
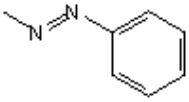


δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
6.40	7.00	6.59	CCl_4

Examples of para substituted Anilines.



δ_a (ppm)	δ_b (ppm)	-x	Solvent
6.34	6.34		$CDCl_3$
6.32	6.50	$-S-CH_3$	CCl_4
6.41	6.55	$-R_2$	$CDCl_3$
6.38	6.57	-SH	$CDCl_3$
6.59	6.59		$CDCl_3$
6.62	6.62		$CDCl_3$

6.49	6.65	-O-R_2	$CDCl_3$
6.68	6.72	-O-CH_3	$CDCl_3$
6.49	6.81		DMSO-d_6
6.75	6.92	-CF_3	$CDCl_3$
6.60	7.02	-Cl	DMSO
6.62	7.09		$CDCl_3$
6.57	7.21	-Br	$CDCl_3$
6.55	7.26		DMSO
6.77	7.36		$CDCl_3$
6.37	7.37	-I	$CDCl_3$
6.70	7.39		DMSO
6.67	7.60	-SO_2-NH-R	DMSO-d_6
6.79	7.77		$CDCl_3$
6.60	7.79		$CDCl_3$

Exchangeable Protons

The NH_2 Group

range (ppm)	-Type	Solvent
0.66-1.52	Aliphatic-NH_2	CCl_4, $CDCl_3$
1.72-1.78	Alicyclic- NH_2	CCl_4, $CDCl_3$

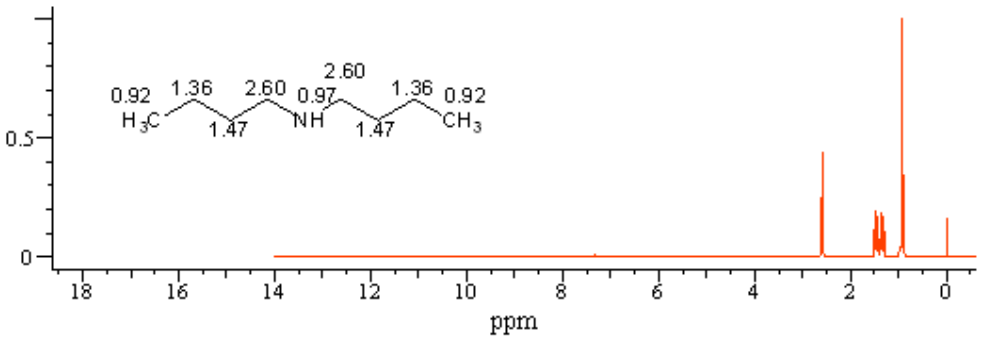
3.30-6. 70	Aromatic- NH_2	CCl_4, $CDCl_3$

2□ Secondary

a. Aliphatic

Secondary Amines

Aliphatics

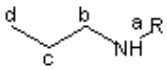


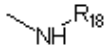
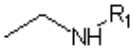
The secondary amines are similar in many respects to the primary amines except for the presence of one instead of two exchangeable hydrogens. A wider range of chemical shifts is observed because of the different types of groups bonded to the nitrogen nucleus. Phenyl substituted secondary amines display a stronger deshielding capability than their aliphatic counterparts.

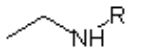
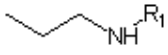
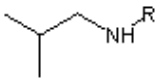
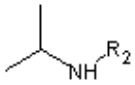
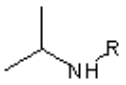
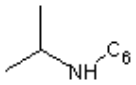
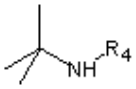
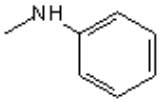
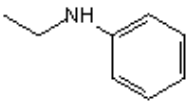
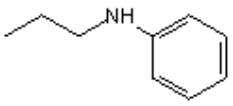
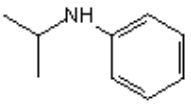
Like the primary and tertiary amines, the secondary type is capable of forming amine-acid salts upon the addition of acid to the sample solution resulting in shifts to lower field of about 0.8 ppm.

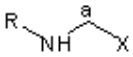
Aliphatic Protons

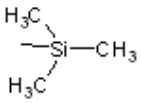
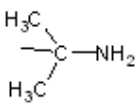
Alkyl secondary amines

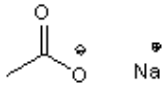
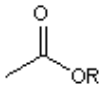
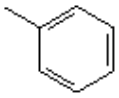
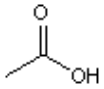


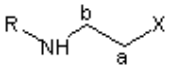
δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		2.32			D_2O
		2.32			D_2O
		2.40	1.49		$CDCl_3$
	1.09	2.60			D_2O

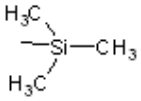
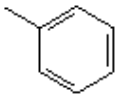
	1.11	2.65	1.23		$CDCl_3$
0.90	1.49	2.58	0.85		$CDCl_3$
(0.88)	1.60	2.31	0.79		CCl_4
	(1.02)	2.76			D_2O
	(1.00)	2.88	0.67		CCl_4
	(1.01)	2.98	1.20		$CDCl_3$
	(1.00)		0.74		$CDCl_3$
		2.67	3.34		CCl_4
	1.12	3.03	3.23		CCl_4
0.92	1.54	2.97	3.31		CCl_4
	(1.12)	3.54	3.19		CCl_4

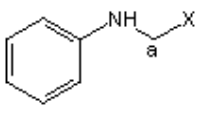


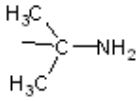
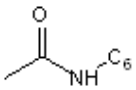
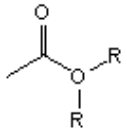
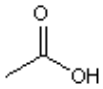
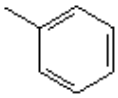
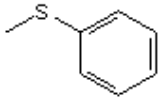
δ_a (ppm)	-X	Solvent
2.07		$CDCl_3$
2.48		$CDCl_3$

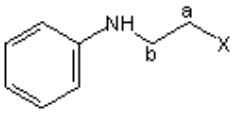
2.60	$-C_4$	$CDCl_3$
2.60	$-CH_3$	D_2O
2.65	$-CH_3$	$CDCl_3$
3.13		D_2O
3.22	$-CH=CH_2$	$CDCl_3$
3.38		CCl_4
3.41		$CDCl_3$
3.70		CCl_4
3.68		D_2O

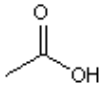


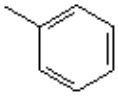
δ_b (ppm)	δ_a (ppm)	-X	Solvent
2.58	1.49	$-CH_3$	$CDCl_3$
2.61	2.61	$-NH_2$	D_2O
2.62	0.80		$CDCl_3$
2.62	3.51	-OH	CCl_4
2.70	3.41	$-O-CH_3$	CCl_4
2.76	2.90	-SH	$CDCl_3$
2.76	2.76	$-NH_2$	$CDCl_3$
2.79	2.79		$CDCl_3$
2.96	2.55	$-C\equiv N$	$CDCl_3$



δ_a (ppm)	-X	Solvent
2.83		CCl_4
3.60	$-CH=CH_2$	$CDCl_3$
3.71		$CDCl_3$
3.77	$-C\equiv N$	$CDCl_3$
3.78		$CDCl_3$
3.81		DMSO-d_6
3.97	$-C\equiv CH$	$CDCl_3$
4.22		$CDCl_3$
4.40	$-SO_2-Na$	DMSO
4.49	$-SO_2-R_8$	$CDCl_3$
4.75		$CDCl_3$



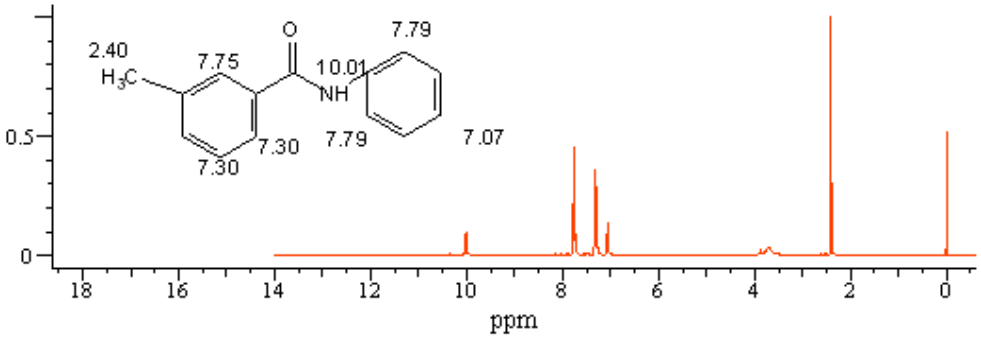
δ_b (ppm)	δ_a (ppm)	-X	Solvent
2.97	1.54	$-CH_3$	CCl_4
3.00	2.75	$-NH_2$	CCl_4
3.22	3.78	-OH	$CDCl_3$
3.28	2.50		DMSO-d_6

3.46	2.55	-C≡N	$CDCl_3$
3.46	2.92		$CDCl_3$

B Aromatic

Secondary Amines

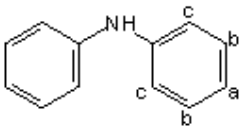
Aromatics

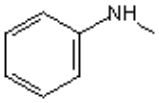


The secondary amines are similar in many respects to the primary amines except for the presence of one instead of two exchangeable hydrogens. A wider range of chemical shifts is observed because of the different types of groups bonded to the nitrogen nucleus. Phenyl substituted secondary amines display a stronger deshielding capability than their aliphatic counterparts.

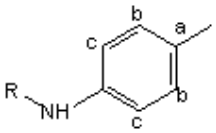
Like the primary and tertiary amines, the secondary type is capable of forming amine-acid salts upon the addition of acid to the sample solution resulting in shifts to lower field of about 0.8 ppm.

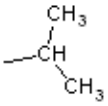
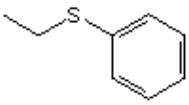
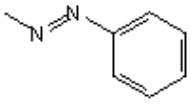
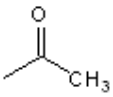
Aromatic Protons

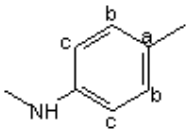


X-	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
CH_3-NH-	7.08	6.57	6.57	CCl_4
	7.20	6.83	6.83	$CDCl_3$

Para-substituted secondary amines



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
6.52	6.52	-NH-R	$CDCl_3$
6.52	6.52	-OH	$CDCl_3$
6.45	6.69	$-O-CH_3$	Polysol
6.80	6.93	$-R_4$	Polysol
6.45	6.96	$-CH_3$	$CDCl_3$
6.47	7.01		$CDCl_3$
6.55	7.07	-Cl	DMSO-d_6
6.83	7.10	$-S-CH_3$	Polysol
6.50	7.11		$CDCl_3$
6.49	7.20	-Br	$CDCl_3$
6.62	7.55	$-SO_2-NH_2$	Polysol
6.47	7.78		$CDCl_3$
6.54	7.80		$CDCl_3$
6.72	7.84	-N=O	Polysol



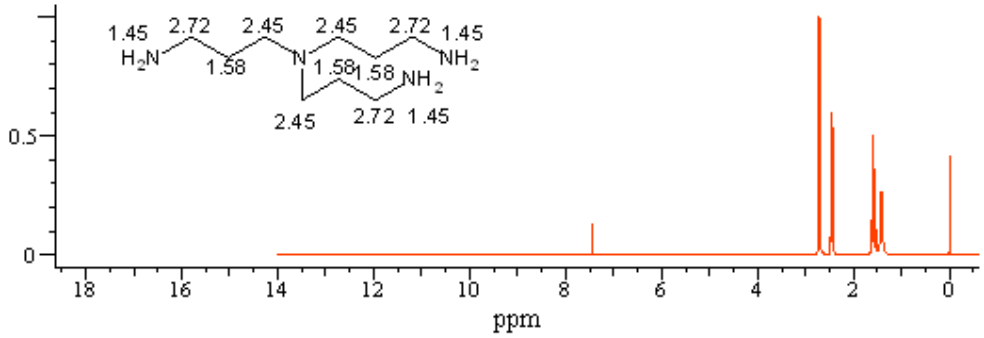
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
6.81	6.47	$-NH_2$	$CDCl_3$
7.20	6.96	$-O-CH_3$	$CDCl_3$
7.45	7.45	-Cl	Polysol
7.08	7.77	-N=O	Polysol
7.09	8.05		Acetone

3□ Tertiary

a. Aliphatic

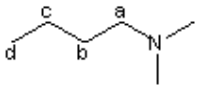
Tertiary Amines

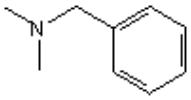
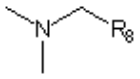
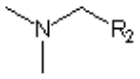
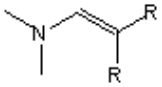
Aliphatics

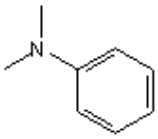
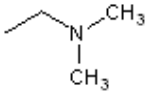
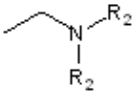
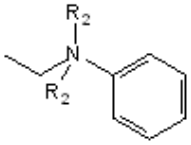
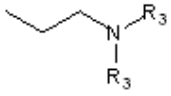
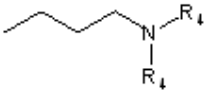
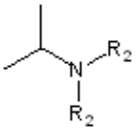


The absence of an exchangeable hydrogen attached to the tertiary amine group makes this amine more difficult to characterize than either the primary or secondary amines. The large number of aliphatic and aromatic beta shift effects produce wider chemical shift ranges than nearly any other common functional group. A simple test for the presence of any amine including the tertiary variety is the addition of a few drops of weak mineral acid. The formation of the amine salt produces significant shifts to lower field.

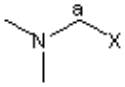
Aliphatic Protons

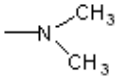
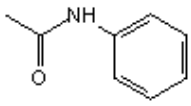


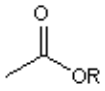
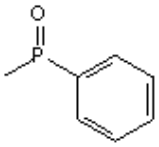
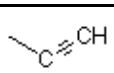
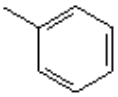
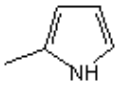
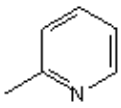
δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
			(2.14)		CCl_4
			(2.21)		$CDCl_3$
			(2.27)		$CDCl_3$
			(2.39)		$CDCl_3$

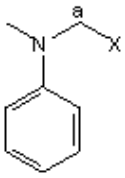
			(2.85)		CCl_4
		1.09	2.33		$CDCl_3$
		0.98	2.42		CCl_4
		1.10	3.27		CCl_4
	0.88	1.36	2.31		CCl_4
0.90	1.25	1.35	2.31		CCl_4
		(0.97)	3.02		CCl_4

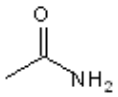
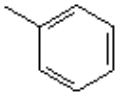
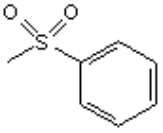
Substituted Trimethylamines

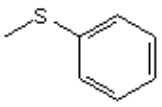


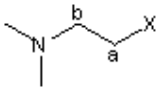
δ_a (ppm)	-X	Solvent
2.33	$-CH_3$	$CDCl_3$
2.72		$CDCl_3$
2.93	$-CH=CH_2$	$CDCl_3$
3.07		$CDCl_3$

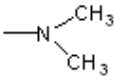
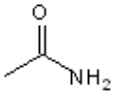
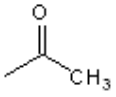
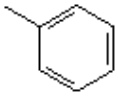
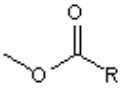
3.07		CCl_4
3.20		$CDCl_3$
3.29		$CDCl_3$
3.33		CCl_4
3.42		$CDCl_3$
3.49	-C≡N	$CDCl_3$
3.69		$CDCl_3$

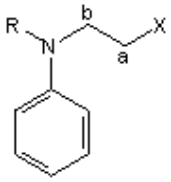


δ_a (ppm)	-X	Solvent
3.30	$-CH_3$	CCl_4
3.84	$-CH=CH_2$	CCl_4
3.95	-C≡C-R	$CDCl_3$
3.99		DMSO-d_6
4.41		CCl_4
4.70		$CDCl_3$

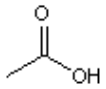
4.89		$CDCl_3$



δ_b (ppm)	δ_a (ppm)	-X	Solvent
2.41	2.41		CCl_4
2.81	2.45		D_2O
2.63	2.63	-SH	$CDCl_3$
2.41	2.69	$-NH_2$	D_2O
2.70	2.70		$CDCl_3$
2.70	2.70		$CDCl_3$
2.70	4.15		CCl_4



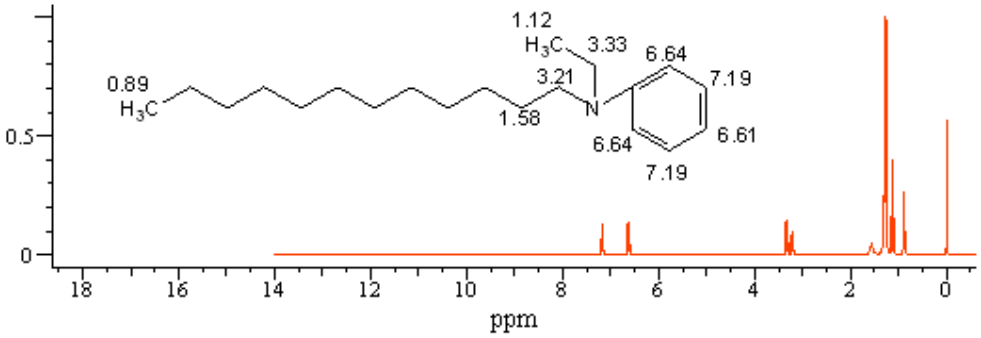
δ_b (ppm)	δ_a (ppm)	-X	Solvent
3.13	1.59	$-CH_3$	CCl_4
3.21	3.50	-OH	CCl_4

3.60	2.49		DMSO-d_6
3.61	3.61	-Cl	Polysol
3.65	2.50	-C≡N	$CDCl_3$

B Aromatic

Tertiary Amines

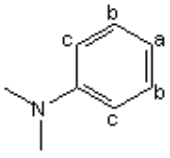
Aromatics

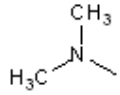


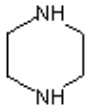
The absence of an exchangeable hydrogen attached to the tertiary amine group makes this amine more difficult to characterize than either the primary or secondary amines. The large number of aliphatic and aromatic beta shift effects produce wider chemical shift ranges than nearly any other common functional group. A simple test for the presence of any amine including the tertiary variety is the addition of a few drops of weak mineral acid. The formation of the amine salt produces significant shifts to lower field.

Aromatic Protons

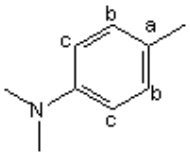
Phenyl Amines

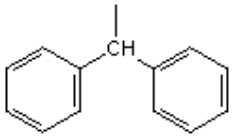
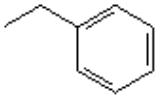
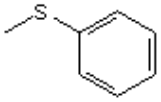
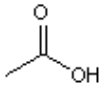


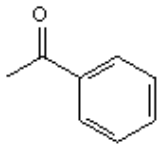
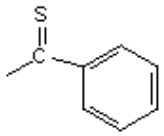
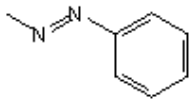
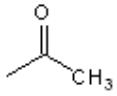
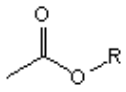
	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
	6.57	7.10	6.57	CCl_4

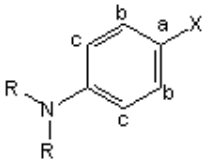
	6.56	7.07	6.48	CCl_4
	6.52	7.02	6.48	CCl_4
	6.86	7.23	6.82	$CDCl_3$
	7.05-7.60			$CDCl_3$
	6.80-7.40			$CDCl_3$

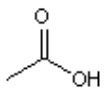
Para substituted aromatics

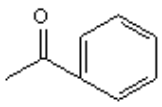
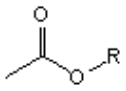


δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
6.62	6.62	$-NH_2$	$CDCl_3$
6.79	6.79	$-O-CH_3$	$CDCl_3$
6.77	7.00		$CDCl_3$
6.62	7.01		$CDCl_3$
6.53	7.25	-Br	$CDCl_3$
6.63	7.33		$CDCl_3$
6.63	7.63		$CDCl_3$
6.60	7.70	-N=O	$CDCl_3$

6.65	7.73		$CDCl_3$
6.61	7.73		$CDCl_3$
6.60	7.80		$CDCl_3$
6.71	7.95		$CDCl_3$
6.69	7.99		$CDCl_3$
6.58	8.08		$CDCl_3$

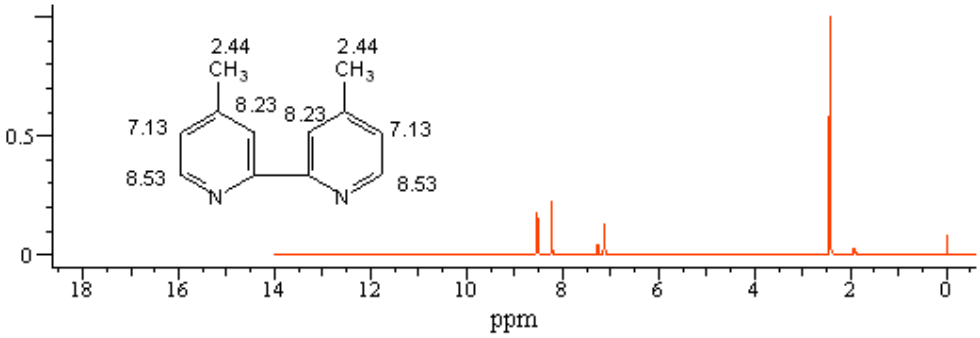


δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
6.59	6.59	$-NH_2$	$CDCl_3$
6.76	6.76	$-O-CH_3$	$CDCl_3$
6.59	7.01	$-CH_3$	$CDCl_3$
6.70	7.15	-Cl	DMSO-d_6
6.48	7.20	-Br	$CDCl_3$
6.58	7.35	-C≡N	$CDCl_3$
6.57	7.56		$CDCl_3$

6.62	7.75		$CDCl_3$
6.78	7.77		$CDCl_3$
6.65	7.79	-N=O	$CDCl_3$
6.71	7.84	-N=N-O	$CDCl_3$
6.70	8.02		$CDCl_3$
6.59	8.08		$CDCl_3$

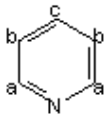
2 Pyridines

Pyridines



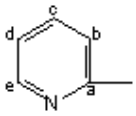
The proton NMR spectra of the pyridines produce characteristic patterns over a wide range of chemical shifts. The chemical shifts of the individual ring protons and the coupling constants with other protons on the ring vary with their position relative to the pyridine nitrogen atom. The characteristic low field chemical shifts observed for the hydrogens at positions 2 and 6 (adjacent to the ring nitrogen atom) are a distinct aid in the identification of the NMR spectra of this class of compounds.

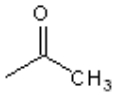
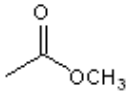
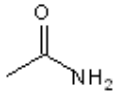
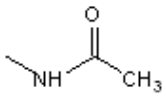
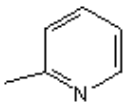
Aromatic Protons



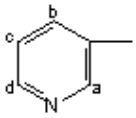
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
7.55	7.14	8.51	Pyridine	CCl_4

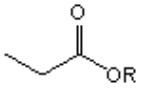
2-Substituted Pyridines



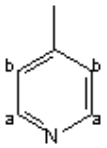
δ_e (ppm)	δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
7.93	6.48	7.22	6.36	$-NH_2$	$CDCl_3$
8.07	6.45	7.36	6.45	-NH-R	$CDCl_3$
8.14	6.83	7.52	6.68	$-O-CH_3$	CCl_4
8.18	7.14	7.77	6.89	-F	CCl_4
8.46	6.98	7.48	7.05	$-CH_2-CH_3$	CCl_4
8.37	7.20	7.68	7.29	-Cl	CCl_4
8.27	7.20	7.48	7.38	-Br	CCl_4
8.76	7.60	7.75	7.89	-C≡N	CCl_4
8.71	7.39	7.81	7.90		CCl_4
8.78	7.58	7.91	7.91		CCl_4
8.70	7.46	7.81	8.03		CCl_4
8.57	7.41	7.83	8.21		$CDCl_3$
8.27	7.03	7.70	8.27		$CDCl_3$
8.67	7.25	7.77	8.42		$CDCl_3$

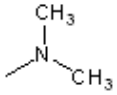
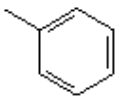
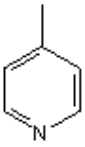
3-Substituted Pyridines



δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	-X	δ_a (ppm)	-X	Solvent
7.92	6.95	6.95	-X	8.04	$-NH_2$	$CDCl_3$
8.32	7.01	7.35	-X	8.36	$-CH_3$	CCl_4
8.33	7.10	7.42	-X	8.38	$-CH_2-CH_3$	CCl_4
8.41	7.15	7.59	-X	8.52	-Cl	CCl_4
8.50	7.21	7.62	-X	8.53		$CDCl_3$
8.48	7.10	7.74	-X	8.66	-Br	CCl_4

4-Substituted Pyridines



δ_b (ppm)	δ_a (ppm)	X	Solvent
8.03	6.50	$-NH_2$	Polysol
8.25	6.50		$CDCl_3$
8.37	6.98	$-CH_3$	CCl_4
8.41	7.02	$-CH_2CH_3$	CCl_4
8.51	7.26	$-CH_2-NH-CH_3$	$CDCl_3$
8.63	7.40		$CDCl_3$
8.71	7.51		$CDCl_3$

8.82	7.64		CCl_4

Coupling and Coupling Constants

The spin-spin couplings of the pyridines is limited to those between hydrogens on the ring. The protons at positions 2 and 6 often display an observable degree of broadening due to the adjacent nitrogen nucleus.

The coupling constants observed for the pyridines are unusual in that long range "para" couplings are observed through five bonds and that the two "ortho" couplings ^{J}2-3 and ^{J}3-4 are different in magnitude.

^{J}2-3 = 4-7 Hz

^{J}3-4 = 7-9 Hz

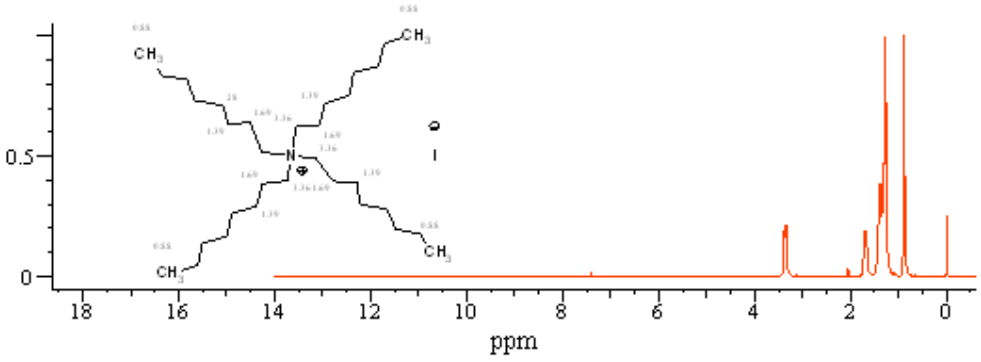
^{J}2-4 = 1-3 Hz

^{J}2-5 = 0.1-1.1 Hz

^{J}3-5 = 1.1-2.5 Hz

3 Quaternary Ammonium Salts

Quaternary Ammonium Compounds

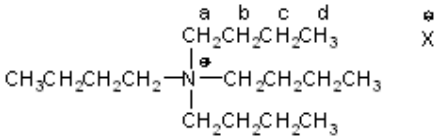


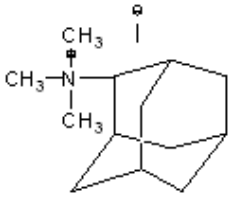
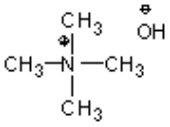
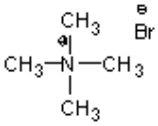
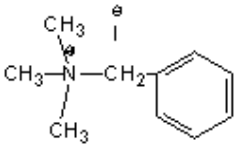
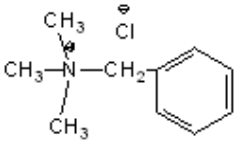
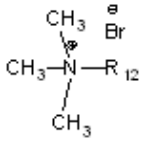
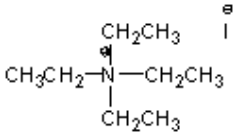
The quaternary ammonium compounds display low field chemical shifts for the aliphatic groups bonded to the nitrogen atom. The groups often show a certain degree of broadening, possibly due to unresolved coupling to the nitrogen nucleus. The compounds are more soluble in $D_2O$and DMSO-d_6 than the corresponding tertiary amines.

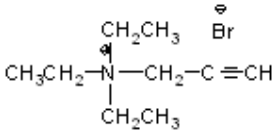
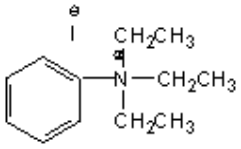
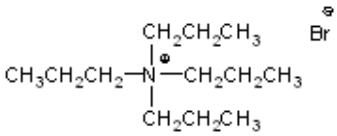
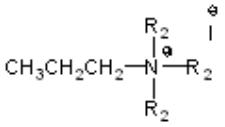
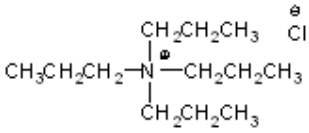
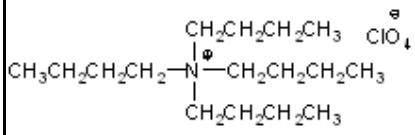
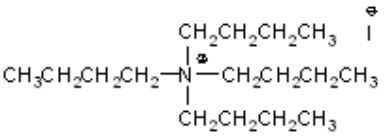
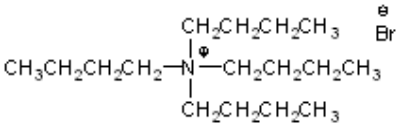
Relatively large ranges of chemical shifts are observed for similar groups on different environments. No consistant

correlation with solvent, concentration or anion has been observed to explain these variations.

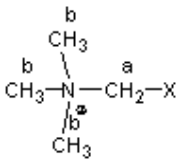
Aliphatic Protons



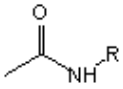
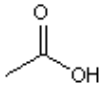
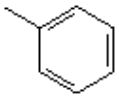
δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
			(2.99)		D_2O
			(3.15)		D_2O
			(3.21)		D_2O
			(3.30)		Polysol
			(3.40)		$CDCl_3$
			(3.48)		$CDCl_3$
		(1.26	3.24)		D_2O

		(1.30	3.40)		Polysol
		(1.28	3.95)		D_2O
	(0.92	1.70	3.16)		D_2O
	(1.08	1.92	3.35)		$CDCl_3$
	(1.08	1.81	3.39)		$CDCl_3$
(1.02	1.45	1.70	3.22)		TFA
(1.03	1.45	1.60	3.41)		$CDCl_3$
(1.01	1.43	1.65	3.42)		$CDCl_3$

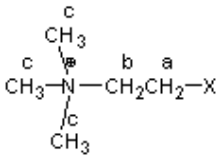
Substituted Methyl Ammonium Compounds

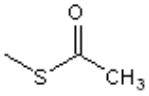
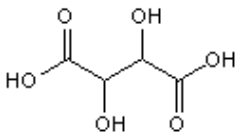
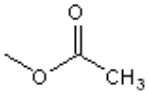
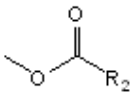


δ_b (ppm)	δ_a (ppm)	-X		Solvent

(3.29)	3.48	$-C_3$	I^-	Polysol
(3.12)	3.95	$-CH=CH_2$	Br^-	D_2O
(3.31)	4.09		Cl^-	D_2O
(3.30)	4.22		Cl^-	D_2O
(3.15)	4.53		Br^-	D_2O

2-Substituted Ethyl Ammonium Compounds



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X		Solvent
3.29	3.55	3.31		I^-	Poly so l
3.19	3.80	3.80	-Br	Br^-	D_2O
3.18	3.49	4.02	-OH		D_2O
3.26	3.81	4.03	-Cl	Cl^-	D_2O
3.26	3.79	4.55		Br^-	D_2O
3.30	3.80	4.57		I^-	D_2O

Olefinic Protons

The trimethylammonium group has an unusually strong and long range deshielding effect on the two terminal olefinic

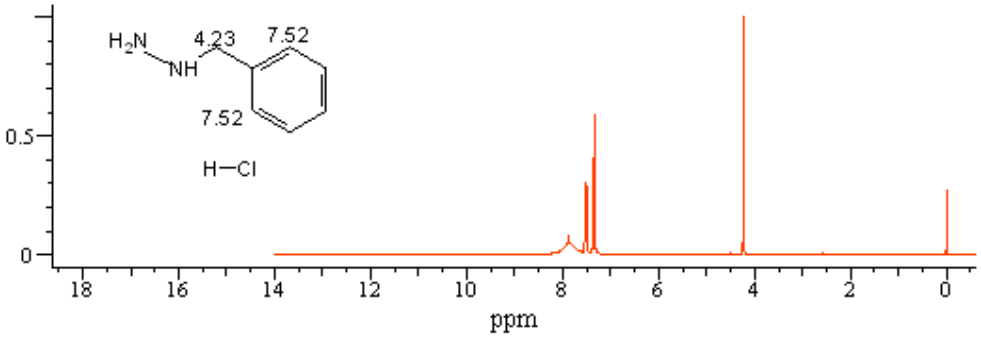
protons of allyl groups. In the spectrum of Allyltrimethylammonium Bromide, all three olefinic protons resonate in the chemical shift range from 5.4 to 6.2 ppm as a higher order ABC pattern. Normally, the terminal olefinic protons of allyl groups resonate at about 5.1 ppm as the AB portion of an ABX system.

Aromatic Protons

The chemical shifts of the quaternary ammonium aromatic compounds are dependent to a significant degree upon the solvent employed and/or the amount of water present in the sample solution. As an example, when benzyl trimethyl ammonium chloride was examined in $CDCl_3$ the ortho protons are strongly deshielded in relation to the meta and para hydrogens. In Polysol and DMSO-d_6 solution, all five protons resonate as a single complex band. In D_2O solution, the five protons appear as a single sharp peak at about 7.5 ppm. A somewhat similar case of solvent deshielding is noted in which the aromatic protons of the compound examined in $CDCl_3$ solution resonate at lower field than those of a similar compound in D_2O.

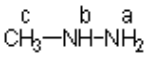
4 Hydrazines

Hydrazines

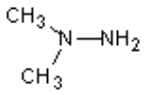


The chemical shifts produced by Hydrazine substituents are similar to those observed for the corresponding primary, secondary or tertiary amines. The hydrazine protons, on the average, resonate midway between the high field resonance of the aliphatic amines and the low field resonance of the aromatic amine protons. The presence of a Hydrazine linkage in a molecule could be detected most easily if the integration ratio indicated either more hydrocarbon groups or more exchangeable hydrogens than a simple amine group could accommodate. As with the amines, the Hydrazine group undergoes salt formation upon the addition of acid to the sample solution producing a shift to lower field for the Hydrazine protons and the protons of aliphatic or aromatic groups bonded to it.

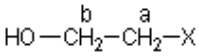
Aliphatic Protons

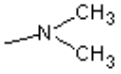


δ_c (ppm)	δ_b (ppm)	δ_a (ppm)		Solvent

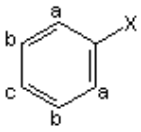
(2.35)		3.00		CCl_4
2.61	3.36	3.36	CH_3-NH-NH_2	CCl_4

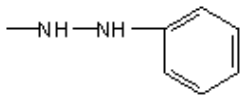
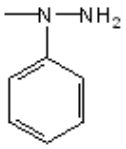
The series of substituted ethanols presented below illustrates the comparative deshielding effect of the amines and hydrazines.



δ_b (ppm)	δ_a (ppm)	-X	Solvent
3.47	2.38		CCl_4
3.69	2.69	-NH-CH_3	D_2O
3.54	2.73	-NH_2	$CDCl_3$
3.74	2.93	-NH-NH_2	D_2O

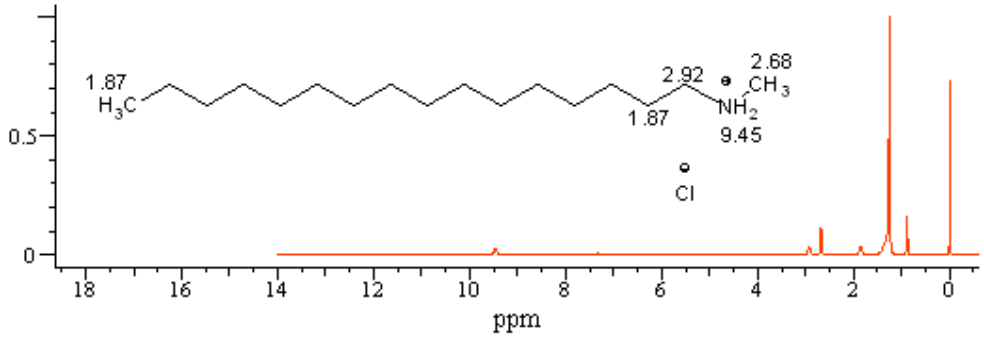
Aromatic Protons



δ_c (ppm)	δ_b (ppm))	δ_a (ppm)	-X	Solvent
6.52	7.00	6.52	-NH-NH_2	CCl_4
6.60	7.07	6.76		DMSO-d_6
1.2-2.1	1.2-2.1	3.72		$CDCl_3$

5 Amine Salts

Amine Salts

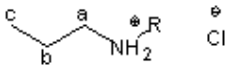


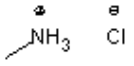
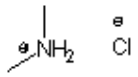
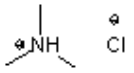
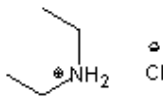
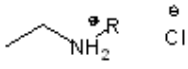
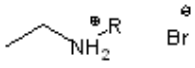
The reaction of mineral acids with primary, secondary and tertiary amines to form amine salts not only makes the compounds more soluble in polar solvents such as D_2O, but increases the deshielding effect of the amine group on both aliphatic and aromatic hydrogens.

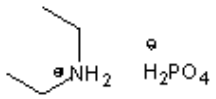
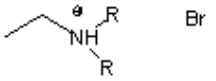
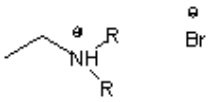
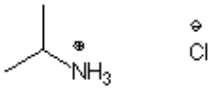
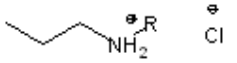
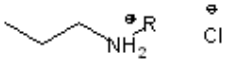
The exchangeable hydrogens attached to the nitrogen nucleus normally resonate at a lower field than the corresponding hydrogens of the free amine.

The amine salts can be neutralized by the addition of a few drops of a sodium bicarbonate solution to the sample. The amine salt is thus converted to the free base form with an attendant shift to higher field for proton containing groups bonded to the nitrogen atom.

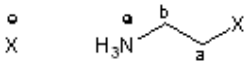
Aliphatic Protons

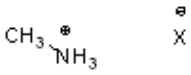
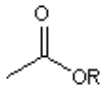
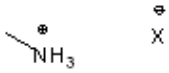
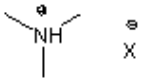


δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		2.62		D_2O
		(2.76)		D_2O
		(2.94)		D_2O
	(1.45	3.03)		$CDCl_3$
	1.30	3.08		D_2O
	1.22	3.10		D_2O

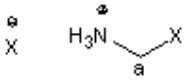
	(1.30	3.10)		D_2O
	1.41	3.31		D_2O
	1.50	3.37		$CDCl_3$
	(1.29)	3.33		DMSO-d_6
0.93	1.76	2.91		$CDCl_3$
1.11	1.99	3.39		TFA

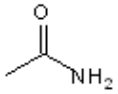
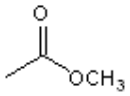
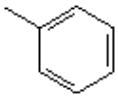
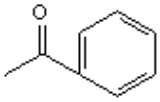
2-Substituted Ethylamine salts



δ_b (ppm)	δ_a (ppm)	-X	Solvent
2.75	1.64	$-CH_3$	DMSO-d_6
3.19	2.22		D_2O
3.22	2.85	-SH	D_2O
3.36	2.85		D_2O
3.27	3.40	$-SO_3H$	D_2O
3.42	3.42		D_2O
3.75	3.55	-Br	D_2O
3.55	3.55		D_2O
3.18	3.85	-OH	D_2O
3.48	4.01	-Cl	D_2O

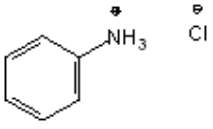
Substituted Methylamine salts

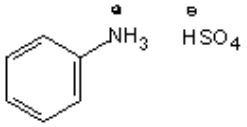
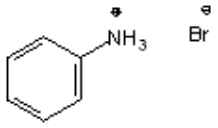
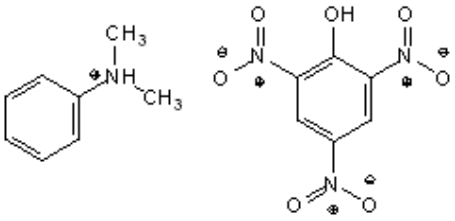
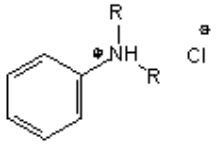


δ_a (ppm)	-X	Solvent
2.90		D_2O
3.08	$-CH_3$	D_2O
3.09	$-R_3$	$CDCl_3$
3.60	$-CH=CH_2$	Polysol
3.88		D_2O
3.99		D_2O
4.19	$-C\equiv N$	D_2O
4.27		D_2O
4.29		D_2O
5.05		TFA

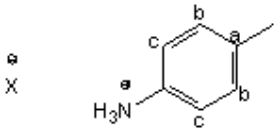
Aromatic Protons

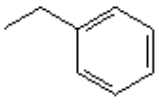
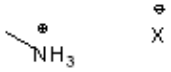
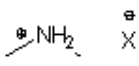
As a substituent on an aromatic ring, the amine salt group has an unusually uniform effect on the chemical shifts of the ortho, meta and para hydrogens. The series of aniline salts presented indicate the minimal effect that the type of acid involved, the solvent employed and the degree of amine substitution have on the chemical shift of the phenyl protons. The aromatic resonance for all of these aniline salts appears as a relatively sharp peak in the narrow chemical shift range from 7.50-7.55 ppm.

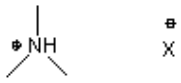
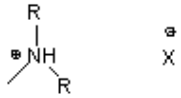
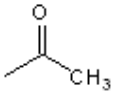
δ (ppm)	Compound	Solvent
7.51		D_2O

7.51		TFA
7.54		D_2O
7.54		DMSO-d_6
7.55		D_2O

Para substituted aniline salts



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
7.19	6.67	-O-R_2	D_2O
7.22	6.88	-OH	DMSO-d_6
7.44	7.09	-O-CH_3	D_2O
7.33	7.33	-CH_3	TFA
7.67	7.39	-Br	D_2O
7.46	7.46		D_2O
7.56	7.56	-Cl	D_2O
7.78	7.78		D_2O
7.78	7.78		D_2O

7.79	7.79		D_2O
7.79	7.79		D_2O
7.20	7.90		DMSO-d_6

Exchangeable Protons

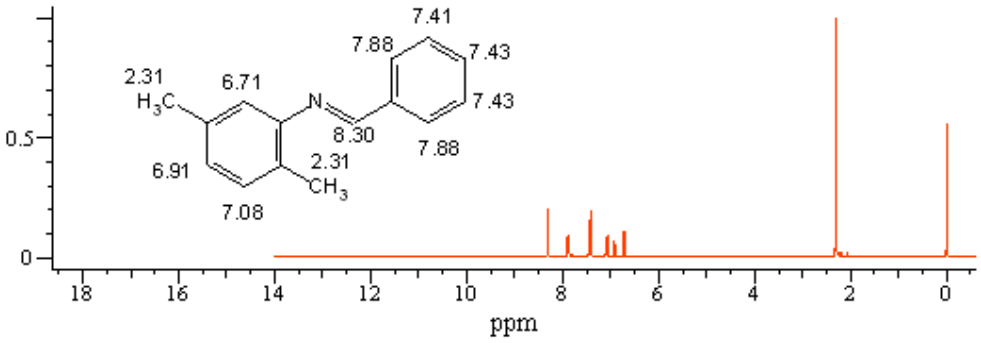
The chemical shifts of the exchangeable protons of the amine salts are especially unreliable. Because they are sensitive to sample concentration, the presence of H_2O and structural differences involving substitution of the amine nitrogen nucleus, they are observed to resonate over a wide range of chemical shifts from 5.0 to 12.0 ppm.

The corresponding chemical shift range for primary and secondary amines (not salts) is about 1.5 ppm (1.0-2.5 ppm).

There does not appear to be any relationship between the type of acid used to form the salt and the chemical shift of the resultant exchangeable hydrogens.

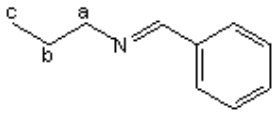
6 Ylidene Compounds (-CH=N-)

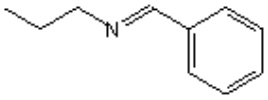
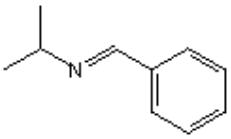
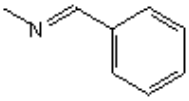
Ylidene Compounds

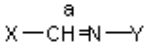


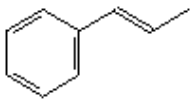
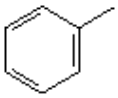
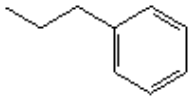
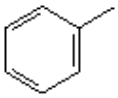
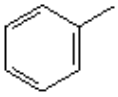
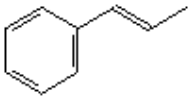
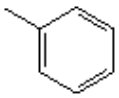
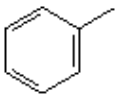
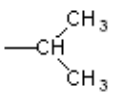
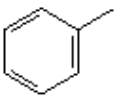
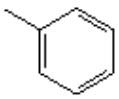
The benzylidene and cinnamylidene compounds correspond to oxime-like structures in which the -OH has been replaced by a hydrocarbon group. Because both sides of the CH=N group are substituted by bulky hydrocarbon groups, syn-/anti- isomerism is not ordinarily observed in the NMR spectra. It is assumed that the compounds exist primarily in the anti- form (substituents on opposite sides of the CH=N bond).

The spectra characteristically display a single band at relatively low field (7.9-8.4 ppm). For the benzylidene compounds the band is a sharp singlet, for the cinnamylide compounds the band appears as a sharp triplet or doublet of doublets.



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
0.95	1.69	3.49		$CDCl_3$
	(1.23)	3.48		CCl_4
		3.41		$CDCl_3$



X	δ_a (ppm)	Y	Solvent
	7.95	-R	$CDCl_3$
	8.07		$CDCl_3$
	8.11	$-CH_3$	$CDCl_3$
	8.13	$-R_3$	$CDCl_3$
	8.15		$CDCl_3$
	8.18		CCl_4
	8.40		$CDCl_3$

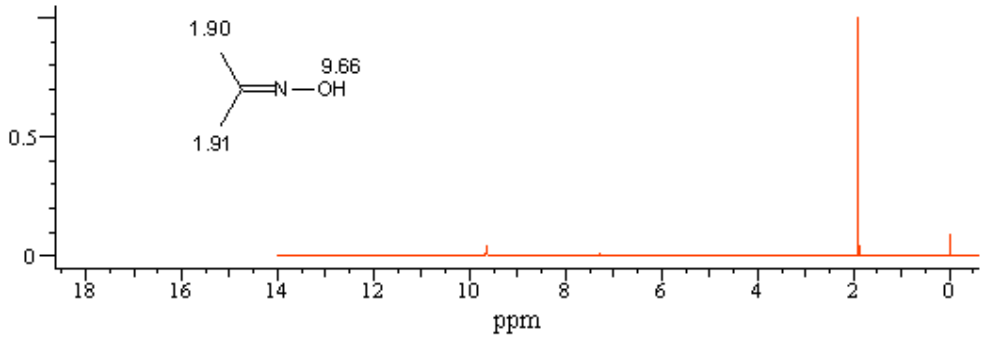
Coupling and Coupling Constants

Aliphatic groups are observed to couple weakly across the—CH=N— bond. The couplings vary from a slight broadening effect (J less than 0.8 Hz) to clear 5 Hz multiplets in the case of the cinnamylidene compounds.

$^{J}CH_3$-N=CH= =2 Hz
$^{J}CH_2$-N=CH- = 0-1 Hz
^{J}C=CH-CH=N- = 4-5 Hz

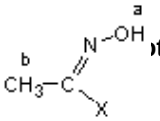
7 Oximes (-CH=N-OH)

Oximes

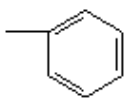


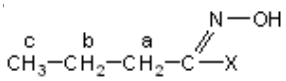
The oximes of aldehydes which contain an HO—N=CH— group are easily identified by the presence of two clear n+1 multiplets in the range from 6.4 to 7.5 ppm arising from the syn and (anti) forms of the CH=N proton. The oximes of ketones (HO—N=C(R)—R) do not possess such a proton and are thus more difficult to characterize. Both forms possess an N—OH hydroxyl group which usually appears as a rather broad resonance band in the chemical shift range from 7.8 to 9.6 ppm.

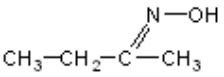
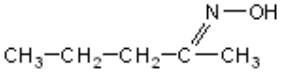
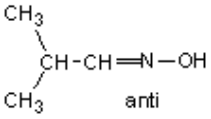
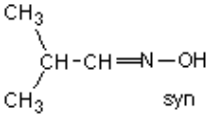
The deshielding effect of the oxime group is similar to that of the C=C group of the alkenes.

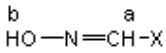


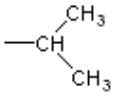
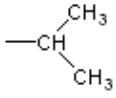
tons

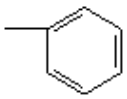
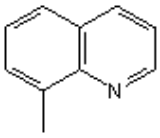
δ_b (ppm)	δ_a (ppm)	X	Solvent
1.88	7.98	-H	$CDCl_3$
1.88	9.08	$-R_3$	$CDCl_3$
1.89	9.55	$-R_2$	$CDCl_3$
2.25			$CDCl_3$

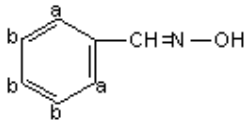


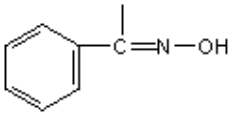
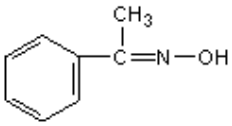
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
	1.09	2.22		$CDCl_3$
0.91	1.56	2.25		$CDCl_3$
	(1.10)	2.44		CCl_4
	(1.08)	3.19		CCl_4



δ_b (ppm)	δ_a (ppm)	-X	Solvent
9.80	6.44	$-R_6$	$CDCl_3$
8.45	6.44		CCl_4
9.80	6.71	$-R_6$	$CDCl_3$
7.98	6.83	$-CH_3$	$CDCl_3$
8.45	7.23		CCl_4
7.98	7.45	$-CH_3$	$CDCl_3$
	7.82	-CH=N-OH	DMSO

9.91	8.21		$CDCl_3$
7.52	9.42		$CDCl_3$



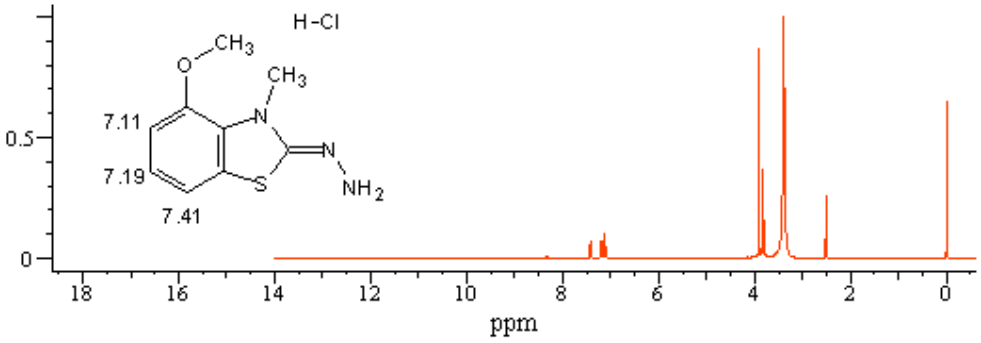
δ_b (ppm)	δ_a (ppm)	X	Solvent
7.1-7.4	7.52	-CH=N-OH	$CDCl_3$
7.2-7.6	7.78		$CDCl_3$
7.2-7.6	7.88		$CDCl_3$

Coupling and Coupling Constants

Coupling between the CH=N proton and adjacent aliphatic groups is similar in magnitude to that of the corresponding coupling of the alkenes, ^{J}CH-CH=N = 6.0-7.0 Hz.

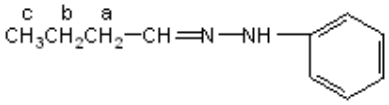
8 Hydrazones (-CH=N-NH_2)

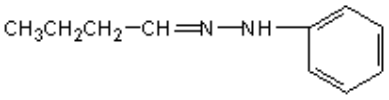
Hydrazones

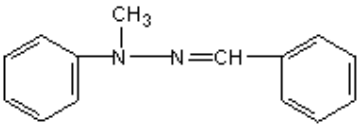
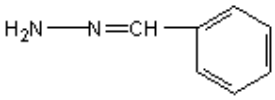
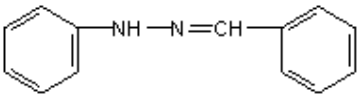
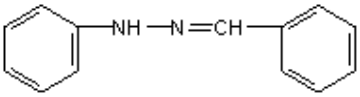


The hydrazones which are primarily used as derivatives for the characterization of ketones and aldehydes produce rather wide ranges of chemical shifts for the —CH=N— proton and for the various types of NH hydrogens. Both groups are quite sensitive to the substituent and its position on adjacent aromatic rings, various nitro-phenyl hydrazones being a common variety.

Aliphatic Protons

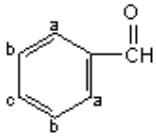


δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
0.96	1.51	2.12		CCl_4

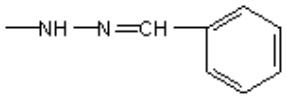
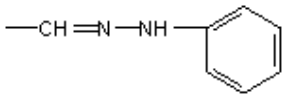
Range (ppm)	Group	Structure
3.35-3.42	CH_3-	
5.37-6.53	NH_2-	
6.90-10.98	-NH-	
7.27-8.06	-N=CH-	

Aromatic Protons

The aromatic hydrogens of phenyl groups bonded to the hydrazone group cover a relatively wide range of

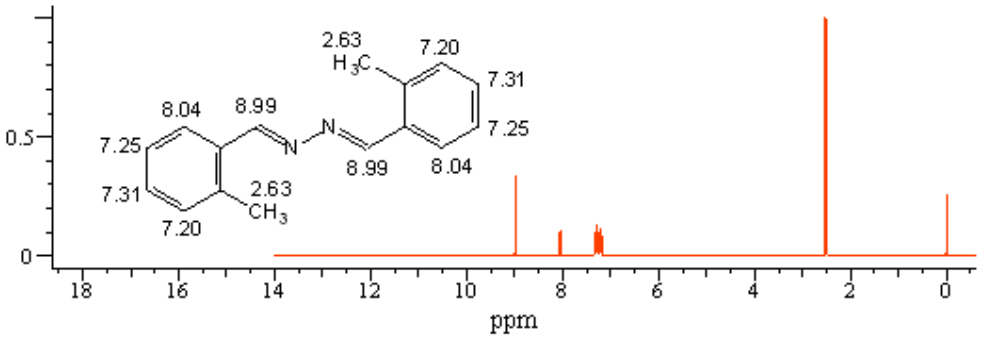


he carbon side of the group is a moderately strong deshielding group in relation to the ortho amine side of the group shields the para hydrogen rather strangely. Because two different esent the aromatic patterns can become quite complex.

δ_c (ppm)	δ_b (ppm)	δ_a (ppm)		Solvent
6.73	6.9-7.4	6.9-7.4		Acetone
6.9-7.4	6.9-7.4	7.60		Acetone

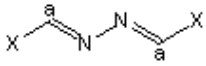
9 Azines (-CH=N-N=CH-)

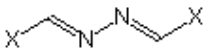
Azines



The symmetrical structure of the azine group generally produces less complex spectra than groups such as the Hydrazones. Azine derivatives are usually produced from only one type of aromatic aldehyde so that the two protons of the azine group are equivalent. In compounds synthesized utilizing two different aromatic aldehydes, the azine protons will appear as separate resonances at low field.

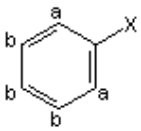
The overall range of chemical shifts for some azines was found to be:

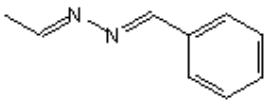


δ_a (ppm)	Compound	Solvent
8.51-9.01 ppm		$CDCl_3$, Polysol

As observed for the Hydrazones, the -CH=N- group deshields the ortho aromatic hydrogens which resonate at about 7.78 ppm for a phenyl group.

Aromatic Protons



δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.1-7.5	7.78		CCl_4

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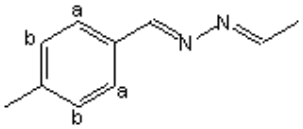
para-substituted Azines



δ_b (ppm)	δ_a (ppm)	para	Solvent
7.78	6.95	$-O-CH_3$	$CDCl_3$
7.72	7.22	$-CH_3$	$CDCl_3$

Coupling and Coupling Constants

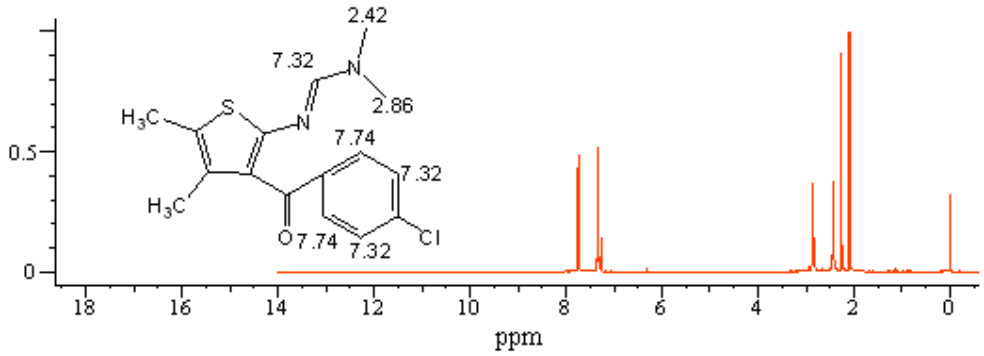
The band arising from the azine protons usually appears slightly broadened indicating the possibility that a very small coupling may exist between it and the ortho aromatic hydrogens. If the coupling in fact does exist it is quite small, less than 0.8 Hz. Derivatives of cinnamaldehyde which result in an olefinic bond adjacent to the azine linkage display clear coupling between the azine protons and the olefinic hydrogens. Although this proton appears as a triplet, equal coupling across the C—C double bond is unlikely and the triplet probably represents a higher order multiplet of the ABX type. A coupling constant of about 5 Hz for the protons of C=CH-CH=N- appears reasonable.

Solvent Effects

The simple aromatic azines are soluble in the halogenated hydrocarbons such as CCl_4 and $CDCl_3$. More polar solvents such as Polysol or DMSO-d_6 may be required depending upon the type of substituents on the aromatic rings. There does not appear to be any special chemical shift relationship between the azine protons and the solvent employed.

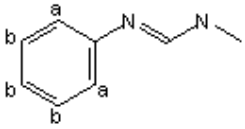
10 Amidines (-N=CH-N)

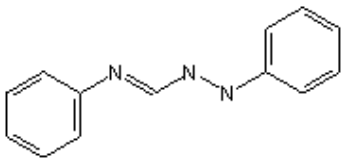
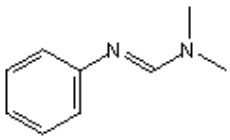
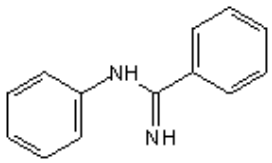
Amidines

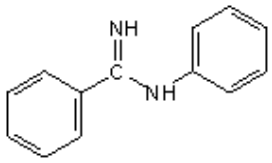


The most characteristic feature of the Amidines is the appearance of the -CH=N- proton as a relatively sharp singlet near 7.3 ppm. The chemical shifts and multiplets observed in the spectra can appear in a large number of possible combinations of aliphatic and aromatic groups.

The methyl resonance of the dimethyl formamidines is fairly constant in chemical shift resonating in the range from 2.8 to 3.0 ppm. As a substituent, the nitrogen nucleus on the N=CH side of the linkage is observed to be a relatively strong shielding group in its effect on the ortho aromatic hydrogens. Exchangeable –NH- protons, when present can appear as very broad bands at low field or as relatively sharp bands at much higher field. Because the CH=N proton is isolated from other proton groups by the two nitrogen atoms, it does not display any clear couplings.



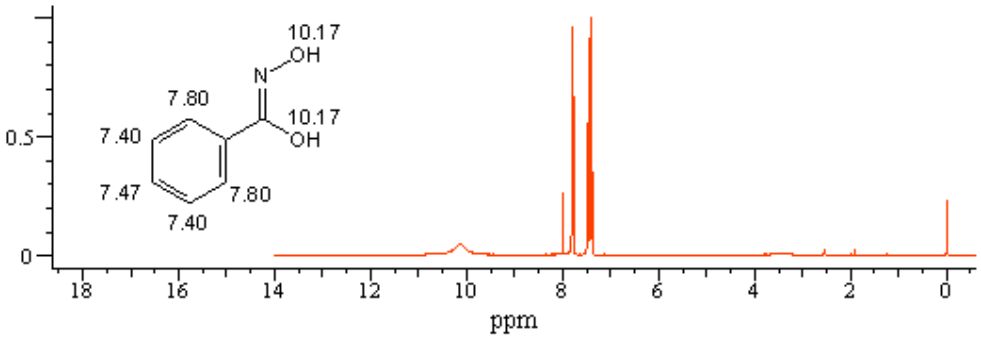
δ_b (ppm)	δ_a (ppm)	Compound	Solvent
6.8-7.3	6.75		CCl_4
6.9-7.3	6.80		CCl_4
6.9-7.5	6.85		DMSO-d_6

7.2-7.5	7.91		DMSO-d_6

Some spectra display extremely similar aromatic patterns for these symmetrically substituted amidine groups. It can be inferred that one is observing an "averaged" structure via resonance in which the double bond is shared by the nitrogen atoms endowing them with identical shielding/deshielding effects. This phenomenon is not observed in the unsymmetrical structures of this type.

11 Hydroxamic Acids

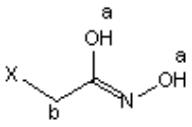
Hydroxamic Acids



Although traditionally structured as N-Hydroxyamides, infrared spectral evidence indicates that the Hydroxamic Acids possess a Hydroxyoxime-like structure of the type R-C(OH)=N-OH. The group has a weakly deshielding effect on adjacent hydrocarbon group protons but a strongly deshielding effect on the ortho aromatic hydrogens. The two OH protons are usually in exchange and resonate as a single, rather broad band at low field (8-11 ppm).

The Hydroxamic acids are generally more soluble in DMSO-d_6, polysol and trifluoroacetic acid than in deuterochloroform or carbon tetrachloride.

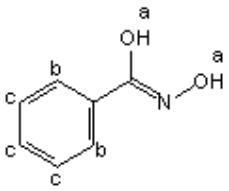
Aliphatic Protons

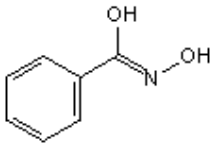


-X	δ_b (ppm)	δ_a (ppm)	Solvent
R_4-	2.20	ca. 8.60	$CDCl_3$
R_{15}-	2.51		TFA
$(R)_2$-C=CH-	2.81	8.1-9.6	Polysol

C_6-O-	4.04	ca. 8.54	Polysol

Aromatic Protons



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.2-7.6	7.80	~10.2		Polysol

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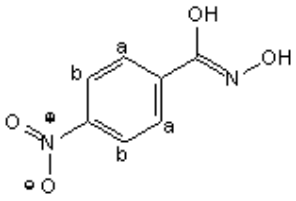
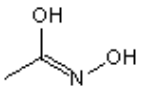
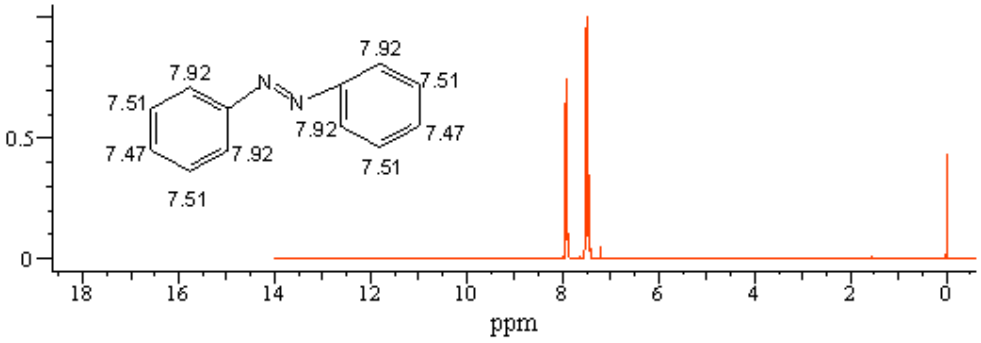


δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
-NO_2	8.29	8.07		Polysol

12 Azo Compounds (-N=N-)

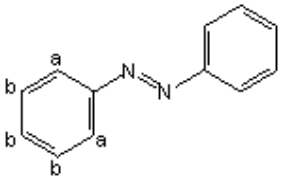
AZO Compounds

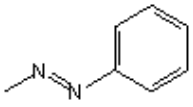


The AZO linkage between aromatic rings acts as a strong deshielding group on the ortho hydrogens. Due to the bulk of the aromatic rings, these compounds most likely exist only in the anti- form.

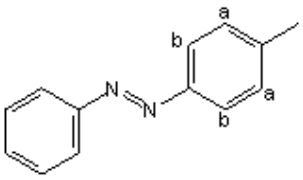
The only major solvent effect upon the deshielding ability of the AZO linkage is observed when these compounds are scanned as solutions in Trifluoroacetic acid. For these solutions, the hydrogens ortho to the AZO linkage are deshielded by an additional 0.3-0.4 ppm. The AZO compounds are readily soluble in $CDCl_3$, depending upon the nature of the other substituents present in the compound.

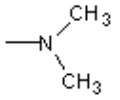
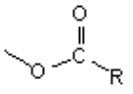
Aromatic Protons

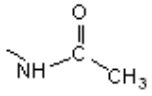
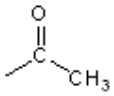
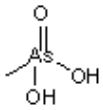
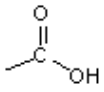


δ_b (ppm)	δ_a (ppm)	X	Solvent
7.4-7.8	7.96		$CDCl_3$

Para substituted Azobenzenes

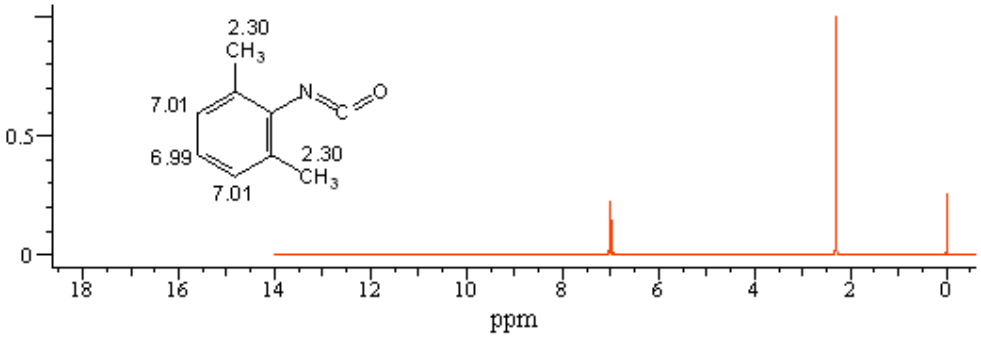


δ_b (ppm)	δ_a (ppm)	para	Solvent
7.78	6.47	-NH-CH_3	$CDCl_3$
7.83	6.63		$CDCl_3$
7.80	7.00	-OH	DMSO-d_6
7.90	7.00	-O-CH_3	$CDCl_3$
7.82	7.11	-F	$CDCl_3$
7.87	7.20		$CDCl_3$

7.80	7.30	$-CH_3$	$CDCl_3$
7.92	7.30	$-R_2$	$CDCl_3$
7.73	7.31	$-S-CH_3$	$CDCl_3$
7.81	7.40	-Cl	$CDCl_3$
7.70	7.70		Poly so l
7.88	7.88	$-SO_3Na$	DMSO
7.79	7.98		$CDCl_3$
8.01	8.01		DMSO
8.08	8.17	$-SO_2-Cl$	$CDCl_3$
7.90	8.21		$CDCl_3$
7.98	8.24		DMSO
7.92	8.32		$CDCl_3$

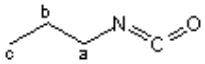
13 Isocyanates (-N=C=O)

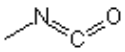
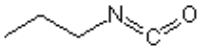
Isocyanates



The isocyanate group has a moderate deshielding effect on aliphatic protons but a slight shielding effect on the ortho aromatic hydrogens.

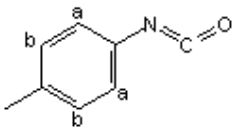
Aliphatic Protons

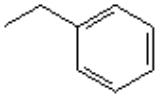


δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
		3.01		$CDCl_3$
0.98	1.61	3.29		$CDCl_3$
(1.1-	1.9)	3.24		CCl_4
(1.1-	1.9)	3.29	CH_3-$(CH_2)_{10}$-CH_2-N=C=O	CCl_4

Aromatic Protons

Phenyl Isocyanates



δ_b (ppm)	δ_a (ppm)	para	Solvent
7.02	6.81	-O-CH_3	$CDCl_3$
6.98	7.07		Polysol
7.10	7.10	-O-CF_3	CCl_4

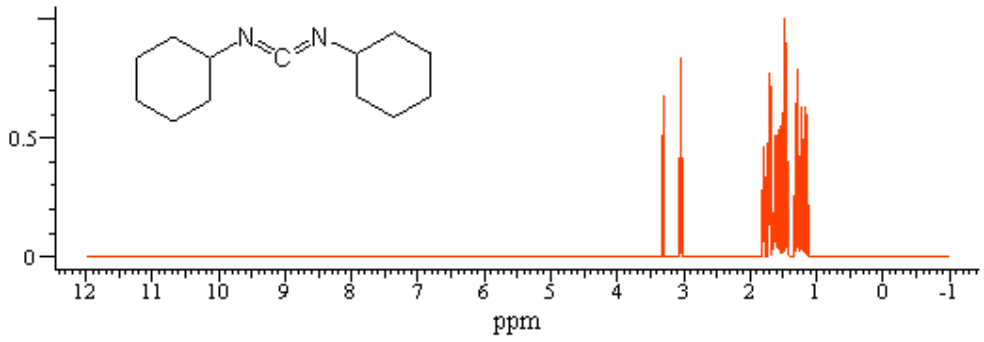
Solubility and Solvent Effects

The Isocyanates are readily soluble in the halogenated solvents normally used to prepare NMR solutions. The aromatic Isocyanates may require more polar solvents such as D_2O or DMSO-d_6 depending on the character of the other substituents on the phenylisocyanate ring.

Characterization

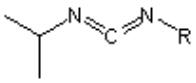
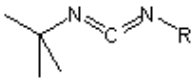
Because the Isocyanate group is neither strongly shielding nor deshielding, possesses no exchangeable protons and displays no coupling to nearby protons, it is a very difficult functional group to identify based only on NMR data. Fortunately, this group is readily identified via its infrared absorption bands.

Carbodiimides



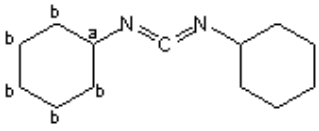
Although relatively few compounds containing the carbodiimide linkage are available, the indication is that the chemical shifts of both the aliphatic and aromatic groups bonded to it are similar to those of the isocyanates (-N=C=O), the benzylidenes (N=CH—Ar) and the isothiocyanates (-N=C=S).

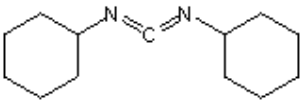
Aliphatic Protons

δ_b (ppm)	δ_a (ppm)	X	Solvent
1.22	3.53		$CDCl_3$
0.98			$CDCl_3$

Alicyclic Protons

Dicyclohexylcarbodiimide



δ_b (ppm)	δ_a (ppm)	X	Solvent
0.9-2.2	3.17		$CDCl_3$

Aromatic Protons

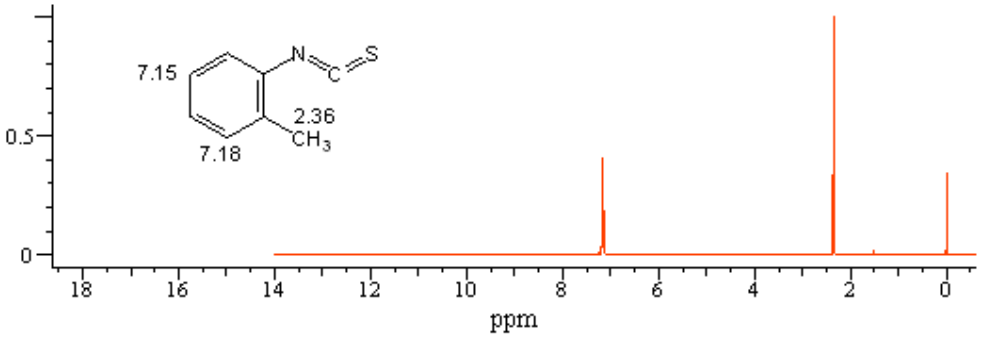
The Carbodiimide group is a weakly shielding group on the ortho aromatic hydrogens similar to a methyl substituent. Its presence in a molecule would be difficult to detect without the corresponding infrared data.

Syn-/Anti- Isomerism

Although both syn- and anti-forms can exist, most of the spectra examined do not display the duplication of resonance bands expected in the spectra of such a mixture. It is assumed that the groups most often exist in the anti- form. One possible exception is noted when one compares the aromatic trityl resonance bands (a single broad band near 7.28 ppm) and the corresponding band of a complex, higher order series of multiplets in the range from 6.8 to 7.3 ppm.

15 Isothiocyanates (-N=C=S)

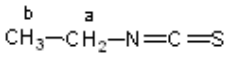
Isothiocyanates



The esters of Isothiocyanic Acid (R—N=C=S) possess chemical shifts similar to those of the other -N=C= groups. The protons of adjacent aliphatic groups resonate in the range from 3.3 to 4.6 ppm.

The —N=C=S group exerts a weakly deshielding effect on the ortho aromatic protons.

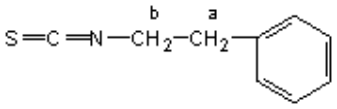
Aliphatic Protons

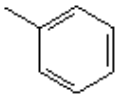


δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
			3.30	CH_3-N=C=S	$CDCl_3$
		1.37	3.55	CH_3-CH_2-N=C=S	$CDCl_3$
0.99	(1.2-2.1)			CH_3-$(CH_2)_2$-CH_2-N=C=S	CCl_4

		(1.45)		$(CH_3)_3$-C-N=C=S	CCl_4

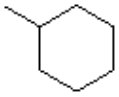
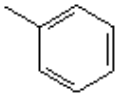
Phenethyl Isothiocyanate



δ_b (ppm)	δ_a (ppm)	X	Solvent
3.48	2.79		CCl_4

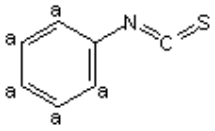
Substituted Methylisothiocyanates

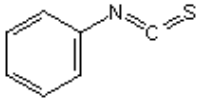
S=C=N=CH_2-X

δ_a (ppm)	Compound	Solvent
3.48		$CDCl_3$
4.15	-CH=CH_2	CCl_4
4.59		$CDCl_3$

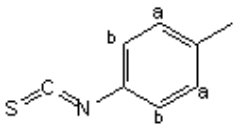
Aromatic Protons

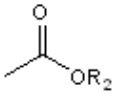
Phenyl Isothiocyanate



δ_a (ppm)	Compound	Solvent
6.95-7.50		CCl_4

Para-substituted aromatics



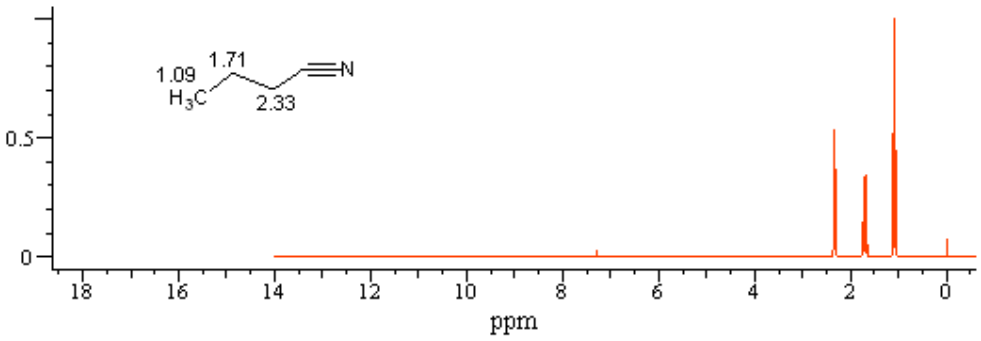
δ_b (ppm)	δ_a (ppm)	para	Solvent
7.15	6.98	-F	CCl_4
7.10	7.25	-Cl	$CDCl_3$
7.08	7.45	-Br	$CDCl_3$
7.25	8.02		$CDCl_3$
7.38	8.28		$CDCl_3$

16 Nitriles (-C≡N)

A Aliphatic

Nitriles

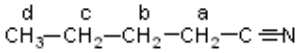
Aliphatics



A large amount of chemical shift data is available for this commercially important group of compounds. The nitrile group is a weak deshielder of aliphatic and aromatic protons, similar to several other unsaturated carbon-carbon and

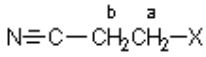
carbon-nitrogen functional groups. Fortunately, the nitrile group is easily characterized by its infrared absorption band allowing the NMR analyst to concentrate his energies on the proton groups in the molecules which are less easily defined by the infrared data.

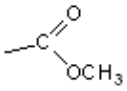
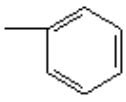
Aliphatic Protons



δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
			1.94	CH_3-C≡N	CCl_4
		1.25	2.34	CH_3-CH_2-C≡N	CCl_4
	1.07	1.67	2.27	CH_3-CH_2-CH_2-C≡N	CCl_4
		(1.30)	2.69	$(CH_3)_2$-CH-C≡N	CCl_4
0.97	(1.2-1.9)		2.30	CH3-$(CH_2)_2$-CH_2-C≡N	CCl_4
	(1.08)	1.97	2.21	$(CH_3)_2$-CH-CH_2-C≡N	CCl_4
		(1.39)		$(CH_3)_3$-C-C≡N	CCl_4

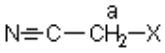
2-Substituted Nitriloethanes

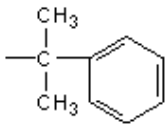
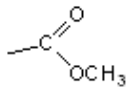
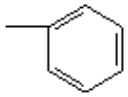
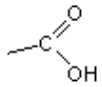


δ_b (ppm)	δ_a (ppm)	X	Solvent
2.27	1.67	-CH_3	CCl_4
2.62	2.62		CCl_4
2.36	2.73		$CDCl_3$
2.78	2.78	-C≡N	$CDCl_3$
2.55	2.96	-NH-$(CH_2)_2$-C≡N	$CDCl_3$
2.49	2.99	-NH_2	$CDCl_3$
2.83	3.20	-NH_2 (TFA salt)	D_2O

2.97	3.53	-Br	CCl_4
2.80	3.70	-Cl	CCl_4
2.67	3.73	$-O-(CH_2)_2-C\equiv N$	$CDCl_3$
2.61	3.85	-OH	$CDCl_3$

Substituted Nitrilomethanes

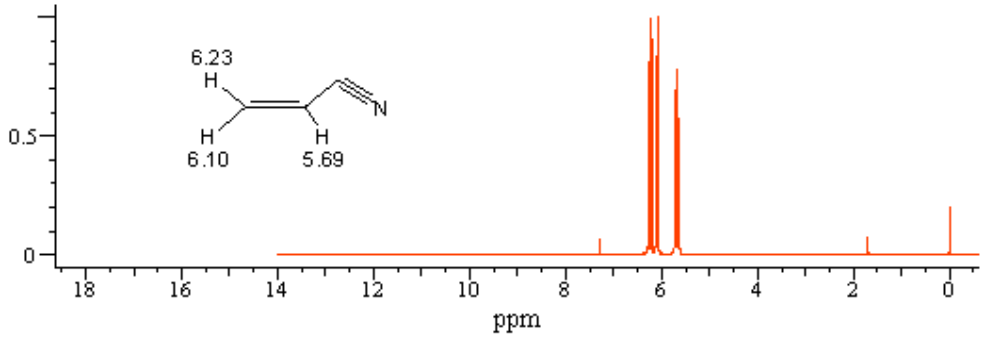


δ_a (ppm)	-X	Solvent
2.34	$-CH_3$	CCl_4
2.48		CCl_4
3.10	$-CH=CH_2$	CCl_4
3.50		$CDCl_3$
3.62		CCl_4
3.79		DMSO-d_6
4.21	-C≡N	DMSO-d_6

B Olefinic

Nitriles

Olefinics

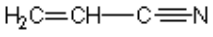


A large amount of chemical shift data is available for this commercially important group of compounds. The nitrile group is a weak deshielder of aliphatic and aromatic protons, similar to several other unsaturated carbon-carbon and carbon-nitrogen functional groups. Fortunately, the nitrile group is easily characterized by its infrared absorption band allowing the NMR analyst to concentrate his energies on the proton groups in the molecules which are less easily defined by the infrared data.

Olefinic Protons

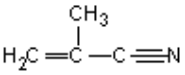
Although the nitrile group deshields all of the vinyl protons, it has an abnormally strong deshielding effect upon the cis olefinic hydrogen.

Acrylonitrile



cis (ppm)	trans (ppm)	geminal (ppm)	-X	Solvent
6.20	5.95	5.60	-C≡N	CCl_4

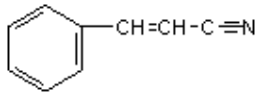
Methacrylonitrile



cis (ppm)	trans (ppm)	-X	Solvent

ca 5.79	1.98	-C≡N	CCl_4

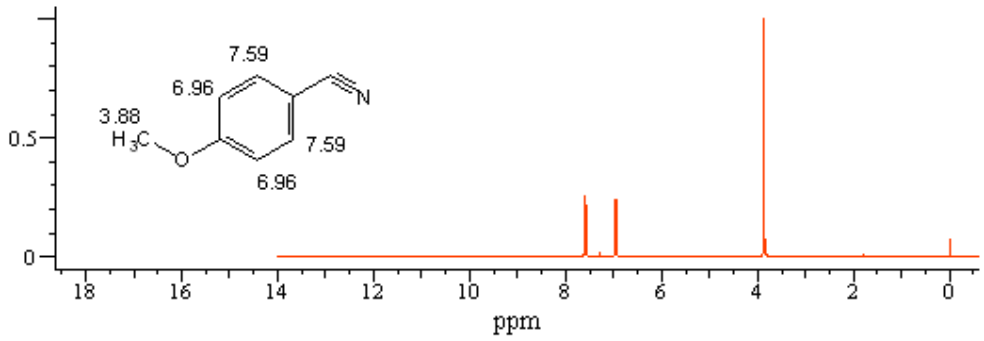
Cinnamonitrile



cis (ppm)	trans (ppm)	-X	Solvent
7.36	5.84	-C≡N	CCl_4

C Aromatic

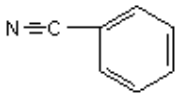
Aromatics



A large amount of chemical shift data is available for this commercially important group of compounds. The nitrile group is a weak deshielder of aliphatic and aromatic protons, similar to several other unsaturated carbon-carbon and carbon-nitrogen functional groups. Fortunately, the nitrile group is easily characterized by its infrared absorption band allowing the NMR analyst to concentrate his energies on the proton groups in the molecules which are less easily defined by the infrared data.

Aromatic Protons

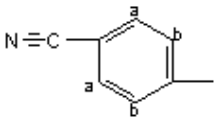
Benzonitrile

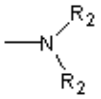
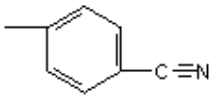


(ppm)	X	Solvent
7.20-7.75	-C≡N	CCl_4

---

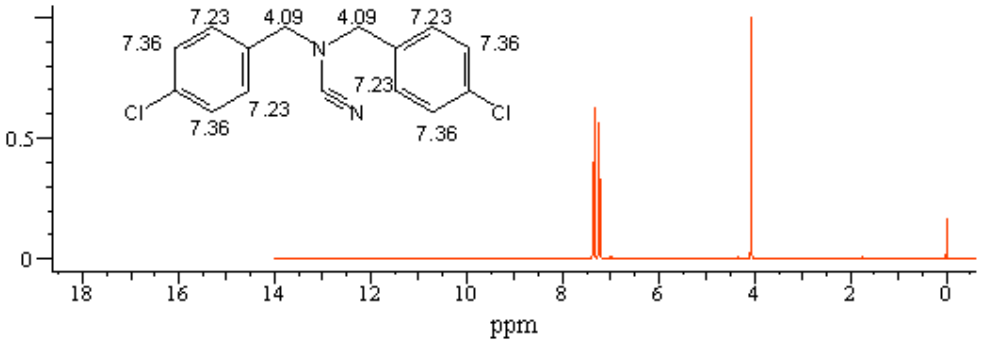
para-Substituted Benzonitriles



δ_b (ppm)	δ_a (ppm)	para	Solvent
7.35	6.58		$CDCl_3$
7.66	7.17	-F	$CDCl_3$
7.47	7.23	$-CH_3$	CCl_4
7.57	7.39	-Cl	$CDCl_3$
7.90	7.90		TFA

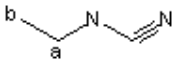
17 Cyanamides (=N-C≡N)

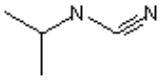
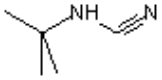
Cyanamides



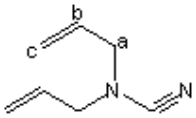
Although the Cyanamid group is of commercial importance, relatively few hydrocarbon derivatives are available for study. The chemical shifts of the aliphatic groups bonded to the Cyanamid group display intermediate deshielding similar to that of the corresponding amines.

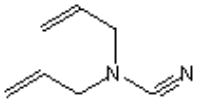
Aliphatic Protons



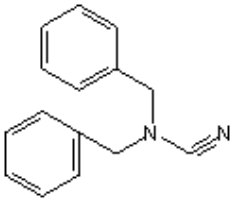
δ_b (ppm)	δ_a (ppm)	X	Solvent
	(2.88)		CCl_4
(1.29)			$CDCl_3$

Diallylcyanamide

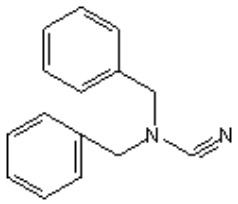


δ_{bc} (ppm)	δ_a (ppm)	Compound	Solvent
(5.0-6.2)	3.60		CCl_4

Dibenzylcyanamide

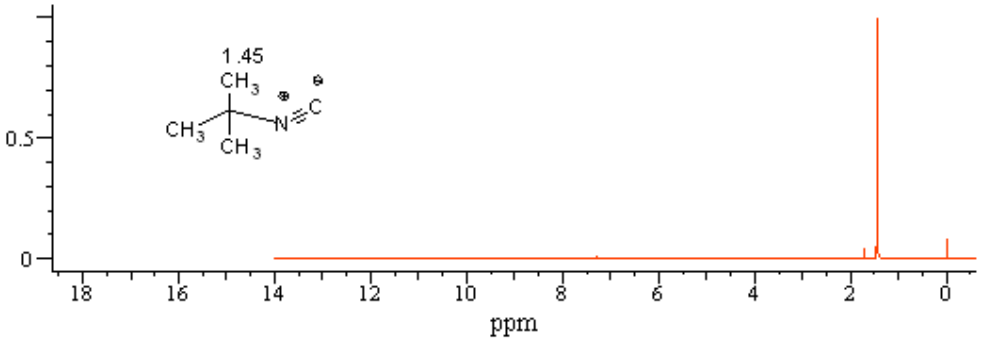


δ_a (ppm)	Compound	Solvent

4.06		$CDCl_3$

18 Isocyanides (-N≡C)

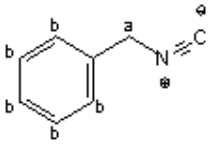
Isocyanides

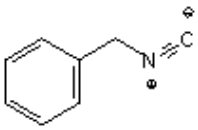


This rather rare functional group is one of the few that may display coupling (2n + 1) between the Nitrogen nucleus and adjacent hydrocarbon groups.

Aliphatic Protons

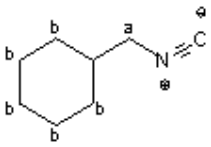
Benzyl isocyanide

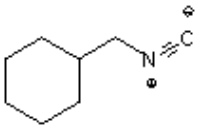


δ_b (ppm)	δ_a (ppm)	Compound	Solvent
ca 7.33	4.59		$CDCl_3$

Alicyclic Protons

Cyclohexyl isocyanide



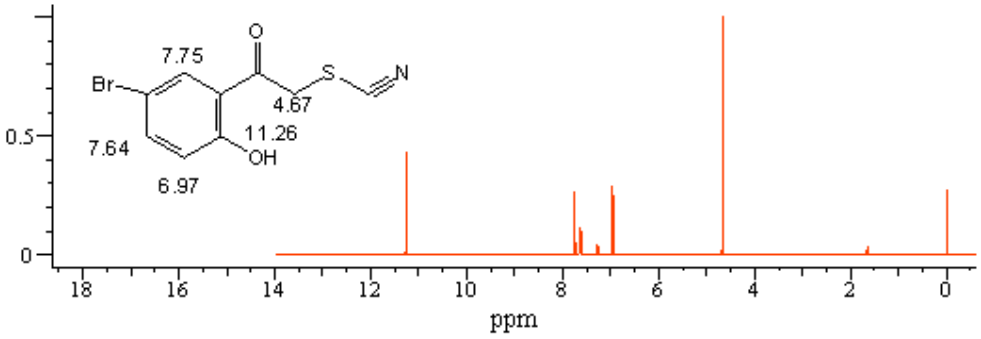
δ_b (ppm)	δ_a (ppm)	Compound	Solvent
0.90-2.27	3.60		$CDCl_3$

Coupling and Coupling Constants

$^{J}C{\equiv}N\text{-}CH_2$ = 2.1 Hz

19 Thiocyanates (-S-C≡N)

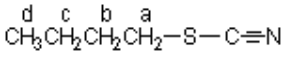
Thiocyanates



The thiocyanate group has an intermediate deshielding effect on adjacent aliphatic groups but little or no shielding/deshielding effect on the aromatic protons.

It is similar to many of the preceding groups in that it is difficult to determine the presence of this group in an NMR spectrum with any degree of certainty, without additional information such as elemental analysis data or infrared information.

Aliphatic Protons

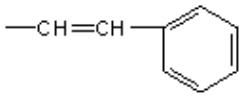
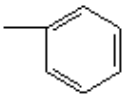
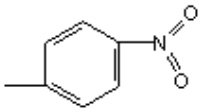
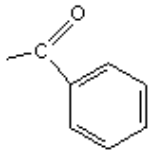


δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent

			2.61	$CH_3—S—C\equiv N$	CCl_4
		1.51	3.00	$CH_3CH_2—S—C\equiv N$	$CDCl_3$
0.99	(1.2-2.1)		2.97	CH_3-$(CH_2)_2$-CH_2-S-C≡N	CCl_4

Substituted Methyl Thiocyanates

$N\equiv C—S—\overset{a}{C}H_2—X$

δ_a (ppm)	-X	Solvent
3.58		$CDCl_3$
4.15		$CDCl_3$
4.23		$CDCl_3$
4.40	-S-C≡N	$CDCl_3$
4.67		$CDCl_3$
4.92	-Cl	CCl_4

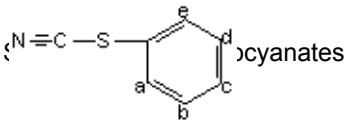
Substituted Ethylthiocyanates

$N\equiv C—\overset{b}{C}H_2\overset{a}{C}H_2—X$

δ_b (ppm)	δ_a (ppm)	X	Solvent
3.01	2.01	$—CH_2CH_2—S—C\equiv N$	$CDCl_3$
3.38	3.38	-S-C≡N	Polysol

3.11	3.78	—O—CH_2CH_2—O—R	CCl_4

Aromatic Protons

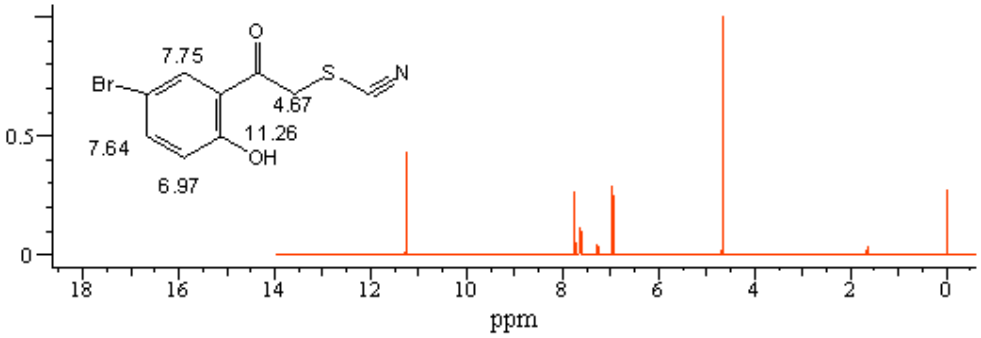


ocyanates

δ_e (ppm)	δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
6.92	6.71	NH_2	O-R_2	7.00	Polysol
7.22	6.89	OH	CH_3	7.30	DMSO-d_6
7.12	CH_3	OH	CH_3	7.12	$CDCl_3$
7.30	CH_3	OH	6.89	7.22	DMSO-d_6
7.35	6.68	OH	CH_3	CH_3	$CDCl_3$
7.48	7.03	NH_2	7.41		DMSO-d_6
7.92	7.61	Cl	8.01		$CDCl_3$
7.93	8.12		8.36	S-C≡N	$CDCl_3$
8.25	8.69		8.99		DMS

20 Nitroso Compounds (-N=O)

Nitroso Compounds



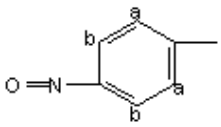
The data for the aliphatic Nitroso compounds is confusing. The spectrum of 2-methyl-2-nitrosopropane presents a

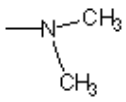
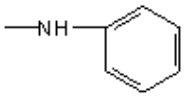
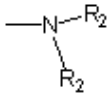
puzzle in that two bands are observed with an intergration ratio of approximately 2:1. One explanation may be that there is restricted rotation about the C-N bond producing a different chemical shift for one of the tert-butyl methyl groups. Such restricted rotation may also be observed in the spectra of the aromatic compounds in that the protons ortho to the -N=O group are always slightly broadened in comparison to the other protons in the aromatic ring.

The effect of the Nitroso group on the chemical shifts of the ortho aromatic compounds is that of a strongly deshielding group.

Aromatic Protons

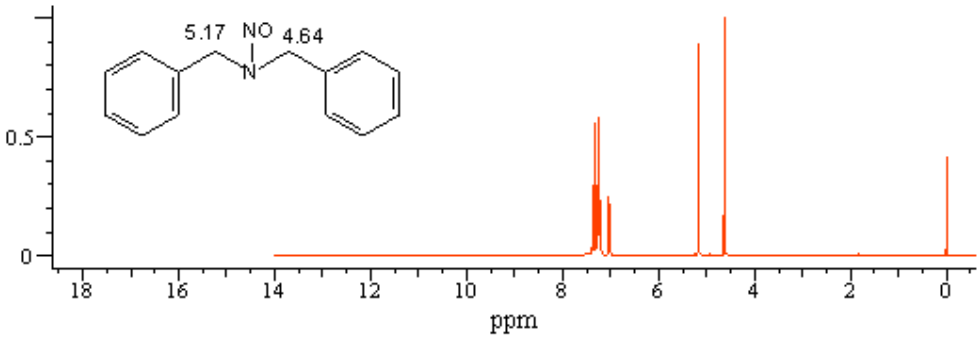
Para substituted nitroso benzenes



δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.73	6.52	-O-Na	D_2O
7.70	6.60		$CDCl_3$
7.67	6.63	-OH	Acetone
7.77	7.08		Polysol
7.79	6.65		$CDCl_3$

21 N-Nitroso Compounds (=N-N=O)

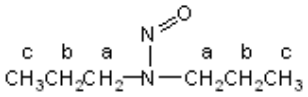
N-Nitroso Compounds

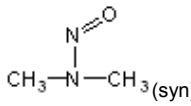
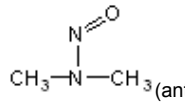
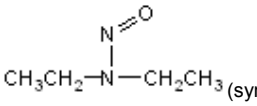
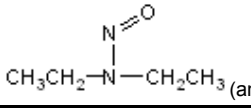
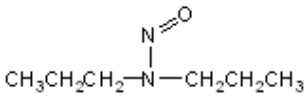
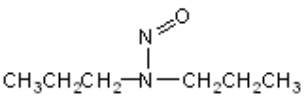


Non-equivalence of similar groups bonded to the nitrosoamine nitrogen nucleus is a characteristic of these compounds. Due to restricted rotation about the N—N bond the groups bonded to the amine nitrogen can reside either syn or anti to the nitroso oxygen atom producing a differentiation in their chemical shifts. The group syn to the oxygen atom usually resonates at higher field and may display a certain degree of broadening in comparison to the group in the anti position.

The differentiation in chemical shift decreases with distance from the amine nitrogen atom, i.e. the alpha groups differ in chemical shift by about 0.6 ppm, the beta groups by about 0.3 ppm and the gamma groups by about 0.1 ppm.

Aliphatic Protons



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
		(2.95)	 (syn)	CCl_4
		(3.71)	 (anti)	CCl_4
	(1.11	3.60)	 (syn)	$CDCl_3$
	(1.41	4.12)	 (anti)	$CDCl_3$
(0.88	1.50	3.48)	 (syn)	CCl_4
(0.97	1.80	4.06)	 (anti)	CCl_4

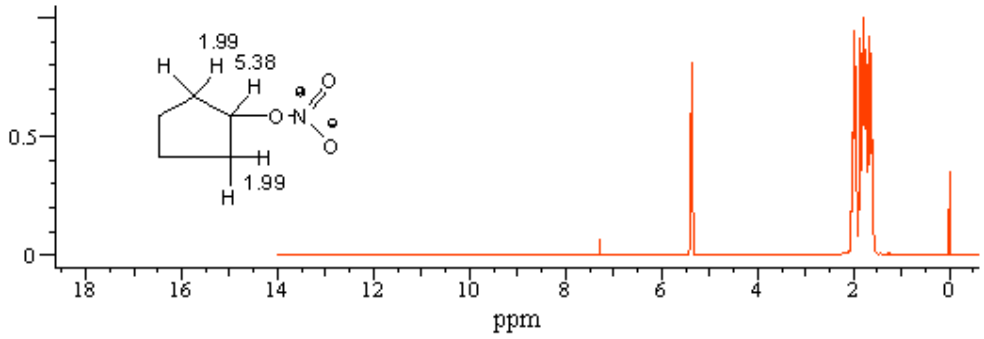
Aromatic Protons

The N-nitroso group deshields all of the aromatic hydrogens of the anti ring forming a complex, higher order pattern centered at about 7.45 ppm. In some examples, two ortho hydrogens are slightly shielded and probably

represent the ortho hydrogens of the ring syn to the N-nitroso oxygen atom.

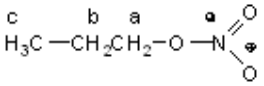
22 Nitrates (-O-NO_2)

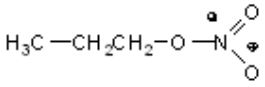
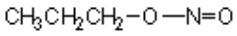
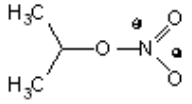
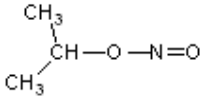
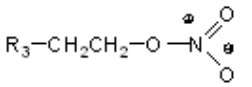
Nitrates



The Nitrates which contain the –O-NO_2 substituent produce lower field shifts than the corresponding N-Nitro compounds. The effect of the – O -NO_2 group is not as strongly deshielding, however, as the –O-N=O group of the Nitrites. Several comparisons of the Nitrate and Nitrite chemical shifts are presented below.

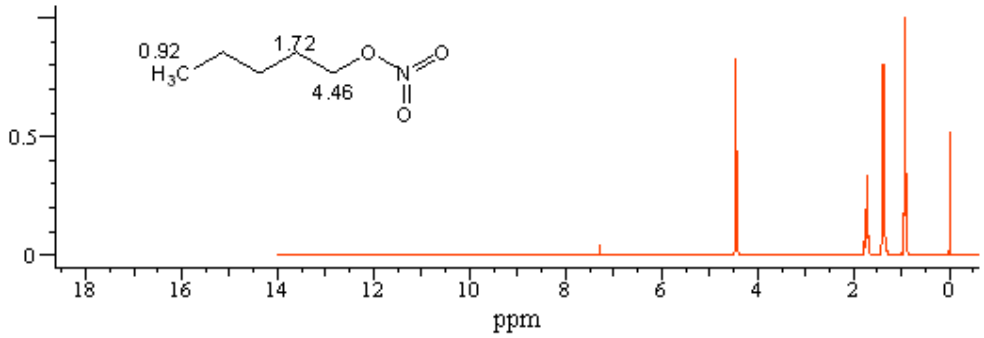
Aliphatic Protons



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
1.01	1.75	4.40		CCl_4
0.97	1.72	4.61		CCl_4
	(1.37)	5.15		CCl_4
	(1.40)	5.59		CCl_4
	1.74	4.47		$CDCl_3$

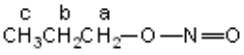
23 Nitrites (-O-N=O)

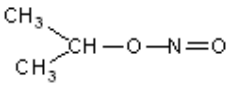
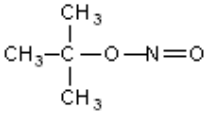
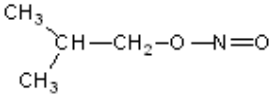
Nitrites



The nitrite group is one of the most strongly deshielding substituents in its effect on the alpha aliphatic groups. Methylene groups are deshielded to about 4.5 ppm and methines to about 5.5 ppm. Such extremes of chemical shift are characteristic of only a few substituents making the identification of a Nitrite compound a relatively easy matter.

Aliphatic Protons



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
0.97	1.72	4.61	$CH_3CH_2CH_2-O-N=O$	CCl_4
	(1.40)	5.59		CCl_4
	(1.57)			$CDCl_3$
(0.98)	1.98	4.45		CCl_4

Coupling and Coupling Constants

The nitrite compounds display no unusual coupling nor coupling constants. The normal vicinal aliphatic proton coupling of about 7 Hz is observed.

Solubility and Solvent Effects

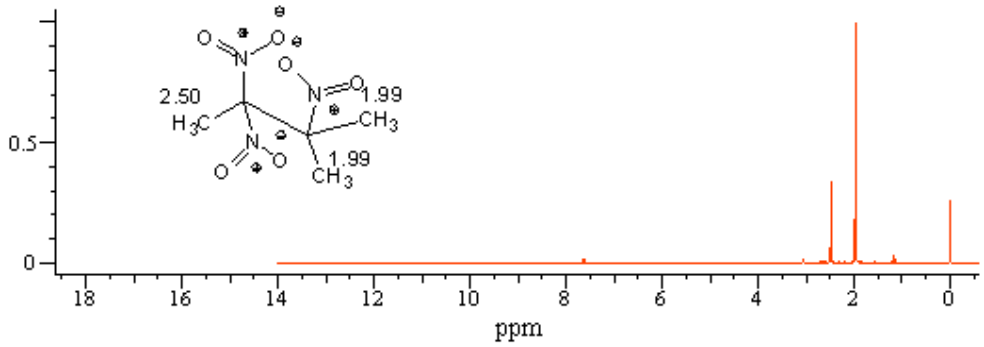
The aliphatic nitrites are readily soluble in the halogenated NMR solvents; carbon tetrachloride and deuterochloroform. No special solvent effects have been noted.

24 Nitro Compounds (-NO_2)

A Aliphatic

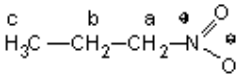
Nitro Compounds

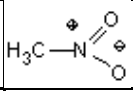
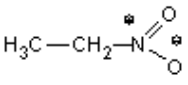
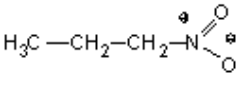
Aliphatics

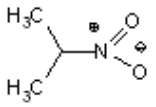
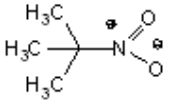


The nitro functional group is one of the very few substituents which strongly deshield both adjacent aliphatic groups and the ortho aromatic protons. The group imparts no other distinguishing characteristics to the proton NMR spectrum.

Aliphatic Protons



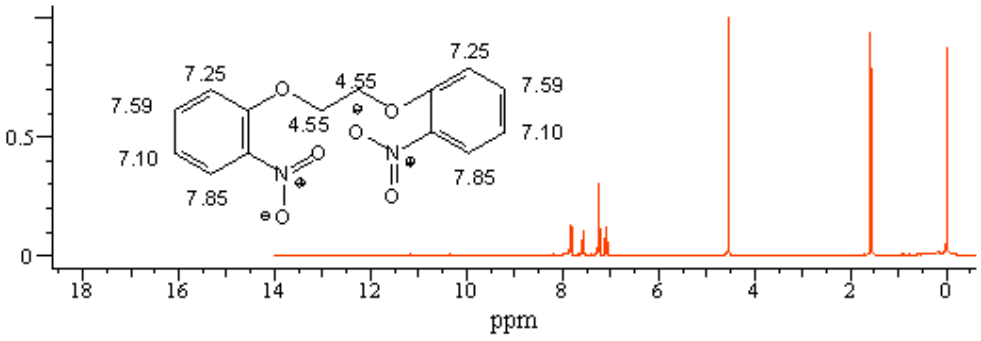
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		4.22		CCl_4
	1.55	4.40		CCl_4
1.01	2.00	4.31		CCl_4

	(1.57)	4.65		$CDCl_3$
	(1.61)			CCl_4

B Aromatic

Nitro Compounds

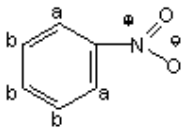
Aromatics

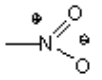


The nitro functional group is one of the very few substituents which strongly deshield both adjacent aliphatic groups and the ortho aromatic protons. The group imparts no other distinguishing characteristics to the proton NMR spectrum.

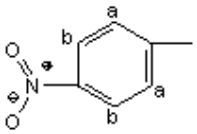
Aromatic Protons

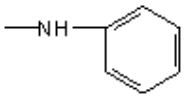
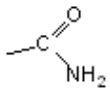
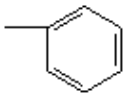
Nitrobenzene



δ_b (ppm)	δ_a (ppm)	X	Solvent
7.3-7.8	8.20		CCl_4

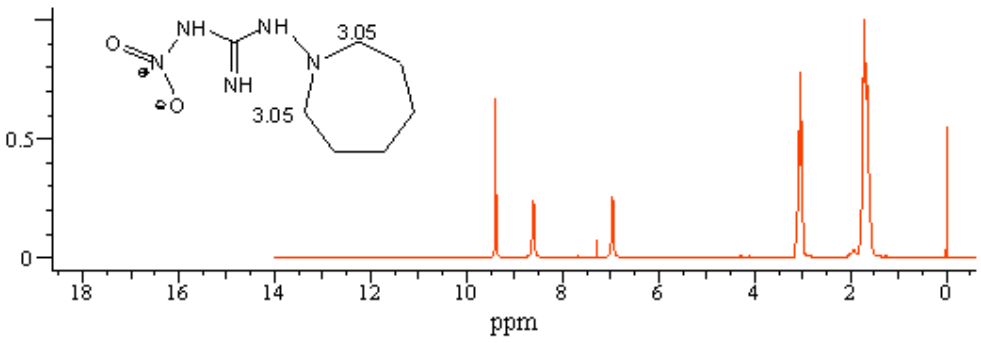
Para-Substituted Nitrobenzenes



δ_b (ppm)	δ_a (ppm)	para	Solvent
7.84	6.19	-O-Na	DMSO
8.09	6.67	$-NH_2$	DMSO-d_6
8.12	6.91	$-O-CH_3$	CCl_4
8.15	7.06	-OH	Acetone
8.05	7.09		Acetone
8.20	7.20	-F	CCl_4
8.10	7.30	$-CH_3$	$CDCl_3$
8.19	7.32	-N=C=S	$CDCl_3$
8.09	7.46	-Cl	$CDCl_3$
8.03	7.62	-Br	$CDCl_3$
7.78	7.62		DMSO
8.26	7.82		Acetone

25 N-Nitro-Compounds (=N-NO_2)

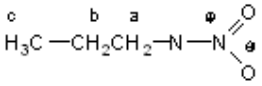
N-Nitro Compounds

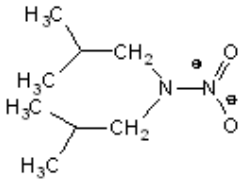
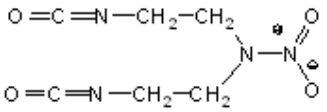
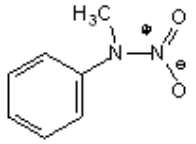


The addition of a nitro group as one of the groups bonded to an amine nitrogen atom increases the deshielding effect of

the amine group. The presence of the N-Nitro group also decreases the relative solubility of these compounds in comparison to the corresponding amines.

Aliphatic Protons



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
0.90	2.25	3.61		$CDCl_3$
	3.71	4.01		$CDCl_3$
		3.65		Polysol

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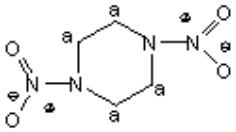
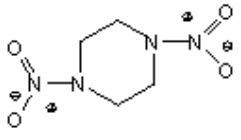
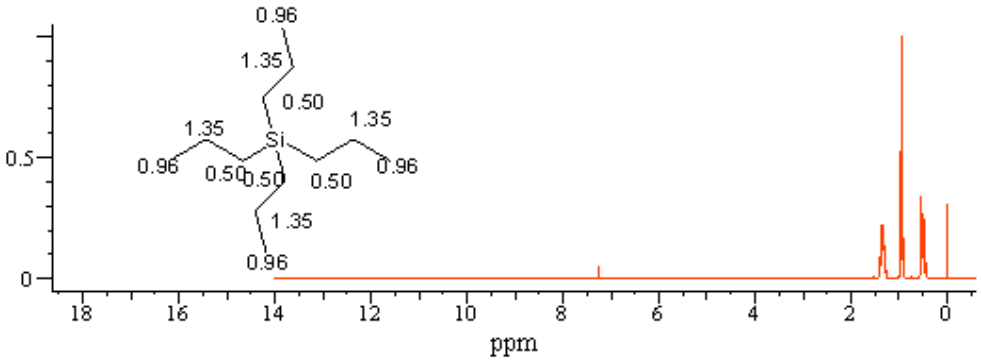
Alicyclic Protons



δ_a (ppm)	Compound	Solvent
4.01		DMSO-d_6

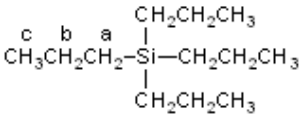
Silicon Containing Compounds (Except Si-O)

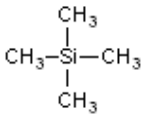
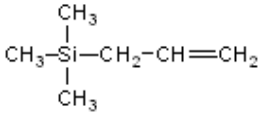
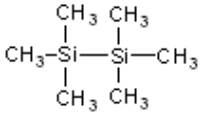
Silicon Compounds

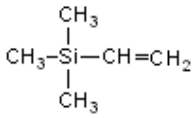
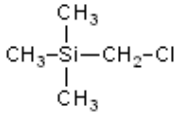
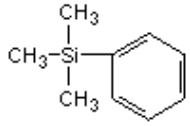
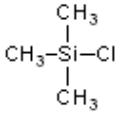
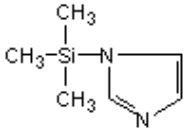
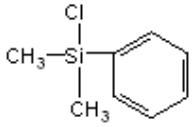
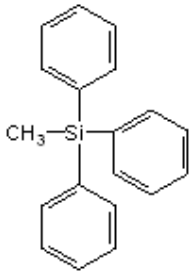
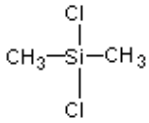
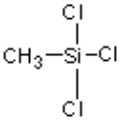
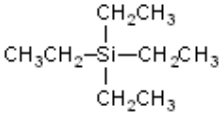


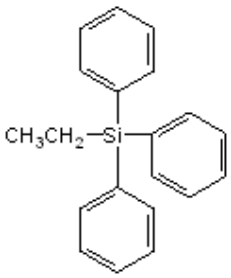
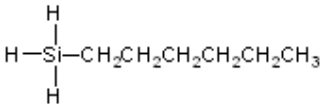
The outstanding characteristic of the silicon compounds is the extremely high-field chemical shifts observed for aliphatic groups bonded to the silicon nucleus. These aliphatic groups resonate at higher fields than any other group in corresponding molecular structures. Additionally, coupling between Si—H protons and adjacent aliphatic groups is observed as clear n+1 multiplets. The silicon compounds are readily soluble in all the normal NMR solvents excluding D_2O.

The chemical shifts of groups bonded to the oxygen atom of the silicon ethers (siloxanes) are described with the other ether oxygen compounds.

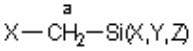


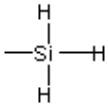
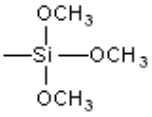
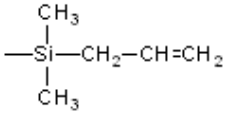
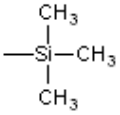
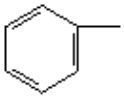
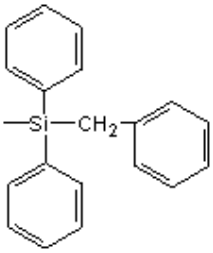
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
		(0.00)		
		(0.03)		CCl_4
		(0.04)		CCl_4

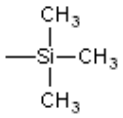
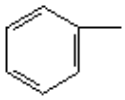
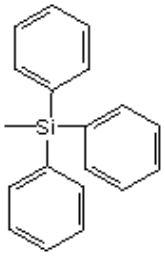
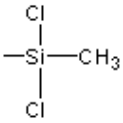
		(0.06)		C_2Cl_4
		(0.12)		CCl_4
		(0.29)		$CDCl_3$
		(0.40)		C_2Cl_4
		(0.48)		$CDCl_3$
		(0.63)		CCl_4
		0.77		$CDCl_3$
		(0.80)		$CDCl_3$
		1.17		CCl_4
	(0.92	0.56)		CCl_4

	1.10	1.30		$CDCl_3$
0.90	(1.1-1.7)	0.90		$CDCl_3$

Substituted Methyl Silanes

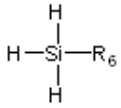
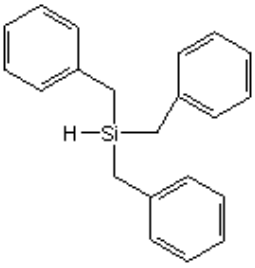
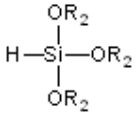
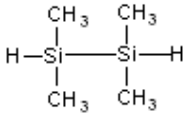


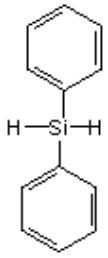
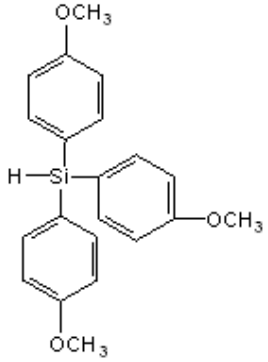
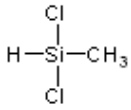
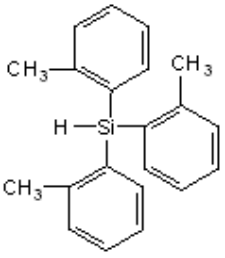
X (ppm)	δ_a (ppm)	-Si(X,Y,Z)	Solvent
R_2-	0.67		$CDCl_3$
R_5-	0.90		CCl_4
CH_2-CH=CH_2-	1.52		C_2Cl_4
CH_2=CH-	1.56		CCl_4
	2.59		$CDCl_3$

Cl-	2.69		CCl_4
	2.91		$CDCl_3$
Cl-	3.11		$CDCl_3$

Silane Protons

Si-H

(ppm)	Compound	Solvent
3.52		$CDCl_3$
4.03		$CDCl_3$
4.14		CCl_4
4.46		CCl_4

4.92		$CDCl_3$
5.39		$CDCl_3$
5.54		CCl_4
5.79		CCl_4

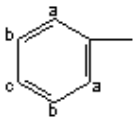
Olefinic Protons

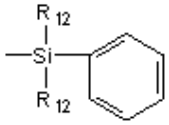
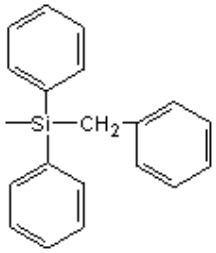
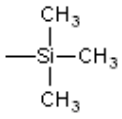
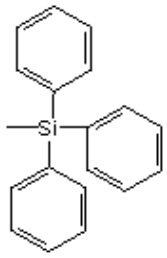
The silicon nucleus deshields all three of the vinyl protons producing a complex ABC pattern centered at about 5.9 ppm.

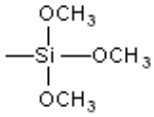
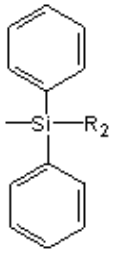
Aromatic Protons

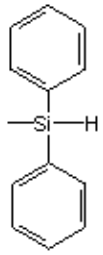
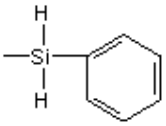
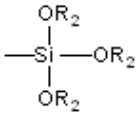
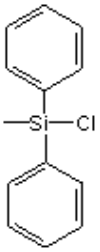
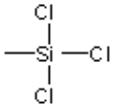
Silicon substituents deshield the ortho aromatic hydrogens which resonate in the range 7.5-7.8 ppm depending on the other groups attached to the silicon nucleus. The chemical shifts of a few representative aromatic silanes are provided.

Phenyl Silanes

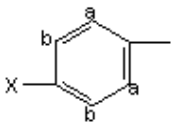


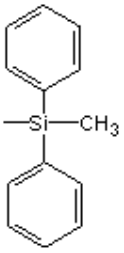
δ_{abc} (ppm)	-Si(X,Y,Z)	Solvent
7.10-7.60		CCl_4
7.10-7.60		$CDCl_3$
7.20-7.65		$CDCl_3$
7.10-7.70		$CDCl_3$

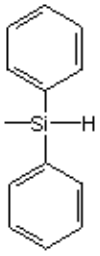
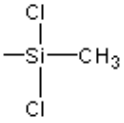
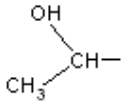
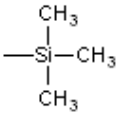
δ_{bc} (ppm)	δ_a (ppm)	-Si(X,Y,Z)	Solvent
7.1-7.5	7.48		CCl_4
7.1-7.4	7.48		$CDCl_3$

7.1-7.4	7.54		$CDCl_3$
7.1-7.4	7.56		$CDCl_3$
7.1-7.5	7.60		CCl_4
7.0-7.4	7.62		$CDCl_3$
7.2-7.7	7.81		$CDCl_3$

Para Substituted Phenylsilanes



X-	δ_b (ppm)	δ_a (ppm)	para	Solvent
CH_3-O-	6.85	7.40		$CDCl_3$

CH_3-O-	6.83	7.41		$CDCl_3$
Cl-	7.35	7.51		CCl_4
	7.33	7.62		$CDCl_3$

Coupling and Coupling Constants

Coupling between the silane protons and adjacent aliphatic groups is observed as clear n+1 multiplets.

^{J}H-Si-CH_2 = 3.1-3.9 Hz

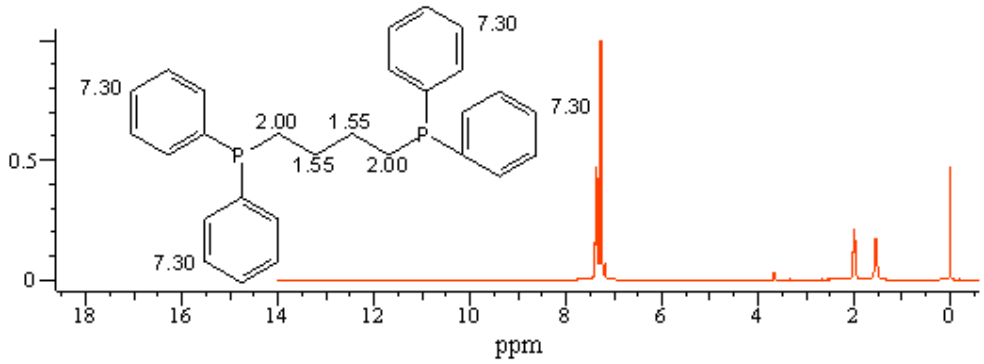
The isotope silicon-29 has a natural abundance of 4.7% and possesses a spin of 1/2. These isotope sidebands can often be observed in the spectra of the silanes if the noise level of the baseline is sufficiently low to allow their definition.

$J^{29}Si\text{-}H_3$ = 184 Hz
$J^{29}Si\text{-}H_2$ = 199 Hz

Phosphorus Containing Compounds (Except P-O and P(=O)-O)

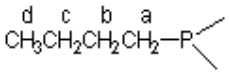
Phosphorus Containing Compounds

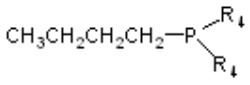
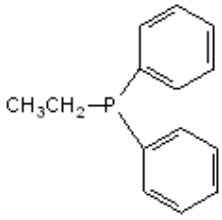
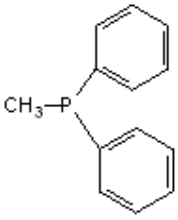
Phosphines



For the sake of comparison, this group of compounds includes not only the Phosphines, but also several other trivalent phosphorus compounds. The phosphine phosphorus nucleus is a very weakly deshielding substituent in its effect on adjacent aliphatic groups, similar in effect to another aliphatic group (CH_3, CH_2, CH). Its effect on the aromatic protons varies, depending on the other groups bonded to the phosphorus nucleus, from a weakly deshielding to a strongly deshielding group. Coupling between the phosphorus atom and adjacent protons is usually present but often difficult to see clearly due to overlap with non-coupled protons.

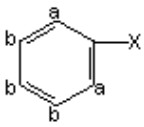
Aliphatic Protons

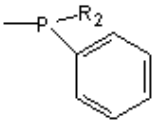
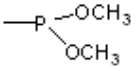
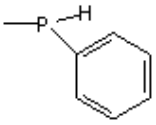
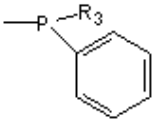


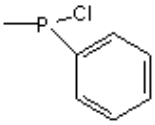
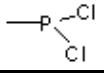
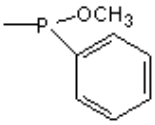
δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
0.94	(1.1-1.9)		1.1-1.9		$CDCl_3$
		1.05	1.99		$CDCl_3$
			1.53		$CDCl_3$

Aromatic Protons

Phenyl Phosphines

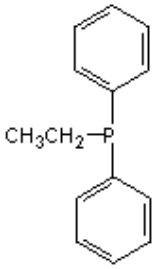


δ_{ab} (ppm)	-X	Solvent
6.99-7.44		$CDCl_3$
7.12-7.59		CCl_4
7.00-7.60		CCl_4
7.10-7.60		$CDCl_3$

δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.1-7.5	7.60		$CDCl_3$
7.1-7.6	7.83		$CDCl_3$
7.3-7.7	8.19		CCl_4

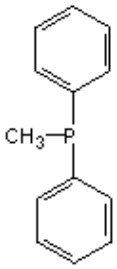
Coupling and Coupling Constants

The phosphorus nucleus of the phosphine compounds couples weakly, if at all, with an alpha aliphatic group, strongly with the beta aliphatic group, and weakly with the gamma group. Certain anomalies appear to exist in the data for those compounds in which two phosphine groups are present. Due to the small number of compounds available for analysis, the data is presented as it was deduced from the spectra via first order analysis.

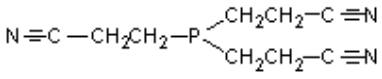


^{J31}P-CH = 0 Hz

^{J31}P-C-CH$_3$ = 17 Hz

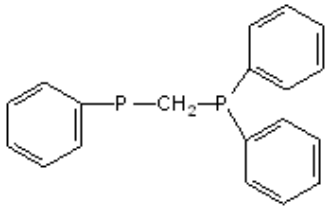


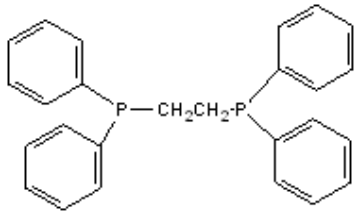
^{J31}P-CH = 4.0 Hz



^{J31}P-CH$_2$ = 0 Hz

^{J31}P-C-CH$_2$ = 9.5 Hz



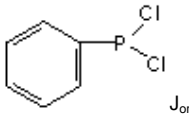


^{J}P-CH = 4-5 Hz,

^{J}P-C-CH$_2$ = 4.5 Hz

^{J}P-CH = ca 1 Hz

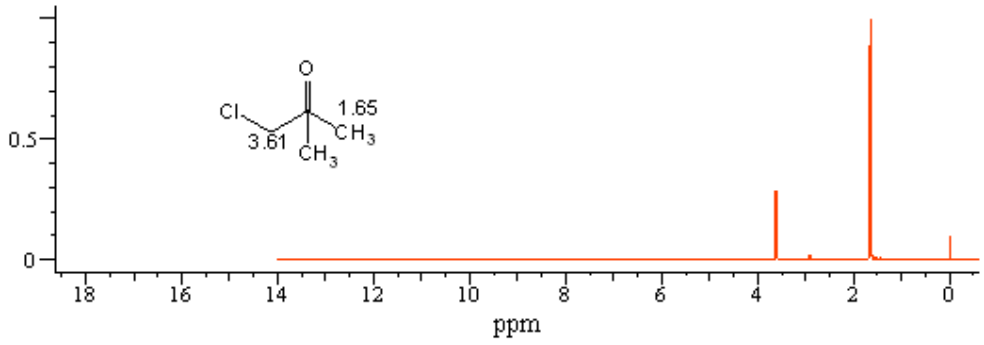
Aromatic Protons



J_{ortho} = 8.5 Hz

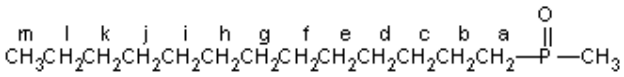
^{J}P-C-C-CH$_3$ = 1-2 Hz

Phosphine Oxides

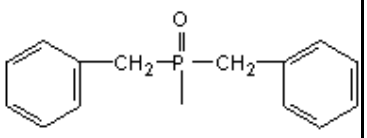
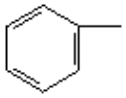
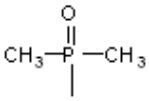


The Phosphine Oxide group produces chemical shifts similar to those of the phosphines but with a significant increase in the magnitude of the coupling constants to the alpha hydrocarbon group. The long chain aliphatic phosphine oxides are often difficult to distinguish from the simple alkanes due to the weak carbon-like deshielding of the alpha methylene group.

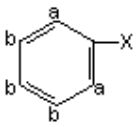
Aliphatic Protons



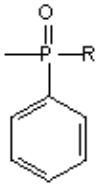
δ_m (ppm)	δ_l -δ_b (ppm)	δ_a (ppm)	-X	Solvent
		(1.44)	$(CH_3)_2$-P(=O)-R_{13}	$CDCl_3$
0.89	(1.1-1.5)	~1.5	CH_3-$(CH_2)_{11}$-CH_2-P(=O)(CH_3)	$CDCl_3$

-X	CH_2- (ppm)	-P (=O)	-X,Y	Solvent
R-	2.59	-P(=O)		$CDCl_3$
	3.00	-P(=O)		$CDCl_3$

Aromatic Protons



The Phosphine Oxide group is a moderately strong deshielding group in its effect on the ortho aromatic hydrogens. Coupling to these hydrogens, when it can be observed, is found to be about 12-13 Hz.

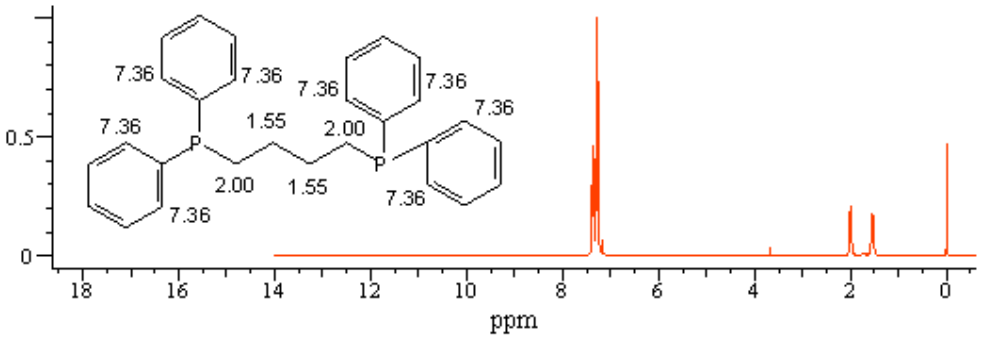
δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.3-7.7	7.72		$CDCl_3$

Coupling and Coupling Constants

$^{J}P\text{-}CH_3$ = 12-13 Hz

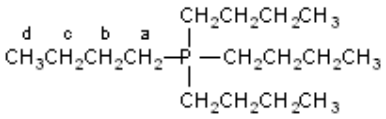
$^{J}P\text{-}CH_2$ = 10-12 Hz

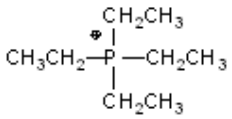
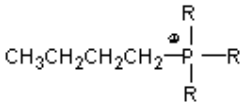
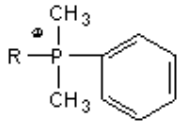
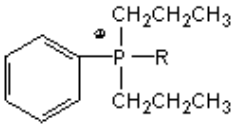
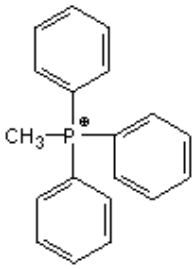
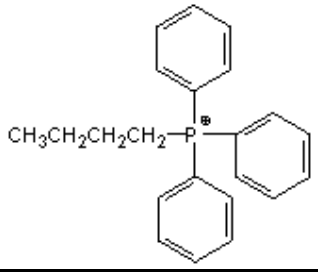
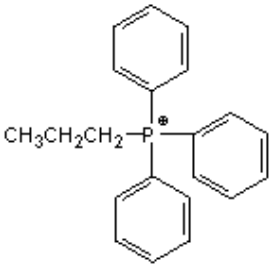
Phosphonium Compounds



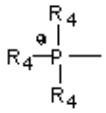
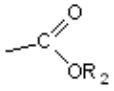
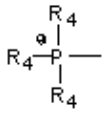
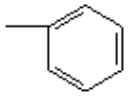
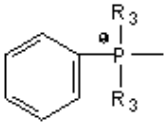
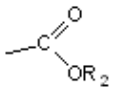
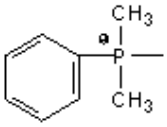
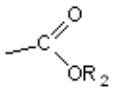
The phosphorus nucleus of the phosphonium compounds is a much more strongly deshielding group than that of the phosphines. Clear coupling to the alpha aliphatic groups is observed which makes this group of compounds more easily identifiable than the phosphines. Although soluble in deutero-chloroform, the spectra as a group suffer from a slightly higher noise level than the other phosphorus containing compounds due to their lower solubility.

Aliphatic Protons



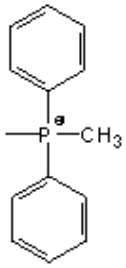
δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound		Solvent
		(1.33	2.52)		$^{-}$I	$CDCl_3$
0.94	(1.1-2.0)		2.55		$^{-}$Cl	$CDCl_3$
			(2.74)		$^{-}$Br	$CDCl_3$
	(1.16	1.71	3.08)		$^{-}$Br	$CDCl_3$
			3.27		$^{-}$Br	$CDCl_3$
0.89	(1.3-1.9)		3.69		$^{-}$Br	$CDCl_3$
	1.24	1.79	3.70		$^{-}$Br	$CDCl_3$

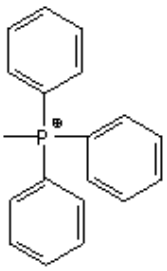
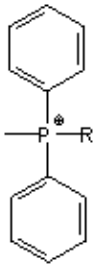
Substituted Methanes

(X,Y,Z)	-P+-	δ_a (ppm)	-X		Solvent
	-P+-	4.13		$^{-}$Br	$CDCl_3$
	-P+-	4.43		$^{-}$Cl	$CDCl_3$
	-P+-	4.58		$^{-}$Br	$CDCl_3$
	-P+-	4.77		$^{-}$Br	$CDCl_3$

Aromatic Protons

The phosphonium group deshields all of the aromatic hydrogens producing a complex, higher order band at low field.

p,m,o (ppm)	-X		Solvent
7.62-8.08		$^{-}$Br	$CDCl_3$

7.50-8.10		$^{-}$I	$CDCl_3$
7.50-8.20		$^{-}$Br	$CDCl_3$

Coupling and Coupling Constants

$^{J}P^{+}$ - CH_3	=	13.6 Hz
$^{J}P^{+}$ -CH_2	=	13.0-15.1 Hz
$^{J}P^{+}$ -C-CH_3	=	18.2 Hz

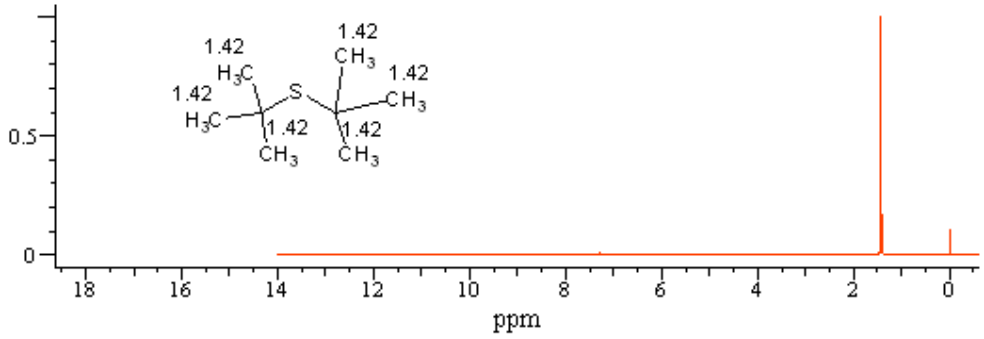
Sulfur Containing Compounds

1 Sulfides (R-S-R)

A Aliphatic

Sulfides

Aliphatics

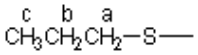


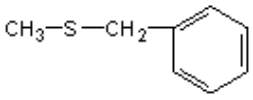
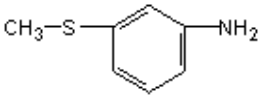
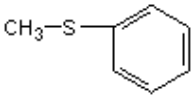
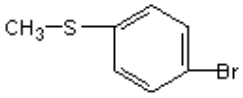
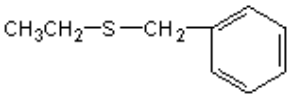
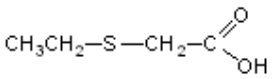
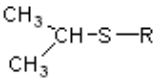
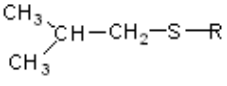
The sulfide linkage has a weakly deshieding effect on adjacent aliphatic groups and a weak shielding effect on the ortho

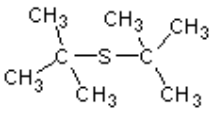
aromatic hydrogens. In both cases, the phenyl sulfide group is a more strongly deshielding group than the corresponding aliphatic sulfide linkage.

Except in the case of the heterocyclic molecules, the coupling constants are the same as those observed for the other substituents discussed thus far.

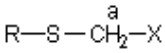
Aliphatic Protons

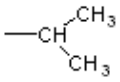
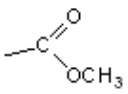
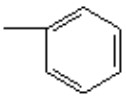


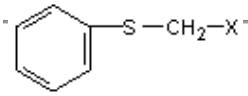
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		1.90		CCl_4
		2.01	CH_3-S-R_{12}	CCl_4
		2.04	CH_3-S-R_2	CCl_4
		2.06	CH_3-S-CH_3	CCl_4
		2.29		CCl_4
		2.39		$CDCl_3$
		2.45		$CDCl_3$
	1.19	2.32		CCl_4
	1.23	2.43	CH_3-CH_2-S-CH_3	CCl_4
	1.23	2.47	CH_3-CH_2-S-R_3	CCl_4
	1.23	2.68		CCl_4
0.98	1.59	2.44	CH_3-CH_2 -CH_2-S-R	CCl_4
	(1.38)	3.12		TFA
(0.99)	1.79	2.32		CCl_4

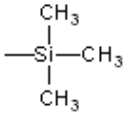
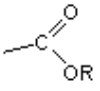
	(1.36)			CCl_4

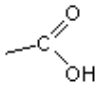
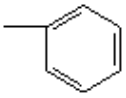
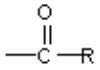
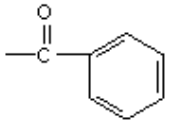
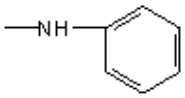
Substituted Methylsulfides



δ_a (ppm)	-X	Solvent
2.32		CCl_4
2.43	$-CH_3$	CCl_4
3.09	$-CH=CH_2$	$CDCl_3$
3.36	-C≡N	CCl_4
3.77		$CDCl_3$
3.80		$CDCl_3$
3.80		CCl_4
4.83	-Cl	$CDCl_3$



δ_a (ppm)	-X	Solvent
2.10		CCl_4
3.49		CCl_4

3.58	-C≡C-R	$CDCl_3$
3.59		$CDCl_3$
3.99		$CDCl_3$
4.00		Polysol
4.10		$CDCl_3$
4.67		Polysol

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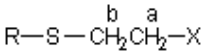
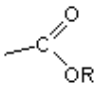
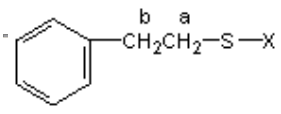
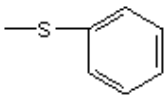
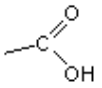
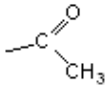
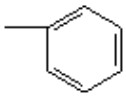
Substituted Ethylsulfides



δ_b (ppm)	δ_a (ppm)	-X	Solvent
2.44	1.59	$-CH_3$	CCl_4
2.52	1.69	$—CH_2CH_2—S—R_2$	$CDCl_3$
2.55	2.66		CCl_4
2.71	2.71	$-S-R_2$	CCl_4
2.75	2.88	-C≡N	$CDCl_3$
2.61	3.63	-OH	CCl_4



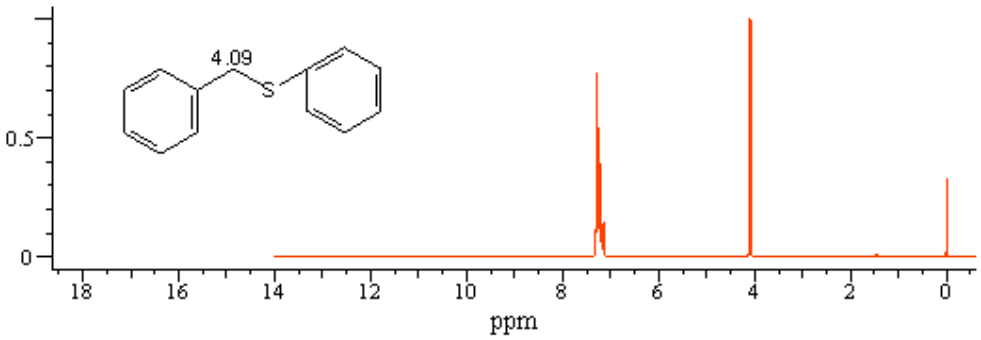
δ_b (ppm)	δ_a (ppm)	-X	Solvent

2.70	2.70		Polysol
3.10	2.58		Polysol
3.11	2.78		Polysol
3.07	2.90		$CDCl_3$
2.89	3.57	-OH	CCl_4

B Aromatic

Sulfides

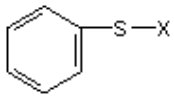
Aromatics



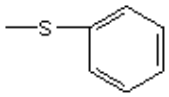
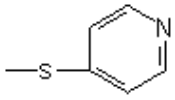
The sulfide linkage has a weakly deshieding effect on adjacent aliphatic groups and a weak shielding effect on the ortho aromatic hydrogens. In both cases, the phenyl sulfide group is a more strongly deshielding group than the corresponding aliphatic sulfide linkage.

Except in the case of the heterocyclic molecules, the coupling constants are the same as those observed for the other substituents discussed thus far.

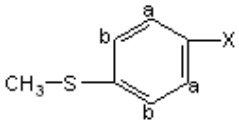
Aromatic Protons

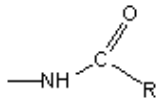
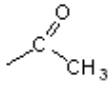
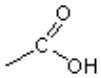


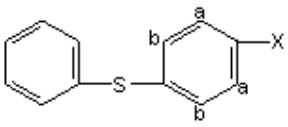
(ppm)	-X	Solvent

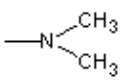
6.90-7.30	-S-CH_3	$CDCl_3$
7.00-7.43		CCl_4
7.10-7.70		$CDCl_3$

Para Substituted Phenylsulfides



δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.22	6.75	-OH	$CDCl_3$
7.10	6.83	-NH-R	Polyso l
7.05	7.05	-CH_3	CCl_4
7.11	7.39	-Br	$CDCl_3$
7.21	7.55		DMSO-d_6
7.24	7.81		Polysol
7.27	7.89		DMSO-d_6

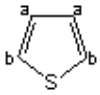


δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.33	6.63		$CDCl_3$

7.23	6.78	$-NH_2$	Polysol
7.08	6.94	$-O-CH_3$	$CDCl_3$
7.28	7.28	-Cl	Polysol
7.21	7.07	$-CH_3$	$CDCl_3$
7.47	7.47	$-NH_2$ (salt)	TFA
7.44	7.97		$CDCl_3$

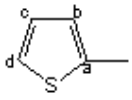
Thiophenes

Due to the small differentiation in chemical shift between the protons of the parent compound and the relatively large coupling constants involved, the multiplets that arise from the substituted thiophenes are usually higher order in character. The coupling constants are unusual in that the ^{J}2-3 coupling constant is normally larger than the ^{J}3-4 situation that does not occur in the spin-spin interactions of the corresponding oxygen and nitrogen heterocyclics.

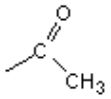
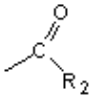
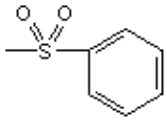
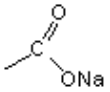


δ_b (ppm)	δ_a (ppm)	Solvent
6.90	7.10	CCl_4

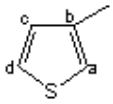
2-Substituted Thiophenes



δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
7.03	6.87	6.72	$-CH_3$	$CDCl_3$
6.92	6.72	6.72	-Cl	$CDCl_3$
7.12	6.79	6.98	-Br	CCl_4
7.19	6.72	7.27	-I	$CDCl_3$

7.53	7.02	7.53		CCl_4
7.60	7.10	7.60	-C≡N	$CDCl_3$
7.54	7.07	7.62		CCl_4
7.62	7.07	7.71		$CDCl_3$
7.67	7.12	7.67		CCl_4
7.56	7.07	7.69		D_2O

3-Substituted Thiophenes



δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
7.11	6.75	$-C_3$	6.78	CCl_4
7.05	6.77	$-CH_3$	6.77	CCl_4
7.18	6.91	-Br	7.11	$CDCl_3$

Coupling and Coupling Constants

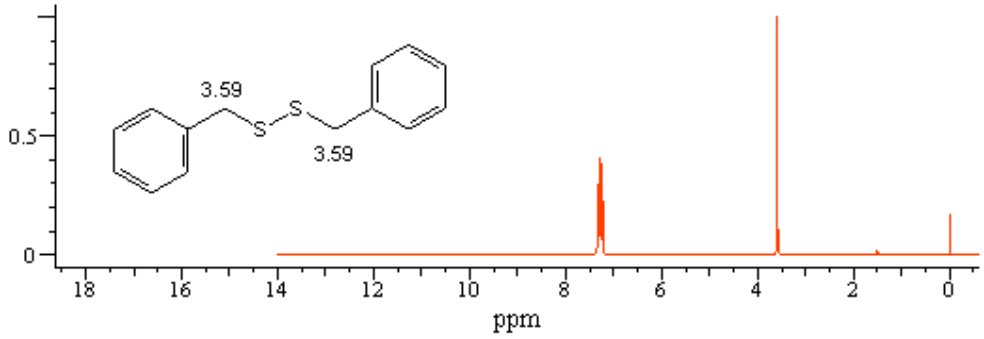
^{J}2-3 = 3-4 Hz

^{J}3-4 = 4-5 Hz

^{J}2-4 = 1-2 Hz

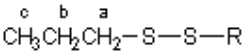
2 Disulfides (R-S-S-R)

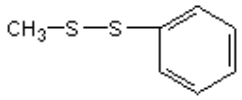
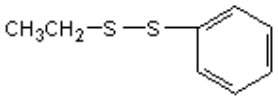
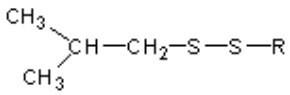
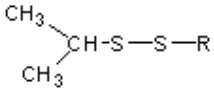
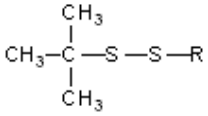
Disulfides



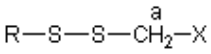
The disulfide group produces chemical shifts similar to those of the sulfides. Its effect on the adjacent aliphatic groups is slightly more deshielding by about 0.1-0.4 ppm while its effect on the ortho aromatic protons is slightly less deshielding by about 0.2 ppm. Without prior knowledge that the element sulfur was present in the molecular formula of an unknown material, both linkages would be difficult to identify because of their weakly deshielding character, their lack of exchangeable protons and the fact that no unusual coupling constants are observed, with the exception of thiophene.

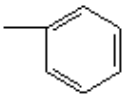
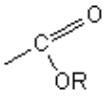
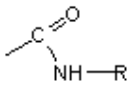
Aliphatic Protons



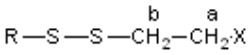
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		2.39	CH_3-S-S-CH_3	CCl_4
		2.33		CCl_4
	1.25	2.66		$CDCl_3$
0.93	1.70	2.69	$CH_3CH_2CH_2$—S—S—R	$CDCl_3$
0.99	(1.2-2.2)	2.96	$CH_3CH_2CH_2CH_2$—S—S—R	$CDCl_3$
(1.01)	1.92	2.55		CCl_4
	(1.30)	2.98		$CDCl_3$
	(1.30)			CCl_4

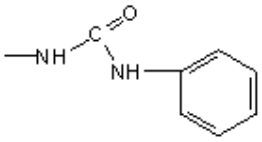
Substituted Methyldisulfides



δ_a (ppm)	-X	Solvent
2.70	$-CH_3$	$CDCl_3$
3.29	$-CH=CH_2$	CCl_4
3.46		CS_2
3.51		CCl4
3.70		TFA
3.70		Polysol

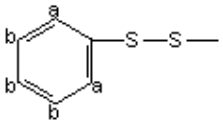
Substituted Ethyldisulfides

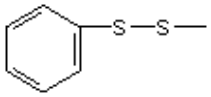


δ_b (ppm)	δ_a (ppm)	X	Solvent
2.69	1.70	$-CH_3$	$CDCl_3$
2.89	2.65		DMSO-d_6
3.07	3.39	$-NH_2(HCl)$	D_2O
2.86	3.49		Polysol

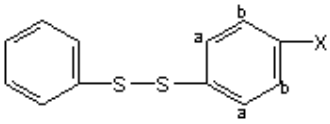
Aromatic Protons

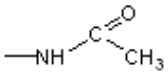
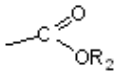
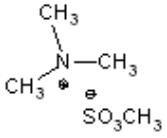
Phenyl Disulfides



	δ_b (ppm)	δ_a (ppm)	Solvent
CH_3-S-S-	7.10-7.35	7.45	CCl_4
	7.00-7.35	7.46	$CDCl_3$

Para Substituted Diphenyl Disulfides



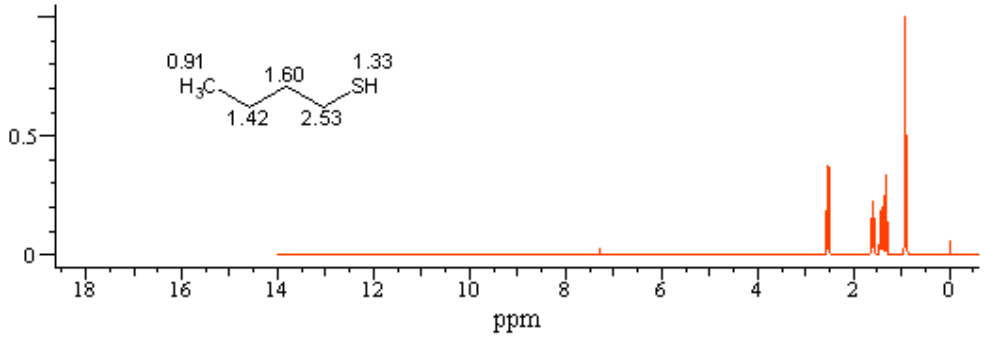
δ_b (ppm)	δ_a (ppm)	X	Solvent
7.12	6.55	$-NH_2$	DMSO-d_6
7.48	6.86	$-O-CH_3$	$CDCl_3$
7.34	7.05	$-CH_3$	$CDCl_3$
7.38	7.20	-Cl	$CDCl_3$
7.39	7.39	-Br	$CDCl_3$
7.48	7.65		DMSO-d_6
7.51	7.99		$CDCl_3$
7.79	8.07		DMSO-d_6

3□Thiols

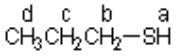
A□Aliphatic

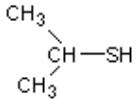
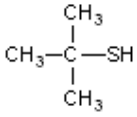
Thiols

Aliphatics

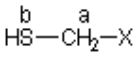


The aliphatic thiols are an especially easy group of compounds to characterize due to the clear coupling between the thiol proton (-S-H) and adjacent aliphatic groups (except in D_2O solution). The aromatic thiols are also relatively easy to characterize in that they contain an exchangeable proton which resonates at relatively high field (3.0-5.0 ppm) but the group does not strongly shield the ortho and para hydrogens as the aromatic amines and phenols do. The thiol group is a weak to intermediate deshielding group in its effect on aliphatic protons but neither shields nor deshields the ortho aromatic hydrogens to any great extent.

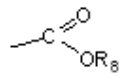
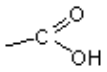
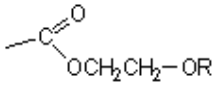
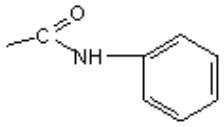
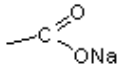
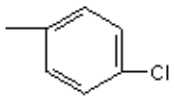
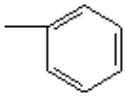


δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
		2.07	1.24	CH_3-SH	$CDCl_3$
	1.31	2.52	1.17	CH_3-CH_2-SH	CCl_4
0.99	1.67	2.52	1.31	CH_3-CH_2-CH_2-SH	CCl_4
	(1.31)	3.07	1.40		TFA
	(1.41)		1.62		CCl_4

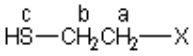
Substituted Methanethiols

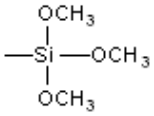
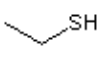
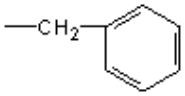


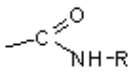
δ_b (ppm)	δ_a (ppm)	X	Solvent

1.99	3.20		CCl_4
2.22	3.31		$CDCl_3$
2.06	3.33		$CDCl_3$
2.06	3.41		$CDCl_3$
	3.51		D_2O
1.58	3.57		CCl_4
1.50	3.64		CCl_4

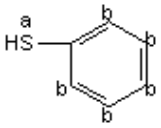
Substituted Ethanethiols



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
1.12	2.43	0.67		CCl_4
1.18	2.50	1.60		CCl_4
1.19	2.49	1.60	$-R_4$	CCl_4
1.31	2.52	1.67	$-CH_3$	$CDCl_3$
1.18	2.51	1.69		CCl_4
1.30	2.51	1.84		$CDCl_3$
1.27	2.67	1.89	$-CH_2-SH$	CCl_4

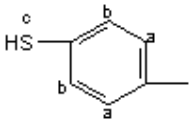
1.58	2.54	2.30		$CDCl_3$
	2.71	2.71	-SH	D_2O
	2.68	3.69	-OH	D_2O

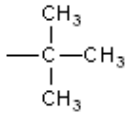
Aromatic Protons



δ_b (ppm)	δ_a (ppm)
3.19	~6.91 (broad, single, peak)

Para Substituted Benzenethiols



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
3.52	7.14	6.52	$-NH_2$	$CDCl_3$
3.37	7.30	6.81	$-O-CH_3$	$CDCl_3$
3.30	7.09	6.91	$-CH_3$	$CDCl_3$
3.40	7.11	7.11	-Cl	$CDCl_3$
3.16	7.13	7.13		CCl_4
3.42	7.07	7.30	-Br	$CDCl_3$

Exchangeable Protons

The thiol protons, being less active than the exchangeable hydrogens of the amines and alcohols, usually display coupling to the adjacent aliphatic groups in all solvents except D_2O. One exception to this fact occurs in the case in which another type of exchangeable is present in the molecule. The thiol-aliphatic group coupling constant is similar to

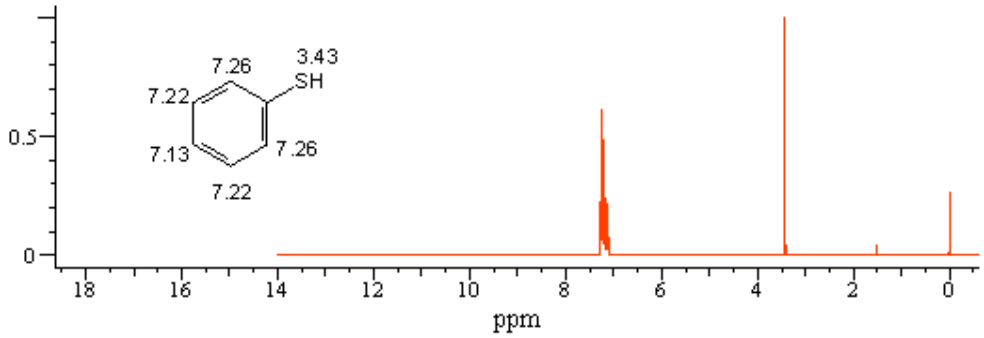
that observed for vicinal CH—CH coupling, J = 5-8 Hz.

These protons undergo deuteration only slowly upon the addition of a few drops of D_2O to a sample solution of $CDCl_3$ or CCl_4 . In D_2O solution, however, they exchange completely and immediately.

B Aromatic

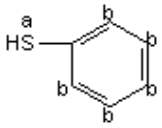
Thiols

Aromatics



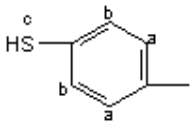
The aromatic thiols are also relatively easy to characterize in that they contain an exchangeable proton which resonates at relatively high field (3.0-5.0 ppm) but the group does not strongly shield the ortho and para hydrogens as the aromatic amines and phenols do. The thiol group is a weak to intermediate deshielding group in its effect on aliphatic protons but neither shields nor deshields the ortho aromatic hydrogens to any great extent.

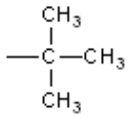
Aromatic Protons



δ_b (ppm)	δ_a (ppm)
3.19	~6.91 (broad, single, peak)

Para Substituted Benzenethiols



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
3.52	7.14	6.52	$-NH_2$	$CDCl_3$
3.37	7.30	6.81	$-O-CH_3$	$CDCl_3$
3.30	7.09	6.91	$-CH_3$	$CDCl_3$
3.40	7.11	7.11	-Cl	$CDCl_3$
3.16	7.13	7.13		CCl_4
3.42	7.07	7.30	-Br	$CDCl_3$

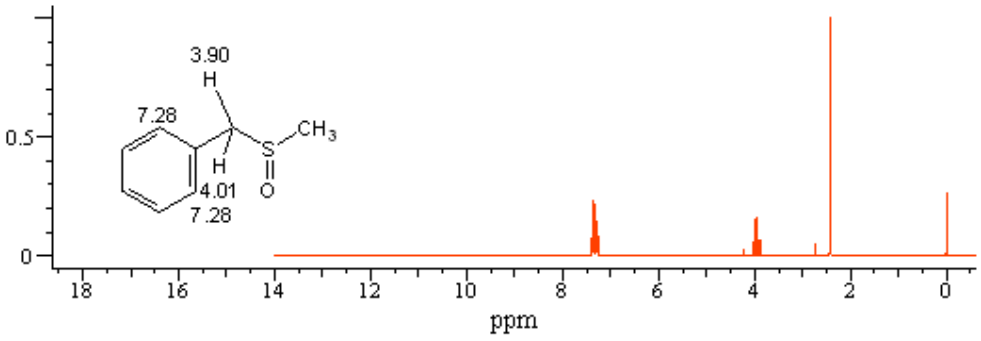
Exchangeable Protons

The thiol protons, being less active than the exchangeable hydrogens of the amines and alcohols, usually display coupling to the adjacent aliphatic groups in all solvents except D_2O. One exception to this fact occurs in the case in which another type of exchangeable is present in the molecule. The thiol-aliphatic group coupling constant is similar to that observed for vicinal CH—CH coupling, J = 5-8 Hz.

These protons undergo deuteration only slowly upon the addition of a few drops of D_2O to a sample solution of $CDCl_3$ or CCl_4 . In D_2O solution, however, they exchange completely and immediately.

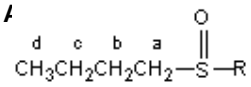
4 Sulfoxides (R-S(=O)-R)

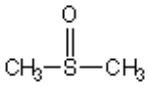
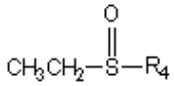
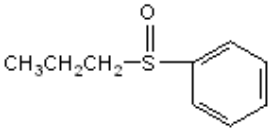
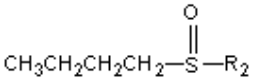
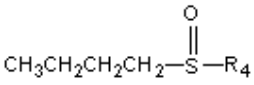
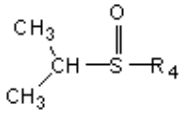
Sulfoxides



The Sulfoxide group imparts no special features to its NMR spectrum. It is an intermediate to strong deshielder of adjacent aliphatic groups and a weak to intermediate deshielder of the ortho aromatic hydrogens.

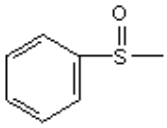
Dimethyl Sulfoxide is well known as a solvent, with its deuterated form a commonly used material in NMR. All of the unsubstituted sulfoxides are readily soluble in the chlorinated solvents such as CCl_4 and $CDCl_3$.

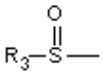


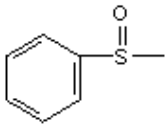
δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
			2.52		CCl_4
		1.28	2.56		CCl_4
	1.02	1.66	2.67		CCl_4
0.99	(1.1-2.0)	(1.1-2.0)	2.51		CCl_4
0.96	(1.1-2.1)	(1.1-2.1)	2.68		$CDCl_3$
		(1.22)	2.67		CCl_4

Aromatic Protons

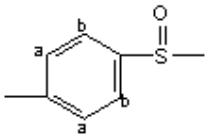
Phenyl Sulfoxides

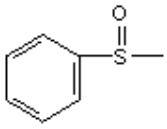
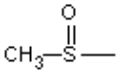
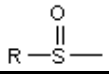
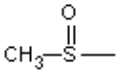
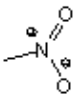


X-	δ_a (ppm)	Solvent
	7.30-7.70	CCl_4

	7.25-7.80	$CDCl_3$

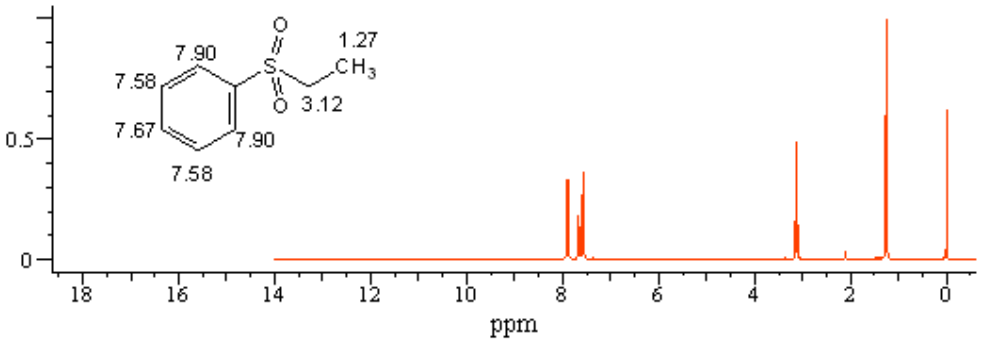
Para-Substituted Phenylsulfoxides



	δ_b (ppm)	δ_a (ppm)	-X	Solvent
	7.56	6.93	$-O-CH_3$	$CDCl_3$
	7.86	7.36	-I	$CDCl_3$
	7.61	7.54	-Cl	$CDCl_3$
	7.86	8.42		$CDCl_3$

5 Sulfones ($R-SO_2-R$)

Sulfones



In comparison to the sulfoxides (-S(=O)-), the sulfones ($-S(=O)_2-$) are a more strongly deshielding substituent in their

effect on both the adjacent aliphatic groups and on the ortho aromatic protons. Some of the relative deshielding effect of the sulfur containing functional groups are displayed.

1.90 ppmCH_3-S-R

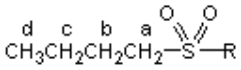
2.39 ppmCH_3-S-S-R

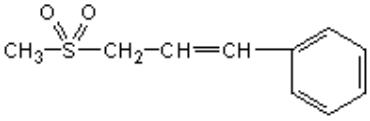
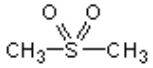
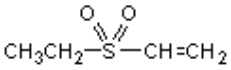
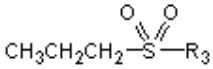
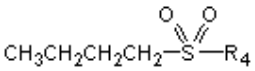
2.52 ppmCH_3-S(=O)-R

2.87 ppmCH_3-S(=O)$_2$-R

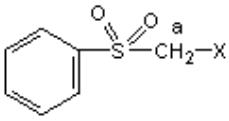
The compounds containing the sulfone group are somewhat less soluble in the chlorinated solvents than the sulfoxides but, are more soluble in solvents such as acetone, DMSO-d_6, Polysol and D_2O.

Aliphatic Protons

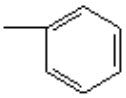


δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
			2.87		$CDCl_3$
			3.11		D_2O
		1.26	2.97		CCl_4
	1.09	1.81	2.91		CCl_4
0.97	(1.2-2.1)	(1.2-2.1)	2.95		$CDCl_3$

Substituted Methanesulfones



δ_a (ppm)	X	Solvent
3.80	-CH=CH_2	$CDCl_3$
4.30	-C≡C-R	Polysol

4.35	-C≡C-H	Polysol
4.44		Polysol
4.60		Polysol
4.88		Polysol

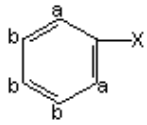
Olefinic Protons

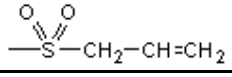
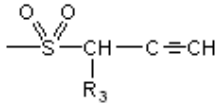
The sulfone group deshields all three vinyl protons, producing a complex, higher order pattern in the chemical shift range from 6.0-7.0 ppm. Analysis of these patterns suggests that the proton trans to the SO_2 group resonates at highest field (about 6.2 ppm), that the proton cis to the SO_2 group resonates at slightly lower field (about 6.4 ppm), and that the geminal proton resonates at lowest field (about 6.8 ppm).

Aromatic Protons

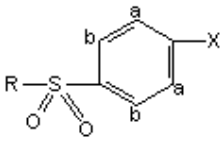
The sulfone substituted phenyl groups produce an aromatic pattern characteristic of a substituent which strongly deshields the ortho protons. The para and meta hydrogens overlap to produce a complex multiplet in the range from about 7.2-7.8 ppm while the ortho hydrogens appear as a higher order doublet of doublets at about 7.9 ppm.

Phenylsulfones

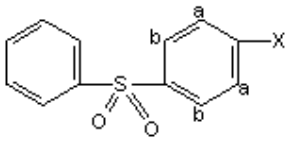


δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.2-7.7	7.89		$CDCl_3$
7.2-7.8	8.02		$CDCl_3$

Para-Substituted Phenylsulfones



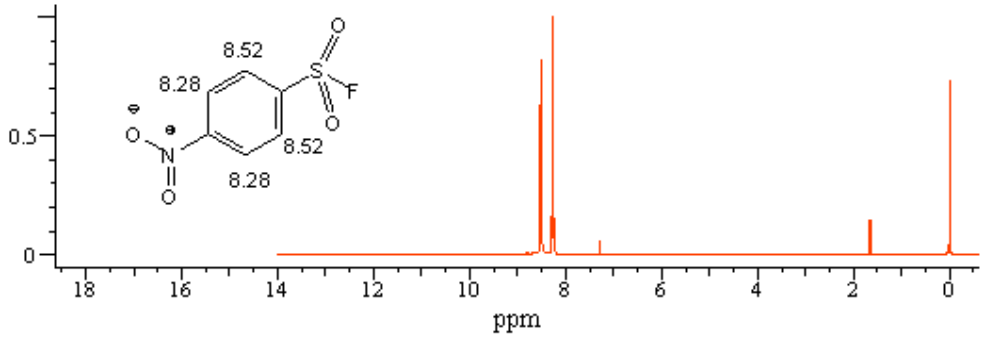
δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.85	7.11	$-O-CH_3$	Polysol
7.78	7.34	$-CH_3$	$CDCl_3$
7.81	7.50	-Cl	$CDCl_3$



δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.79	6.91	$-O-CH_3$	$CDCl_3$
7.95	7.18	-F	$CDCl_3$
7.80	7.23	$-CH_3$	$CDCl_3$
7.82	7.42	-Cl	$CDCl_3$
7.82	7.65	-Br	$CDCl_3$
8.08	8.30		$CDCl_3$

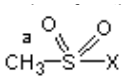
6 Sulfonyl Halides ($R-SO_2-X$)

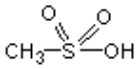
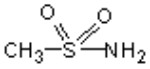
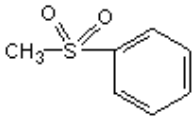
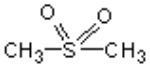
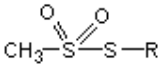
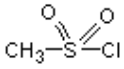
Sulfonyl Halides



We present chemical shift data only for the sulfonyl fluorides and chlorides.

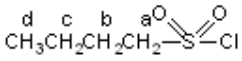
While the type of halogen present appears to have a significant effect on the chemical shifts of aliphatic groups, the effect is much less pronounced in relation to the ortho aromatic hydrogens. For the sake of comparison, a ıyl substituted SO_2 groups of various types is presented.



δ_a (ppm)	Compound	Solvent
2.82		D_2O
3.03		Polysol
3.07		$CDCl_3$
3.11		D_2O
3.49		DMSO-d_6
3.65		CCl_4

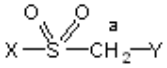
It is interesting to note that when the sulfonyl chloride undergoes hydrolysis to form the corresponding sulfonic acid, the methyl resonance is converted from the most strongly deshielded (3.65 ppm) to the least deshielded group of this series (2.82 ppm).

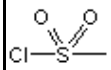
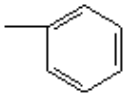
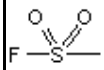
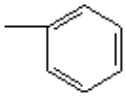
Aliphatic Protons



δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
			3.65	CH_3-SO_2-Cl	CCl_4
		1.54	3.65	CH_3-CH_2-SO_2-Cl	CS_2
	1.17	2.09	3.68	CH_3-CH_2-CH_2-SO_2-Cl	CCl_4
1.02	1.50	2.00	3.69	CH_3- CH_2-CH_2-CH_2-SO_2-Cl	CCl_4

Substituted Methane Sulfonyl Halides

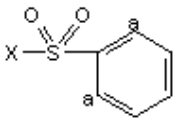


-X	δ_a (ppm)	-Y	Solvent
	4.83		$CDCl_3$
	5.07		Polysol

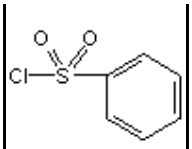
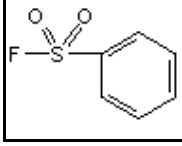
Aromatic Protons

Both the chlorine and fluorine sulfonyl compounds strongly deshield the ortho aromatic hydrogens. The chemical shifts observed for the two phenyl compounds are extremely similar. A comparison of the para substituted compounds indicates identical shifts for the two para substituted methyl compounds, higher field shifts for the chlorine substituted sulfonyl fluoride but lower field shifts for the corresponding carboxylic acid substituted sulfonyl fluoride compared to the corresponding sulfonyl chlorides.

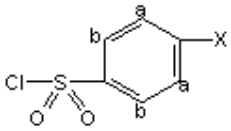
Phenylsulfonyl Halides

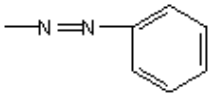
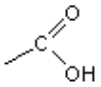
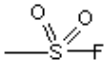
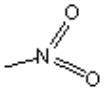


	δ_a (ppm)	Solvent

	8.03	CCl_4
	8.00	CCl_4

Para-Substituted Phenylsulfonyl Halides



δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.98	7.07	$-O-CH_3$	$CDCl_3$
7.90	7.41	$-CH_3$	$CDCl_3$
8.05	7.67	-Cl	$CDCl_3$
7.99	7.69	-I	$CDCl_3$
7.90	7.77	-Br	$CDCl_3$
8.17	8.08		$CDCl_3$
7.90	8.09		Polysol
8.13	8.13		Polysol
8.01	8.28		Polysol

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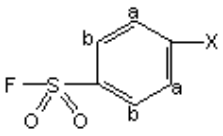
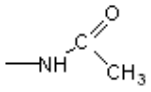
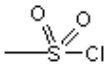
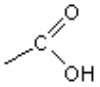


δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.73	6.71	$-NH_2$	$CDCl_3$
7.90	7.41	$-CH_3$	$CDCl_3$
7.98	7.62	-Cl	$CDCl_3$
8.01	8.01		DMSO-d_6
8.13	8.13		Polysol
8.14	8.33		Polysol

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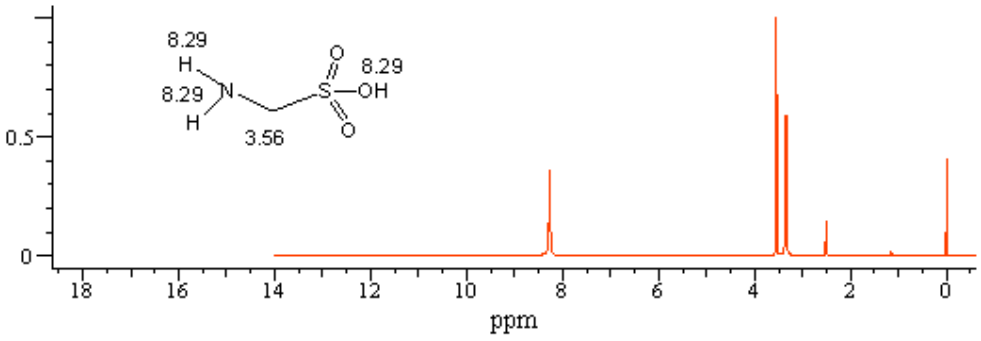
Coupling and Coupling Constants

The only unusual coupling constant associated with the sulfonyl halides is that observed between the sulfonyl fluoride group and the adjacent-aliphatic group

$^{J}F\text{-}S(O_2)\text{-}CH_2$ = 4.5 Hz

7 Sulfonic Acids ($R\text{-}SO_2\text{-}OH$)

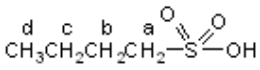
Sulfonic Acids

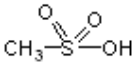
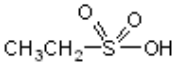
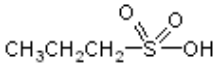
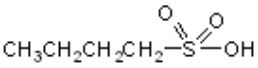


The sulfonic acids are similar to the other sulfone ($-S(O_2)-$) compounds in their chemical shift effects, in that, they are a moderately strong deshielding group for adjacent aliphatic groups and a strong deshielding group for ortho aromatic hydrogens.

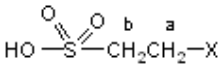
The lower molecular weight members of the series are soluble in both the chlorinated solvents as well as DMSO-d_6, polysol and D_2O. When an amine group is present in the molecule, they form an internal salt which makes these compounds soluble almost exclusively in D_2O or DMSO-d_6.

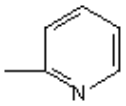
Aliphatic Protons



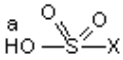
δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
			2.82		D_2O
		1.45	3.26		CCl_4
	1.11	1.97	3.24		$CDCl_3$
0.97	1.55	1.90	3.23		$CDCl_3$

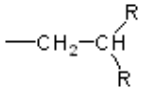
Substituted Ethanesulfonic Acids



δ_b (ppm)	δ_a (ppm)	-X	Solvent
3.42	3.30	$-NH-CH_3$	D_2O
3.51	3.51		D_2O
3.40	3.27	$-NH_2$	D_2O

Sulfonic Acid Protons



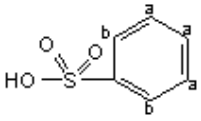
δ_a (ppm)	-X	Solvent
8.75		CCl_4
10.70	$-R_2$	CCl_4
10.71	$-R_3$	$CDCl_3$

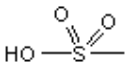
10.72	-R_4	$CDCl_3$

Aromatic Protons

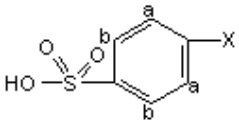
The sulfonic acid group strongly deshields the ortho aromatic hydrogens. The ortho protons resonate near 7.9 ppm as a distorted doublet of doublets while the meta and para hydrogens appear as a complex higher order band in the chemical shift range from 7.4-7.7 ppm.

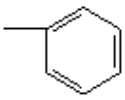
Benzenesulfonic acid



	δ_b (ppm)	δ_a (ppm)	Solvent
	7.93	7.4-7.7	D_2O

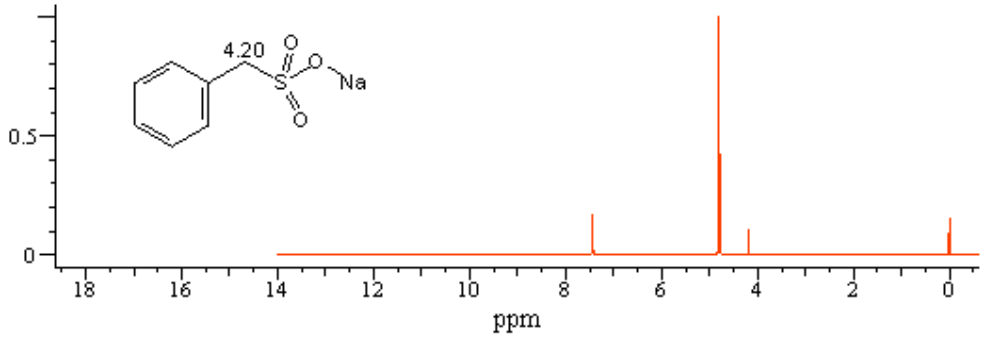
Para-Substituted benzenesulfonic acids



δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.61	7.19	$-CH_3$	DMSO-d_6
7.81	7.81		DMSO-d_6

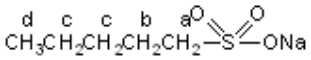
A Sulfonic Acid Salts (R-SO_2-O-M)

Salts of Sulfonic Acid



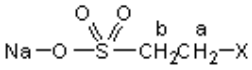
The water soluble metallic salts of sulfonic acid display aromatic chemical shifts very similar to those of the free acid with the aliphatic groups adjacent to the sulfonate group resonating at slightly higher field. Although of commercial importance, relatively small number of compounds are available for the preparation of their NMR spectra.

Aliphatic Protons



δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
0.91	(1.2-1.6)	1.72	2.87	$CH_3CH_2CH_2CH_2CH_2—S(=O)(=O)—ONa$	D_2O

2-Substituted Ethanesulfonic Acid Salts

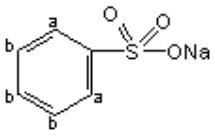


δ_b (ppm)	δ_a (ppm)	X	Solvent
2.89	1.72	$-R_3$	D_2O
3.15	2,96	-C≡N	D_2O
3.27	3.27	$-SO_3$-Na	D_2O
3.41	3.66	-Br	D_2O
3.37	3.89	-Cl	D_2O
3.15	3.95	-OH	D_2O

Aromatic Protons

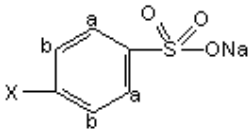
The aromatic chemical shifts of the sulfonic acid salts are similar to those of the parent acids. The shifts of benzenesulfonic acid, sodium salt are listed below followed by those of several para substituted derivatives

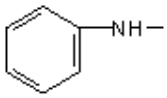
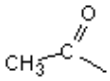
Benzenesulfonic acid, sodium salt

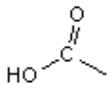


δ_b (ppm)	δ_a (ppm)		Solvent
7.4-7.7	7.92	$-SO_3$-Na	D_2O

Para substituted benzenesulfonic acid salts

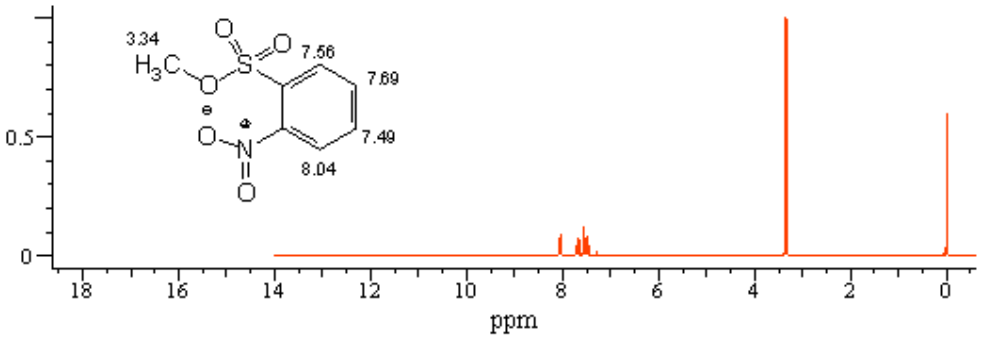


X-	δ_b (ppm)	δ_a (ppm)		Solvent
H_2N-	6.79	7.62	$-SO_3$-Na	D_2O
HO-	6.80	7.72	$-SO_3$-K	D_2O
R_{14}-	7.06	7.67	$-SO_3$-Na	D_2O
	7.10	7.91	$-SO_3$-Na	D_2O
CH_3-	7.28	7.81	$-SO_3-NH_4$	D_2O
Cl-	7.45	7.83	$-SO_3$-Na	D_2O
Br-	7.68	7.79	$-SO_3$-Na	D_2O
	7.88	7.88	$-SO_3$-Na	D_2O

	8.09	8.09	-SO_3-K	D_2O

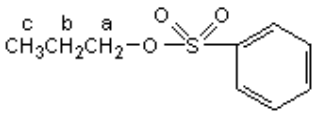
B Sulfonic Acid Esters ($R-SO_2-O-R$)

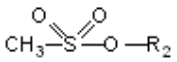
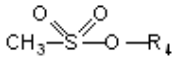
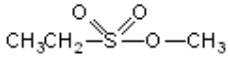
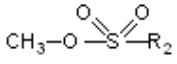
Esters of Sulfonic Acid

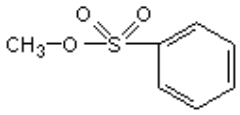
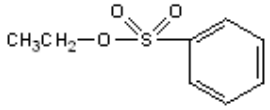
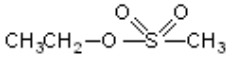
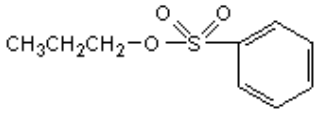
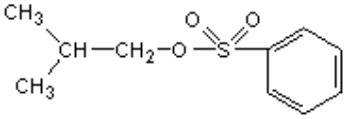


The sulfonic acid functional group produces two distinct sets of chemical shifts for the adjacent aliphatic groups. The groups bonded to the acid side of the linkage are weakly deshielded but those bonded to the alcohol side are very strongly deshielded. This situation is analogous to that which is encountered with the esters of carboxylic acids. The sulfonic acid esters, unlike the free acids and their salts, are readily soluble in $CDCl_3$ and CCl_4, and relatively insoluble in deuterium oxide.

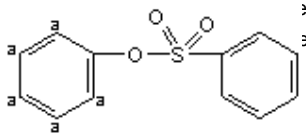
Aliphatic Protons



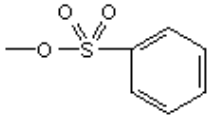
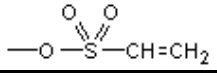
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		2.94		CCl_4
		3.00		$CDCl_3$
	1.39	3.09		CCl_4
		3.85		CCl_4

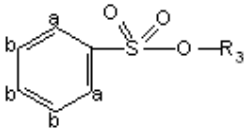
		3.89		$CDCl_3$
	1.25	4.01		CCl_4
	1.39	4.21		CCl_4
0.89	1.59	3.99		$CDCl_3$
0.89	1.91	3.71		CCl_4

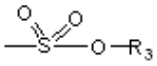
Aromatic Protons



ens, the effect of the sulfonic acid ester linkage is opposite to that observed for
en side of the linkage weakly shields the ortho protons while the sulfur side

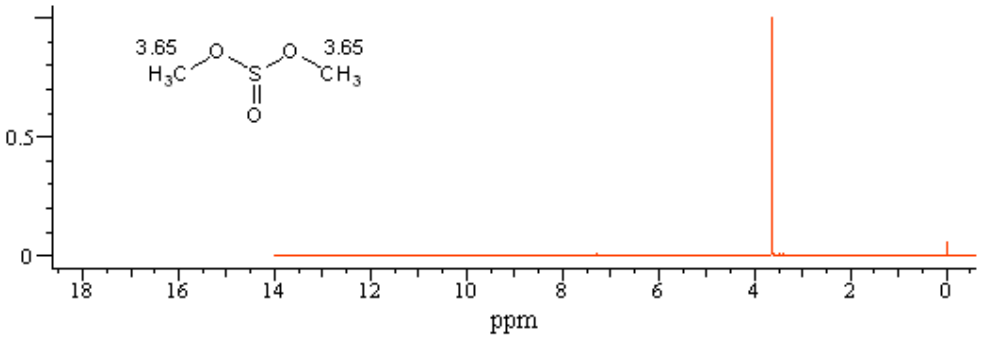
δ_a (ppm)	-X	Solvent
6.9-7.5		$CDCl_3$
7.0-7.5		CCl_4



δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.3-7.7	7.83		$CDCl_3$

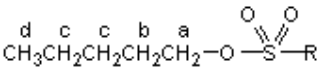
C Sulfuric Acid Esters (R-O-S(=O)-O-R)

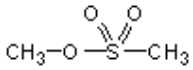
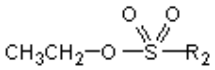
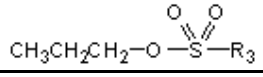
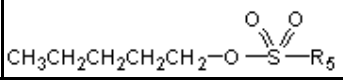
Esters of Sulfurous Acid



The esters of sulfurous acid are a small group of compounds for which only a few aliphatic derivatives are available commercially. As with all of the esters, the oxygen atom adjacent to the alpha carbon group has a strong deshielding effect upon the protons bonded to it.

Aliphatic Protons



δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
			3.59		CCl_4
		1.34	4.04		CCl_4
	0.96	1.67	3.92		$CDCl_3$
0.92	(1.2-2.0)		3.94		CCl_4

Coupling and Coupling Constants

No unusual couplings nor coupling constants have been noted for the esters of sulfurous acid. The aliphatic

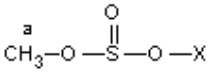
patterns are similar in appearance to those of similarly strong deshielding groups such as the ether group.

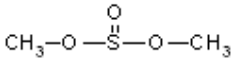
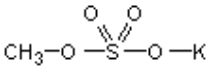
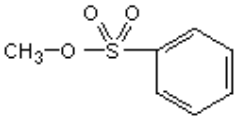
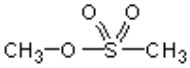
Solubility and Solvent Effects

The sulfites are readily soluble in the chlorinated solvents such as carbon tetrachloride and deutero-chloroform.

Characterization

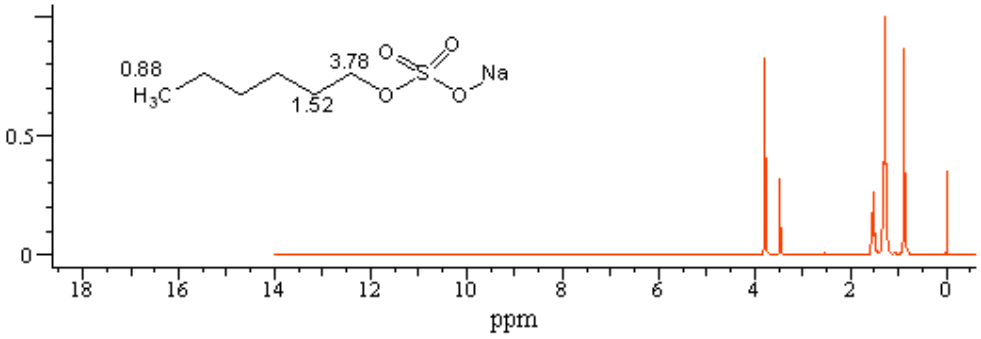
Because of the relatively narrow range of chemical shifts observed for the esters of the various sulfur containing acids, the functional group of such compounds is best characterized through the analysis of their infrared



δ_a (ppm)	Compound	Acid	Solvent
3.59		Sulfurous acid	CCl_4
3.73		Sulfuric acid	D_2O
3.73		Benzenesulfonic acid	$CDCl_3$
3.88		Methanesulfonic acid	CCl_4

D Sulfuric Acid Salts (R-O-SO_2-O-M)

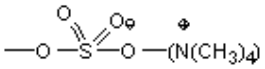
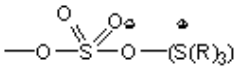
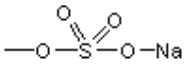
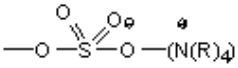
Salts of Sulfuric Acid

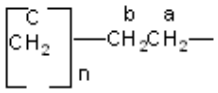


The mono-salts of sulfuric acid display a strong deshielding effect on the aliphatic groups of the ester portion of the molecule. This deshielding effect is similar to that noted for the esters of Sulfurous acid.

Aliphatic Protons

Methyl Esters

δ_a (ppm)	-X	Solvent
3.71		D_2O
3.72		D_2O
3.73		D_2O
3.95		TFA



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		3.73	CH_3-O-S(O_2)-O-K	D_2O
	1.31	4.12	CH_3-CH_2-O-S(O_2)-O-K	Polysol
$(1.1\text{-}1.6)_2$	1.69	4.06	$CH_3(CH_2)_2$-CH_2-CH_2-O-S(O_2)-O-Na	D_2O
$(1.1\text{-}1.5)_5$	1.61	4.01	$CH_3(CH_2)_5$-CH_2-CH_2-O-S(O_2)-O-Na	D_2O
$(1.1\text{-}1.5)_7$	1.61	3.46	$CH_3(CH_2)_7$-CH_2-CH_2-O-S(O_2)-O-Na	Polysol
$(1.1\text{-}1.6)_{11}$	1.61	3.82	$CH_3(CH_2)_{10}$-CH_2-CH_2-O-S(O_2)-O-Na	Polysol

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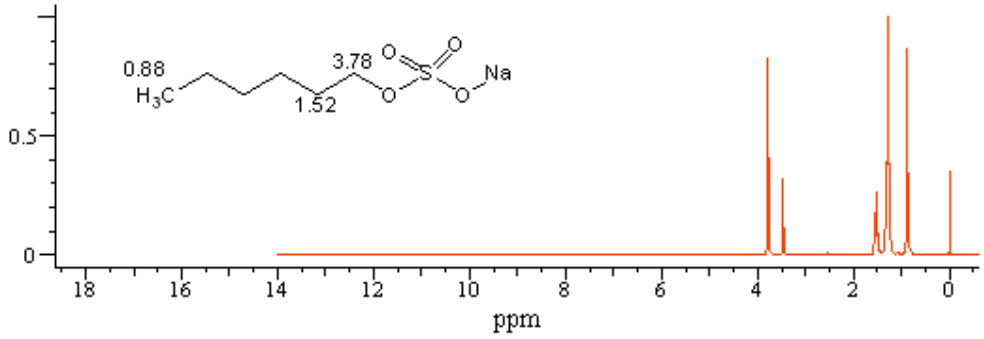
Solubility and Solvent Effects

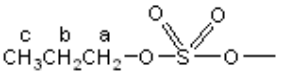
The presence of the mono-salt function makes the mono-esters much more soluble in solvents such as Polysol, DMSO-d_6 and D_2O than the corresponding diesters. The rather wide divergence in chemical shift noted for the compounds examined in Polysol solution most probably arises from the varying amounts of H_2O which are often present in such solutions. Based upon the information supplied in the table above, it can be inferred that the chemical shifts of the sulfuric acid ester/salts appear at highest field in relatively dry Polysol solution shifting to lower field as the amount of H_2O increases and finally reach maximum deshielding when the solvent is 1OO% H_2O (D_2O).

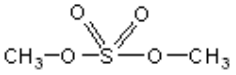
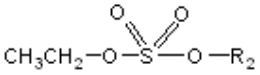
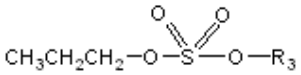
Diesters of Sulfuric Acid



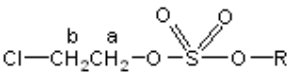
The diesters of sulfuric acid exhibit chemical shifts similar to those of the ester/salts with minor variations due to the different solvents employed. The diesters are found to be much more soluble in the chlorinated hydrocarbons than the more polar ester/salts.

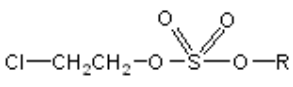
Aliphatic Protons

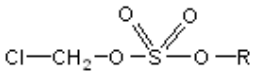


δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		3.87		CCl_4
	1.45	4.28		CCl_4
1.00	1.75	4.15		CCl_4

Chlorinated Sulfate Esters



δ_b (ppm)	δ_a (ppm)	Compound	Solvent
3.80	4.52		$CDCl_3$

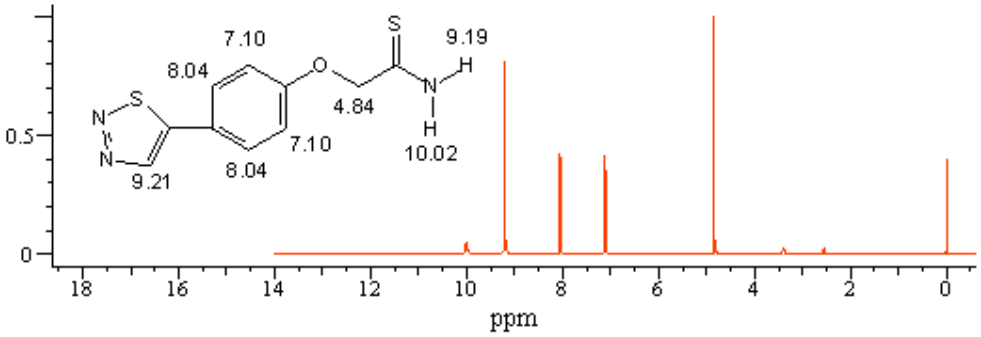
	5.79		CCl_4

Coupling and Coupling Constants

The diesters of sulfuric acid do not display any additional or different couplings from the protons of the other normal aliphatic groups. Vicinal coupling is observed (^{J}HC-CH = 6-8 Hz), but longer range coupling if present is too small in magnitude to be detected.

8 Thioamides ($R\text{-}C(=S)\text{-}NH_2$)

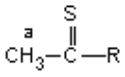
Thioamides

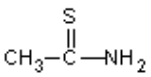


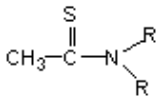
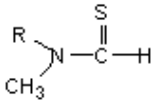
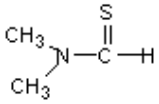
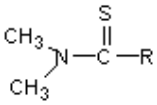
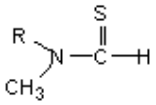
The Thioamide functional group is interesting in that a wide variety of chemical shifts may be observed depending upon the substituents and the side of the group to which they are bonded. Non-equivalence is commonly observed for the primary amide protons and also in the case in which two different groups are bonded to the tertiary amide nitrogen atom.

The thioamides tend to be less soluble in the chlorinated solvents than most of the sulfur-containing groups but are usually quite soluble in Polysol or DMSO-d_6.

Aliphatic Protons

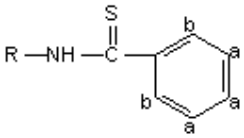


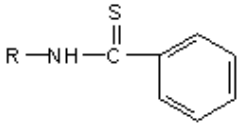
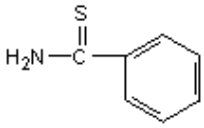
δ_a (ppm)	Compound	Solvent
2.40		DMSO-d_6

2.62		$CDCl_3$
3.13		$CDCl_3$
(3.27, 3.30)		$CDCl_3$
(3.31, 3.48)		$CDCl_3$
3.34		$CDCl_3$

Aromatic Protons

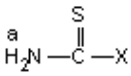
The Thioamide carbon of this functional group has a moderately strong deshielding effect on the ortho aromatic hydrogens. They appear as a distorted doublet-of-doublets near 7.85 ppm while the para and meta protons produce a complex, higher order band at higher field.

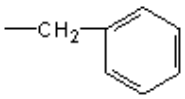
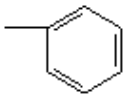


Compound	δ_b (ppm)	δ_a (ppm)
	7.81	7.3-7.6
	7.89	7.1-7.5

Exchangeable Protons

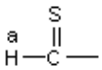
The Thioamide protons usually appear as very broad bands at low field. They are often non-equivalent and thus may appear separated in chemical shift by 1-2 ppm.

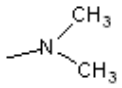
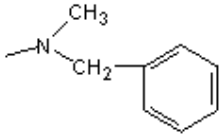
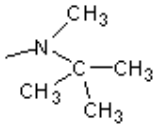


δ_a (ppm)	-X	Solvent
ca. 8.45		Polysol
9.20	$-CH_3$	DMSO-d_6
9.32, 9.65		DMSO-d_6

Thioformaldehyde Protons

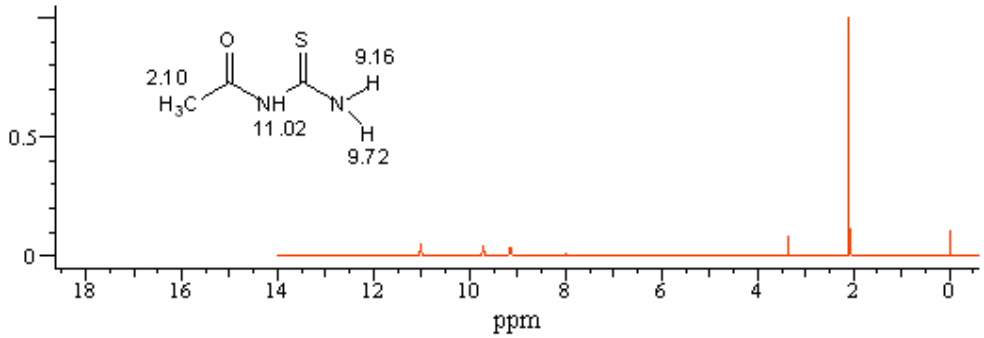
The Thioformaldehyde protons resonate at very low field as a sharp to slightly broadened single peak. If the nitrogen atom is substituted by two different groups, it is possible for two stable forms to exist in which one group is syn to the aldehydic proton and the other group anti, and vice versa. Clear coupling between the aldehydic proton and aliphatic groups bonded to the nitrogen atom is usually not observed.



δ_a (ppm)	-X	Solvent
9.19		$CDCl_3$
9.32, 9.46		$CDCl_3$
9.53		$CDCl_3$

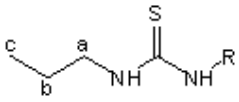
9 Thioureas (R-NH-C(=S)-NH_2)

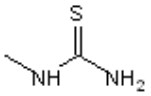
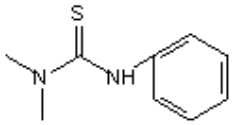
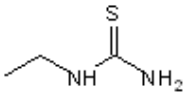
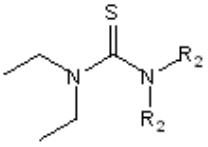
Thioureas

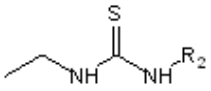
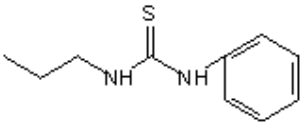
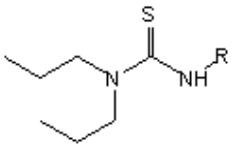
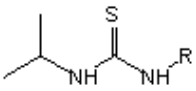
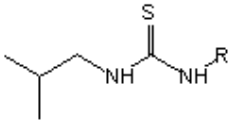


The Thioureas have a moderately strong deshielding effect on adjacent aliphatic groups and they usually display clear coupling to them in the case of the secondary thiourea linkage (J = 4-5 Hz). The presence of the C(=S) thiocarbonyl group greatly reduces the shielding effect of the NH group on ortho aromatic hydrogens in comparison to the effect noted for the secondary amines. The chemical shift of the various NH hydrogens varies widely depending primarily on the type of substitution present in the molecule. In the case of the primary thiourea protons, the two hydrogens bonded to the nitrogen atom may be non-equivalent leading to different chemical shifts for each proton.

Aliphatic Protons



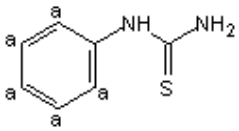
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		2.80		DMSO-d_6
		(3.29)		Poly so l
	1.04	3.28		DMSO-d_6
	(1.20	3.52)		$CDCl_3$

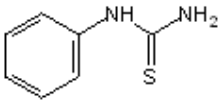
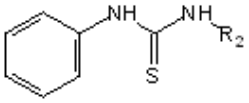
	1.22	3.52		CCl_4
	1.19	3.66		$CDCl_3$
(0.92	1.64	3.61)		Polysol
	(1.24)	4.32		$CDCl_3$
(0.95)	1.92	3.30		Polysol

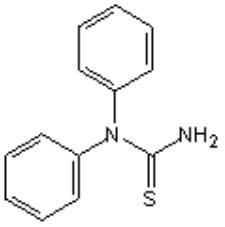
Aromatic Protons

The aromatic protons bonded to the nitrogen nuclei of the thiourea group are neither strongly shielded nor deshielded. They appear in the spectrum as a complex band in the chemical shift range from about 6.9 to 7.7 ppm. The shape and complexity of this higher order pattern is quite sensitive to the presence and type of other substituents bonded to the thiourea linkage.

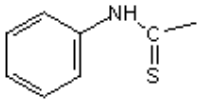
Thiourea substituted phenyl groups

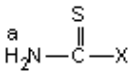


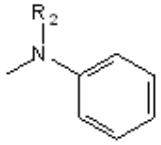
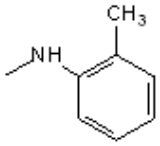
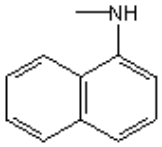
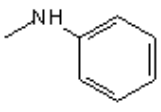
δ_a (ppm)	Compound	Solvent
6.90-7.60		DMSO-d_6
7.00-7.70		$CDCl_3$

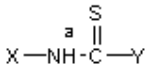
7.10-7.60		DMSO

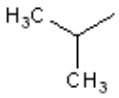
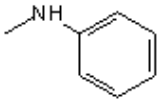
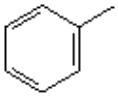
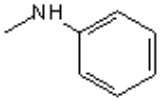
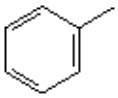
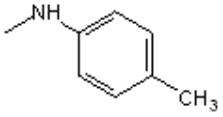
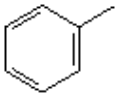
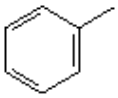
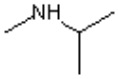
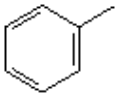
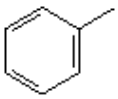
Exchangeable Protons

Although the chemical shifts of the exchangeable protons of the thioureas vary markedly with solvent, temperature and the presence of H_2O in solution, the tables below indicate a trend in shift with the type of substitution of the thiourea nitrogen atoms. It is noted that the primary amide protons resonate at highest field (H_2N-C(=S)-), that alkyl substituted secondary amide protons resonate at slightly lower field (R-NH-C(=S)-), and that the phenyl substituted secondary groups resonate at lowest field  .



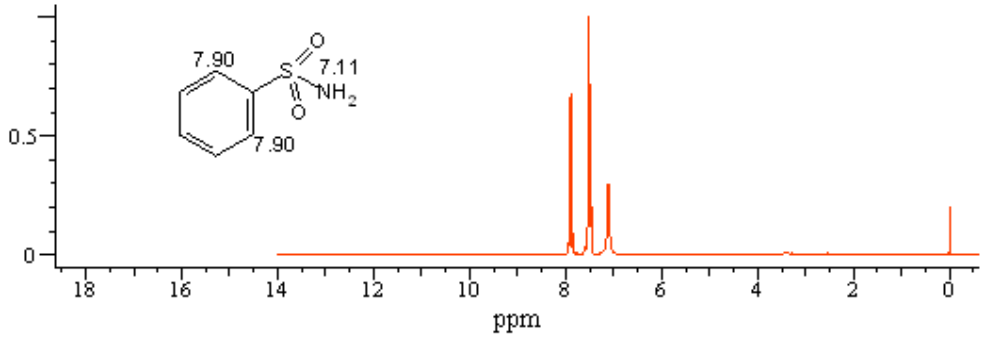
δ_a (ppm)	-X	Solvent
5.0-8.0	-NH-CH_3	DMSO-d_6
6.31		Polysol
6.88		DMSO-d_6
6.93	-NH-R_2	DMSO-d_6
7.00		Polysol
7.11	-NH_2	DMSO
7.32		DMSO-d_6



-X	δ_a (ppm)	-Y	Solvent
	6.10	-NH-R	$CDCl_3$
R_2-	6.19		$CDCl_3$
R_2-	6.67	-NH-R_2	CCl_4
R_{10}-	7.10	-NH-R_{10}	Polysol
CH_3-	7.50	-NH_2	DMSO-d_6
R_2-	7.50	-NH_2	DMSO-d_6
	7.97		$CDCl_3$
	8.04		$CDCl_3$
	8.62	-NH-R_2	$CDCl_3$
	9.13		Polysol
	9.57	-NH_2	Polysol
	9.66	-NH_2	DMSO-d_6

11 Sulfonamides (R-SO_2-NH_2)

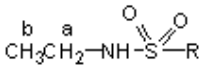
Sulfonamides

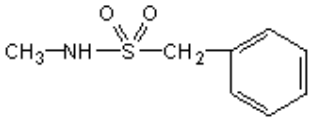
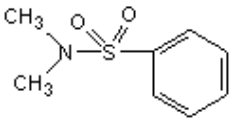
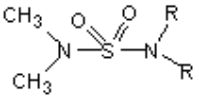
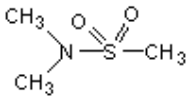
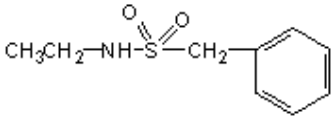


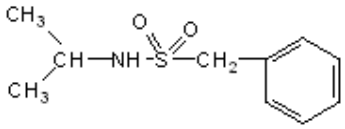
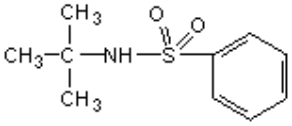
The Sulfonamides produce two distinct sets of chemical shifts. The protons of hydrocarbon groups bonded to the nitrogen side of the linkage resonate at higher field than the corresponding protons of groups bonded to the SO_2 side. In addition to the characteristic chemical shifts thus produced, the sulfonamides usually display clear coupling between an aliphatic group and the NH proton adjacent to it.

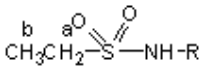
These compounds are generally more soluble in DMSO-d_6 and Polysol than in the chlorinated solvents. There appears to be a distinct deshielding of the NH protons in DMSO-d_6 and Polysol in comparison to similar protons in $CDCl_3$.

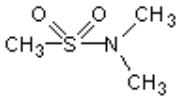
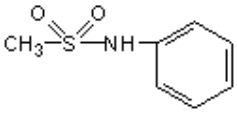
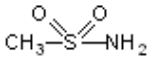
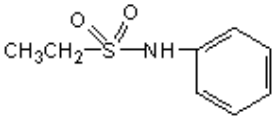
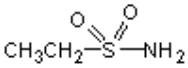
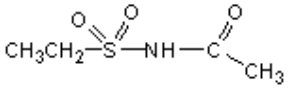
Aliphatic Protons



δ_b (ppm)	δ_a (ppm)	Compound	Solvent
	2.60		Polysol
	(2.69)		$CDCl_3$
	(2.83)		$CDCl_3$
	(2.85)		$CDCl_3$
1.08	2.97		DMSO-d_6

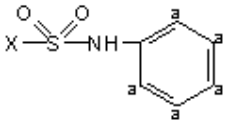
(1.13)	3.40		Polysol
(1.20)			$CDCl_3$

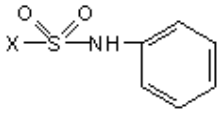
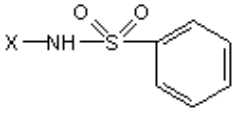


δ_b (ppm)	δ_a (ppm)	Compound	Solvent
	2.78		$CDCl_3$
	3.00		$CDCl_3$
	3.03		Polysol
1.33	3.10		$CDCl_3$
1.40	3.18		$CDCl_3$
1.40	3.47		$CDCl_3$

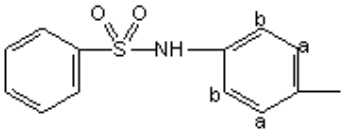
Aromatic Protons

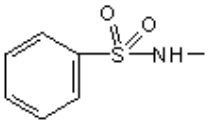
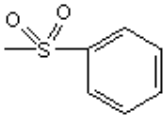
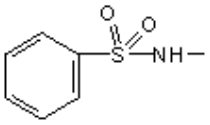
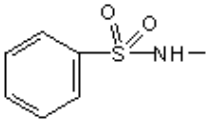
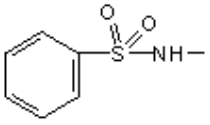
The SO_2 side of the sulfonamide linkage is a strong deshielding group in its effect on the ortho aromatic hydrogens. These protons usually resonate in the range from 7.5-7.9 ppm. The nitrogen side of the sulfonamide group is a weakly shielding substituent on all the aromatic protons and they appear as a broad single peak near 7.1 ppm.

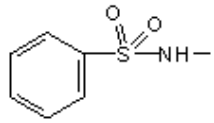
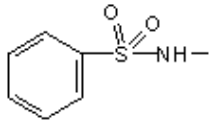
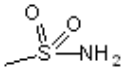
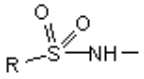


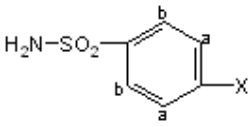
Compound	δ_a (ppm)	Solvent
	ca. 7.12	$CDCl_3$
	7.87, 7.5-7.8	DMSO-d_6

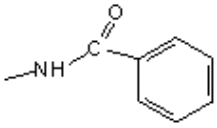
Para Substituted Sulfonamides



	δ_b (ppm)	δ_a (ppm)	para	Solvent
	7.19	6.88		Poly so l
	6.95	6.95	-CH_3	$CDCl_3$
	6.98	7.09	-R_2	TFA
R-SO_2-NH-	7.21	7.2	-Cl	DMSO-d_6
	7.01	7.31	-Br	$CDCl_3$

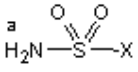
	7.01	7.54	-I	Acetone
	7.26	7.73		Poly so l
	7.40	8.03		Acetone



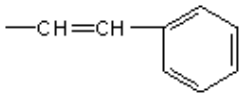
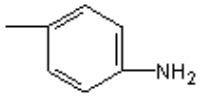
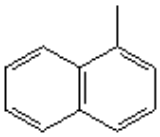
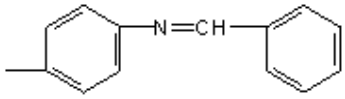
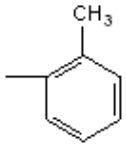
δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.50	6.64	$-NH_2$	DMSO-d_6
7.75	6.98	$-O-CH_3$	Poly so l
8.07	7.37	-F	Acetone
7.90	7.57	-Cl	Acetone
7.89	7.89		Polysol
7.99	8.11		Polysol
8.10	8.43	$-NO_2$	DMSO-d_6

Exchangeable Protons

Primary Sulfonamides



δ_a (ppm)	-X	Solvent

5.24	-R_2	$CDCl_3$
6.50		Polysol
6.89		DMSO-d_6
7.11		Poly so l
7.11		DMSO-d_6
7.21		DMSO-d_6

Coupling and Coupling Constants

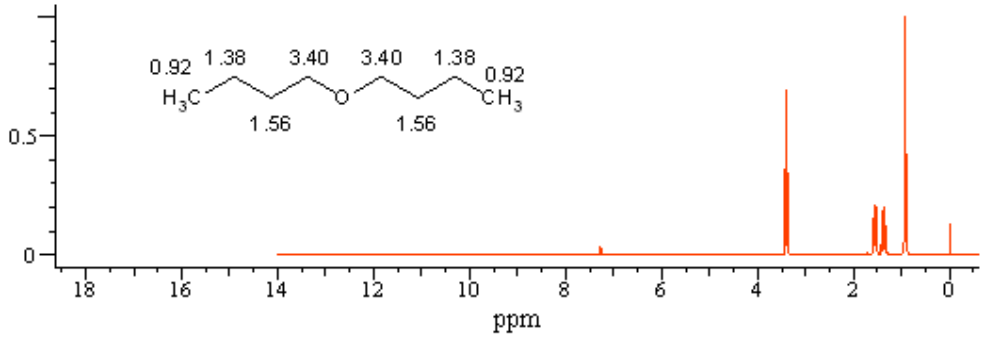
Coupling between aliphatic groups and the adjacent NH proton is usually observed. The coupling constant is similar in magnitude to normal vicinal CH-CH coupling, ^{J}CH—NH = 6-8 Hz

Oxygen Containing Compounds (Except -C(=O)-)

1□ Ethers

1□Aliphatic Ethers (R-O-R)

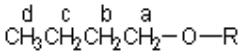
Aliphatic and Olefinic Ethers

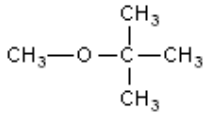
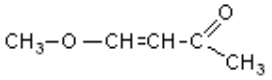


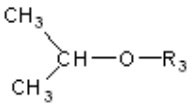
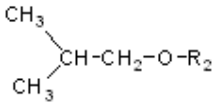
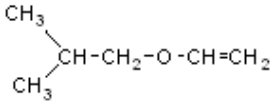
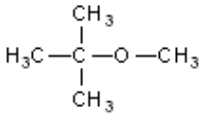
Because the compounds containing an ether linkage are of such commercial importance and because such a large number of compounds are available, the chemical shifts of this group have been divided into five separate sections; Aliphatic and Olefinic, Alicyclic, Aromatic, Heterocyclic and, the Silicon and Phosphorus Ethers.

Aliphatic Protons

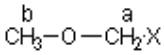
The aliphatic groups bonded to the ether linkage are moderately strongly deshielded. In addition, the aliphatic groups bonded to an olefinic ether linkage are more strongly deshielded than those of an aliphatic ether substituent.

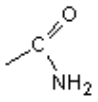
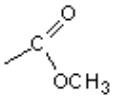
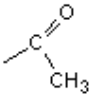
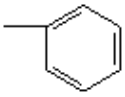


δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
			3.11		CCl_4
			3.22	CH_3-O-R_5	CCl_4
			3.30	CH_3-O-R_4	$CDCl_3$
			3.72		CCl_4
		1.13	3.38	CH_3-CH_2-O-R_2	CCl_4
		1.23	3.71	CH_3-CH_2-O-CH=CH-CH_3	CCl_4
	0.93	1.60	3.37	CH_3-CH_2-CH_2-O-R_3	$CDCl_3$

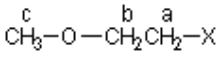
		(1.12)	3.51		CCl_4
0.91	(1.1-1.8)	(1.1-1.8)	3.37	$CH_3CH_2CH_2CH_2—O—CH_3$	$CDCl_3$
0.91	(1.1-1.8)	(1.1-1.8)	3.60	$CH_3CH_2CH_2CH_2—O—CH=CH_2$	CCl_4
	(0.89)	1.80	3.09		CCl_4
	(0.97)	1.90	3.38		CCl_4
		(1.12)			CCl_4

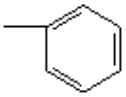
Substituted Methyl Ethers



δ_b (ppm)	δ_a (ppm)	X	Solvent
3.30	3.37	$-R_3$	$CDCl_3$
3.43	3.89		$CDCl_3$
3.38	3.90		CCl_4
3.30	3.99	-C≡C-H	CCl_4
3.47	4.02		$CDCl_3$
3.46	4.14	-C≡N	CCl_4
3.49	4.30		CCl_4
3.29	4.35		$CDCl_3$
3.23	4.40	$-O-CH_3$	$CDCl_3$

Substituted Methyl Ethyl Ethers

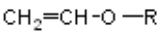


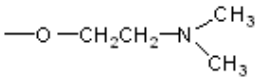
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
3.38	3.54	2.52	-C≡N	CCl_4
3.26	3.53	2.73		$CDCl_3$
3.37	3.42	2.86	$-NH_2$	$CDCl_3$
3.39	3.65	3.40	-Br	CCl_4
3.38	3.51	3.71	-OH	$CDCl_3$

Olefinic Protons

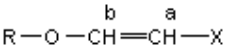
In regard to the vinyl protons, the ether linkage is a strongly deshielding substituent in its effect on the chemical shift of the proton attached to the alpha carbon (the geminal hydrogen), but is a strong shielding group in its effect on the cis and trans protons.

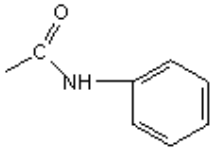
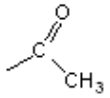
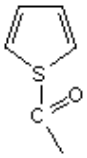
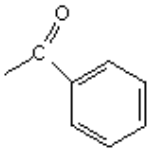
Vinyl Ethers



cis (ppm)	trans (ppm)	geminal (ppm)	-R	Solvent
4.01	3.84	6.32	$-O-R_4$	CCl_4
4.08	3.89	6.35		CCl_4

Substituted Vinyl Ethers



δ_b (ppm)	δ_a (ppm)	-X	Solvent
5.82	4.27	$-CH_3$ (cis)	CCl_4
6.12	4.68	$-CH_3$ (trans)	CCl_4
7.54	5.42		$CDC!_3$
7.50	5.52		CCl_4
7.76	6.68		Polysol
7.79	6.72		Poly so l

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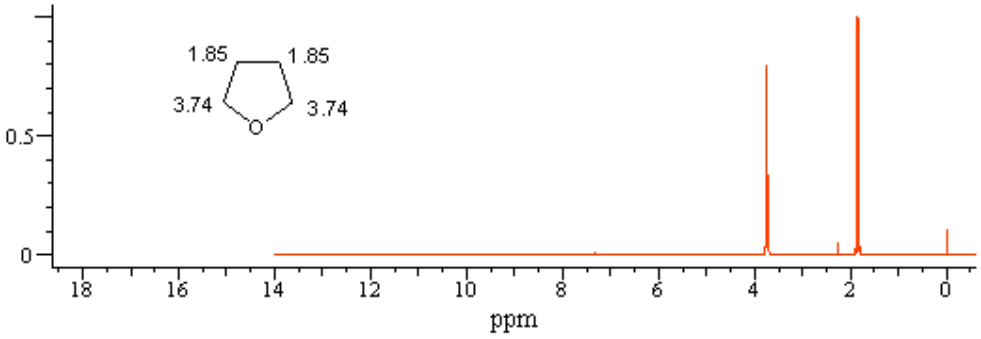
Vinyl Coupling and Coupling Constants

Because of the clear separation in chemical shifts produced by ether substituents on the vinyl protons, the various coupling constants are often clearly displayed.

	J values	
Geminal	$^{J}H_2C=C$	= 1.7 Hz
Cis	$^{J}H-C=C-H$	= 7.0 Hz
Trans	$^{J}H-C=C-H$	= 14.5 Hz
Geminal	$^{J}CH_3-C-H$	= 6.9 Hz
Cis	$^{J}CH_3-C=C-H$	= 1.6 Hz
Trans	$^{J}CH_3-C=C-H$	= 1.6 Hz

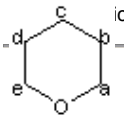
2 Alicyclic Ethers

Alicyclic Ethers

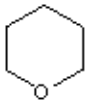


The broadening of multiplets due to the lack of rotation about the carbon-carbon bonds of the protons in the ring and the absence of terminal methyl groups are often sufficient evidence to characterize the HNMR spectra of the alicyclic compounds. The cyclic ethers are all readily soluble in the chlorinated solvents CCl_4 and $CDCl_3$.

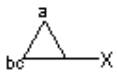
The three ring protons of the epoxide group are non-equivalent and appear as three distinct multiplets in the chemical shift range from 2.3 to 3.8 ppm delta. The two protons bonded to C-1 resonate at higher field than the proton attached to C-2. The appearance and chemical shifts of these bands are readily recognizable and quite



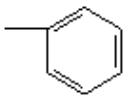
ic of this group.

δ_e (ppm)	δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		4.62	2.64	4.62		CCl_4
	3.71	1.81	1.81	3.71		$CDCl_3$
3.56	1.59	1.59	1.59	3.56		CCl_4

ıg Protons



cis δ_c (ppm)	trans δ_b (ppm)	δ_a (ppm)	X	Solvent
2.31	2.55	2.69	$-R_2$	CCl_4

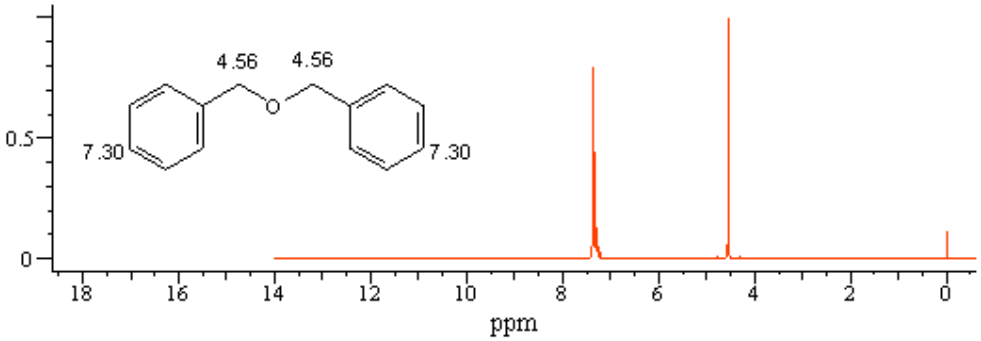
2.28	2.56	2.74	$-R_{10}$	CCl_4
2.23	2.59	2.80	$-CH_3$	CCl_4
2.46	2.63	2.98	$-CH_2-O-R$	CCl_4
2.58	2.79	3.17	$-CH_2-Cl$	CCl_4
2.60	2.90	3.30	$-CH=CH_2$	$CDCl_3$
2.58	2.84	3.40	$-CH_2-Br$	CCl_4
2.61	2.96	3.69		CCl_4

Coupling and Coupling Constants

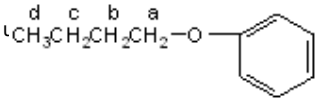
Due to the high degree of strain in the three membered ring, the coupling constants between the three hydrogens of the epoxide group are observed to be somewhat smaller than normally expected. The coupling constants can be J = 5, 4 and 3 Hz for the geminal, cis and trans couplings.

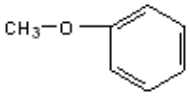
3 Aromatic Ethers

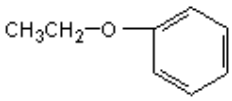
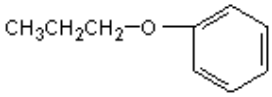
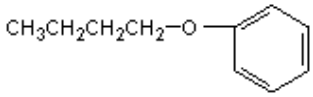
Aromatic Ethers

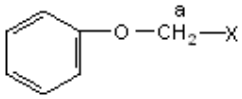


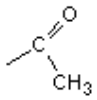
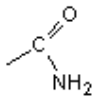
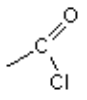
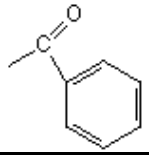
The HNMR spectra of the phenyl ethers are often easily characterized by means of the low field shifts observed for aliphatic groups bonded to the phenoxy moiety and from the high field shifts observed for the ortho and para protons.

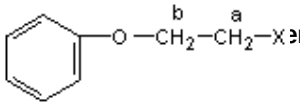
The compounds are normally soluble in CCl_4, $CDCl_3$ and DMSO-d_6. The spectra of the aromatic ethers possess no  of the chemical shifts noted.

δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
			3.70		CCl_4

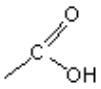
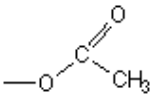
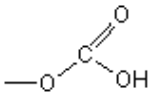
		1.31	3.89		CCl_4
	0.90	1.71	3.85		$CDCl_3$
0.99	1.45	1.70	3.87		CCl_4

 **Phenyl Ethers**

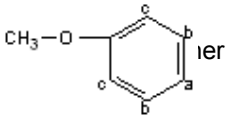
δ_a (ppm)	-X	Solvent
3.89	$-CH_3$	CCl_4
4.36		CCl_4
4.47		$CDCl_3$
4.80		CCl_4
4.81	-C≡C-H	DMSO-d_6
4.92	-C≡N	$CDCl_3$
5.18		$CDCl_3$

 **enyl Ethers**

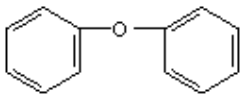
δ_b (ppm)	δ_a (ppm)	-X	Solvent

3.85	1.71	$-CH_3$	$CDCl_3$
4.21	2.79		$CDCl_3$
3.89	2.99	$-NH_2$	$CDCl_3$
4.19	3.52	-Br	$CDCl_3$
4.00	3.59	$-O-CH_3$	CCl_4
4.05	3.63	-Cl	CCl_4
4.06	4.29		CCl_4
4.08	4.39		$CDCl_3$

Aromatic Protons

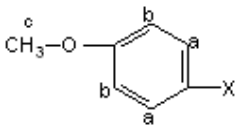


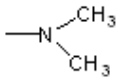
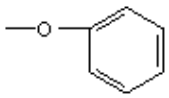
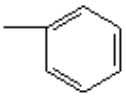
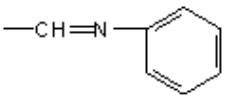
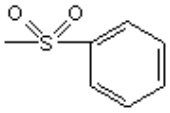
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
6.78	7.19	6.80	CCl_4



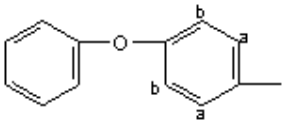
(ppm)	Solvent
6.78-7.40	CCl_4

Para Substituted Methyl Phenyl Ethers

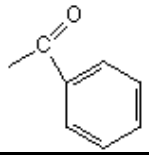
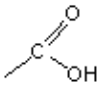


δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
3.75	6.79	6.79		$CDCl_3$
3.71	6.79	6.79	-O-CH_3	$CDCl_3$
3.71	6.80	6.90		$CDCl_3$
3.61	6.65	7.08	-CH=CH-CH_3	CCl_4
3.77	6.79	7.09	-CH_3	$CDCl_3$
3.70	6.72	7.18	-Cl	CCl_4
3.71	6.69	7.29	-Br	CCl_4
3.76	6.81	7.30	-SH	$CDCl_3$
3.76	6.93	7.49		$CDCl_3$
3.74	6.68	7.53	-I	$CDCl_3$
3.65	6.81	7.73		$CDCl_3$
3.79	6.91	7.79		$CDCl_3$
3.89	6.91	8.12		CCl_4

Para Substituted Diphenyl Ethers

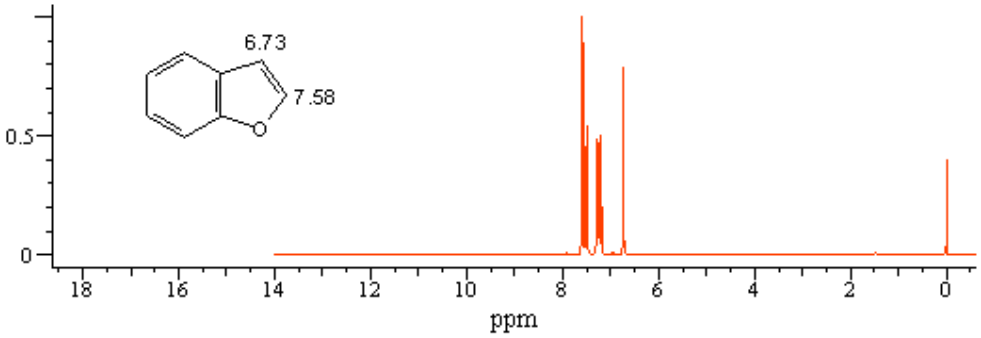


δ_b (ppm)	δ_a (ppm)	-X	Solvent
6.85	6.55	-NH_2	$CDCl_3$

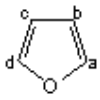
6.91	6.77	-OH	$CDCl_3$
6.90	6.80	$-O-CH_3$	$CDCl_3$
6.75	7.29	-Br	CCl_4
7.02	7.39	-Cl	$CDCl_3$
7.03	7.80		$CDCl_3$
6.98	8.07		$CDCl_3$
7.10	8.27		CCl_4

4 Furans

Furans

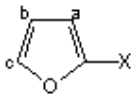


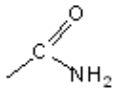
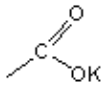
Furan and its derivatives are the major heteroaromatic group of the ether compounds. Their NMR spectra display characteristic chemical shifts and coupling constants producing spin-spin coupling patterns similar to those of the pyrroles and thiophenes. The oxygen atom in the ring strongly deshields the hydrogens on the adjacent carbons (C-2 and C-5) but shields the protons bonded to positions C-3 and C-4.



δ_d(ppm)	δ_c(ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
7.37	6.30	6.30	7.37	CCl_4

2-Substituted Furans



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
6.85	6.23	5.11	$-O-CH_3$	$CDCl_3$
7.15	6.13	5.83	$-CH_3$	CCl_4
7.30	6.25	6.14	$-CH_2-SH$	$CDCl_3$
7.82	7.29	6.67		DMSO-d_6
7.59	6.58	6.92	$-CH=CH-NO_2$	$CDCl_3$
7.64	6.59	7.05		D_2O
7.60	6.55	7.11	$-C\equiv N$	CCl_4
7.82	6.70	7.52		CCl_4

Coupling and Coupling Constants

The furan coupling constants are much smaller in magnitude than the corresponding ortho and meta coupling constants of the benzene derivatives. It is characteristic of the furans and the other heteroaromatic compounds that the "ortho" couplings, J_{2-3} and J_{3-4} are not the same.

$^{J}2\text{-}3$ = 1.7-2.0 Hz

$^{J}3\text{-}4$ = 3.0-4.0 Hz

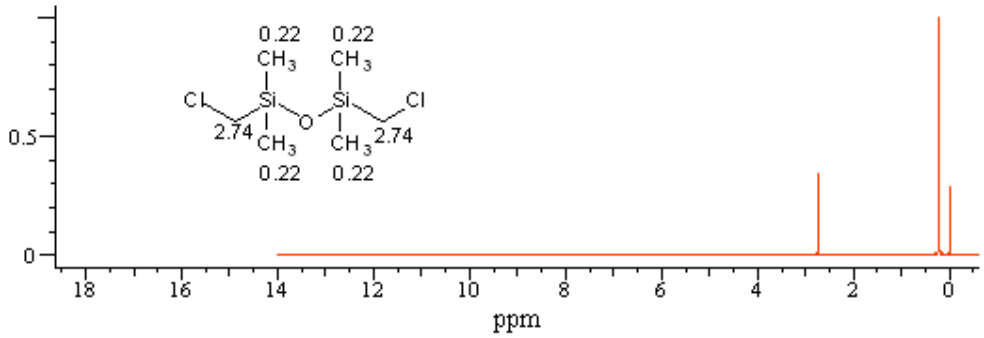
$^{J}2\text{-}4$ = 0.7-1.0 Hz

Solubility and Solvent Effects

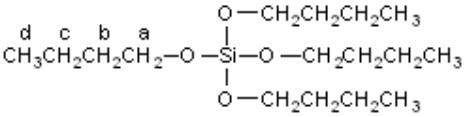
Excluding the solubility limitations imposed by the substituents that may be bonded to the furan ring system, the compounds are readily soluble in the chlorinated solvents normally utilized as NMR solvents (CCl_4 and $CDCl_3$).

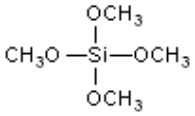
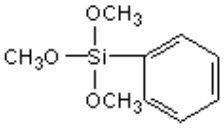
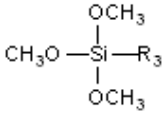
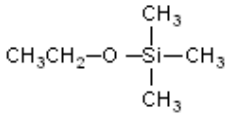
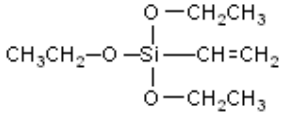
5 Silicon Ethers (R_3-Si-O-R)

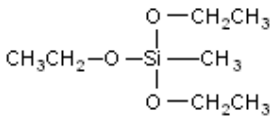
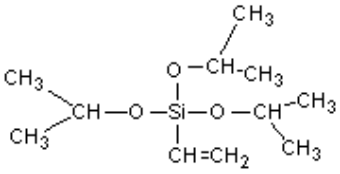
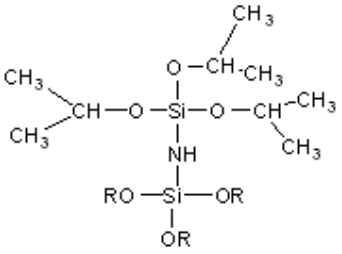
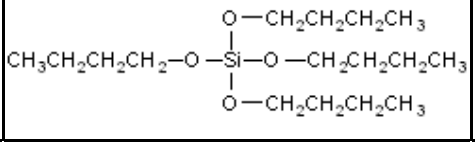
Silicon Ethers



The HNMR spectra of the silicon ethers appear quite similar to those of the aliphatic ethers. The presence of the silicon nucleus can normally be detected only when a hydrocarbon group is bonded directly to it. The silicon ethers are readily soluble in carbon tetrachloride and deuterochloroform.

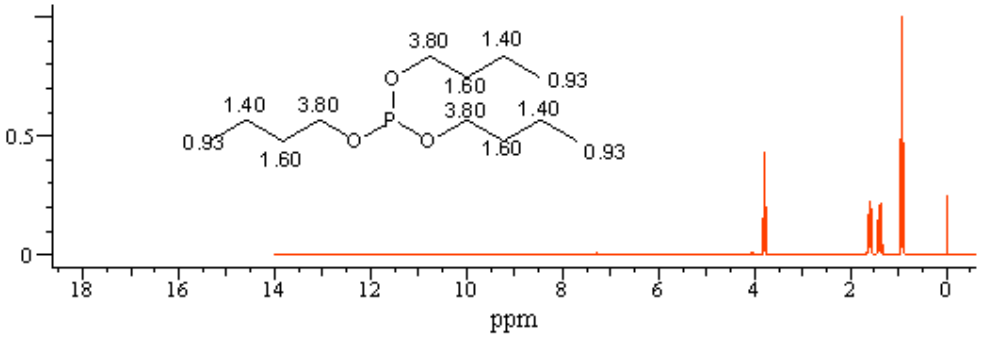


δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
			3.52		CCl_4
			3.56		CCl_4
			3.57		$CDCl_3$
		1.13	3.59		CCl_4
		1.20	3.77		CCl_4

		1.22	3.81		$CDCl_3$
		1.15	4.17		CCl_4
		1.17	4.21		CCl_4
0.94	1.35	1.55	3.71		CCl_4

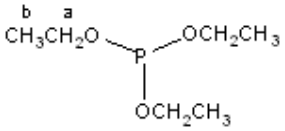
6 Phosphorus Ethers ($(R\text{-}O)_3\text{-}P$)

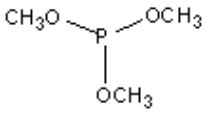
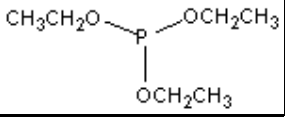
Phosphorus Ethers



The esters of phosphorus acid (P- $(O\text{-}R)_3$) possess chemical shifts characteristic of the oxygen substituent and in addition display additional coupling across the oxygen linkage to the phosphorus atom. This coupling to the first aliphatic group is usually similar to that of three bond proton-proton coupling (J = 6-8 Hz). The magnitude of the coupling constant between phosphorus atom and the second aliphatic group is usually too small to be clearly observed.

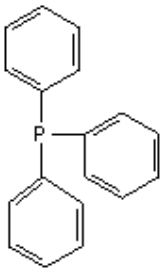
Aliphatic Protons



δ_b (ppm)	δ_a (ppm)	X	Solvent
	3.41		CCl_4
1.21	3.80		CCl_4

Aromatic Protons

Triphenyl Phosphite



δ_a (ppm)	Solvent
6.90-7-50	$CDCl_3$

Coupling and Coupling Constants

^{J}P-O-CH_2 = 6.8 Hz

^{J}P-O-C-CH_3 = 0-1 Hz

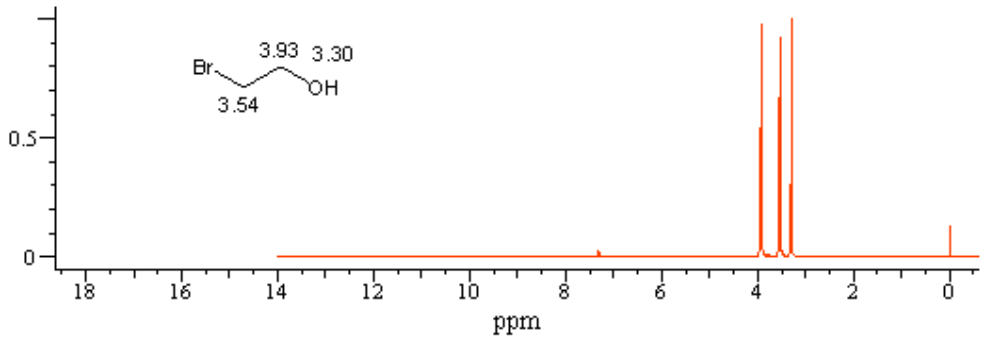
2□ Alcohols (R-OH)

1□ Primary

A□Aliphatic

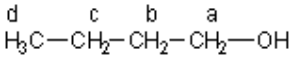
Primary Alcohols

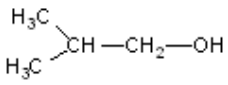
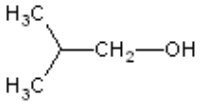
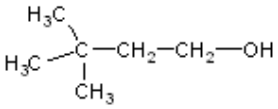
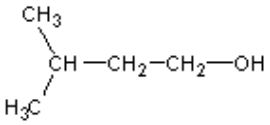
Aliphatics



The primary alcohols characteristically produce HNMR spectra containing a methylene group in the chemical shift range from 3.3 to 5.4 ppm and one exchangeable proton which normally resonates over the range from 1.0 to 6.0 ppm. Both groups may be significantly broadened by partial coupling with each other. This coupling and the attendant broadening is easily eliminated by the addition of either acid or D_2O to the sample solution.

Aliphatic Protons

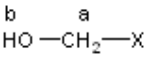


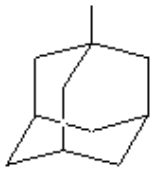
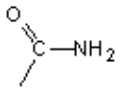
δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
			3.34	CH_3-OH	CCl_4
		1.17	3.58	CH_3-CH_2-OH	CCl_4
	0.94	1.49	3.50	CH_3-CH_2-CH_2-OH	CCl_4
	(0.89)	1.67	3.27		CCl_4
	(0.87)		3.20		CCl_4
0.91	1.35	1.55	3.52	CH_3-CH_2-CH_2-CH_2-OH	CCl_4
(0.95)		1.50	3.71		$CDCl_3$
(0.91)	1.38	1.72	3.52		CCl_4

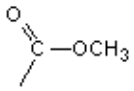
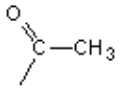
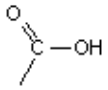
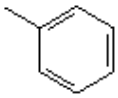
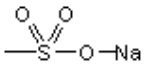
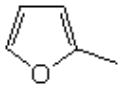
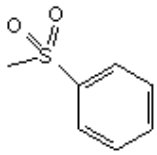
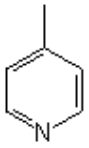
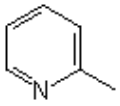
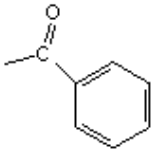
The Hydroxy Group

As with the other exchangeable protons, the chemical shift of the hydroxyl groups varies with concentration, temperature, solvent and the presence of impurities such as acid, base of H_2O. The trend for hydroxyl groups to resonate at a lower field as their concentration in solution increases, can be illustrated by the selection of straight chain alcohols listed below. Note that as the molecular weight of the compound decreases with decreasing chain length, the chemical shift of the hydroxyl resonance increases proportionately.

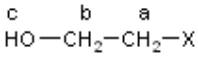
HO (ppm)	-X	Solvent
1.62	$-R_{20}$	$CDCl_3$
2.05	$-R_{18}$	$CDCl_3$
3.24	$-R_{11}$	CCl_4
3.67	$-R_6$	CCl_4
4.11	$-R_4$	CCl_4
4.40	$-R_2$	CCl_4

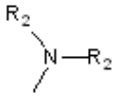
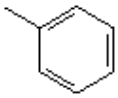
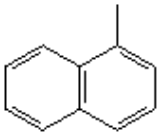
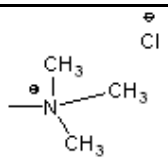


δ_b (ppm)	δ_a (ppm)	-X	Solvent
3.49	3.07		Polysoll
3.48	3.32		CCl_4
4.40	3.58	$-CH_3$	CCl_4
	3.62	$-(CH_2-OH)_3$	D_2O
4.46	3.90	$-CF_3$	$CDCl_3$
4.11	3.92	$-CH=CH-CH_3$	CCl_4
4.60	4.05	$-CH=CH_2$	CCl_4
	4.06		D_2O

3.76	4.07		CCl_4
3.99	4.11	-C≡C-CH_3	CCl_4
4.01	4.23	-C≡C-H	$CDCl_3$
3.80	4.27		$CDCl_3$
	4.29		D_2O
3.10	4.41		CCl_4
	4.46		D_2O
3.32	4.50		$CDCl_3$
4.45	4.61		$CDCl_3$
6.27	4.71		$CDCl_3$
5.02	4.78		$CDCl_3$
3.63	4.86		$CDCl_3$

2-Substituted Ethanols



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
3.71	3.50	1.49	$-CH_3$	CCl_4
3.52	3.45	2.50		CCl_4
2.57	3.65	2.37	$-CH=CH_2$	$CDCl_3$
3.67	3.67	2.38	$-C\equiv C-H$	CCl_4
3.99	3.80	2.58	$-C\equiv N$	$CDCl_3$
	3.69	2.68	-SH	D_2O
2.82	3.54	2.73	$-NH_2$	$CDCl_3$
2.44	3.71	2.77		$CDCl_3$
3.41	3.69	3.01		CCl_4
	3.93	3.12	-SO-K	D_2O
	3.85	3.18	$-NH_2$ (HCl)	D_2O
4.29	3.85	3.45	-Br	CCl_4
2.49	3..71	3.51	$-O-CH_3$	$CDCl_3$
4.61	4.05	3.56		$CDCl_3$
4.50	3.79	3.63	-Cl	$CDCl_3$

Coupling and Coupling Constants

Clearly defined coupling between the hydroxyl group and the adjacent hydrocarbon group is usually not observed in solutions of the alcohols in CCl_4 and $CDCl_3$. It appears that in these solvents, the hydroxyl protons are exchanging at an intermediate rate resulting in a broadening of both resonance bands. Sometimes a relatively clear coupling is observed (^{J} CH_2-OH = 5 Hz) indicating a much slower rate of exchange.

In solutions of alcohols in acetone and DMSO, clear coupling between the hydroxyl protons and adjacent hydrocarbon groups is the rule rather than the exception and it appears to result from the presence of the small amount of water that is usually present in these solvents.

The addition of a small amount of D_2O or acid will remove any coupling or broadening that appears in the HNMR

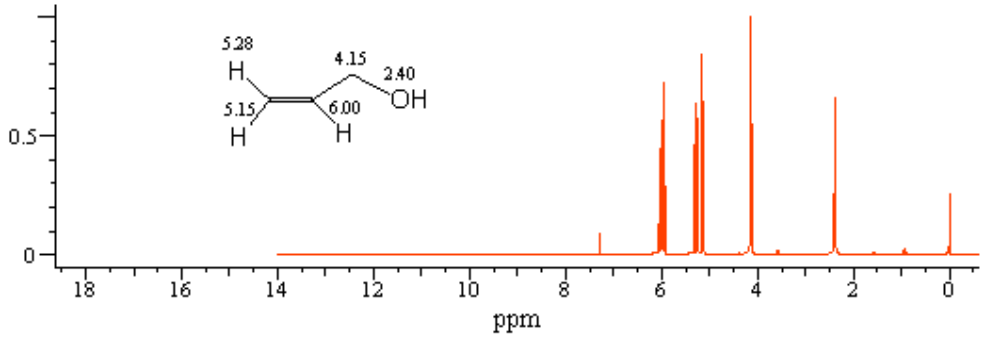
spectra of the alcohols. The exchange rate can be increased by heating the sample solutions, resulting in sharp single peaks for the hydroxyl resonance.

The hydroxyl protons often interchange with other types of exchangeable protons present in the same molecular structure.

B Olefinic

Primary Alcohols

Olefinics



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The Hydroxy Group

As with the other exchangeable protons, the chemical shift of the hydroxyl groups varies with concentration, temperature, solvent and the presence of impurities such as acid, base of H_2O. The trend for hydroxyl groups to resonate at a lower field as their concentration in solution increases, can be illustrated by the selection of straight chain alcohols listed below. Note that as the molecular weight of the compound decreases with decreasing chain length, the chemical shift of the hydroxyl resonance increases proportionately.

HO (ppm)	-X	Solvent
1.62	$-R_{20}$	$CDCl_3$
2.05	$-R_{18}$	$CDCl_3$
3.24	$-R_{11}$	CCl_4
3.67	$-R_6$	CCl_4
4.11	$-R_4$	CCl_4
4.40	$-R_2$	CCl_4

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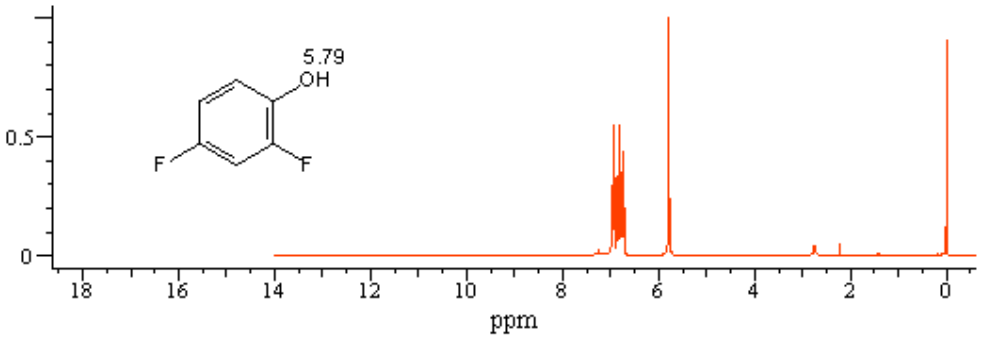
C Aromatic

Primary Alcohols

Aromatics



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The Hydroxy Group

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4.11	$-R_4$	CCl_4
4.40	$-R_2$	CCl_4

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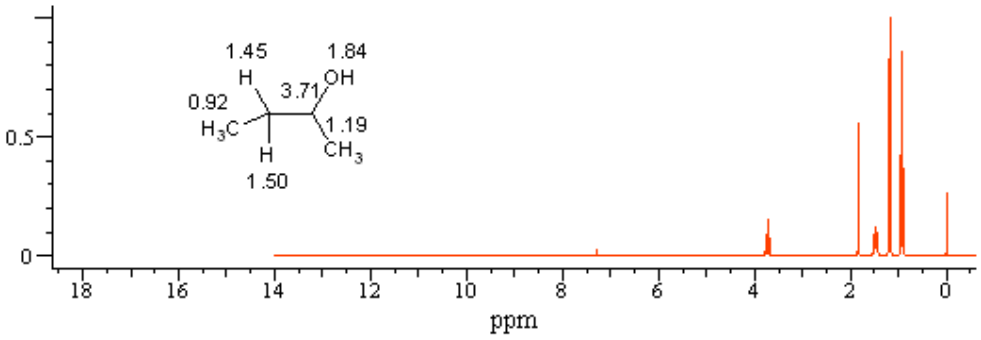
2□Secondary

a. Aliphatic

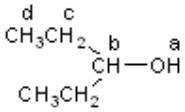
Secondary Alcohols

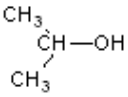
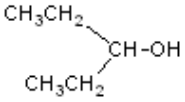
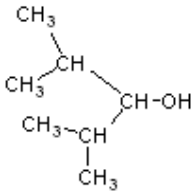
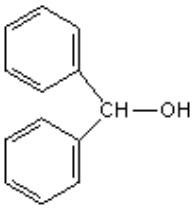
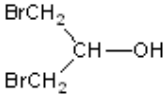


The methine proton adjacent to the hydroxyl group of the secondary alcohols is very strongely deshielded and may appear as any of a wide variety of multiplets depending upon the aliphatic groups bonded to it. The highest degree of multiplicity that is observed is octet produced by the two methyl groups of isopropanol with additional coupling to the

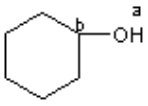
hydroxyl group.

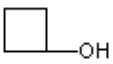
Aliphatic Protons

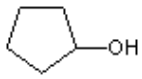
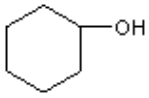
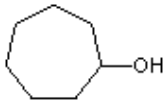


δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
	(1.29)	3.99	2.90		CCl_4
(0.90	1.9)	3.36	3.30		CCl_4
(0.92	1.62)	3.01	1.64		$CDCl_3$
		5.59	2.28		CCl_4
	(3.59)	4.03	3.27		$CDCl_3$

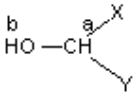
Alicyclic Protons

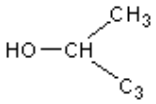
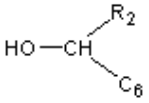
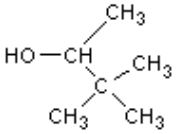
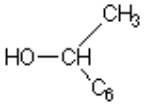
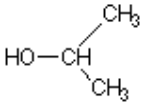
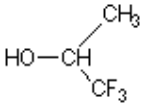
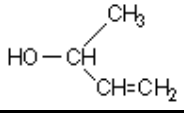


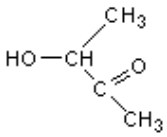
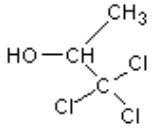
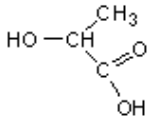
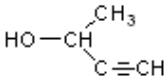
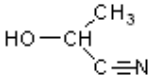
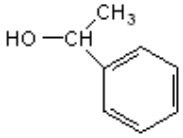
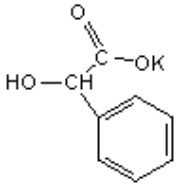
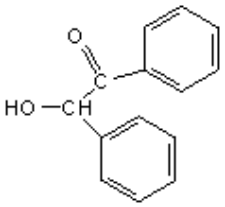
$(CH_2)n$ (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
1.1-2.5	4.16	5.48		CCl_4

1.3-2.1	4.21	3.58		CCl_4
0.8-2.5	3.49	4.20		CCl_4
1.2-2.3	3.80	2.69		$CDCl_3$

Disubstituted Methanols

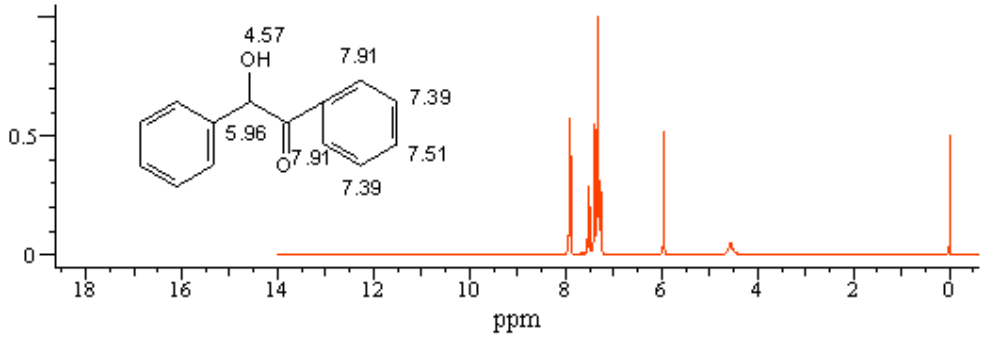


δ_b (ppm)	δ_a (ppm)	X(Y)(	Solvent
2.77	3.11		$CDCl_3$
1.95	3.18		CCl_4
2.59	3.38		CCl_4
3.05	3.43		CCl_4
2.90	3.99		CCl_4
3.63	4.03		CCl_4
3.88	4.20		CCl_4

3.73	4.22		$CDCl_3$
3.41	4.30		$CDCl_3$
	4.40		D_2O
4.08	4.50		CCl_4
4.05	4.60		$CDCl_3$
2.76	4.65		CCl_4
	4.94		D_2O
4.60	5.91		$CDCl_3$

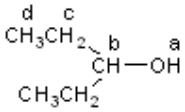
B Aromatic

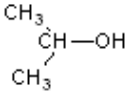
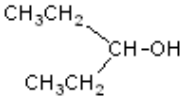
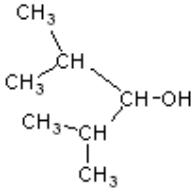
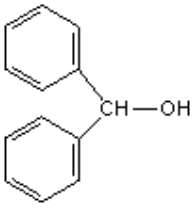
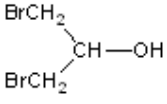
Secondary Alcohols



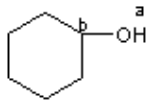
The methine proton adjacent to the hydroxyl group of the secondary alcohols is very strongely deshielded and may appear as any of a wide variety of multiplets depending upon the aliphatic groups bonded to it. The highest degree of multiplicity that is observed is octet produced by the two methyl groups of isopropanol with additional coupling to the hydroxyl group.

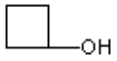
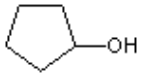
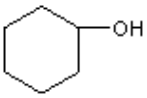
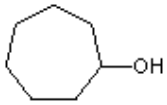
Aliphatic Protons



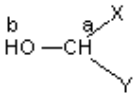
δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
	(1.29)	3.99	2.90		CCl_4
(0.90	1.9)	3.36	3.30		CCl_4
(0.92	1.62)	3.01	1.64		$CDCl_3$
		5.59	2.28		CCl_4
	(3.59)	4.03	3.27		$CDCl_3$

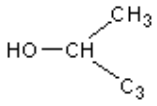
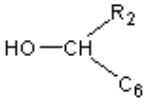
Alicyclic Protons

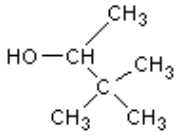
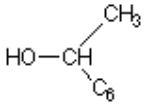
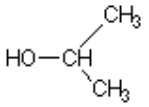
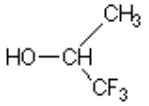
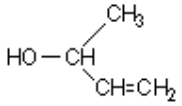
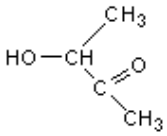
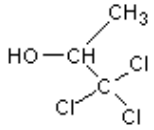
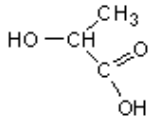
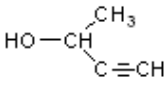
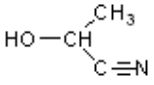
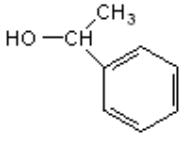
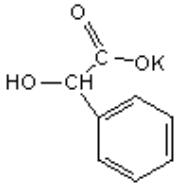


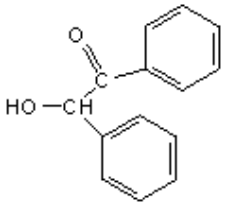
$(CH_2)n$ (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
1.1-2.5	4.16	5.48		CCl_4
1.3-2.1	4.21	3.58		CCl_4
0.8-2.5	3.49	4.20		CCl_4
1.2-2.3	3.80	2.69		$CDCl_3$

Disubstituted Methanols



δ_b (ppm)	δ_a (ppm)	X(Y)(	Solvent
2.77	3.11		$CDCl_3$
1.95	3.18		CCl_4

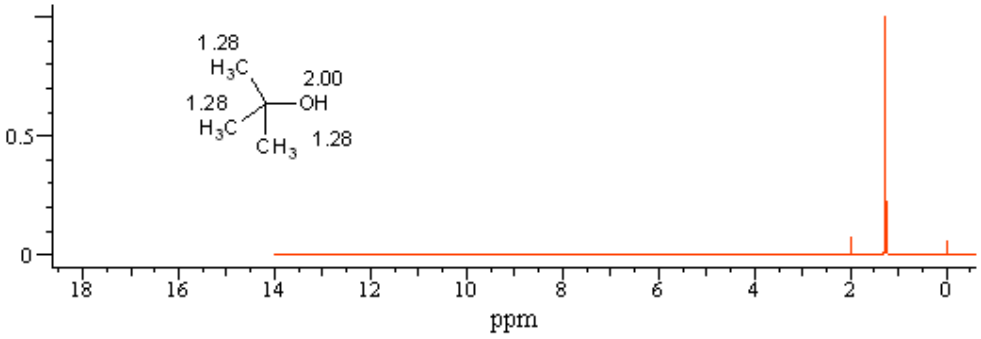
2.59	3.38		CCl_4
3.05	3.43		CCl_4
2.90	3.99		CCl_4
3.63	4.03		CCl_4
3.88	4.20		CCl_4
3.73	4.22		$CDCl_3$
3.41	4.30		$CDCl_3$
	4.40		D_2O
4.08	4.50		CCl_4
4.05	4.60		$CDCl_3$
2.76	4.65		CCl_4
	4.94		D_2O

4.60	5.91		$CDCl_3$

3□Tertiary

a. Aliphatic

Tertiary Alcohols



The tertiary alcohols are a difficult group of compounds to identify using only their NMR spectra. Their most characteristic feature is the presence of a single exchangeable proton which does not display any couplings since there are no protons on the adjacent carbon atom.

The phenols will be treated as a separate group. The series of 1-substituted-2-propanols listed below illustrates the relatively narrow range of chemical shifts (less than 1 ppm) that is observed for the hydrocarbon groups of the tertiary alcohols.

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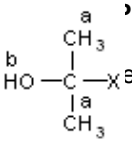
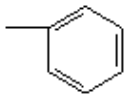
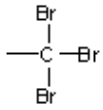
rotons



ed-2-propanols

δ_b (ppm)	δ_a (ppm)	-X	Solvent
2.89	1.15	$-R_2$	CCl_4
1.40	1.18	$-R_3$	CCl_4
2.40	1.20	$-CH_3$	CCl_4
2.14	1.23	$-CH=CH_2$	CCl_4
2.34	1.51		$CDCl_3$

2.30	1.53	-C≡C-H	$CDCl_3$
	1.54	$-SO_2-O-Na$	D_2O
3.49	1.61	-C≡N	$CDCl_3$
2.62	1.77		$CDCl_3$

Coupling and Coupling Constants

The coupling constants between protons on adjacent carbons (CH-CH) are similar to those of the corresponding structures of other types of substituents. Because none of the hydrocarbon groups are strongly deshielded by the hydroxyl group, complex higher order patterns at high field are to be expected.

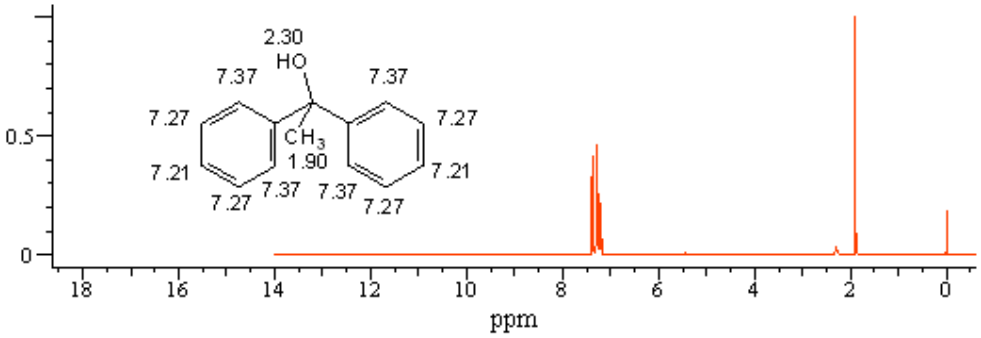
Solubility and Solvent Effects

Except for compounds containing water soluble groups such as the sodium and potassium salts of organic acids, the simple tertiary alcohols are normally soluble in the chlorinated solvents, CCl_4 and $CDCl_3$.

The use of hydroscopic solvents such as acetone and DMSO should be avoided whenever possible because the relatively weak hydroxyl resonance may exchange with water in the solvent and its presence could go undetected.

B Aromatic

Tertiary Alcohols



The tertiary alcohols are a difficult group of compounds to identify using only their NMR spectra. Their most characteristic feature is the presence of a single exchangeable proton which does not display any couplings since there are no protons on the adjacent carbon atom.

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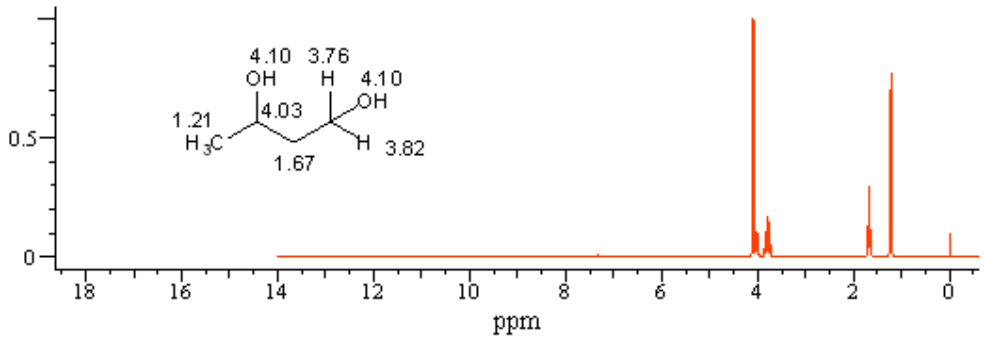
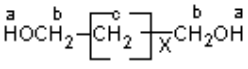
4 Diols and Polyols

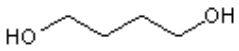
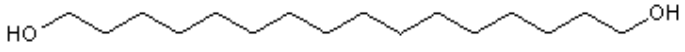
Diols and Polyols



The polyols are one of the groups of compounds for which the proton NMR integration ratios are most useful in determining their molecular structure. The polyols characteristically display the resonance of two or more exchangeable protons with three or more hydrocarbon groups resonating at low field in the range from 3 to 4 ppm. The straight chain polyols, and their cyclic counterparts, possess no methyl absorption bands at high field making their identification somewhat easier than the corresponding branched chain compounds.



1,n-Alkanediols	n	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
	0		3.68		D_2O
	1	1.78	3.65		D_2O

	2	1.43	3.39	4.34	DMSO-d_6
	3	1.2-1.9	3.60		D_2O
	4	1.1-1.8	3.65	4.52	$CDCl_3$
	7	1.1-1.8	3.60	3.05	$CDCl_3$
	14	ca 1.32	3.40	3.92	DMSO-d_6

Coupling and Coupling Constants

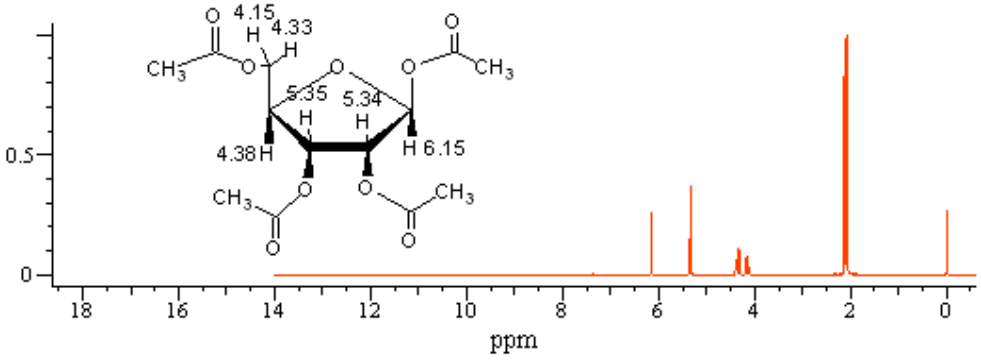
As with the primary and secondary alcohols, coupling between the hydroxyl group and adjacent methylene or methine groups may or may not be observed depending to a great extent on the solvent employed. In D_2O solution, of course, the hydroxyl proton will be replaced by deuterium and no coupling will be observed. In acetone and dimethyl sulfoxide solutions coupling between the OH and adjacent aliphatic groups is usually clearly observed (^{J}CH- OH $=$ 4-6 Hz). In carbon tetrachloride and deuterochloroform solutions, the coupling across the oxygen group of the polyols is usually not observed or at most, both groups may be badly broadened.

Solubility and Solvent Effects

With the exception of the very high molecular weight varieties, the polyols are readily soluble in one of the usually employed NMR solvents. The compounds containing approximately equal numbers of carbon and oxygen atoms are soluble in D_2O. At ratios of about three carbons per hydroxyl group, acetone or DMSO-d_6 will be found to be most effective. When the ratio of carbon to oxygen atoms exceeds 7 or 8, $CDCl_3$ and CCl_4 become more useful in dissolving such compounds containing large hydrocarbon fragments.

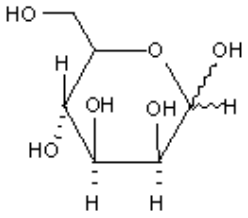
5 Carbohydrates

Sugars and Carbohydrates



This specialized group of polyols characteristically displays few resonance bands at high field. Their NMR spectra usually consist of a complex higher order pattern in the chemical shift range from 3-4 ppm, with the cyclic varieties displaying one or two additional doublets at lower field (4-6 ppm). These doublets represent the axial and equatorial protons bonded to the carbon nucleus adjacent to the ether linkage of the furanosides and pyranosides. All of the carbohydrates are readily soluble in deuterium oxide although they may dissolve only slowly. Proton NMR is useful in determining the relative percentages of alpha and beta forms, but the spectra are not otherwise readily interpretable except for direct comparison of the pattern with that of a reference compound.

The chemical shift data for several selected pyranosides which appear in this database are presented.



Pyranosides	CH-2,3,4,5 (ppm)	Axial (ppm)	Equatorial (ppm)	Solvent
Arabinopyranose	3.3-4.2	4.51	5.24	D_2O
Glucose	3.0-4.1	4.60	5.20	D_2O
Galactose	3.3-4.3	4.60	5.30	D_2O
Xylose	3.1-4.2	4.68	5.28	D_2O
Mannose	3.2-4.0	4.89	5.19	D_2O

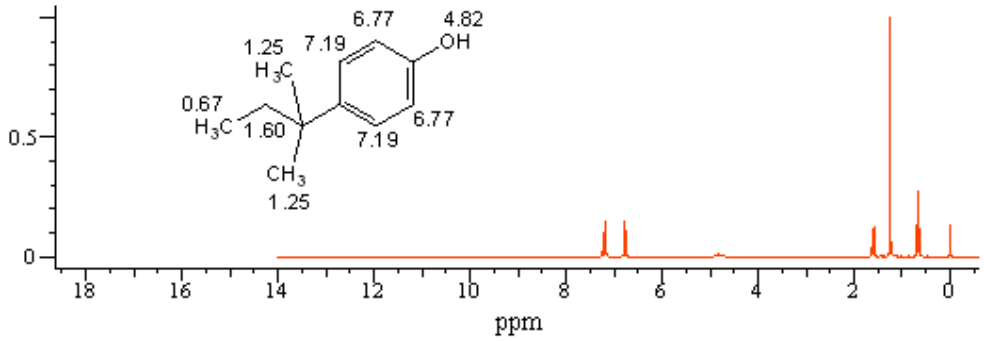
Coupling and Coupling Constants

Three types of coupling can occur in the spectra of the cyclic sugars; axial-axial, axial-equatorial and equatorial-equatorial. Because the size of the coupling constant varies with the dihedral angle between the coupled protons, the axial-axial interaction is significantly larger than the other two types. Ranges of observed coupling constants for these three couplings are presented.

^{J} values	Hz
^{J}axial-axial	5-8
^{J}axial-equatorial	1-4
^{J}equatorial-equatorial	1-4

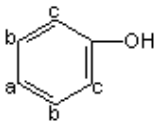
6 Phenols

Phenols



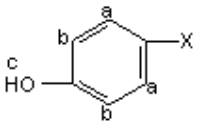
The phenolic compounds characteristically display high field chemical shifts for the aromatic hydrogens ortho and para to the hydroxyl substituent. The single hydroxyl proton resonates at much lower field than the corresponding OH group of the alcohols but at higher field than that of the carboxylic acids.

Phenol

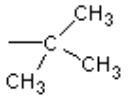
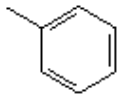
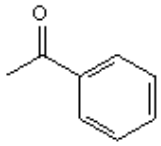
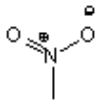


HO- (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
6.11	6.75	7.14	6.79	$CDCl_3$

Para-Substituted Phenols



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)		Solvent
5.77	6.62	6.62	-O-CH_3	CCl_4
	6.79	6.79	-OH	D_2O
6.45	6.69	6.92	-CH_3	$CDCl_3$
6.53	6.79	6.91	-F	$CDCl_3$
6.39	6.78	7.03	—CH(CH_3)$_2$	$CDCl_3$
4.95	6.75	7.08	-C_6	$CDCl_3$
6.33	6.71	7.10	-Cl	$CDCl_3$

4.73	6.75	7.22	-S-CH_3	$CDCl_3$
4.91	6.75	7.23		$CDCl_3$
5.20	6.69	7.30	-Br	$CDCl_3$
9.49	6.87	7.43		DMSO
6.80	6.91	7.46	-CF_3	$CDCl_3$
5.41	6.59	7.48	-I	$CDCl_3$
6.84	6.88	7.58		DMSO-d_6
8.70	6.63	7.67	-N=O	Acetone
10.50	6.93	7.72	-SO_2-O	DMSO-d_6
	7.05	7.87	-SO_2-O-Na	D_2O
9.76	7.07	8.11		Acetone
9.32	7.06	8.15		Acetone

Solubility and Solvent Effects

Phenol and the simple aliphatic substituted phenols are soluble in CCl_4 and $CDCl_3$. As indicated above in the table of chemical shifts, the presence of other functional groups may require the use of D_2O, Poiysol, Acetone or DMSO-d_6.

Characterization

The presence of an exchangeable proton band at relatively low field and the relatively high field chemical shifts produced by the hydroxyl group on the ortho and para aromatic hydrogens makes the phenols a relatively simple group of compounds to characterize.

Only the anilines, produce similar chemical shifts, however, the resonance bands of the anilines are sensitive to the addition of acid to the sample solution while the phenols are not affected in the same manner.

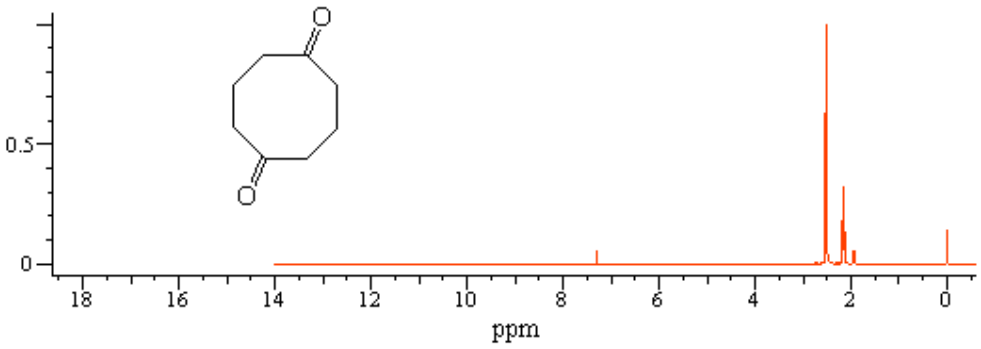
VIII. Compounds Containing Carbon To Oxygen Double Bonds

1□ Ketones (R-C(=O)-R)

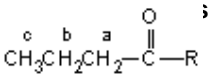
1□Aliphatic and Alicyclic

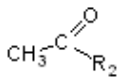
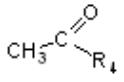
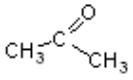
Ketones

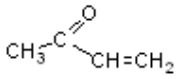
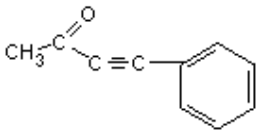
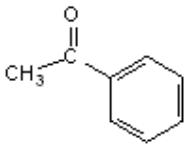
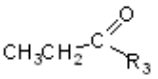
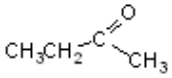
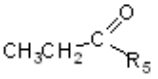
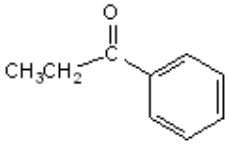
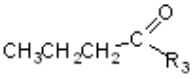
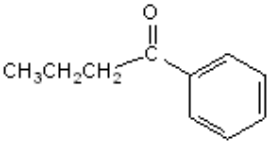
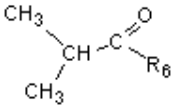
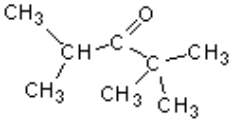
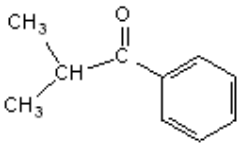
Aliphatics and Alicyclics

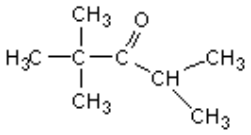
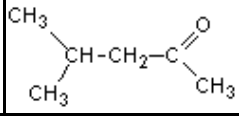
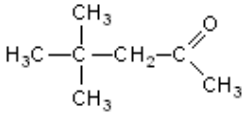


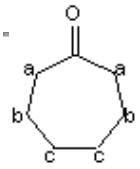
The Ketone linkage weakly deshields the protons of adjacent aliphatic groups but strongly deshields the ortho aromatic protons. The ketones are readily soluble in carbon tetrachloride and deutero-chloroform.



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		2.05		CCl_4
		2.07		CCl_4
		2.11		

		2.20		CCl_4
		2.40		$CDCl_3$
		2.43		CCl_4
	1.03	2.29		CCl_4
	0.99	2.40		CCl_4
	0.92	2.43		$CDCl_3$
	1.18	2.94		$CDCl_3$
0.90	1.58	2.31		CCl_4
0.95	1.72	2.82		CCl_4
	(1.05)	2.50		CCl_4
	(1.00)	3.07		CCl_4
	(1.18)	3.47		CCl_4

	(1.11)			CCl_4
(0.91)	2.00	2.22		CCl_4
(1.02)		2.28		CCl_4



otons

n	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Ring	Solvent
0		2.02	2.02	Cyclopentanone	CCl_4
1	ca. 1.79	ca 1.79	2.25	Cyclohexanone	CCl_4
2	ca. 1.71	ca 1.71	2.49	Cycloheptanone	$CDCl_3$
3	ca. 1.47	1.82	2.31	Cyclooctanone	CCl_4
8	ca. 1.29	1.62	2.36	Cyclotridecanone	CCl_4
10	ca. 1.33	1.64	2.43	Cyclopentadecanone	$CDCl_3$

Coupling and Coupling Constants

No unusual couplings nor coupling constants are observed in the NMR spectra of the Ketones. The aliphatic three bond vicinal coupling ^{J}HC-CH is 6-8 Hz, the aromatic ortho coupling constant varies from 8-9 Hz, and the olefinic coupling constants display the values listed.

^{J}CH=CH = 14-18 Hz (trans)

^{J}CH=CH = 7-12 Hz (cis)

^{J}H-C-H = 1-4 Hz (geminal)

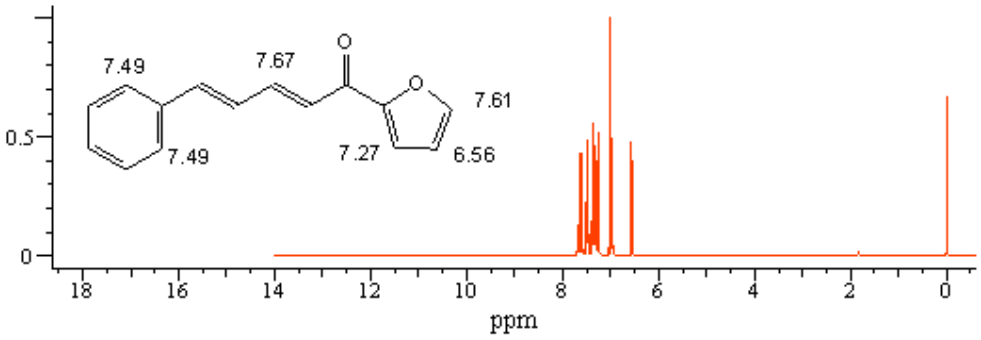
$^{J}CH_3$-CH = 5-7 Hz

$^{J}CH_3$-C=CH= 0-2 Hz

2 Olefinic

Ketones

Olefinics

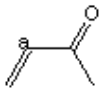


The Ketone linkage weakly deshields the protons of adjacent aliphatic groups but strongly deshields the ortho aromatic protons. The ketones are readily soluble in carbon tetrachloride and deutero-chloroform.

Olefinic Protons

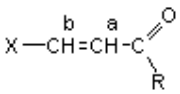
The carbonyl group of the ketones weakly deshields the geminal olefinic proton but strongly de-shields the cis and trans hydrogens bonded to the beta carbon atom. Its effect is similar to that of the unsaturated carbon atom of the nitrile (-C≡N) functional group.

3-Buten-2-one

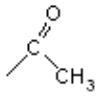
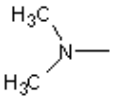
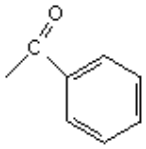
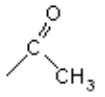
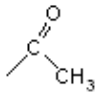
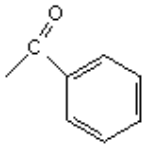
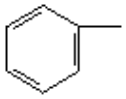
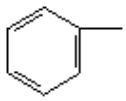
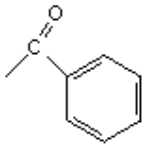
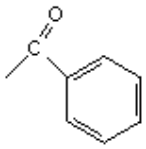
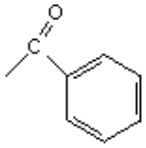
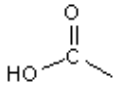
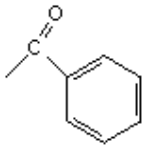
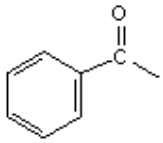
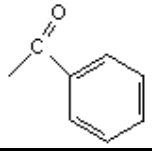


trans (ppm)	cis (ppm)	δ_a (ppm)	Compound	Solvent
ca 6.1	ca 6.1	5.80	H_2C=CH-C(=O)-CH_3	CCl_4

Substituted Olefinc Ketones



X-	δ_b (ppm)	δ_a (ppm)	X	Solvent

CH_3-O-	7.50	5.52		CCl_4
	7.55	5.69		$CDCl_3$
	6,47	5.92		CCl_4
CH_3-	6.70	6.00		CCl_4
CH_3-	6.70	6.00		CCl_4
	7.51	6,68		$CDCl_3$
	7.72	7.05		$CDCl_3$
Cl-	7.42	7.27		$CDCl_3$
N≡C-S-	7.36	7.32		$CDCl_3$
	6.86	7.95		$CDCl_3$
	7.95	7.95		$CDCl_3$

Coupling and Coupling Constants

No unusual couplings nor coupling constants are observed in the NMR spectra of the Ketones. The aliphatic three bond vicinal coupling ^{J}HC-CH is 6-8 Hz, the aromatic ortho coupling constant varies from 8-9 Hz, and the olefinic coupling constants display the values listed.

^{J}CH=CH = 14-18 Hz (trans)

^{J}CH=CH = 7-12 Hz (cis)

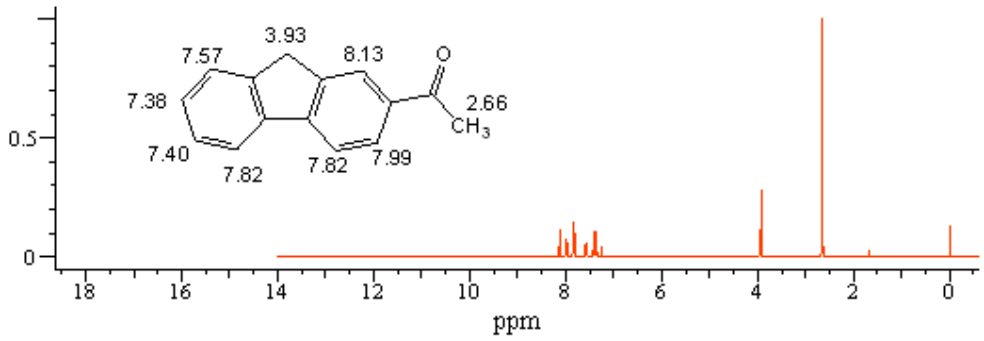
^{J}H-C-H = 1-4 Hz (geminal)

^{J}CH_3-CH = 5-7 Hz

^{J}CH_3-C=CH= 0-2 Hz

3 Aromatic

Aromatics

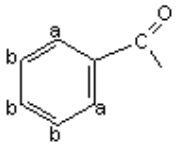


The Ketone linkage weakly deshields the protons of adjacent aliphatic groups but strongly deshields the ortho aromatic protons. The ketones are readily soluble in carbon tetrachloride and deutero-chloroform.

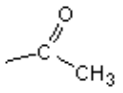
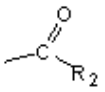
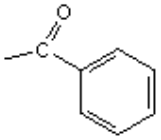
Aromatic Protons

The Ketone functional group is one of the strongly deshielding groups in its effect on the ortho aromatic protons, deshielding them about 0.3 ppm in relation to the meta and para hydrogens. The ortho hydrogens of the phenyl ketones resonate at about 7.8 ppm while the meta and ortho hydrogens overlap to form a complex band in the range from 7.1- 7.5 ppm (CCl_4 solution).

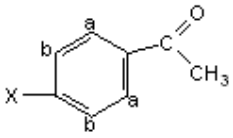
Phenyl Ketones

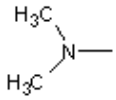
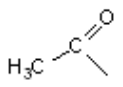


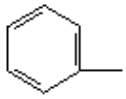
δ_b (ppm)	δ_a (ppm)	X	Solvent

7.1-7.5	7.80		CCl_4
7.2-7.6	7.92		$CDCl_3$
7.2-7.6	7.78		$CDCl_3$

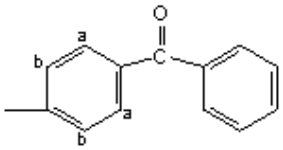
Para Substituted Acetophenones

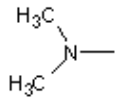
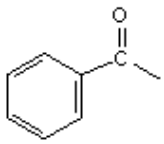
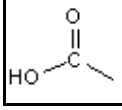


X-	δ_b (ppm)	δ_a (ppm)	Solvent
CH_3-	7.09	7.69	CCl_4
Br-	7.50	7.73	CCl_4
CH_3- CH_2 -	7.17	7.75	CCl_4
H_2N-	6.62	7.77	$CDCl_3$
R-NH-	6.54	7.80	$CDCl_3$
HO-	6.83	7.80	DMSO-d_6
Cl-	8.05	8.05	$CDCl_3$
CH_3-S-	7.24	7.81	Polysol
	6.71	7.95	$CDCl_3$
CH_3-O-	6.98	7.97	$CDCl_3$
F-	7.11	7.99	$CDCl_3$
	8.05	8.05	$CDCl_3$

	7.64	8.00	$CDCl_3$
O_2N-	8.32	8.19	$CDCl_3$

Para Substituted Benzophenones



X-	δ_b (ppm)	δ_a (ppm)	Solvent
HO-	6.88	7.56	DMSO-d_6
Br-	7.60	7.60	$CDCl_3$
CH_3-	7.22	7.69	$CDCl_3$
	6.65	7.73	$CDCl_3$
	7.92	7.92	$CDCl_3$
	8.39	7.99	TFA

Coupling and Coupling Constants

No unusual couplings nor coupling constants are observed in the NMR spectra of the Ketones. The aliphatic three bond vicinal coupling ^{J}HC-CH is 6-8 Hz, the aromatic ortho coupling constant varies from 8-9 Hz, and the olefinic coupling constants display the values listed.

^{J}CH=CH = 14-18 Hz (trans)

^{J}CH=CH = 7-12 Hz (cis)

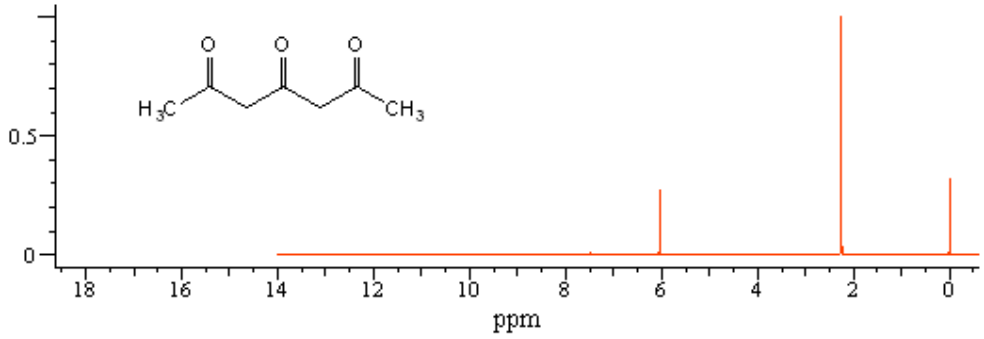
^{J}H-C-H = 1-4 Hz (geminal)

$^{J}CH_3$-CH = 5-7 Hz

$^{J}CH_3$-C=CH= 0-2 Hz

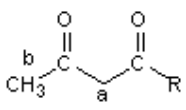
4 a-Diketones and b-Diketones

Beta Diketones

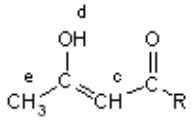


The beta Diketones are unusual in that two distinct forms with different chemical shifts exist in solution. Their concentration changes with time, normally the keto form predominates when the sample is first dissolved but upon standing, the keto form increases until it becomes the form at higher concentration. The chemical shifts of aliphatic groups bonded to the diketone fragment are weakly deshielded with the aliphatic groups of the enol form resonating at slightly higher field than those of the keto form.

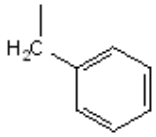
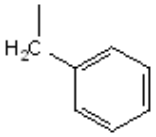
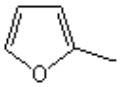
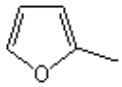
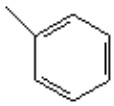
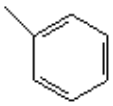
Because the enol hydroxyl group is often quite weak and broadened, it is often difficult to locate its resonance in the offset range beiow 10 ppm.



keto



enol

δ_b (ppm)	δ_a (ppm)	-R	δ_e (ppm)	δ_d (ppm)	δ_c (ppm)	-R	Solvent
1.98	3.32		1.88	15.0	5.29		CCl_4
2.17	3.54	$-CH_3$	1.99		5.38	$-CH_3$	CCl_4
2.20	3.86		2.08	15.0	6.00		CCl_4
2.24	4.03		2.13		6.12		$CDCl_3$

Exchangeable Protons

The hydroxyl group formed during enolization resonates at lower field than nearly any other type of proton. The range of chemical shifts extends from about 11-20 ppm depending upon the structure of the beta diketone and the amount of H_2O present in the solution. The high field values are usually observed for solutions containing a relatively large percentage of H_2O.

Coupling and Coupling Constants

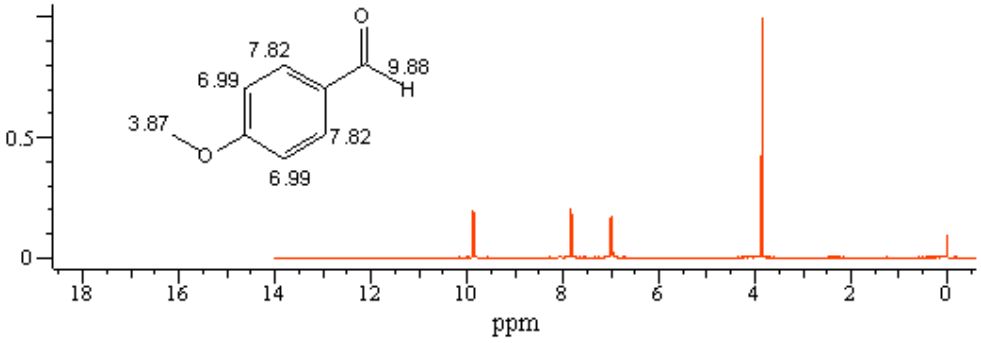
As with the mono-ketones, coupling between groups on opposite sides of the carbonyl carbon is usually not observed. Similarly, coupling across the enolized carbonyl group (-C(OH)=CH) is not observed.

Solubility and Solvent Effects

The beta Diketones are readily soluble in carbon tetrachloride and deuterochloroform. Because these solvents are least likely to contain large amounts of water which could exchange with and mask the enol -OH resonance, their use is preferable under normal circumstances.

2 Aldehydes (R-C(=O)-H)

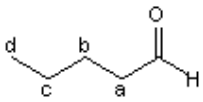
Aldehydes

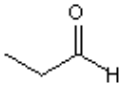
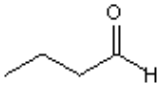
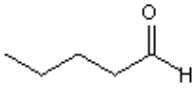
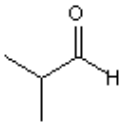
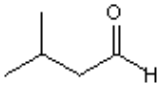


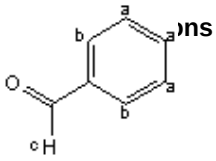
The aldehydic functional group produces a characteristic band at very low field arising from the resonance of the proton bonded to the carbonyl group. Coupling between this proton and the adjacent aliphatic groups is usually observed in the HNMR spectra of the aliphatic aldehydes.

The aldehydic group weakly deshields aliphatic protons but has a relatively strong deshielding effect on the ortho aromatic protons. The aldehydes oxidize easily and their HNMR spectra often display impurity bands arising from the presence of the corresponding carboxylic acid.

Aliphatic Protons

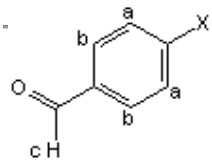


δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
			2.12		CCl_4
		1.09	2.45		$CDCl_3$
	0.95	1.61	2.36		CCl_4
0.90	1.35	1.55	2.43		DMSO-d_6
		(1.12)	2.38		CCl_4
	(0.98)	2.12	2.29		$CDCl_3$



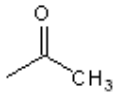
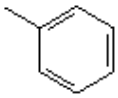
ons

δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
9.94	7.79	7.2-7.6	CCl_4

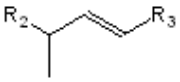
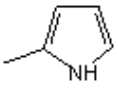
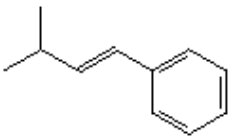


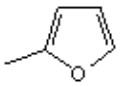
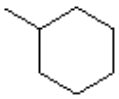
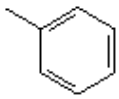
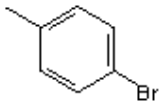
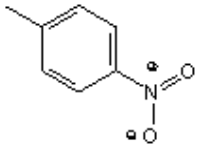
Benzaldehydes

δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent

9.66	7.63	6.63		$CDCl_3$
9.78	7.69	6.89	-O-R_3	$CDCl_3$
9.80	7.71	6.92	-O-R_5	CCl_4
9.82	7.72	6.92		CCl_4
9.89	7.80	7.04	-OH	Acetone
9.91	7.80	7.19		CCl_4
10.00	7.91	7.21	-F	$CDCl_3$
9.97	7.76	7.31	-CH_3	$CDCl_3$
9.91	7.73	7.40	-Cl	$CDCl_3$
10.00	7.88	7.67		$CDCl_3$
9.97	7.68	7.68	-Br	$CDCl_3$
10.13	7.89	8.01	-C≡N	$CDCl_3$
10.18	8.09	8.39		$CDCl_3$

lic Protons

δ_a (ppm)	-X	Solvent
9.33		CCl_4
9.48		$CDCl_3$
9.53		$CDCl_3$
9.57		CCl_4

9.58		CCl_4
9.63		CCl_4
9.66		$CDCl_3$
9.68	$-R_3$	CCl_4
9.69	$-CH_3$	CCl_4
9.94		CCl_4
9.97		$CDCl_3$
10.18		$CDCl_3$

There is a general trend in the chemical shift of the aldehydic proton in relation to the type of group to which it is bonded. In general, the aldehydic protons bonded to vinyl or heteroaromatic groups resonate at slightly higher field than those bonded to aliphatic groups. At the lowest field appear the benzaldehyde protons which are further differentiated in chemical shift by the deshielding effect of other substituents on the aromatic ring as indicated in the table of chemical shifts for para substituted benzaldehydes.

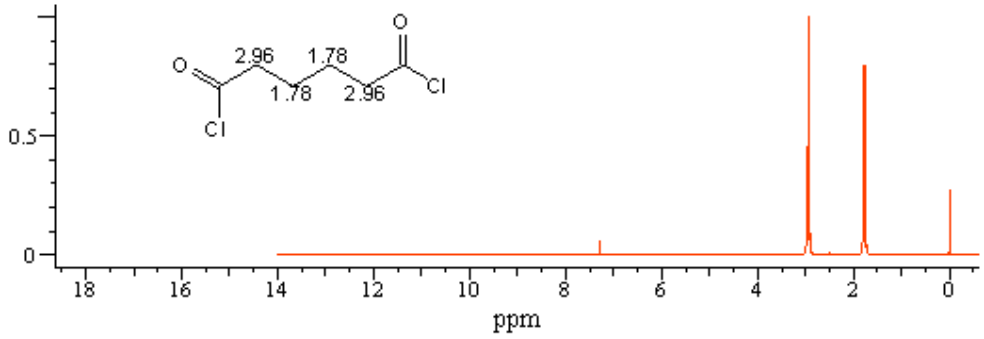
Coupling and Coupling Constants

The aldehydic proton normally displays coupling to protons bonded to the carbon atom alpha to the carbonyl group. The coupling constants for such vinyl protons tend to be significantly larger than the corresponding coupling constant observed for aliphatic protons.

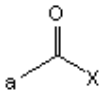
J	=	7.6 Hz	H-C(=O)-CH=C
J	=	1.4-1.8 Hz	H-C(=O)-CH_2-R
J	=	2.5 Hz	H-C(=O)-$CH(R)_2$

3 Acid Halides (R-C(=O)-X)

Acid Halides

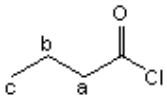


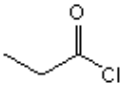
Due to the limited availability of compounds containing Acid Fluoride, Acid Bromide or Acid Iodide groups, their spectra will deal primarily with the HNMR parameters encountered in the spectra of the Acid Chlorides. The relative deshielding effect of three of the acetyl halides and their hydrolysis product, acetic acid, are presented.

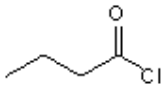
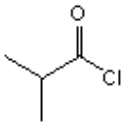
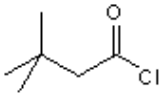


δ_a (ppm)	-X	Solvent
2.06	-OH	CCl_4
2.18	-I	CCl_4
2.66	-Cl	CCl_4
2.79	-Br	$CDCl_3$

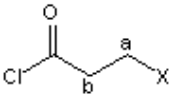
Aliphatic Protons

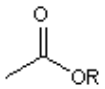
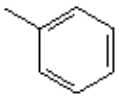


δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		2.66		CCl_4
	1.22	2.93		$CDCl_3$

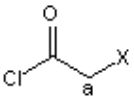
0.99	1.75	2.88		$CDCl_3$
	(1.21)	2.59		$CDCl_3$
(1.10)		2.79		CCl_4

2-Substituted Propionyl Chlorides

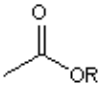
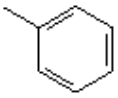
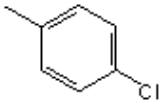
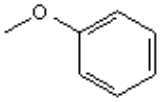


δ_b (ppm)	δ_a (ppm)	-X	Solvent
2.88	1.75	$-CH_3$	$CDCl_3$
2.88	1.77	$-C_5$	CCl_4
2.62	2.62		CCl_4
3.02	2.89		CCl_4
3.28	3.28		$CDCl_3$
3.51	3.51	-Br	CCl_4

Substituted Acetyl Chlorides

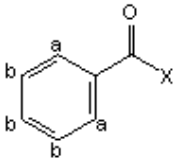


δ_a (ppm)	-X	Solvent

2.79		CCl_4
2.93	$-CH_3$	$CDCl_3$
3.80		CCl_4
4.02		CCl_4
4.10		$CDCl_3$
4.80		CCl_4

Aromatic Protons

Benzoyl Halides

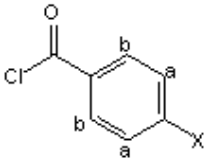


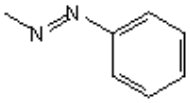
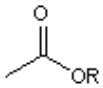
δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.2-7.7	7.94	-F	CCl_4
7.2-7.7	8.02	-Br	CCl_4
7.2-7.7	8.04	-Cl	CCl_4

Para Substituted Benzoyl Chlorides

Solubility and Solvent Effects

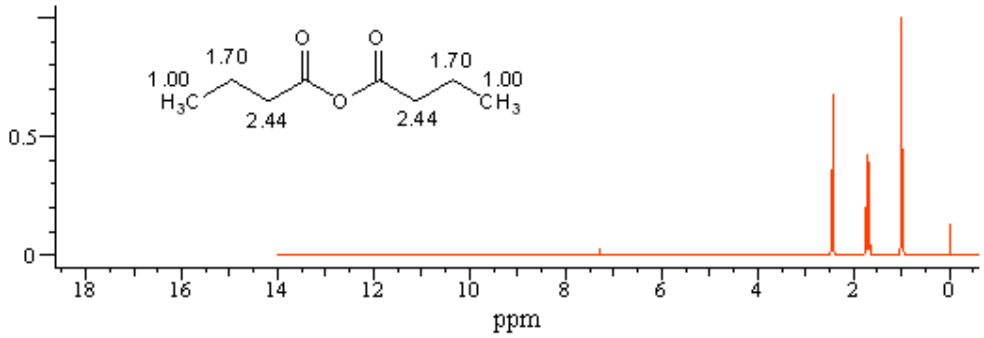
The Acid Halides are readily soluble in the chlorinated solvents carbon tetrachloride and deuterochloroform. Due to the ease with which the acid halides hydrolyze to form the corresponding carboxylic acid, these solvents are preferable to those such as Polysol, Acetone or DMSO-d_6 which may contain traces of water.



δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.98	6.89	-O-R_5	CCl_4
8.02	6.90	-O-CH_3	CCl_4
7.96	7.24	-CH_3	CCl_4
8.02	7.46	-Cl	$CDCl_3$
8.06	7.52		$CDCl_3$
7.94	7.61	-Br	$CDCl_3$
8.20	7.73	-CF_3	$CDCl_3$
8.22	7.81	-C≡N	$CDCl_3$
8.21	7.90		$CDCl_3$
8.10	8.10		CCl_4
8.26	8.26		$CDCl_3$
8.38	8.38		Acetone

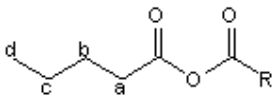
4 Anhydrides (R-C(=O)-O-C(=O)-R)

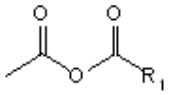
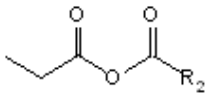
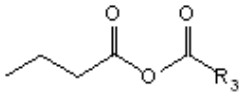
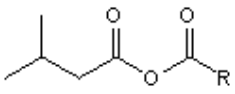
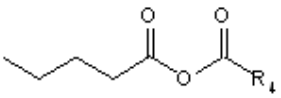
Anhydrides

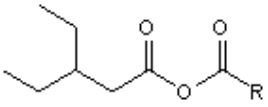
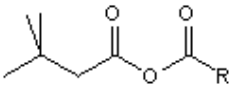


The anhydrides are similar to other carbonyl containing compounds in that, adjacent aliphatic groups are weakly deshielded while the ortho aromatic protons are strongly deshielded. Their HNMR spectra are similar to those of the carboxylic acids. Because the anhydrides hydrolyze easily to form the corresponding carboxylic acid, the chemical shift range from 10-12 ppm should be checked carefully to determine the presence of the carboxylic acid -OH group which would indicate that hydrolysis has occurred and to what extent such decomposition products are present in solution.

Aliphatic Protons

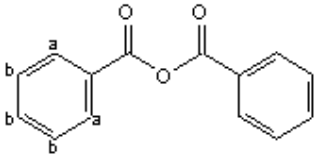


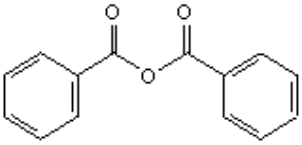
δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
			2.20		CCl_4
		1.17	2.43		CCl_4
	1.01	1.69	2.40		CCl_4
		(1.24)	2.68		$CDCl_3$
0.95	1.45	1.65	2.48		$CDCl_3$

	(0.97	1.60)	2.29		CCl_4
		(1.25)			CCl_4

Aromatic Protons

Benzoic Anhydride



δ_b (ppm)	δ_a (ppm)	Compound	Solvent
7.2-7.7	8.11		$CDCl_3$

Coupling and Coupling Constants

The anhydrides display no special couplings nor coupling constants, other than the usual aliphatic H—C—C—H coupling and the normal aromatic ortho and meta couplings that are commonly observed for most functional groups.

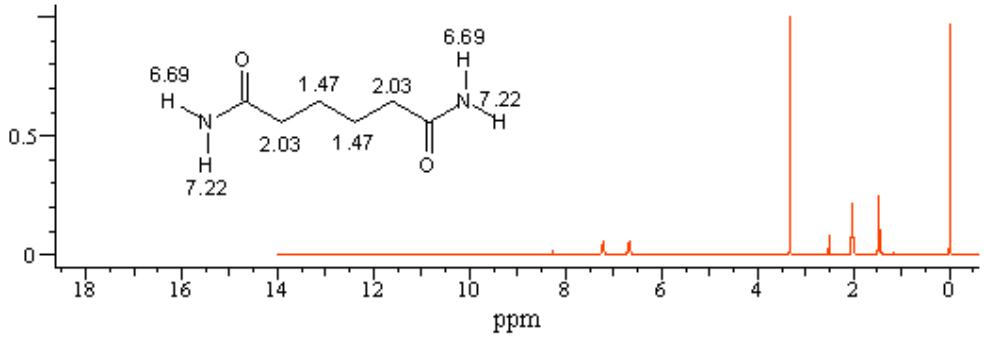
Solubility and Solvent Effects

The anhydrides are readily soluble in carbon tetrachloride and deuterochloroform which are the solvents of preference. Solvents such as DMSO-d_6, Polysol and Acetone-d_6 could contain sufficient amounts of water to lead to the decomposition of the sample.

5 Amides

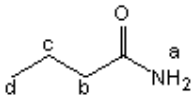
1 Primary (R-C(=O)-NH_2)

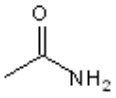
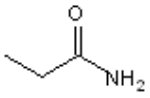
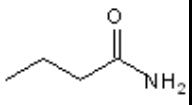
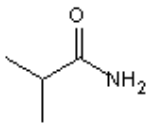
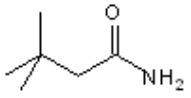
Primary Amides



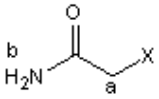
Although similar in chemical shifts to the other carbonyl containing compounds, the Primary Amides can be distinguished by the presence of one or two very broad bands at low field (5.5-8.9 ppm) arising from the resonance of the two -NH_2 protons. These bands are exchangeable and will not be observed if D_2O or TFA are used as the solvent. Due to the partial double bond character of the amide—C(=O)—NH_2 bond, the two NH protons may be non-equivalent resulting in two distinct but overlapping resonance bands.

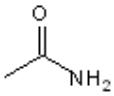
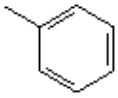
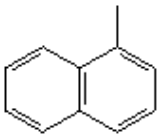
Aliphatic Protons



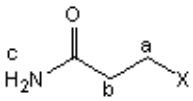
δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		1.98			D_2O
	1.12	2.23	6.0-7.5		$CDCl_3$
0.94	1.62	2.28			D_2O
	(1.19)	2.39	5.6-6.2		$CDCl_3$
(0.98)		2.11			D_2O

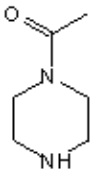
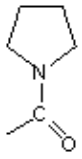
Substituted Acetamides

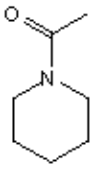
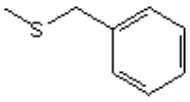
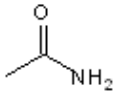
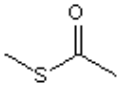
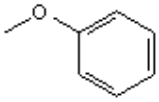


δ_b (ppm)	δ_a (ppm)	-X	Solvent
6.0-7.5	2.23	$-CH_3$	$CDCl_3$
	2.28		D_2O
7.0, 7.4	3.00		DMSO-d_6
5.1-5.7	3.56		$CDCl_3$
7.3, 7.6	3.59	-C≡N	DMSO-d_6
5.5-8.0	3.89	$-O-CH_3$	$CDCl_3$
	4.18	-Cl	D_2O
	4.19		TFA

2-Substituted Propionamides

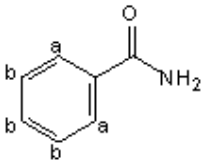


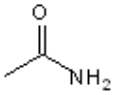
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
6.5-7.1	2.43	2.43		DMSO-d_6
6.2, 6.9	2.59	2.59		CCl_4

6.1-6.7	2.61	2.61		$CDCl_3$
6.6-7.3	2.48	2.62		DMSO-d_6
	3.00	3.00		TFA
5.7-6.7	2.54	3.12		$CDCl_3$
6.6-7.2	2.72	3.85	-Cl	Acetone-d_6
5.9, 6.4	2.74	4.38		$CDCl_3$

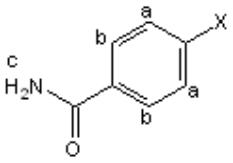
Aromatic Protons

Benzamide



δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.3-7.9	8.00		TFA

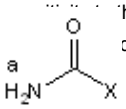
Para Substituted Benzamides

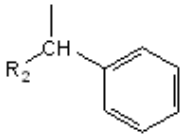
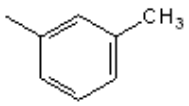
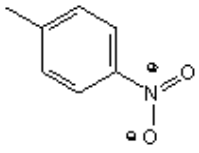


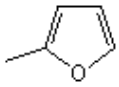
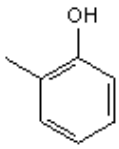
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
6.5-7.0	7.62	6.60	$-NH_2$	Poly so l
7.1-7.7	7.90	6.94	$-O-CH_3$	Poly so l
7.1-7.8	7.87	7.61	-Br	DMSO-d_6
	7.92	7.43	$-CH_3$	TFA
6.8-7.6	7.62	7.78		DMSO-d_6

Exchangeable Protons

The two exchangeable Primary Amide protons resonate at low field as either one or two very broad bands. The table of chemical shifts provided below indicates that the aliphatic Primary Amides resonate at slightly higher field than the aromatic compounds. The chemical shift(s) of these protons vary over a relatively wide range of values due to their [illegible] the concentration of the sample solution, the solvent employed and the temperature at which the solution [illegible]d, in addition to any possible hydrogen bonding effects and other structural considerations.

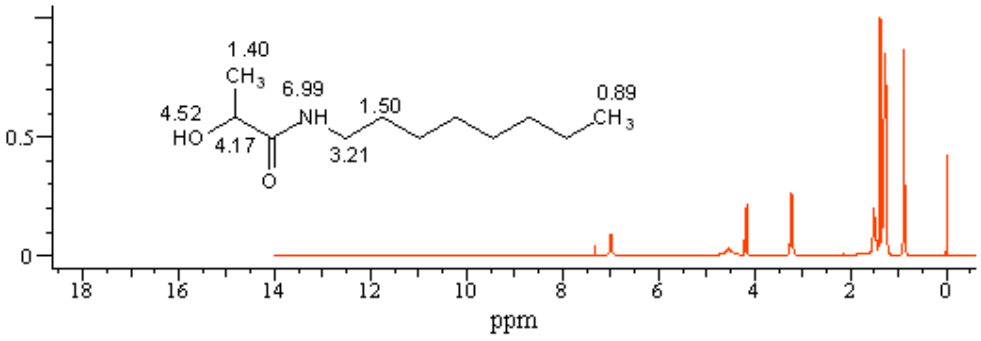


δ_a (ppm)	-X	Solvent
5.5-6.9	$-R_7$	$CDCl_3$
5.8-6.9	$-R_6$	$CDCl_3$
5.9, 6.5		CCl_4
6.0-7.5	$-R_2$	$CDCl_3$
6.0-7.0		$CDCl_3$
6.8-7.5		DMSO

7.3-8.3		DMSO
7.6-8.9		DMSO-d_6

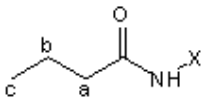
2 Secondary (R-C(=O)-NH-R)

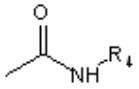
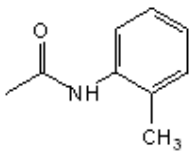
Secondary Amides

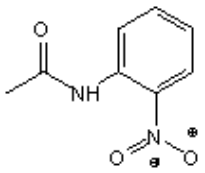
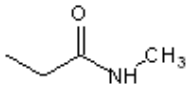
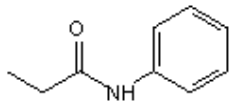
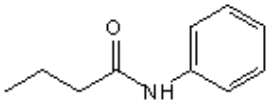
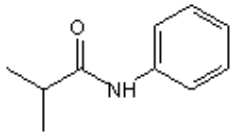
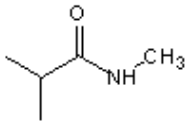
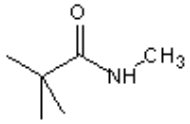
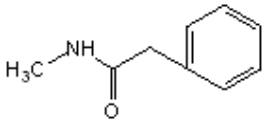
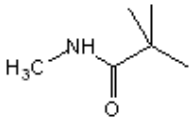
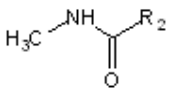
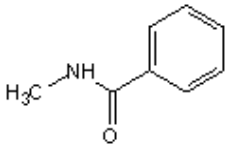


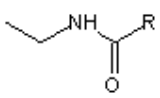
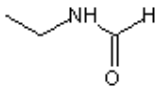
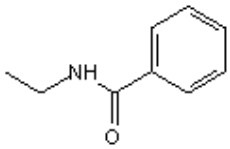
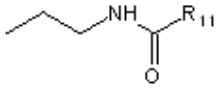
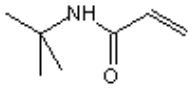
The HNMR spectra of the Secondary Amides are usually more complex than the primary amides due to the presence of a substituent bonded to the amide nitrogen atom. These substituents produce a much wider range of chemical shifts for the amide proton which may, in addition, display coupling to aliphatic groups bonded to it. The chemical shifts of aliphatic groups bonded to the carbonyl side of this functional group are similar to those observed for the Primary Amides, while those groups bonded to the-nitrogen side of the linkage resonate at slightly lower field than the corresponding amines (ca 0.4 ppm).

Aliphatic Protons



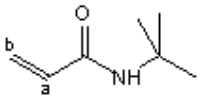
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		1.99		D_2O
		2.27		$CDCl_3$

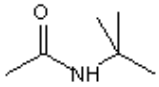
		2.27		$CDCl_3$
	1.17	2.24		$CDCl_3$
	1.19	2.35		$CDCl_3$
0.92	1.64	2.29		$CDCl_3$
	(1.12)	2.54		Poly so l
	(1.20)			$CDCl_3$
	(1.23)			Poly so l
		2.66		$CDCl_3$
		2.79		$CDCl_3$
		2.80		$CDCl_3$
		2.97		$CDCl_3$

	1.10	3.21		Polysol
	1.15	3.29		D_2O
	1.20	3.39		$CDCl_3$
0.90	1.51	3.20		$CDCl_3$
	(1.40)			$CDCl_3$

Olefinic Protons

The olefinic protons of the Acrylamides display the same differentiation in chemical shifts noted for the other carbonyl containing groups, i.e. the protons bonded to the beta carbon are deshielded in comparison to the geminal proton which is bonded to the alpha carbon.

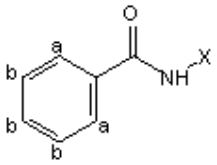


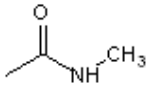
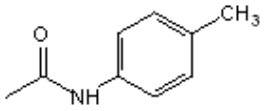
δ_b (ppm)	δ_a (ppm)	-X	Solvent
5.9-6.3	5.52		$CDCl_3$

Aromatic Protons

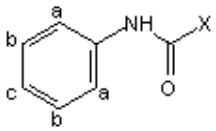
Both sides of the Secondary Amide linkage deshield the ortho aromatic protons. The protons ortho to the NH group resonate near 7.5 ppm while the protons ortho to the carbonyl group resonate at slightly lower field near 7.8 ppm.

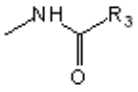
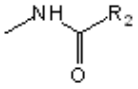
N-Substituted Benzamides



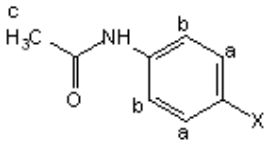
δ_b (ppm)	δ_a (ppm)	-X	Solvent
6.8-7.7	7.81		$CDCl_3$
7.2-7.6	7.74		$CDCl_3$

N-Phenyl Amides

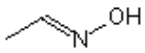


δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.20	7.05	7.52		$CDCl_3$
7.25	7.12	7.54		$CDCl_3$

Para Substituted Acetanilides



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
2.03	7.30	6.71	-OH	Polysol

2.02	7.48	6.85	-O-CH_3	DMSO-d_6
2.11	7.40	6.99	-F	$CDCl_3$
2.05	7.45	7.03	-CH_3	DMSO-d_6
2.07	7.32	7.04		$CDCl_3$
2.10	7.68	7.32	-Cl	DMSO-d_6
2.10	7.40	7.28		$CDCl_3$
2.18	7.60	7.60	-CF_3	$CDCl_3$
2.10	7.45	7.61	-Br	DMSO-d_6
2.11	7.47	7.61		Polysol
2.44	7.19	7.70	-I	TFA
2.48	7.82	8.35		TFA

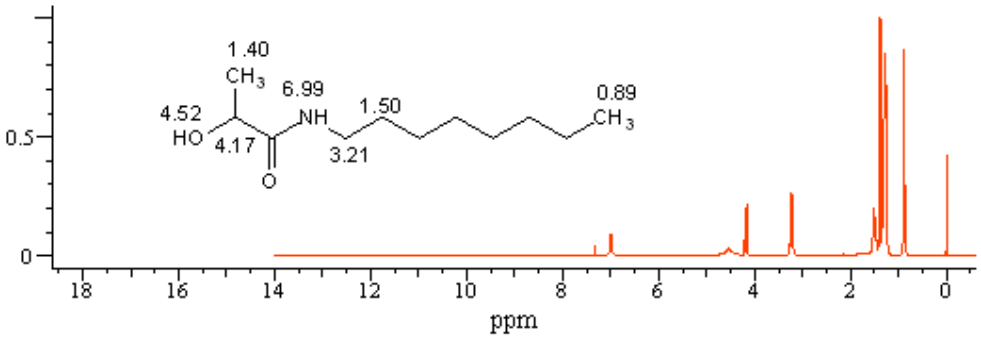
Coupling and Coupling Constants

Clear coupling is normally observed between the NH group and the protons of adjacent hydrocarbon groups.

^{J}HN-CH = 4.8-5.2 HZ

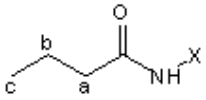
3 Tertiary (R-C(=O)-N-R_2)

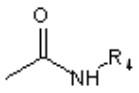
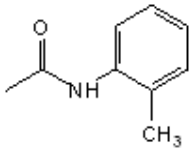
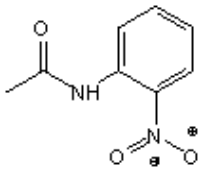
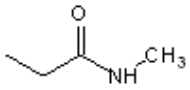
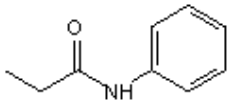
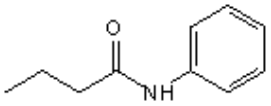
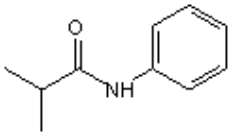
Secondary Amides

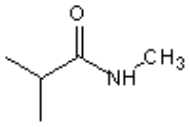
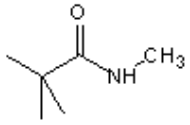
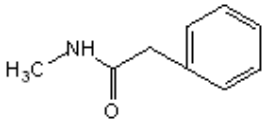
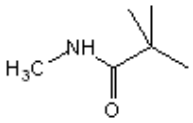
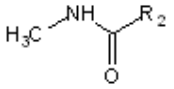
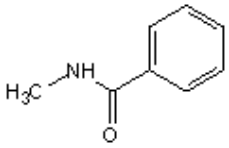
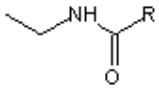
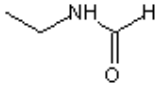
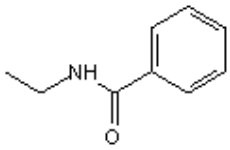
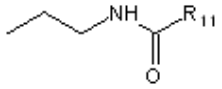
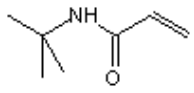


The HNMR spectra of the Secondary Amides are usually more complex than the primary amides due to the presence of a substituent bonded to the amide nitrogen atom. These substituents produce a much wider range of chemical shifts for the amide proton which may, in addition, display coupling to aliphatic groups bonded to it. The chemical shifts of aliphatic groups bonded to the carbonyl side of this functional group are similar to those observed for the Primary Amides, while those groups bonded to the-nitrogen side of the linkage resonate at slightly lower field than the corresponding amines (ca 0.4 ppm).

Aliphatic Protons



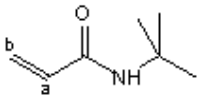
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		1.99		D_2O
		2.27		$CDCl_3$
		2.27		$CDCl_3$
	1.17	2.24		$CDCl_3$
	1.19	2.35		$CDCl_3$
0.92	1.64	2.29		$CDCl_3$
	(1.12)	2.54		Poly so l

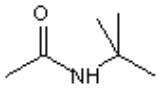
	(1.20)			$CDCl_3$
	(1.23)			Poly so I
		2.66		$CDCl_3$
		2.79		$CDCl_3$
		2.80		$CDCl_3$
		2.97		$CDCl_3$
	1.10	3.21		Polysol
	1.15	3.29		D_2O
	1.20	3.39		$CDCl_3$
0.90	1.51	3.20		$CDCl_3$
	(1.40)			$CDCl_3$

Olefinic Protons

The olefinic protons of the Acrylamides display the same differentiation in chemical shifts noted for the other carbonyl

containing groups, i.e. the protons bonded to the beta carbon are deshielded in comparison to the geminal proton which is bonded to the alpha carbon.

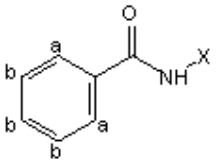


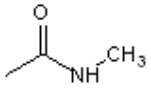
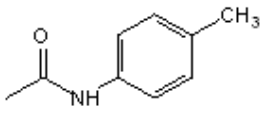
δ_b (ppm)	δ_a (ppm)	-X	Solvent
5.9-6.3	5.52		$CDCl_3$

Aromatic Protons

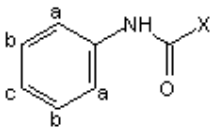
Both sides of the Secondary Amide linkage deshield the ortho aromatic protons. The protons ortho to the NH group resonate near 7.5 ppm while the protons ortho to the carbonyl group resonate at slightly lower field near 7.8 ppm.

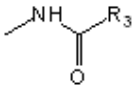
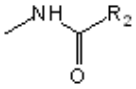
N-Substituted Benzamides



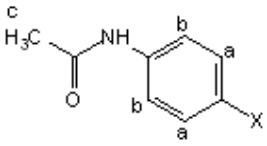
δ_b (ppm)	δ_a (ppm)	-X	Solvent
6.8-7.7	7.81		$CDCl_3$
7.2-7.6	7.74		$CDCl_3$

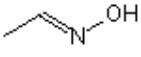
N-Phenyl Amides



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.20	7.05	7.52		$CDCl_3$
7.25	7.12	7.54		$CDCl_3$

Para Substituted Acetanilides



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
2.03	7.30	6.71	-OH	Polysol
2.02	7.48	6.85	$-O-CH_3$	DMSO-d_6
2.11	7.40	6.99	-F	$CDCl_3$
2.05	7.45	7.03	$-CH_3$	DMSO-d_6
2.07	7.32	7.04		$CDCl_3$
2.10	7.68	7.32	-Cl	DMSO-d_6
2.10	7.40	7.28		$CDCl_3$
2.18	7.60	7.60	$-CF_3$	$CDCl_3$
2.10	7.45	7.61	-Br	DMSO-d_6
2.11	7.47	7.61		Polysol

2.44	7.19	7.70	-I	TFA
2.48	7.82	8.35		TFA

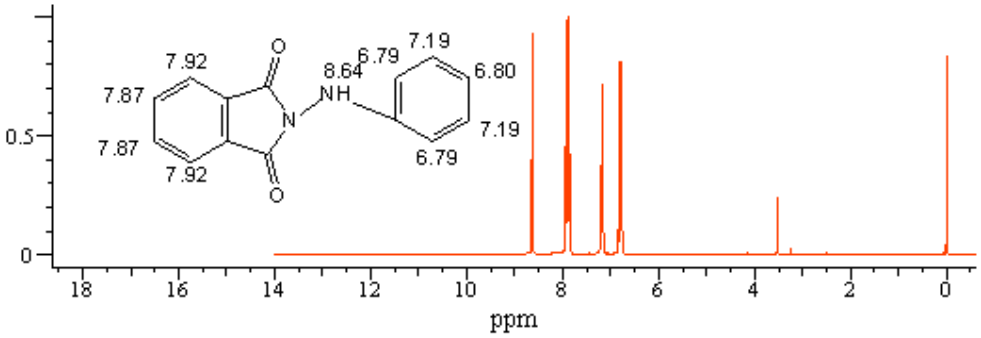
Coupling and Coupling Constants

Clear coupling is normally observed between the NH group and the protons of adjacent hydrocarbon groups.

^{J}HN-CH = 4.8-5.2 HZ

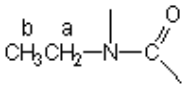
6 Imides (R-C(=O)-NH-C(=O)-R)

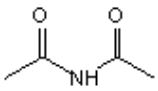
Imides

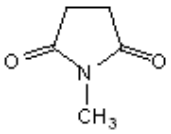
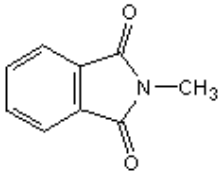
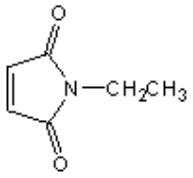
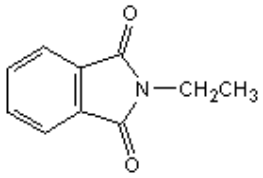


The Imides are nitrogen containing analogs of the Anhydrides. They contain the -C(=O)-NH-C(=O)-linkage and are usually cyclic in structure. As with the other carbonyl containing compounds, the protons of aliphatic groups alpha to the C(=O) group are weakly deshielded. The Imide NH proton resonates at low field (8-12 ppm) and is usually a very broad absorption band.

Aliphatic Protons



δ_b (ppm)	δ_a (ppm)	Compound	Solvent
	2.30		$CDCl_3$

	2.99		$CDCl_3$
	3.23		TFA
1.18	3.55		$CDCl_3$
1.29	3.71		$CDCl_3$

Olefinic Protons

The ring olefinic protons of Maleimide appear as a single sharp peak in the chemical shift range from 6.6 to 7.2 ppm. The olefinic protons of a vinyl group bonded to the Imide nitrogen atom are well differentiated in chemical shift. The hydrogen in the geminal position resonates at lowest field (6.83 ppm) as a doublet of doublets due to coupling to the hydrogens cis and trans to it. These hydrogens resonate at higher field, the cis proton at 5.01 ppm as a 10 Hz doublet and the trans proton at 6.02 ppm as a 16 Hz doublet.

Aromatic Protons

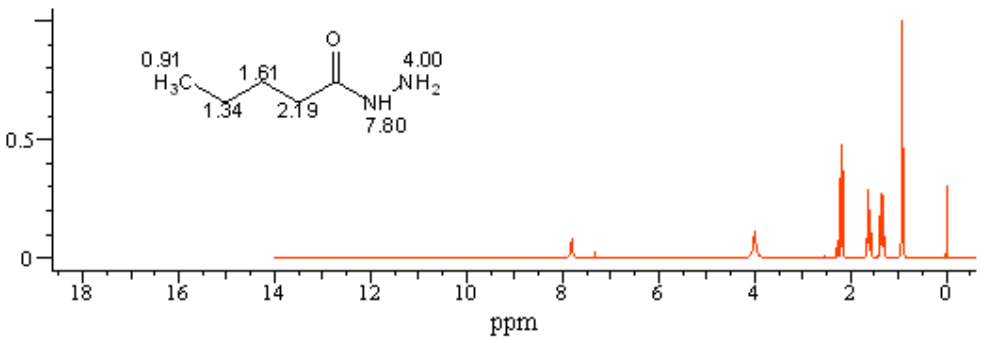
Phenyl groups bonded to the Imide nitrogen atom usually appear as a single, relatively sharp band near 7.4 ppm. The four aromatic hydrogens of the Phthalimides are observed as a symmetrical, higher-order series of bands centered at about 7.8 ppm.

Exchangeable Protons

The chemical shift of the Imide NH proton, as noted above resonates over a range of about 4 ppm at low field. The major determining factor producing this range is the type of ring system in which the Imide group is found. Generally the alicyclic systems, Succinimide and Glutarimide contain NH protons resonating at highest field, the Maleimides occupy the middle of the range, while the Phthalimides appear at the low field end of the range.

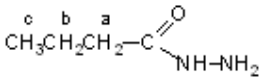
7 Hydrazides (R-C(=O)-NH-NH_2)

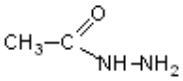
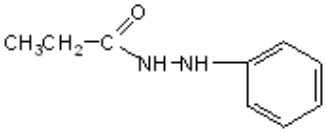
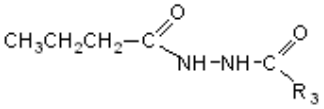
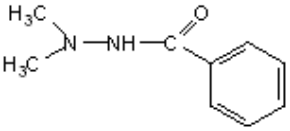
Hydrazides



The Hydrazides are similar to the other Amide-like structures in the chemical shifts of protons bonded to carbons alpha to the carbonyl group. The most distinguishing feature of the Hydrazides is the very broad two or three proton band in the range from 3-6 ppm which represents the resonance of the -NH_2 exchangeable hydrogens. The NH proton may be in exchange with the NH_2 and may resonate in the same range or, if not in exchange, will appear at lower field (7-10 ppm).

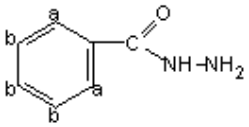
Aliphatic Protons

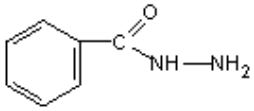
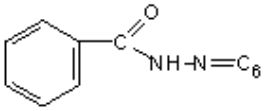


δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		1.93		$CDCl_3$
	1.11	2.21		Polysol
0.90	1.58	2.11		DMSO-d_6
		(2.66)		$CDCl_3$

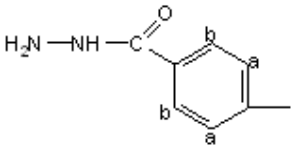
Aromatic Protons

Benzoic Acid, Hydrazides



δ_b (ppm)	δ_a (ppm)	Compound	Solvent
7.2-7.6	7.88		DMSO
7.1-7.5	7.82		$CDCl_3$

Para Substituted Benzoic Acid, Hydrazides

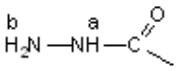


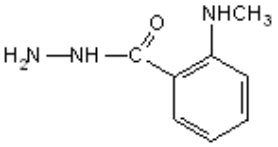
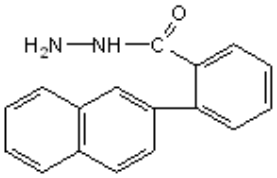
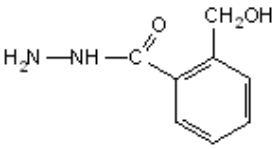
δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.72	7.23	$-CH_3$	$CDCl_3$
7.88	7.62	-Br	DMSO
8.07	8.22		Polysol

Exchangeable Protons

Because the Hydrazides are soluble in solvents which may contain significant amounts of water, it is often difficult to characterize the exchangeable proton resonances with confidence. In general, it appears that the NH_2 group resonates at intermediate field and is often in exchange with any water which may be present in the solution producing an erroneous 3-hydrogen integration value. In addition, the C(=O)-NH proton may resonate at much lower field (7-9

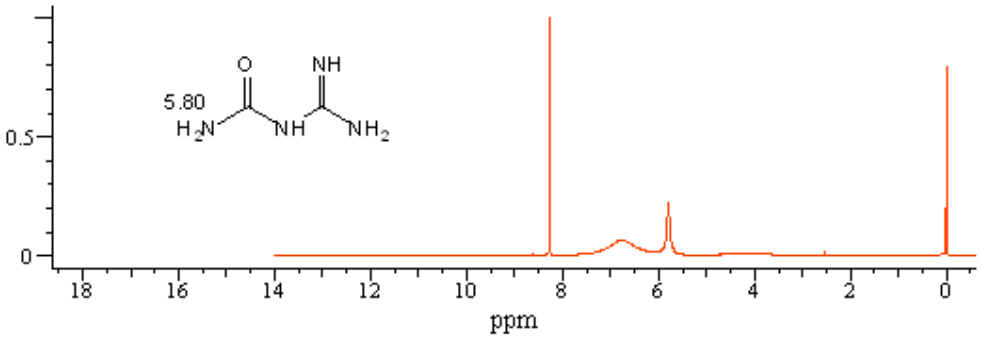
ppm) as a very broad band which may be difficult to locate.



δ_b (ppm)	δ_a (ppm)	Compound	Solvent
4.5	7.7		DMSO-d_6
3.9	8.0		Polysol
4.5	9.1		DMSO-d_6

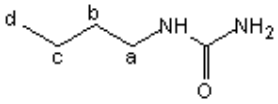
8 Ureas (R-NH-C(=O)-NH_2)

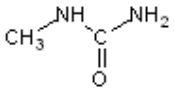
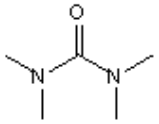
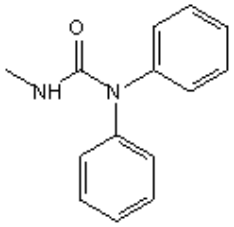
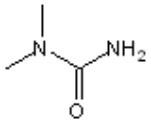
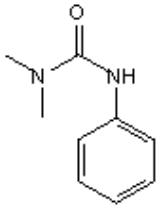
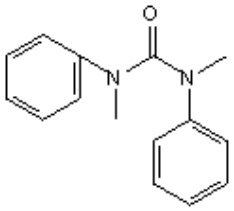
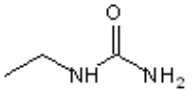
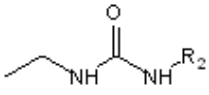
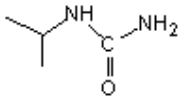
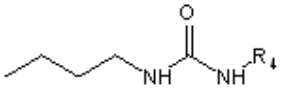
Ureas

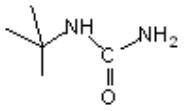
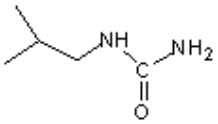


The monosubstituted aliphatic ureas characteristically display separate resonance bands for the two different types of NH protons. Coupling is usually observed between the NH and the protons of the adjacent hydrocarbon group ($NH-CH_2$). The chemical shift of aliphatic groups adjacent to the Urea nitrogen nucleus varies with the degree of substitution of the urea moiety as well as the other types of substituents in the molecule.

Aliphatic Protons



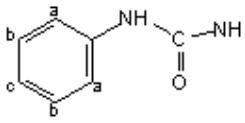
δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
	(1.29)	3.99	2.70		D_2O
			(2.75)		CCl_4
			2.78		$CDCl_3$
			(2.91)		$CDCl_3$
			(2.97)		$CDCl_3$
			3.16		$CDCl_3$
		1.11	3.18		$CDCl_3$
		1.22	3.50		$CDCl_3$
		(1.09)	3.72		Polysol
0.96	1.35	1.50	3.15		$CDCl_3$

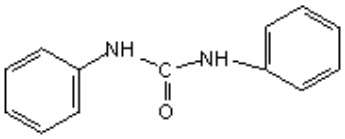
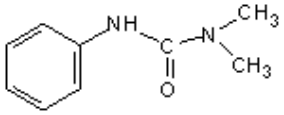
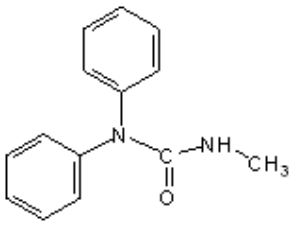
		(1.29)			Polysol
	(0.90)	1.69	2.91		Polysol

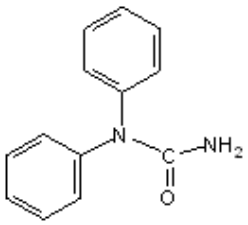
Aromatic Protons

The 1-phenyl ureas display an unusual type of aromatic shielding, i.e. the para proton is shielded while the ortho protons are deshielded. This shielding is not observed when two phenyl groups are bonded to the same nitrogen atom. In this case, a single peak is often observed near 7.3 ppm.

Phenyl Substituted Ureas

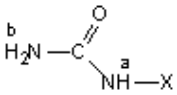


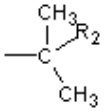
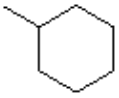
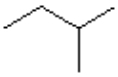
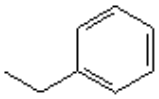
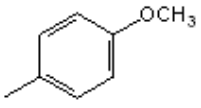
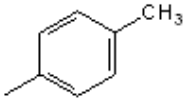
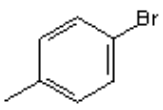
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.02	7.32	7.58		DMSO
	6.8-7.5			$CDCl_3$
	ca 7.25			$CDCl_3$

	ca 7.27			Polysol

Exchangeable Protons

Substitution of a urea molecule deshields the adjacent NH proton in comparison to the unsubstituted NH_2 group in the same molecule.



δ_b (ppm)	δ_a (ppm)	-X	Solvent
5.21	5.63		DMSO-d_6
5.21	5.74		Polysol
5.39	5.92		Polysol
5.22	6.00		Polysol
5.29	6.35		Polysol
6.79	6.79	-H	Polysol
5.53	8.19		Polysol
5.79	8.39		DMSO-d_6
5.88	8.62		DMSO-d_6

Coupling and Coupling Constants

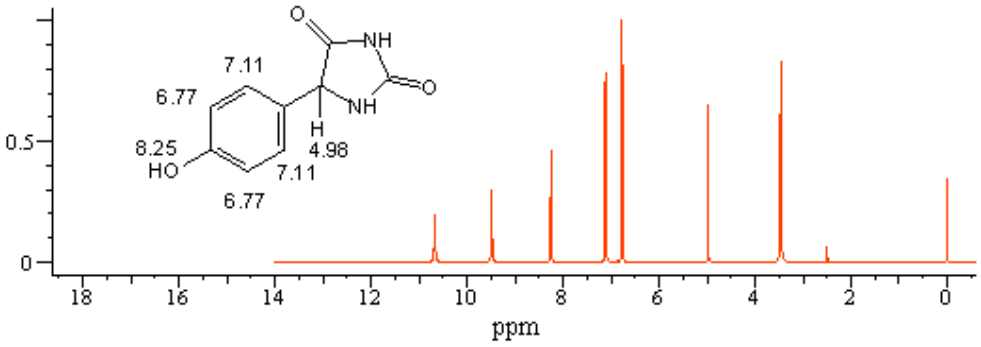
Coupling is usually observed between the NH proton and the hydrogens of adjacent hydrocarbon groups. The coupling constant varies over the range from 6-8. It is interesting to note that the type of non-equivalence so common in the spectra of N,N-dimethylamides is not observed in the HNMR spectra of the N,N-dimethylureas.

Solubility and Solvent Effects

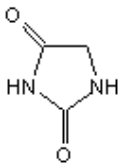
The solubility of the ureas varies primarily with the degree of substitution and the type of substituent(s). Urea and its monosubstituted derivatives are generally more soluble in solvents such as D_2O, DMSO-d_6 and Polysol. The trisubstituted and tetrasubstituted compounds, as well as those with large hydrocarbon groups tend to be more soluble in carbon tetrachloride or deuterochloroform. There does not appear to be any unusual solvent effects when CCl_4, $CDCl_3$, DMSO-d_6 and Polysol are used. As with most compounds, D_2O exchanges with the labile hydrogens in the molecule resulting in the loss of their resonance bands, and the use of trifluoroacetic acid produces unusually low field chemical shifts.

9 Hydantoins, Uracils, Barbiturates

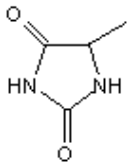
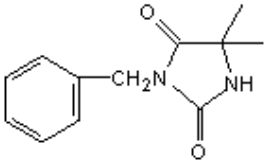
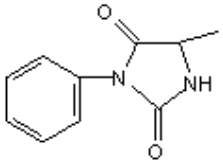
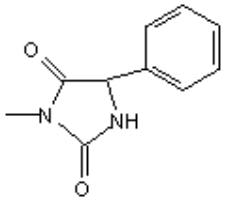
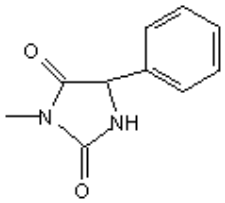
Hydantoins and Uracils



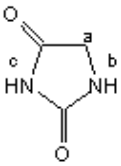
The Hydantoins and Uracils are cyclic structures containing the group – NH-C(=O-NH-C(=O)-. Hydantoin is a five membered ring while Uracil is a six membered ring. When present, the NH proton at position one (adjacent to one carbonyl) resonates at higher field than the NH proton at position three (adjacent to two carbonyl groups). Aliphatic groups bonded to the rings possess chemical shifts determined by their position on the ring.

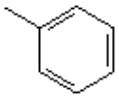


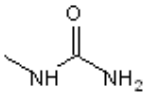
δ_b (ppm)	δ_a(ppm)	Group	Ring System	Solvent

	1.31	CH_3-		Polysol
	(1.38)	$(CH_3)_2$-		$CDCl_3$
	1.68	CH_3-		DMSO-d_6
	3.00	CH_3-		$CDCl_3$
1.12	3.47	CH_3-CH_2-		$CDCl_3$

Cyclic



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.44	9.52	4.03	$-CH_3$	Polysol
		4.29	-H	TFA
8.34	10,74	5.14		DMSO-d_6

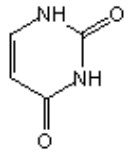
6.94	7.92	5.39		DMSO-d_6

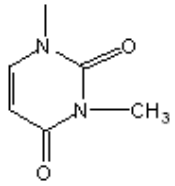
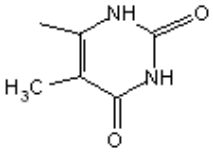
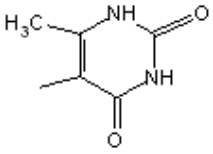
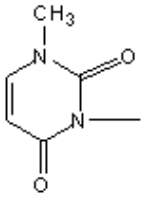
Uracil

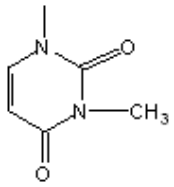
s

Aliphati

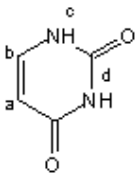
c



δ_a (ppm)	Group	Ring System	Solvent
1.75	CH_3		DMSO-d_6
2.05	CH_3		TFA
2.38	CH_3		TFA
3.30	CH_3		$CDCl_3$

3.41	CH_3		$CDCl_3$

Cyclic Protons



δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
		$-CH_3$	7.21	DMSO
$-CH_3$	$-CH_3$	5.71	7.29	$CDCl_3$
10.55	10.56	-Br	7.71	DMSO
9.10	9.10	-I	7.88	DMSO
11.69	11.69		8.80	DMSO
10.10		$-CH_3$	$-CH_3$	TFA
10.19		6.02	$-CH_3$	TFA

Solubility and Solvent Effects

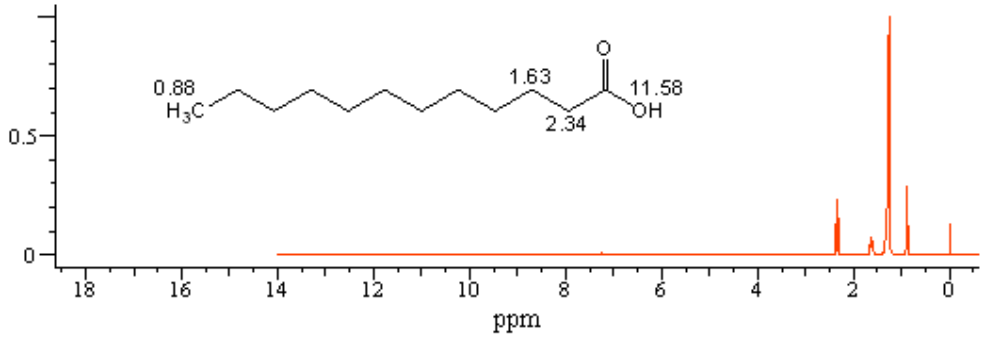
The cyclic diamides such as Hydantoin and Uracil are normally not soluble in carbon tetrachloride nor deuterochloroform unless one or both of the nitrogen atoms are substituted by an aliphatic group. The compounds are usually readily soluble in Polysol, DMSO-d_6, acetone and trifluoroacetic acid.

Trifluoroacetic acid is usually the solvent of last choice since one or both of the NH resonance bands may not be observed due to overlap with the acid proton band at low field.

10 Carboxylic Acids (R-C(=O)-OH)

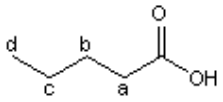
1 Aliphatic and Alicyclic

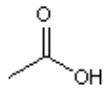
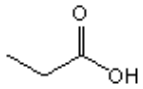
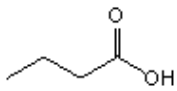
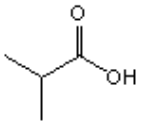
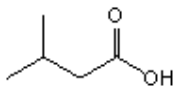
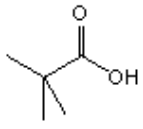
Aliphatics

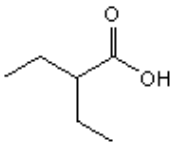


The carboxylic acid functional group (-C(=O)-OH) has a weakly deshielding effect on the protons of adjacent aliphatic groups but a strongly deshielding effect on the ortho aromatic protons.

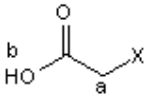
A distinguishing feature of this group of compounds is the carboxylic acid -OH group which normally resonates at very low field (10-13 ppm). This band may appear at higher field when a significant amount of water is present in the solution.

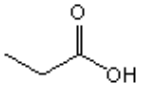
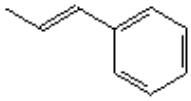
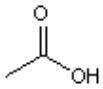
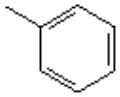
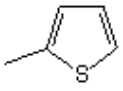
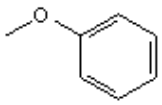


δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		2.06	11.90		CCl_4
	1.14	2.37	10.49		$CDCl_3$
0.90	1.67	2.29	11.97		CCl_4
	(1.20)	2.55	12.08		CCl_4
(0.98)	2.08	2.19	11.00		CCl_4
	(1.21)		12.01		$CDCl_3$

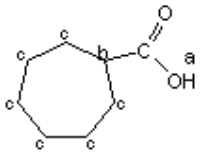
(0.93 1.55)		2.21	12.08		CCl_4

Substituted Acetic Acids



δ_b (ppm)	δ_a (ppm)	-X	Solvent
10.49	2.37	$-CH_3$	$CDCl_3$
11.80	2.43		DMSO-d_6
10.08	3.12	$-CH=CH_2$	$CDCl_3$
11.28	3.25		$CDCl_3$
11.50	3.37		Polysol
10.88	3.61		$CDCl_3$
10.80	3.71	-I	$CDCl_3$
11.49	3.79		$CDCl_3$
11.75	3.79	-C≡N	DMSO-d_6
10.59	3.92	-Br	$CDCl_3$
11.22	4.05	-Cl	CCl_4
	4.10	$-O-CH_3$	D_2O
	4.29	-OH	D_2O
8.78	4.67		Acetone

Alicyclic Protons



	n	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
	2	(0.7-1.2)	1.58	11.72	CCl_4
	3	(1.6-2.7)	3..19	11.99	$CDCl_3$
	4	(1.2-2.2)	2.69	11.25	CCl_4
	5	(1.1-26)	2.25	12.00	CCl_4
	6	(1.1-2.2)	2.53	11.55	$CDCl_3$

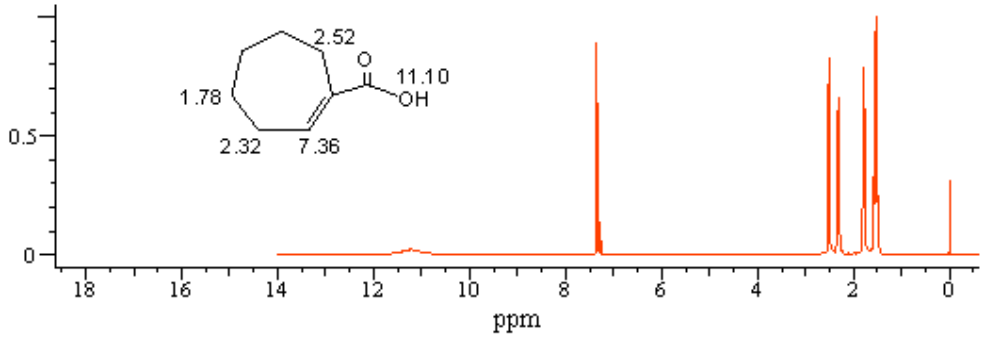
Exchangeable Protons

The carboxylic acid protons which are extremely labile hydrogens exchange with many other types of labile hydrogen to produce an averaged chemical shift for the protons involved in the exchange.

In addition, they will be in exchange with any water present in the solution resulting in either higher-field chemical shifts than expected and/or very broad resonance bands covering several ppm. The latter case is much more noticeable in the HNMR spectra of the Benzoic acids than in the spectra of the more soluble aliphatic compounds.

2 Olefinic

Olefinics



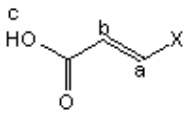
The carboxylic acid functional group (-C(=O)-OH) has a weakly deshielding effect on the protons of adjacent aliphatic groups but a strongly deshielding effect on the ortho aromatic protons.

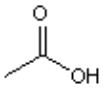
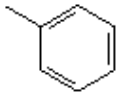
A distinguishing feature of this group of compounds is the carboxylic acid -OH group which normally resonates at very low field (10-13 ppm). This band may appear at higher field when a significant amount of water is present in the solution.

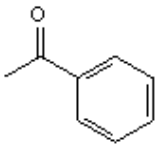
Olefinic Protons

The three olefinic protons of acrylic acid resonate as a complex higher-order pattern in the chemical shift range from 5.7-6.8 ppm. The most deshielded of these protons is the hydrogen that is cis to the carboxylic acid group, while the geminal proton resonates at higher field. This order of chemical shifts is the reverse of that observed for simple alkenes.

3-Substituted acrylic acids



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-X		Solvent
12.28	6.66	6.66		(trans)	DMSO-d_6
12.27	6.27	6.84	-Cl	(cis)	Polysol
11.91	5.77	7.03	-R_3	(trans)	CCl_4
11.79	5.82	7.04	-CH_3	(trans)	$CDCl_3$
11.34	6.28	7.50	-Cl	(trans)	$CDCl_3$
11.90	6.41	7.73		(trans)	$CDCl_3$

11.00	6.90	7.75		(trans)	$CDCl_3$

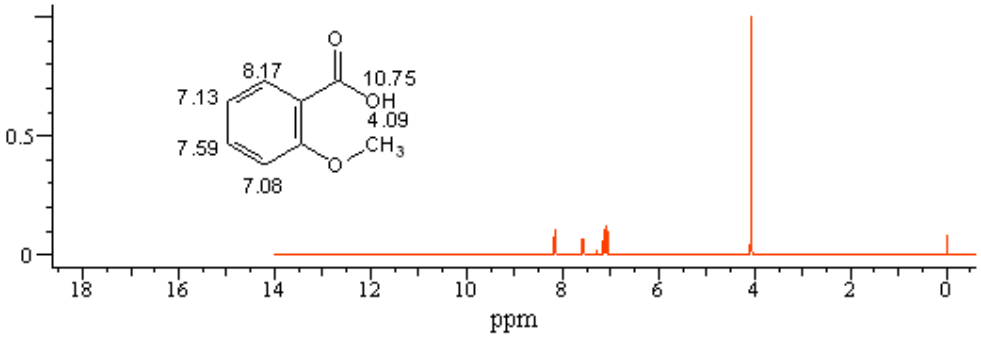
Exchangeable Protons

The carboxylic acid protons which are extremely labile hydrogens exchange with many other types of labile hydrogen to produce an averaged chemical shift for the protons involved in the exchange.

In addition, they will be in exchange with any water present in the solution resulting in either higher-field chemical shifts than expected and/or very broad resonance bands covering several ppm. The latter case is much more noticeable in the HNMR spectra of the Benzoic acids than in the spectra of the more soluble aliphatic compounds.

3 Aromatic

Aromatics

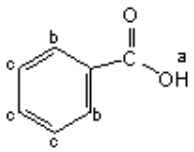


The carboxylic acid functional group (-C(=O)-OH) has a weakly deshielding effect on the protons of adjacent aliphatic groups but a strongly deshielding effect on the ortho aromatic protons.

A distinguishing feature of this group of compounds is the carboxylic acid -OH group which normally resonates at very low field (10-13 ppm). This band may appear at higher field when a significant amount of water is present in the solution.

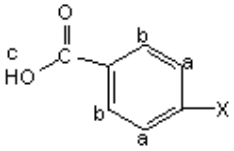
Aromatic Protons

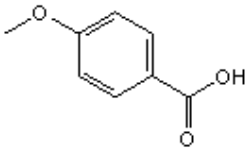
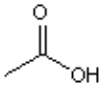
Benzoic Acid



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Solvent
7.2-7.8	8.14	12.82	CCl_4

Para Substituted Benzoic Acids



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	-para	Solvent
6.55	7.83	6.76	$-NH_2$	Acetone
10.95	7.95	6.90	$-O-R_3$	Polysol
	7.91	7.00	$-O-CH_3$	DMSO-d_6
9.76	8.11	7.07	-OH	Acetone
12.02	8.09	7.20		DMSO
9.72	8.02	7.30	-F	Acetone
	8.02	7.30	$-CH_3$	TFA
8.27	8.00	7.56	-Cl	DMSO
7.28	7.90	7.71	-Br	DMSO-d_6
	7.90	7.71	-I	DMSO-d_6
9.41	8.11	8.11		DMSO-d_6
	8.21	8.30		DMSO-d_6

Exchangeable Protons

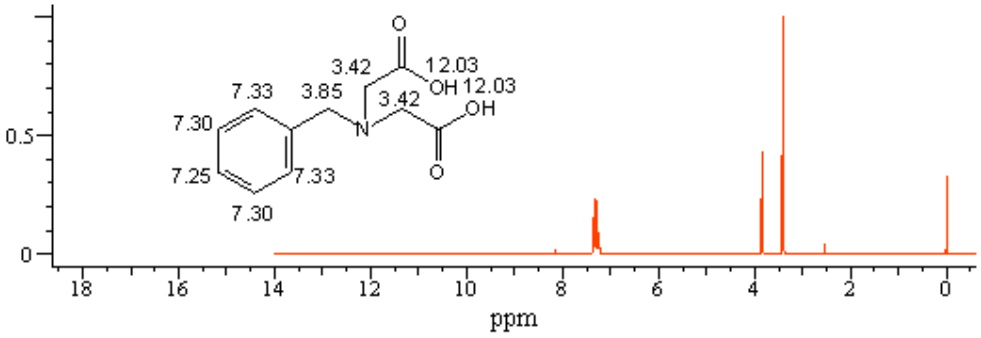
The carboxylic acid protons which are extremely labile hydrogens exchange with many other types of labile hydrogen to

produce an averaged chemical shift for the protons involved in the exchange.

In addition, they will be in exchange with any water present in the solution resulting in either higher-field chemical shifts than expected and/or very broad resonance bands covering several ppm. The latter case is much more noticeable in the HNMR spectra of the Benzoic acids than in the spectra of the more soluble aliphatic compounds.

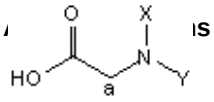
4 Amino Acids

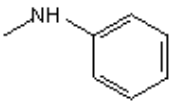
Amino Acids

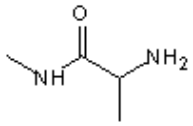
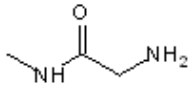
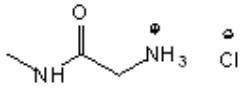
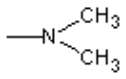


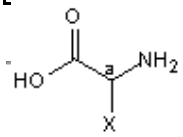
The Amino Acids, and especially the alpha amino acid's, are distinguished by their high degree of solubility in water (D_2O) and that many of these compounds contain a methine resonance band at relatively low field (3.3-4.5 ppm).

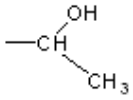
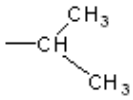
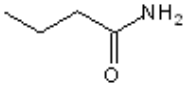
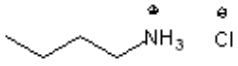
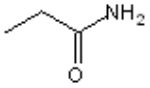
Because the methine proton of the alpha Amino Acids is an asymmetric carbon, an adjacent methylene group may display clear non-equivalence in chemical shift for the two hydrogens bonded to it. As a result, the methine proton may appear as a doublet of doublets rather than as a triplet.



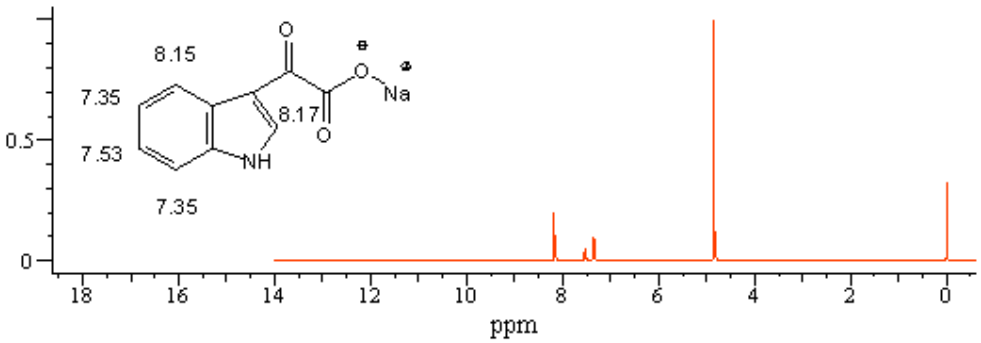
δ_a (ppm)	-N (X,Y)	Solvent
3.58	$-NH_2$	D_2O
3.62	$-NH-CH_3$	D_2O
3.68		D_2O
3.81		D_2O

3.81		D_2O
3.90		D_2O
3.92		D_2O
3.98		D_2O



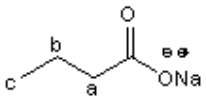
δ_a (ppm)	-X	Solvent
3.30		D_2O
3.50		D_2O
3.55		D_2O
3.70	$-CH_3$	D_2O
3.70	$- CH_2 - CH_3$	D_2O
3.71	$-R_3$	D_2O
3.79		D_2O
3.82		D_2O
3.91		D_2O
4.00		D_2O
4.47	$-CH_2-SH$	D_2O

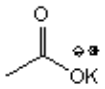
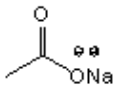
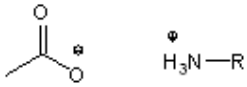
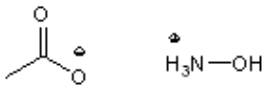
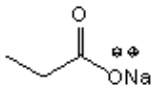
Salts of Carboxylic Acids

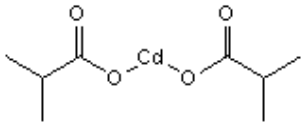
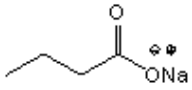


The Salts of the Carboxylic Acids are very similar in most respects to their corresponding Carboxylic acids with the exception of their increased solubility in water (D_2O). The chemical shifts listed vary over a relatively wide range due to the different solvents employed. The solubility of the Carboxylic Acid Salts, in turn, is directly related to the metal which is present in the compound.

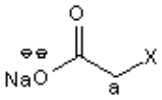
Aliphatic Protons

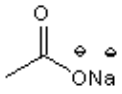
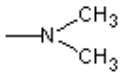
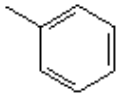
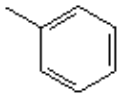
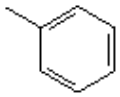
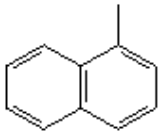


δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
		1.88		D_2O
		1.90		DMSO-d_6
		1.90		$CDCl_3$
		1.99		D_2O
	1.01			D_2O

	(1.09	2.30)		D_2O
0.90	1.56	2.17		D_2O

Substituted Acetic Acid Salts



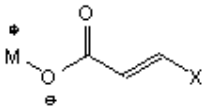
Group	δ_a (ppm)	X	Solvent
Na-O-C(=O)-	3.11		D_2O
Na-O-C(=O)-	3.19		D_2O
-Sn-O-C(=O)-	3.50		CCl_4
Na-O-C(=O)-	3.51	-SH	D_2O
K-O-C(=O)-	3.53		D_2O
-Hg-O-C(=O)-	3.60		Poly so l
Na-O-C(=O)-	3.63	-I	D_2O
Na-O-C(=O)-	4.25		D_2O
Na-O-C(=O)-	4.73	-F	D_2O

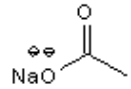
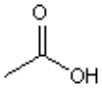
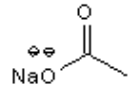
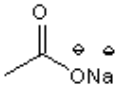
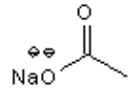
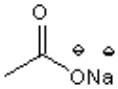
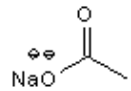
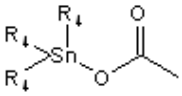
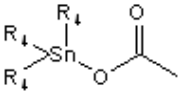
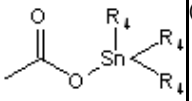
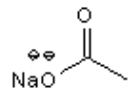
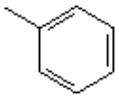
Olefinic Protons

The vinyl protons of Acrylic Acid salts appear as a higher-order series of peaks in the chemical shift range from 5.5-6.3

ppm. Characteristically, the two protons on the beta carbon are more strongly deshielded than the proton on the alpha carbon atom.

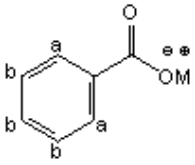
2-Substituted Acrylic Acid Salts

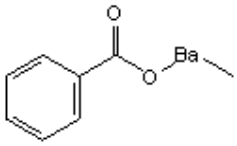
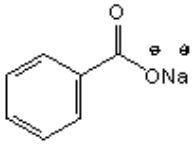
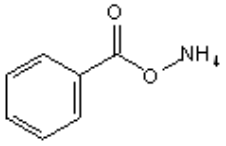
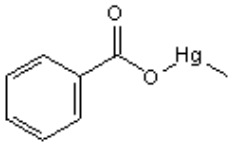


	δ_b (ppm)	δ_a (ppm)	-X		Solvent
	6.02	6.02		(cis)	D_2O
	6.10	6.10		(cis)	D_2O
	6.50	6.50		(trans)	D_2O
	5.84	6.59	$-CH_3$		D_2O
	5.75	6.75	$-CH_3$	(trans)	CCl_4
	6.76	6.76		(trans)	$CDCl_3$
	6.53	7.54		(trans)	D_2O

Aromatic Protons

Salts of Benzoic Acid



δ_b (ppm)	δ_a (ppm)	Compound	Solvent
7.3-7.7	7.91		D_2O
7.3-7.6	7.98		D_2O
7.3-7.7	7.99		D_2O
7.2-7.7	8.05		Poly so l

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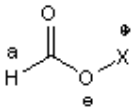
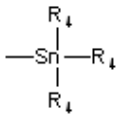
Aldehydic Protons

Salts of Formic Acid

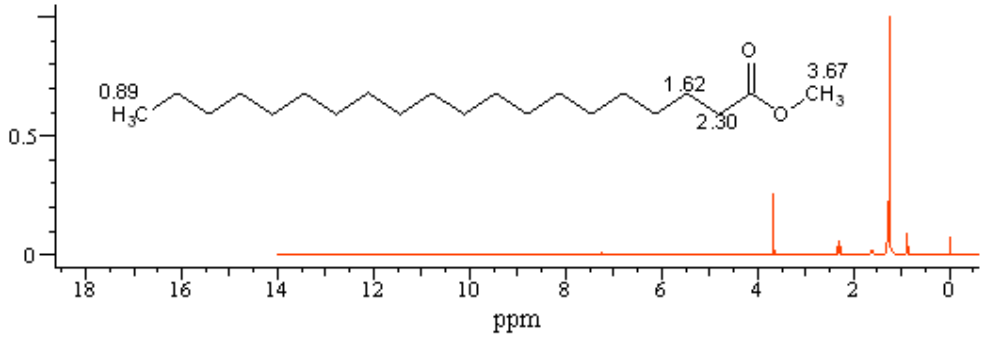


δ_a (ppm)	-X	Solvent
8.08		CCl_4
8.17	-Na	TFA
8.46	-Li	D_2O
8.48	-Ca-	D_2O

11□Esters

1□□Aliphatic Esters of Aliphatic Acids

Aliphatic Esters

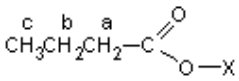


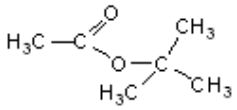
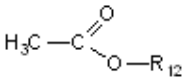
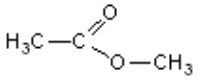
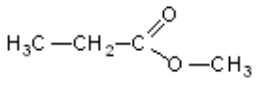
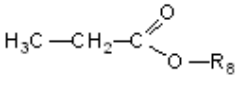
The Esters are one of the most important functional groups with a wide variety of combinations of aliphatic, olefinic and aromatic acids and alcohols.

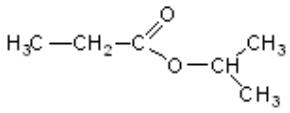
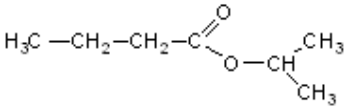
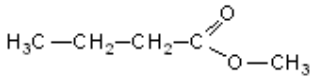
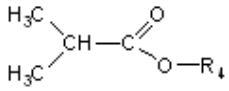
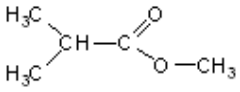
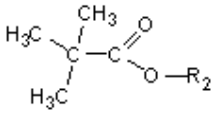
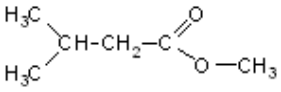
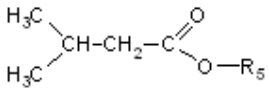
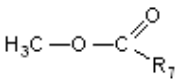
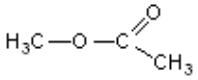
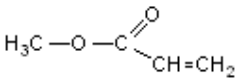
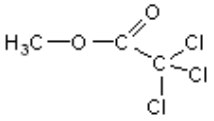
The carbonyl side of the ester functional group has a weakly deshielding effect on the protons of adjacent aliphatic groups, while the oxygen side of the linkage has a strongly deshielding effect.

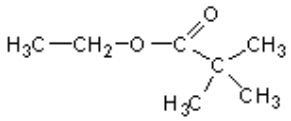
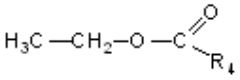
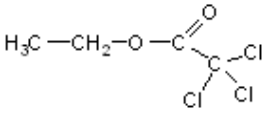
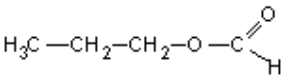
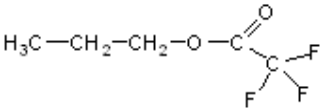
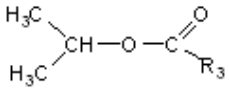
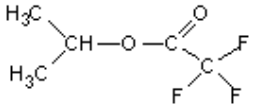
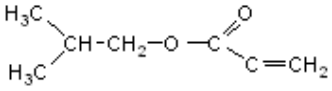
The Esters are readily soluble in carbon tetrachloride and deuterochloroform unless substituted by more polar functional groups.

Aliphatic Protons



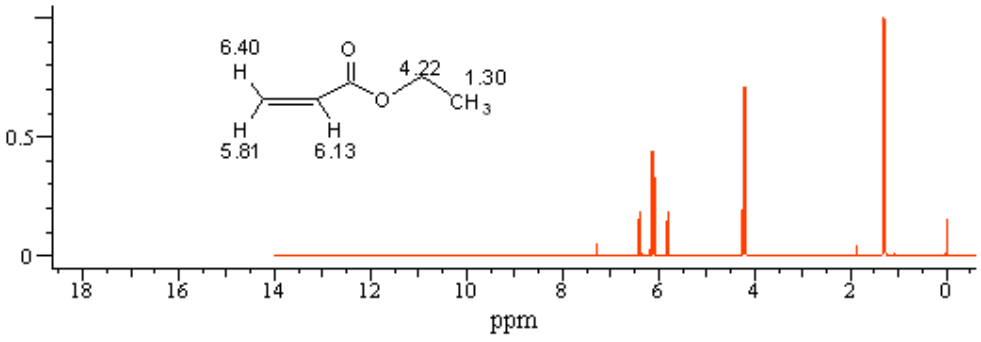
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		1.90		CCl_4
		1.95		CCl_4
		2.00		CCl_4
	1.10	2.27		CCl_4
	1.10	2.27		CCl_4

	1.16	2.30		$CDCl_3$
0.95	1.70	2.18		CCl_4
0.91	1.61	2.21		CCl_4
	(1.13)	2.44		CCl_4
	(1.14)	2.49		CCl_4
	(1.17)			CCl_4
(0.96)	1.97	2.12		CCl_4
(0.93)	1.99	2.18		$CDCl_3$
		3.61		CCl_4
		3.65		CCl_4
		3.70		CCl_4
		4.00		CCl_4

	1.23	4.07		CCl_4
	1.29	4.19		CCl_4
	1.41	4.41		$CDCl_3$
0.98	1.67	4.08		CCl_4
0.98	1.78	4.30		$CDCl_3$
	(1.22)	4.92		CCl_4
	(1.39)	5.20		CCl_4
(0.96)	1.97	3.89		CCl_4

2 Olefinic Esters of Aliphatic Acids

Olefinic Esters



The Esters are one of the most important functional groups with a wide variety of combinations of aliphatic, olefinic and aromatic acids and alcohols.

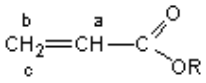
The carbonyl side of the ester functional group has a weakly deshielding effect on the protons of adjacent aliphatic groups, while the oxygen side of the linkage has a strongly deshielding effect.

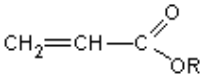
The Esters are readily soluble in carbon tetrachloride and deuterochloroform unless substituted by more polar functional groups.

Olefinic Protons

The olefinic protons of Acrylic Acid Esters appear in the HNMR spectrum as a higher-order ABC pattern in the chemical shift range from 5.6-6.1 ppm. The proton which is trans to the carbonyl group resonates at highest field, the geminal proton resides at slightly lower field, and the hydrogen which is cis to the carbonyl appears at lowest field.

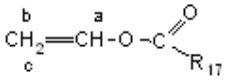
Acrylate Esters

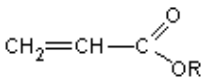


δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
6.34	5.72	6.09		CCl_4

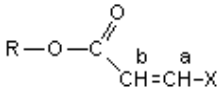
The Vinyl Esters of aliphatic carboxylic acids produce a much clearer pattern than the corresponding Acrylic Acid protons. The three olefinic protons of the Vinyl Esters produce resonance bands over the range from 4.3 to 7.5 ppm. The two protons bonded to the beta carbon resonate at highest field while the geminal proton which is bonded to the alpha carbon resonates at lower field.

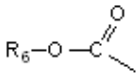
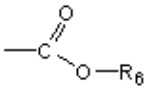
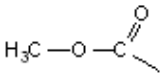
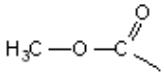
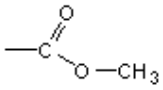
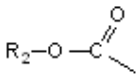
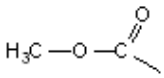
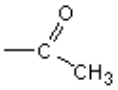
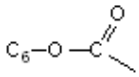
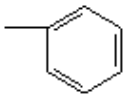
Vinyl Esters of Aliphatic Acids



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
4.82	4.51	7.23		$CDCl_3$

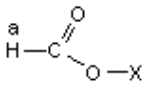
2-Substituted Acrylate Esters

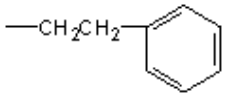


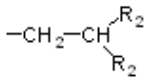
R-	δ_b (ppm)	δ_a (ppm)	-X		Solvent
	6.79	6.79		(trans)	CCl_4
	5.71	6.84	$-R_7$	(trans)	CCl_4
	6.86	6.86		(trans)	$CDCl_3$
	5.79	6.90	$-CH_3$	(trans)	CCl_4
	6.59	7.03		(trans)	$CDCl_3$
	6.40	7.67		(trans)	CCl_4

The Aldehydic Protons

The Aldehydic protons of the Formic Acid esters appears as a sharp singlet at low field in the range from 7.9 to 8.10 ppm.

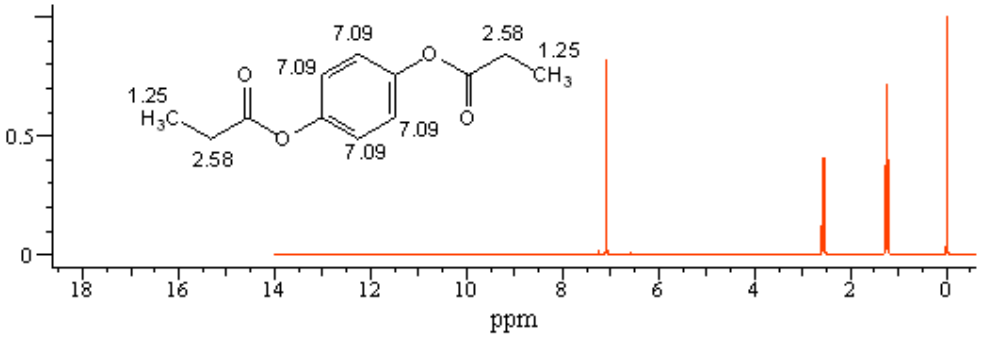


δ_a (ppm)	-X	Solvent
7.90		CCl_4
7.91	$-R_7$	CCl_4
7.96	$-R_8$	CCl_4
7.98	$-CH_3$	CCl_4

8.07		$CDCl_3$
8.10	$-CH_2CH_2-OR$	$CDCl_3$

3 Aromatic Esters of Aliphatic Acids

Aromatic Esters



The aliphatic esters of Benzoic Acid are more highly deshielded by the adjacent oxygen atom than those of the aliphatic and olefinic carboxylic acids.

The ortho aromatic protons are also strongly deshielded by the adjacent carbonyl group and resonate about 0.5 ppm to lower field than the meta and para protons.

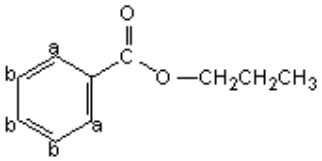
The aromatic esters are readily soluble in the halogenated solvents normally used as solvents in NMR and do not exhibit any unusual solvent effects. These compounds do not display any special spin-spin couplings.

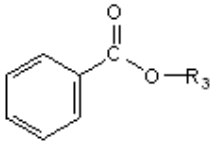
Aromatic Protons

The carbonyl side of the ester linkage strongly deshields the ortho aromatic protons producing a series of multiplets similar to those observed for the ketones and amides.

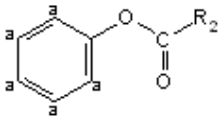
The oxygen side of the group has a much weaker shielding effect than the oxygen atom of the aliphatic ethers, resulting in a broad, complex higher-order series of multiplets in the chemical shift range from 6.9-7.5 ppm.

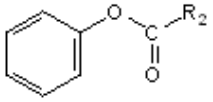
Benzoic Acid, Propyl Ester



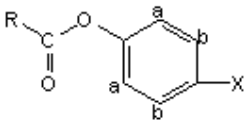
δ_b (ppm)	δ_a (ppm)	Compound	Solvent
7.1-7.6	8.01		CCl_4

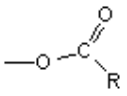
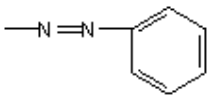
Propionic Acid, Phenyl Ester



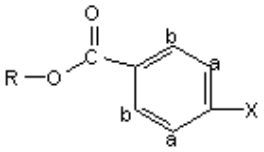
δ_a (ppm)	Compound	Solvent
6.9-7.5		CCl_4

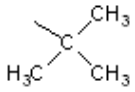
Para Substituted Phenyl Esters



δ_b (ppm)	δ_a (ppm)	-X	Solvent
6.82	7.01	$-CH_3$	CCl_4
7.06	7.06	-F	$CDCl_3$
7.09	7.09		$CDCl_3$
7.19	7.80		CCl_4
7.19	7.88		$CDCl_3$
7.32	8.29		$CDCl_3$

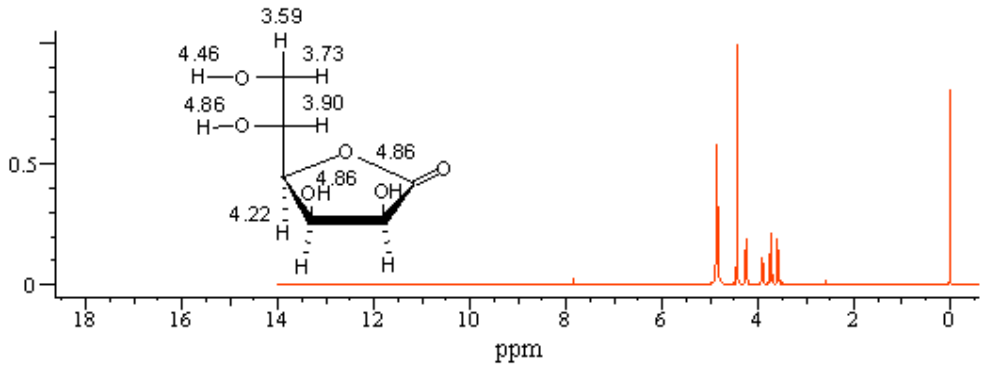
Para Substituted Benzoic Acid Esters



δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.83	6.63	$-NH_2$	$CDCl_3$
7.87	6.84	-OH	$CDCl_3$
7.99	6.88	$-O-CH_3$	$CDCl_3$
7.95	7.06	-N=C=O	$CDCl_3$
7.88	7.36		CCl_4
7.95	7.38	-Cl	$CDCl_3$
7.83	7.49	-Br	CCl_4
7.82	7.70	-I	Polyso l
8.32	7.91	-N=O	$CDCl_3$
8.07	8.07		$CDCl_3$
8.26	8.26		$CDCl_3$

4 Cyclic Esters (Lactones)

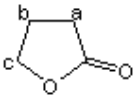
Lactones



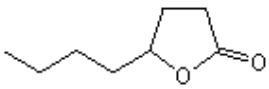
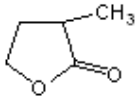
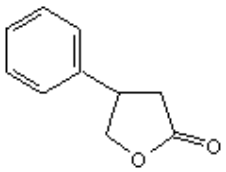
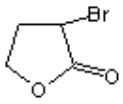
Due to their cyclic structure, the aliphatic cyclic esters often display non-equivalence in chemical shift for the two protons of the methylene group in the ring system.

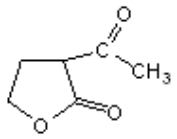
This situation is clearly observed in compounds in which the five ring hydrogens each display distinctly different chemical shifts. The aromatic protons of the aromatic lactones generally produce complex patterns in the chemical shift range from 6.5 to 8.0 ppm depending upon which group of the ester moiety is bonded to the aromatic ring. When the oxygen atom is bonded to the ring, the resonance bands tend to be in the high field portion of the range, 6.8 -7.4. When the carbonyl group is bonded to the aromatic ring, then the resonance bands tend to occupy the lower half of the range.

The Lactones, like the other esters are readily soluble in the chlorinated NMR solvents, carbon tetrachloride and deuterochloroform.



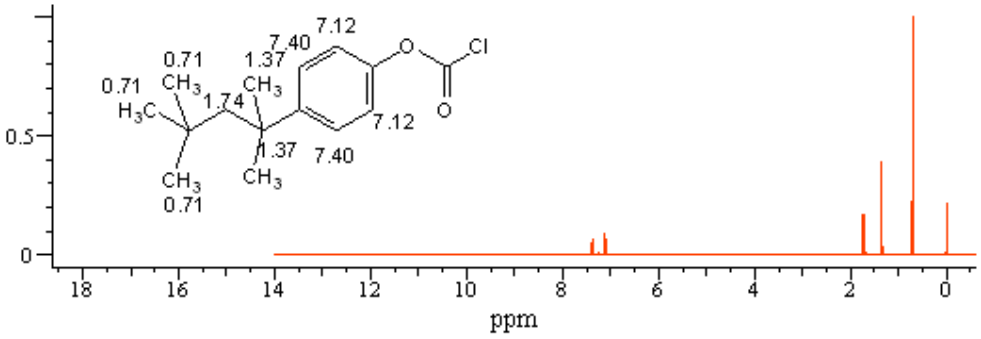
otons

δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
4.40	1.5-2.1	2.1-2.7		CCl_4
3.9-4.4	1.9, 2.4	2.60		CCl_4
4.2, 4.6	3.69	2.6, 2.8		$CDCl_3$
4.3, 4.6	2.2-2.8	3.00		CCl_4

4.29	1.9-3.0	3.71		CCl_4

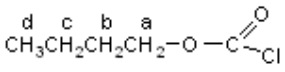
5 Chloroformates

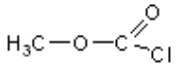
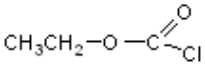
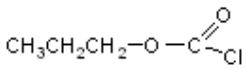
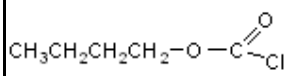
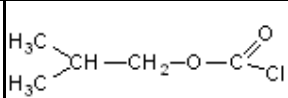
Chloroformates



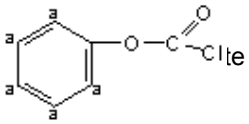
The aliphatic esters of Chloroformic Acid are notable in that their alpha hydrocarbon groups are more strongly deshielded than either the esters of simple aliphatic or aromatic carboxylic acids.

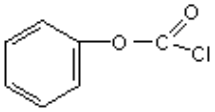
The Chloroformates are readily soluble in the chlorinated solvents. Their spectra display no unusual couplings nor coupling constants.



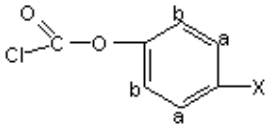
δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
			3.93		CCl_4
		1.40	4.39		$CDCl_3$
	1.00	1.76	4.22		CCl_4
1.01	1.75	1.45	4.31		CCl_4
	(0.99)	2.08	4.11		$CDCl_3$

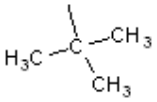
Aromatic Protons



δ_a (ppm)	Compound	Solvent
7.0-7.6		CCl_4

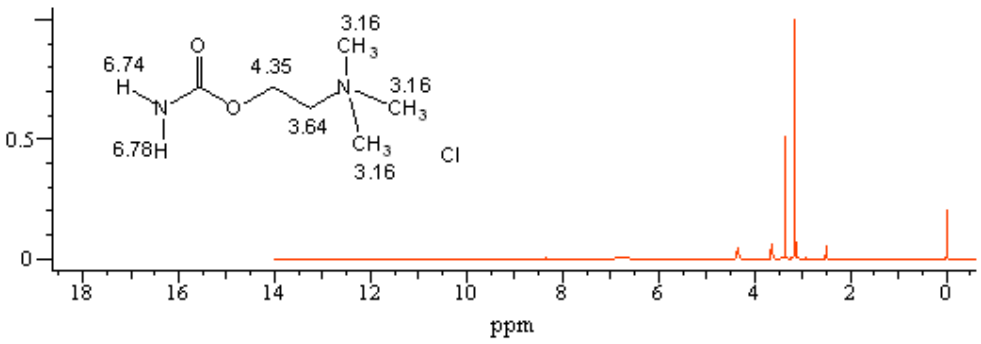
Para Substituted Phenyl Chloroformates



δ_b (ppm)	δ_a (ppm)	-X	Solvent
7.03	6.77	-O-CH_3	CCl_4
7.10	7.30	-Cl	CCl_4
7.07	7.33		CCl_4
7.11	8.12		DMSO-d_6

6 Carbamates

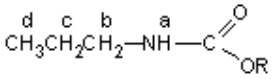
Carbamates

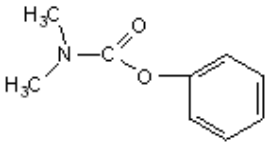
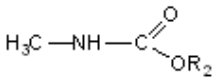
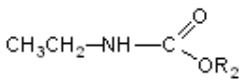
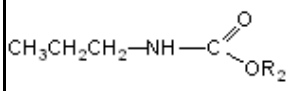
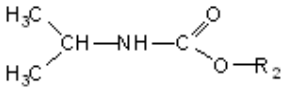


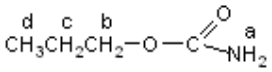
The NMR spectra of the Carbamates are often quite complex in appearance since up to three aliphatic or aromatic groups may be present in the molecule. In addition, the secondary Carbamates (R-NH-C(=O)-O-) often display coupling between the NH proton and the hydrogens bonded to the adjacent carbon atom. The coupling constant for this interaction is about 7.5 Hz.

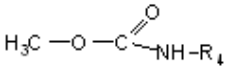
Hydrocarbon groups adjacent to the nitrogen side of the linkage are deshielded to intermediate field (about 3 ppm) while those adjacent to the oxygen side are deshielded by an additional 1 ppm to about 4 ppm.

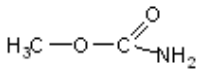
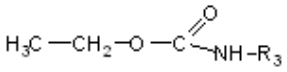
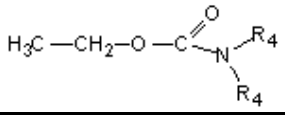
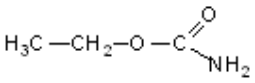
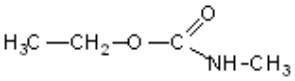
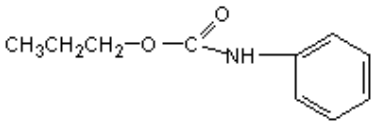
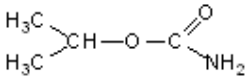
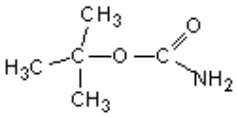
Aliphatic Protons



δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	X	Solvent
		(3.06)			$CDCl_3$
		2.78	5.09		$CDCl_3$
	1.12	3.15	5.57		CCl_4
0.90	1.45	3.08	5.25		CCl_4
	(1.15)	3.71	4.66		$CDCl_3$

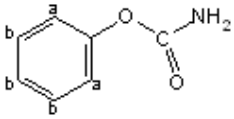


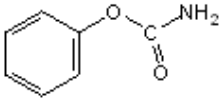
δ_d (ppm)	δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		3.60	5.30		CCl_4

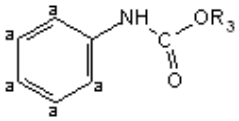
		3.63	5.13		$CDCl_3$
	1.20	4.03	5.25		CCl_4
	1.21	4.07			CCl_4
	1.22	4.08	5.20		$CDCl_3$
	1.24	4.11	5.09		$CDCl_3$
0.94	1.68	4.10	6.90		$CDCl_3$
	(1.22)	4.89	4.97		$CDCl_3$
	(1.45)		4.88		$CDCl_3$

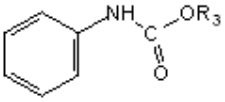
Aromatic Protons

Phenyl Carbamates



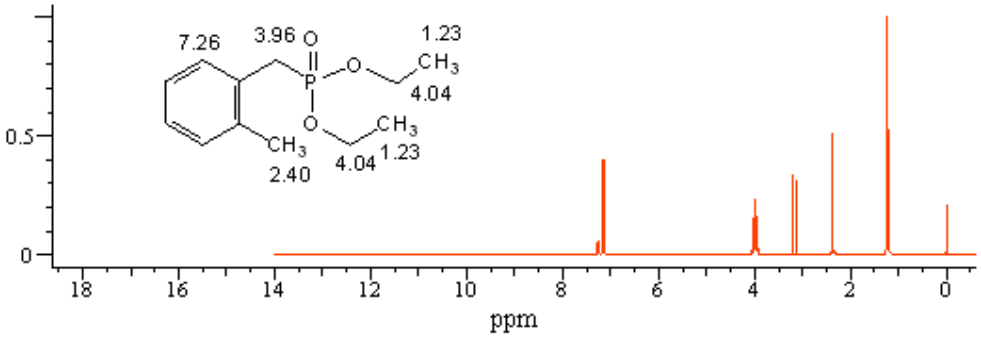
δ_b (ppm)	δ_a (ppm)	Compound	Solvent
6.8-7.4	7.51		DMSO



δ_a (ppm)	Compound	Solvent
6.6-7.5		$CDCl_3$

7 Esters of Phosphorus Acids

Esters of the Phosphorus Acids



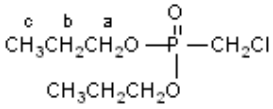
The chemical shifts of the Esters of Phosphonic and Phosphoric Acid are similar to those of the carboxylic acids, however, their spectra are distinguished by the spin-spin coupling interactions of the nearby hydrocarbon groups with the Phosphorus nucleus. As noted, many of these couplings and their associated coupling constants are quite sensitive to structural and substituent differences. Both groups of compounds are quite soluble in carbon tetrachloride and deuterochloroform and no unusual solvent effects have been noted for these two solvents.

The

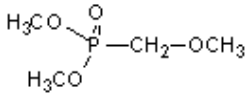
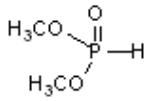
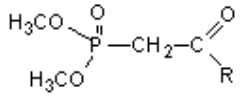
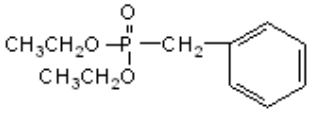
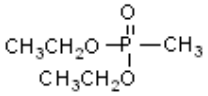
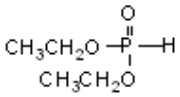
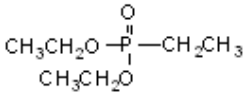
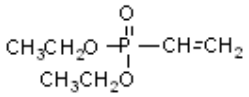
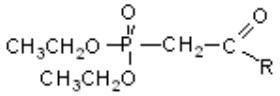
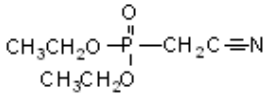
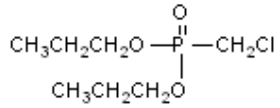
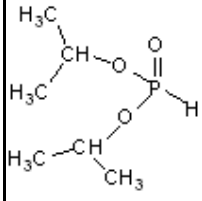
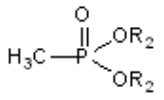
Phosphon

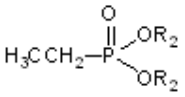
ates

Aliphatic

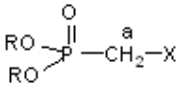


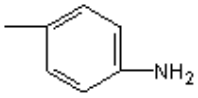
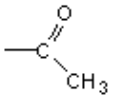
δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent

		(3.71)		CCl_4
		(3.72)		CCl_4
		(3.80)		$CDCl_3$
	(1.22	4.01)		$CDCl_3$
	(1.29	4.04)		CCl_4
	(1.36	4.08)		CCl_4
	(1.31	4.11)		$CDCl_3$
	(1.36	4.11)		$CDCl_3$
	(1.35	4.17)		CCl_4
	(1.40	4.22)		$CDCl_3$
(0.99	1.65	3.51)		CCl_4
	(1.32	4.64)		CCl_4
		1.33		CCl_4

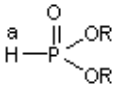
	1.19	1.91		$CDCl_3$

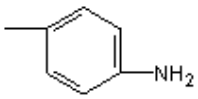
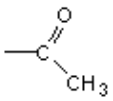
Substituted Methyl Phosphonates



δ_a (ppm)	X	$^{J}P(=O)-CH_2$ (Hz)	Solvent
1.91	$-CH_3$	0	$CDCl_3$
2.98	-C≡N	20.9	$CDCl_3$
3.05		21.3	$CDCl_3$
3.10		23.1	$CDCl_3$
3.51	-Cl	11.5	CCl_4
3.69	$-O-CH_3$	8.0	CCl_4

Phosphonyl Protons



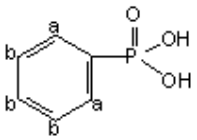
δ_a (ppm)	R	$^{J}P(=O)-H$ (Hz)	Solvent
4.40	$-CH_3$	411 Hz	CCl_4
5.69	-C≡N	342 Hz	CCl_4
5.80		697 Hz	CCl_4
6.11		733 Hz	$CDCl_3$

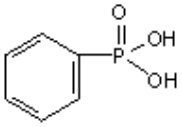
6.76	-Cl	691 Hz	$CDCl_3$

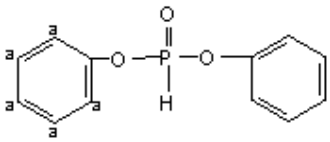
Aromatic Protons

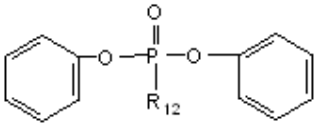
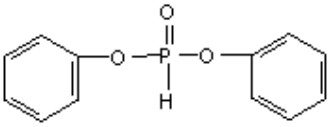
The aromatic protons of the phenyl esters of Phosphonic Acid resonate as a broad, single peak or a complex series of bands centered at about 7.2 ppm. Phenyl groups bonded to the Phosphorus nucleus display a strong deshielding of the ortho protons which resonate near 7.8 ppm and couple to the Phosphorus nucleus with a coupling constant of about 13 Hz.

Phenyl Phosphonates



δ_b (ppm)	δ_a (ppm)	Compound	Solvent
7.3-7.6	7.80		Acetone



δ_a (ppm)	Compound	Solvent
ca. 7.21		$CDCl_3$
7.3-7.6		$CDCl_3$

Coupling and Coupling Constants

$^{J}P\ (=O)\text{-}C\text{-}O\text{-}CH_3$ = 1.1 Hz

$^{J}P(=O)\text{-}O\text{-}CH_2$ = 7.3-8.1 Hz

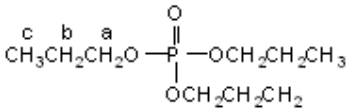
$^{J}P(=O)\text{-}O\text{-}CH_3$ = 10.8 Hz

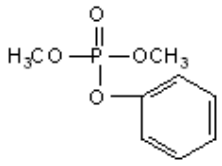
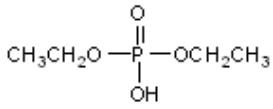
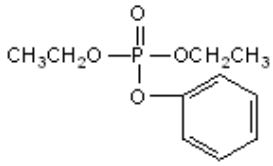
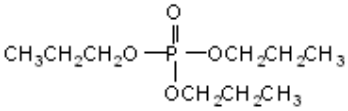
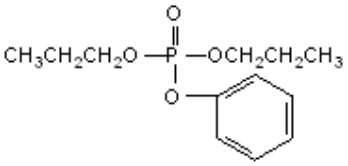
$^{J}P(=O)\text{-}CH_2$ = 11-24 Hz

$^{J}P(=O)\text{-}CH_3$ = 17.5 Hz

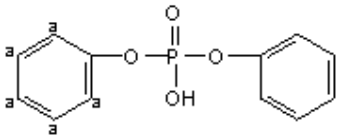
$^{J}P(=O)\text{-}H$ = 340-740 Hz

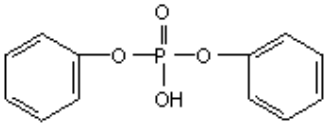
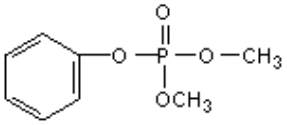
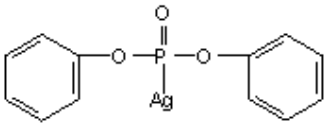
Aliphatic Protons



δ_c (ppm)	δ_b (ppm)	δ_a (ppm)	Compound	Solvent
		(3.75)		CCl_4
	(1.33	4.06)		CCl_4
	(1.31	4.11)		CCl_4
(0.99	1.70	3.99)		$CDCl_3$
(0.92	1.62	4.00)		CCl_4

Aromatic Protons



δ_a (ppm)	Compound	Solvent
ca 7.20		$CDCl_3$
ca 7.21		CCl_4
6.8-7.4		Polysol

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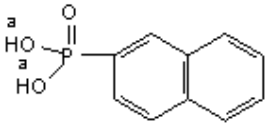
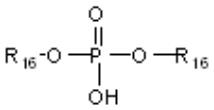
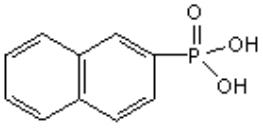
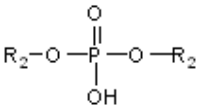
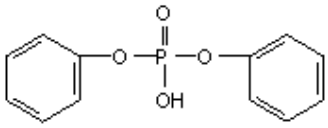
Exchangeable Protons



δ_a (ppm)	Compound	Solvent
8.83		$CDCl_3$
(10.19)		Polysol
11.06		CCl_4

12.22		$CDCl_3$

Coupling and Coupling Constants

$^{J}P(=O)\text{-}O\text{-}CH_3$ = 10-12 Hz

$^{J}P(=O)\text{-}O\text{-}CH_2$ = 6-7 Hz