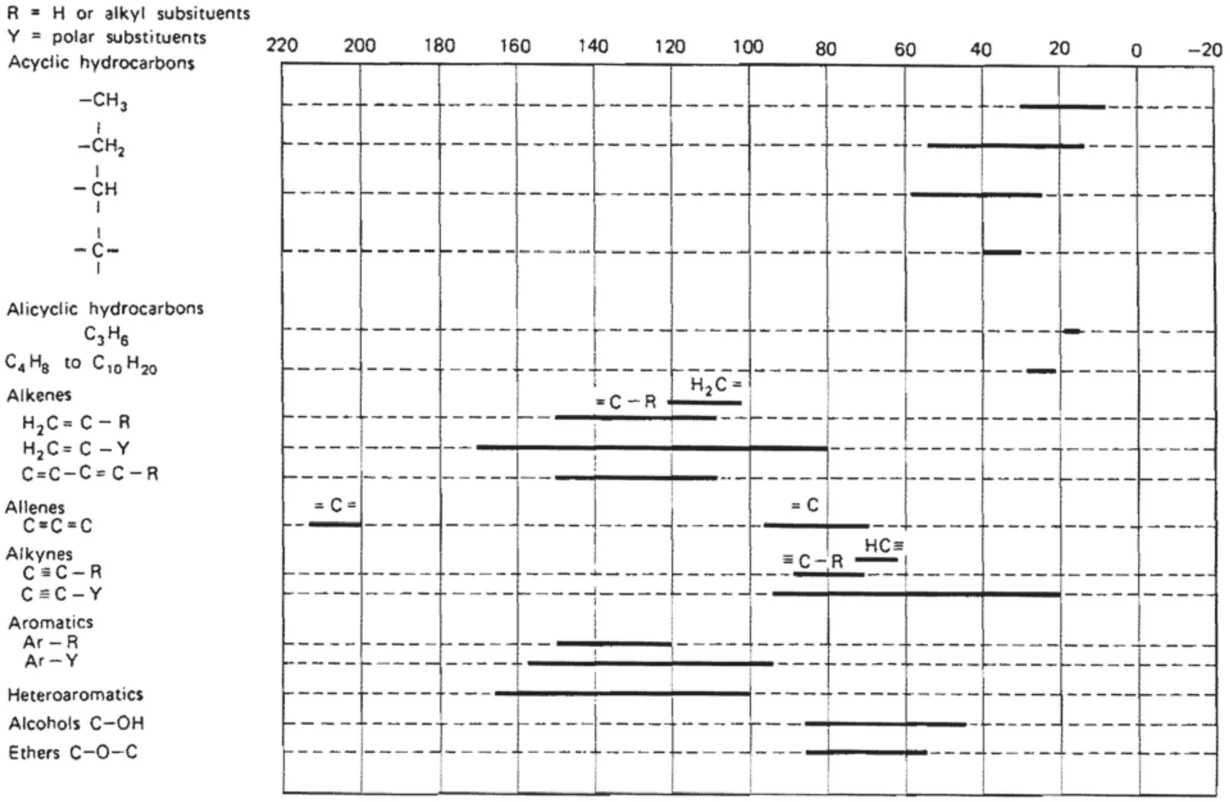
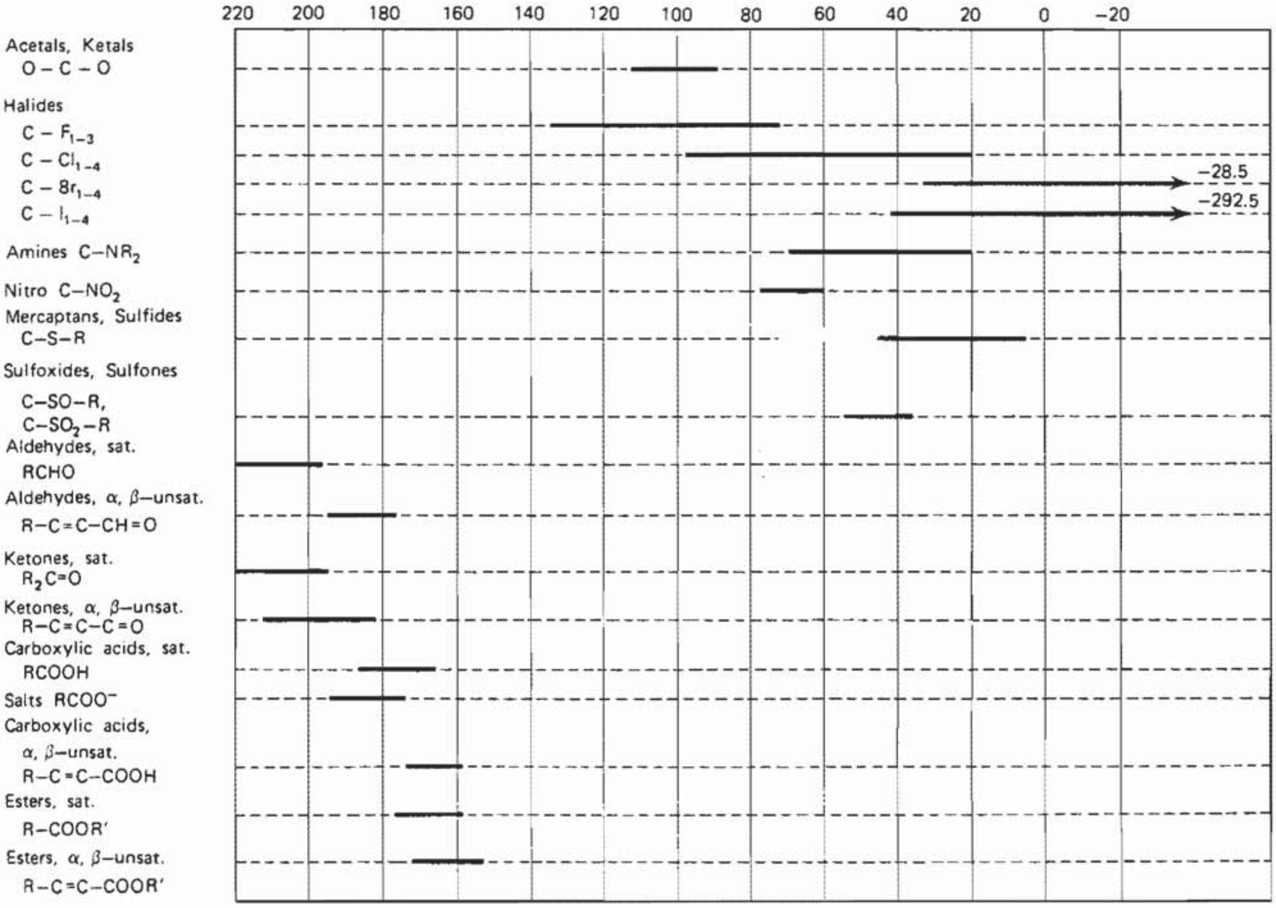
APPENDIX B *(Continued)*

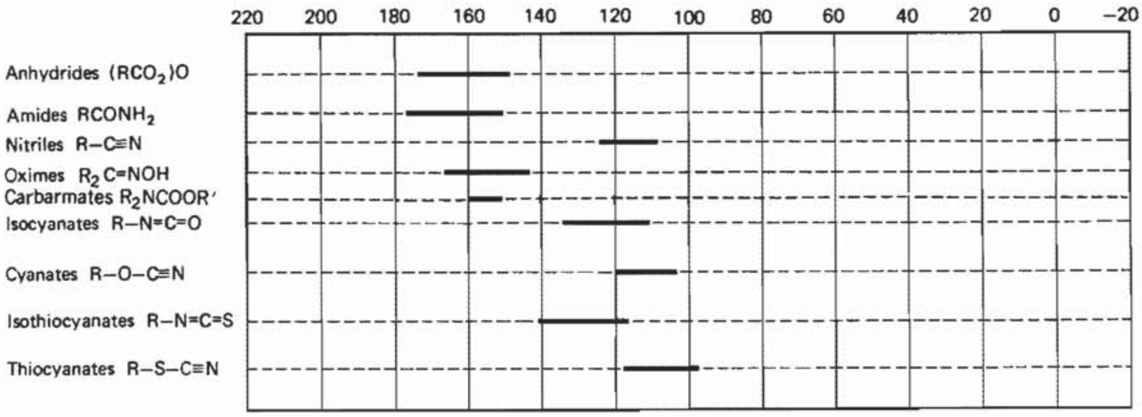
n-hexane	CH_3	14.14	14.34	13.88	14.32	14.43	14.45	
	$CH_2(2)$	22.70	23.28	22.05	23.04	23.40	23.68	
	$CH_2(3)$	31.64	32.30	30.95	31.96	32.36	32.73	
HMPA	CH_3	36.87	37.04	36.42	36.88	37.10	37.00	36.46
methanol	CH_3	50.41	49.77	48.59	49.97	49.90	49.86	49.50
nitromethane	CH_3	62.50	63.21	63.28	61.16	63.66	63.08	63.22
n-pentane	CH_3	14.08	14.29	13.28	14.25	14.37	14.39	
	$CH_2(2)$	22.38	22.98	21.70	22.72	23.08	23.38	
	$CH_2(3)$	34.16	34.83	33.48	34.45	34.89	35.30	
2-propanol	CH_3	25.14	25.67	25.43	25.18	25.55	25.27	24.38
	CH	64.50	63.85	64.92	64.23	64.30	64.71	64.88
pyridine	CH(2)	149.90	150.67	149.58	150.27	150.76	150.07	149.18
	CH(3)	123.75	124.57	123.84	123.58	127.76	125.53	125.12
	CH(4)	135.96	136.56	136.05	135.28	136.89	138.35	138.27
silicone grease	CH_3	1.04	1.40		1.38		2.10	
tetrahydrofuran	CH_2	25.62	26.15	25.14	25.72	26.27	26.48	25.67
	CH_2O	67.97	68.07	67.03	67.80	68.33	68.83	68.68
toluene	CH_3	21.46	21.46	20.99	21.10	21.50	21.50	
	C(*i*)	137.89	138.48	137.35	137.91	138.90	138.85	
	CH(*o*)	129.07	129.76	128.88	129.33	129.94	129.91	
	CH(*m*)	128.26	129.03	128.18	128.56	129.23	129.20	
	CH(*p*)	125.33	126.12	125.29	125.68	126.28	126.29	
triethylamine	CH_3	11.61	12.49	11.74	12.35	12.38	11.09	9.07
	CH_2	46.25	47.07	45.74	46.77	47.10	46.96	47.19

APPENDIX C THE ^{13}C CORRELATION CHART FOR CHEMICAL CLASSES



APPENDIX C *(Continued)*





the high-frequency peak at the left end of the main spectrum, we note that there are no peaks directly aligned above in the subspectra; therefore this peak in the main spectrum is a C peak—i.e., no attached proton atoms. The next peak to the right in the main spectrum is a CH peak, since the peak aligned in the lower subspectrum is pointed up, as is the aligned peak in the upper subspectrum. The next two peaks in the main spectrum are CH_2 peaks, since the aligned peaks in the lower subspectrum are pointed down. The next peak to the right of the solvent, triplet peak ($CDCl_3$) is now obviously another CH peak. The next two peaks are CH_2 peaks. The next peak is again CH. The next two are CH_3 since the aligned peaks in the lower subspectrum are pointed up, and there are no aligned peaks in the upper subspectrum. Summing up, we have (in order of frequency):

6 7 8 10 4 5 3 2 1 9
C, CH, CH_2, CH_2, solvent, CH, CH_2, CH_2, CH, CH_3, CH_3

Yes, interpretation of a DEPT spectrum takes a bit of practice, but the results are most instructive. Not only do we have the number of carbon and hydrogen atoms, but now we have the frequency distribution of carbon atoms with the number of hydrogen atoms attached to each carbon. However, there is a discrepancy between the proton count (see Figure 3.55 for ^1H spectrum for confirmation) in the proton spectrum and in the DEPT spectrum, since the OH is not recorded in the DEPT spectrum; nor are protons that are attached to such atoms as ^{15}N, ^{33}S, ^{29}Si, and ^{31}P. It is not difficult to correlate the DEPT spectrum with the ^1H spectrum. In fact, it is striking to observe how the olefinic and alkyl systems are widely separated in both spectra.

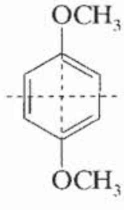
4.7 CHEMICAL CLASSES AND CHEMICAL SHIFTS

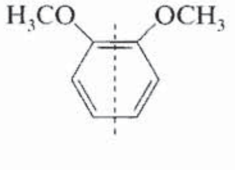
In this section, chemical shifts will be discussed under the headings of the common chemical classes of organic compounds. As noted earlier, the range of shifts generally encountered in routine ^{13}C studies is about 220 ppm.

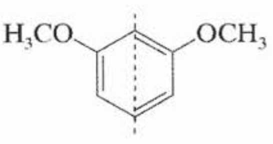
As a first reassuring statement, we can say that trends in chemical shifts of ^{13}C are somewhat parallel to those of ^1H, so that some of the "feeling" for ^1H spectra may carry over to ^{13}C spectra. Furthermore, the concept of additivity of substituent effects (see Sections 4.7.1 and 4.7.6) is useful for both spectra. The ^{13}C shifts are related mainly to hybridization, substituent electronegativity, and diamagnetic anisotropy (to a lesser extent); solvent effects are important in both spectra. Chemical shifts for ^{13}C are affected by substitutions as far removed as the δ position; in the benzene ring, pronounced shifts for ^{13}C are caused by substituents at the point of attachment and at the *ortho*, *meta*, and *para* positions. The ^{13}C chemical shifts are also moved significantly to the right by the γ-*gauche* effect (see Section 4.7.1). Shifts to the right as much as several parts per million may occur on dilution. Hydrogen-bonding effects with polar solvents may cause shifts to the left.

As in other types of spectrometry, peak assignments are made on the basis of reference compounds. Reference material for many classes of compounds has accumulated in the literature. The starting point is a general correlation chart for chemical shift regions of ^{13}C atoms in the major chemical classes (see Figure 4.3 and Appendix C): then, minor changes within these regions are correlated with structure variations in the particular chemical class. The chemical shift values in the following tables must not be taken too literally because of the use of various solvents and concentration. For example, the C=O absorption of acetophenone in $CDCl_3$ appears at 2.4 ppm further to the left than in CCl_4; the effect on the other carbon atoms of acetophenone ranges from 0.0 to 1.1 ppm. Furthermore, much of the early work used various reference compounds, and the values were corrected to give parts per million from TMS.

A ^{13}C spectrum will often distinguish substitution patterns on an aromatic ring. If, for example, there are two identical (achiral) substituents, the symmetry elements alone will distinguish among the *para, ortho,* and *meta* isomers if the chemical shifts of the ring carbon atoms are sufficiently different. The *para* isomer has two simple axes and two planes. The *ortho* and *meta* isomers have one simple axis and one plane, but in the *meta* isomer the elements pass through two atoms. There is also a symmetry plane in the plane of the ring in each compound, which does not affect the ring carbon atoms.







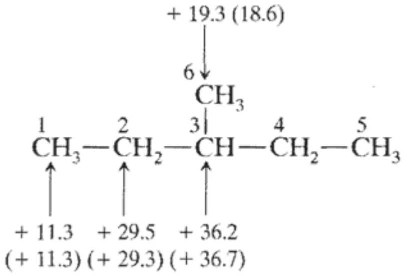
The aromatic region of the ^{13}C spectrum for the *para* isomer shows two peaks: for the *ortho* isomer, three peaks: and for the *meta* isomer, four peaks. The quaternary carbon peaks are much less intense than the unsubstituted carbon peaks.

The additivity of shift increments is demonstrated in Section 4.7.6.

4.7.1 Alkanes

4.7.1.1 *Linear and Branched Alkanes* We know from the general correlation chart (Appendix C) that alkane groups unsubstituted by heteroatoms absorb to about 60 ppm. (Methane absorbs at −2.5 ppm). Within this range, we can predict the chemical shifts of individual ^{13}C atoms in a straight-chain or branched-chain hydrocarbon from the data in Table 4.4 and the formula given below.

This table shows the additive shift parameters (A) in hydrocarbons: the α effect of +9.1, the β effect of +9.4 ppm, the γ effect of −2.5, the δ effect of +0.3, the ϵ effect of +0.1, and the corrections for branching effects. The calculated (and observed) shifts for the carbon atoms of 3-methylpentane are:



Calculations of shift are made from the formula: $\delta = -2.5 + \Sigma nA$, where δ is the predicted shift for a carbon atom; A is the additive shift parameter; and n is the number of carbon atoms for each shift parameter (−2.5 is the shift of the ^{13}C of methane). Thus, for carbon atom 1, we have 1 α-, 1 β-, 2 γ-, and 1 δ-carbon atoms.

$$\delta_1 = -2.5 + (9.1 \times 1) + (9.4 \times 1) + (-2.5 \times 2) + (0.3 \times 1) = 11.3$$

Carbon atom 2 has 2 α-, 2 β-, and 1 γ-carbon atoms. Carbon atom 2 is a 2° carbon with a 3° carbon attached [2°(3°) = −2.5].

$$\delta_2 = -2.5 + (9.1 \times 2) + (9.4 \times 2) + (-2.5 \times 1) + (-2.5 \times 1) = 29.5$$

Carbon atom 3 has 3 α- and 2 β-carbon atoms, and it is a 3° atom with two 2° atoms attached [3°(2°) = − 3.7]. Thus,

$$\delta_3 = -2.5 + (9.1 \times 3) + (9.4 \times 2) + (-3.7 \times 2) = 36.2.$$

Carbon atom 6 has 1 α-, 2 β-, and 2 γ-carbon atoms, and it is a 1° atom with a 3° atom attached [1°(3°) = −1.1]. Thus,

$$\delta_6 = -2.5 + (9.1 \times 1) + (9.4 \times 2) + (-2.5 \times 2) + (-1.1 \times 1) = 19.3$$

The agreement with the determined values for such calculations is very good. Another useful calculation has been given.* The ^{13}C γ shift to lower frequency resulting from the γ carbon has been attributed to the steric compression of a γ *gauche* interaction but has no counterpart in ^1H spectra. It accounts, for example, for the shift to the right of an axial methyl substituent on a conformationally rigid cyclohexane ring, relative to an equatorial methyl, and for the shift to the right of the γ carbon atoms of the ring. Table 4.5 lists the shifts in some linear and branched alkanes.

TABLE 4.4 The ^{13}C Shift Parameters in Some Linear and Branched Hydrocarbons

^{13}C Atoms	Shift (ppm) (A)
α	9.1
β	9.4
γ	−2.5
δ	0.3
ϵ	0.1
1°(3°)[a]	−1.1
1°(4°)[a]	−3.4
2°(3°)[a]	−2.5
2°(4°)	−7.2
3°(2°)	−3.7
3°(3°)	−9.5
4°(1°)	−1.5
4°(2°)	−8.4

[a] The notations 1° (3°) and 1° (4°) denote a CH_3 group bound to a R_2CH group and to a R_3C group, respectively. The notation 2° (3°) denotes a RCH_2 group bound to a R_2CH group, and so on.

4.7.1.2 *Effect of Substituents on Alkanes* Table 4.6 shows the effects of a substituent on linear and branched alkanes. The effect on the α-carbon parallels the electronegativity of the substituent except for bromine and iodine.† The effect at the β-carbon seems fairly constant for all the substituents except for the carbonyl, cyano, and nitro groups. The shift to the right at the γ carbon results (as above) from steric compression of a *gauche* interaction. For Y = N, O, and F, there is also a shift to the right with Y in the *anti* conformation, attributed to hyperconjugation.

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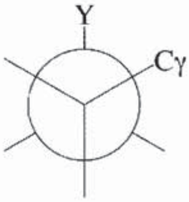
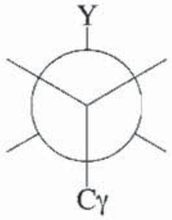
* Lindeman. L.P. and Adams. J.Q. (1971). *Anal. Chem.*, 43,1245.

† See Section 3.4, Table 3.2 (Pauling table of electronegativity).

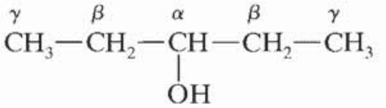


gauche



anti

Table 4.6 provides the functional-group increments that must be added to the appropriate shift values for alkanes given in Table 4.5. For example, we can calculate the ^{13}C shifts for 3-pentanol.



$$\overset{\gamma}{CH_3}-\overset{\beta}{CH_2}-\underset{OH}{\overset{\alpha}{CH}}-\overset{\beta}{CH_2}-\overset{\gamma}{CH_3}$$

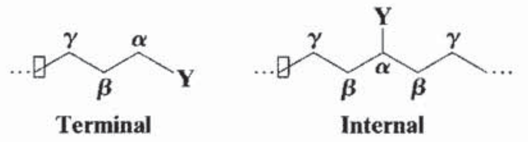
The OH substituent is attached "internally" (rather than "terminally") to the linear alkane chain of pentane; the point of attachment is labeled α, which corresponds to C-3 of pentane, for which the shift value of 34.7 is given in Table 4.6. To this value is added the increment +41, this being the increment for an OH group attached internally to the α-carbon of 3-pentanol (see line 12, 2nd column of numbers). The shift, therefore, for the point of attachment (the α-carbon) is calculated as 75.7. The β and γ shifts are calculated as follows. All of the calculated shifts are in reasonable agreement with the experimental values (Table 4.14).

TABLE 4.5 The ^{13}C Shifts for Some Linear and Branched-Chain Alkanes (ppm from TMS)

Compound	C-1	C-2	C-3	C-4	C-5
Methane	−2.3				
Ethane	5.7				
Propane	15.8	16.3			
Butane	13.4	25.2			
Pentane	13.9	22.8	34.7		
Hexane	14.1	23.1	32.2		
Heptane	14.1	23.2	32.6	29.7	
Octane	14.2	23.2	32.6	29.9	
Nonane	14.2	23.3	32.6	30.0	30.3
Decane	14.2	23.2	32.6	31.1	30.5
Isobutane	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Isohexane	22.7	28.0	42.0	20.9	14.3
Neopentane	31.7	28.1			
2,2-Dimethylbutane	29.1	30.6	36.9	8.9	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH_3)	
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
2,3-Dimethylpentane	7.0	25.3	36.3	(14.6, 3-CH_3)	

	Calculated	Experimental (See Table 4.14)
C_α	34.7 + 41 = 75.7	73.8
C_β	22.8 + 8 = 30.8	29.7
C_γ	13.9 − 5 = 8.9	9.8

TABLE 4.6 Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes. Y is Terminal or Internal[a]



	α		β		γ
Y	Terminal	Internal	Terminal	Internal	
CH_3	9	6	10	8	−2
$CH{=}CH_2$	20		6		−0.5
$C{\equiv}CH$	4.5		5.5		−3.5
COOH	21	16	3	2	−2
COO^-	25	20	5	3	−2
COOR	20	17	3	2	−2
COCl	33	28		2	
$CONH_2$	22		2.5		−0.5
COR	30	24	1	1	−2
CHO	31				−2
Phenyl	23	17	9	7	−2
OH	48	41	10	8	−5
OR	58	51	8	5	−4
OCOR	51	45	6	5	−3
NH_2	29	24	11	10	
NH_3^+	26	24	8	6	−5
NHR	37	31	8	6	−4
NR_2	42		6		−3
NR_3^+	31		5		−7
NO_2	63	57	4	4	
CN	4	1	3	3	−3
SH	11	11	12	11	−4
SR	20		7		−3
F	68	63	9	6	−4
Cl	31	32	11	10	−4
Br	20	25	11	10	−3
I	−6	4	11	12	−1

[a] Add these increments to the shift values of the appropriate carbon atom in Table 4.5 or to the shift value calculated from Table 4.4.

Source: Wehrli, F.W., Marchand, A.P., and Wehrli, S. (1983). *Interpretation of Carbon-13 NMR Spectra.* 2nd ed. London: Heyden.

1-Pentanol would be treated similarly but as a "terminal" alcohol, and the carbon atom to which the OH group is attached would again be labeled α.

4.7.1.3 Cycloalkanes and Saturated Heterocyclics

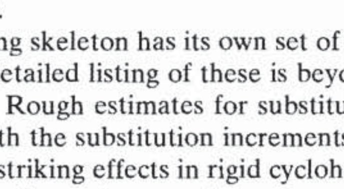
The chemical shifts of the CH_2 groups in monocyclic alkanes are given in Table 4.7. The striking feature here is the strong shift to the right of cyclopropane, analogous to the shift of its proton absorptions.

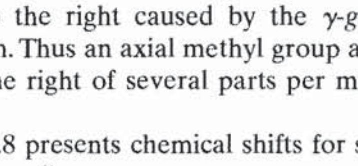
Each ring skeleton has its own set of shift parameters, but a detailed listing of these is beyond the scope of this text. Rough estimates for substituted rings can be made with the substitution increments in Table 4.6. One of the striking effects in rigid cyclohexane rings is the shift to the right caused by the *γ-gauche* steric compression. Thus an axial methyl group at C-1 causes a shift to the right of several parts per million at C-3 and C-5.

Table 4.8 presents chemical shifts for several saturated heterocyclics.

4.7.2 Alkenes

The sp^2 carbon atoms of alkenes substituted only by alkyl groups absorb in the range of about 110–150 ppm. The double bond has a rather small effect on the shifts of the sp^3 carbons in the molecule as the following comparisons demonstrate.


$\mathrm{H_3C{-}C(CH_3)_2{-}CH_2{-}C(CH_3){=}CH_2}$

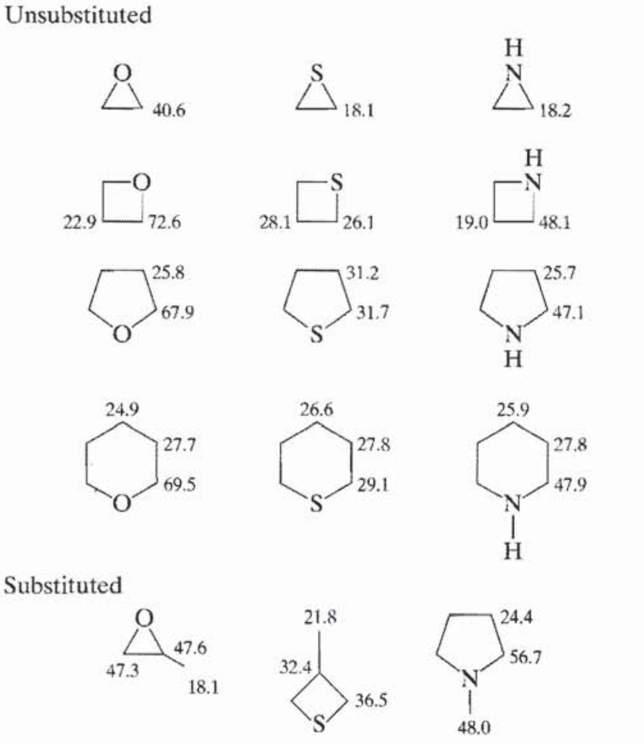

$\mathrm{H_3C{-}C(CH_3)_2{-}CH_2{-}CH(CH_3){-}CH_3}$

The methyl signal of propene is at 18.7 ppm, and of propane at 15.8 ppm. In (*Z*)-2-butene, the methyl signals are at 12.1 ppm, compared with 17.6 ppm in (*E*)-2-butene, because of the γ effect. (For comparison, the methyl signals of butane are at 13.4 ppm). Note the γ effect on one of the geminal methyl groups in 2-methyl-2-butene (Table 4.9).

TABLE 4.7 Chemical Shifts of Cycloalkanes (ppm from TMS)

C_3H_6	−2.9	C_7H_{14}	28.4
C_4H_8	22.4	C_8H_{16}	26.9
C_5H_{10}	25.6	C_9H_{18}	26.1
C_6H_{12}	26.9	$C_{10}H_{20}$	25.3

TABLE 4.8 Chemical Shifts for Saturated Heterocyclics (ppm from TMS, neat)

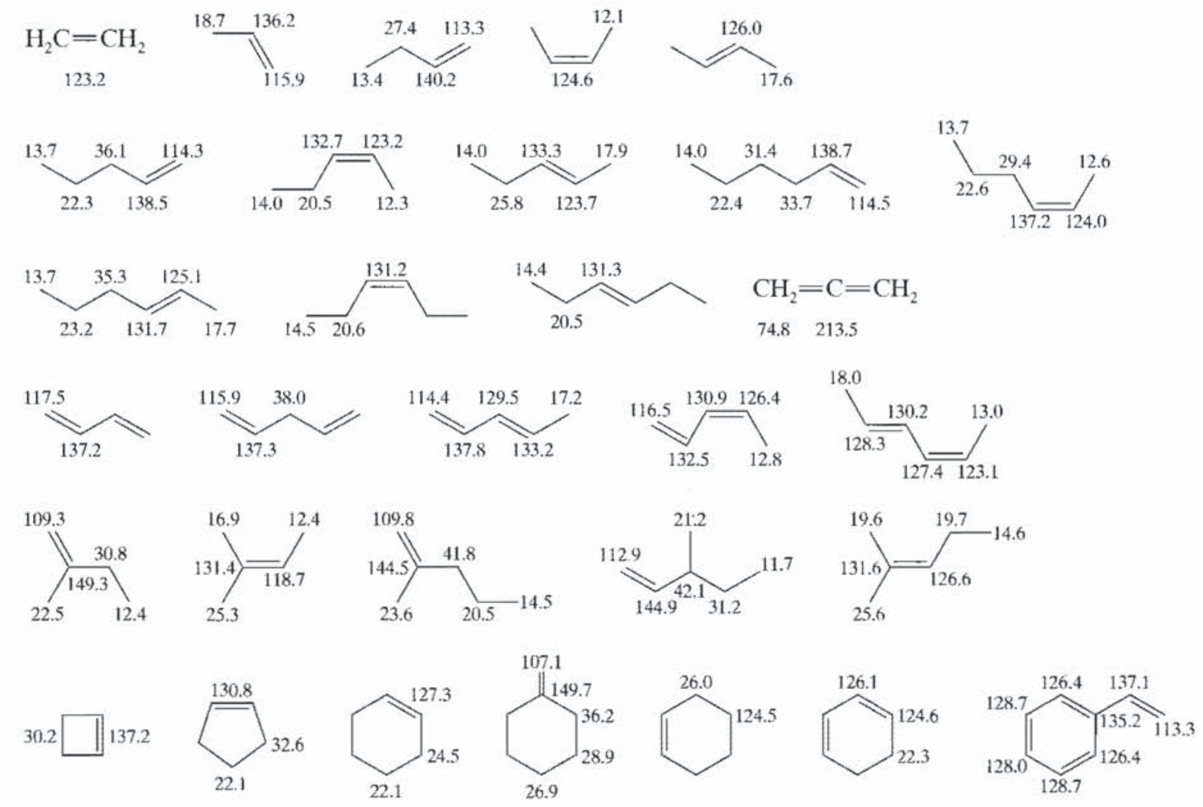


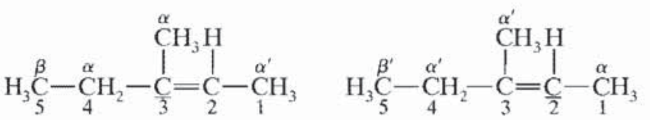
In general, the terminal $=CH_2$ group absorbs to the right relative to an internal $=CH-$ group, and (*Z*)$-CH=CH-$ signals are to the right from those of corresponding *E* groups. Calculations of approximate shifts can be made from the following parameters where α, β, and γ represent substitutents on the same end of the double bond as the alkene carbon of interest, and α′, β′, and γ′ represent substitutents on the far side.

α	10.6
β	7.2
γ	−1.5
α'	−7.9
β'	−1.8
γ'	−1.5
Z(*cis*) correction	−1.1

These parameters are added to 123.3 ppm, the shift for ethylene. We can calculate the values of C-3 and C-2 for (*Z*)-3-methyl-2-pentene as follows:

TABLE 4.9 Alkene and Cycloalkene Chemical Shift (ppm from TMS)





$$H_3\overset{\beta}{\underset{5}{C}}-\overset{\alpha}{\underset{4}{CH_2}}-\underset{3}{\overset{\overset{\alpha}{CH_3}}{C}}=\underset{2}{\overset{H}{C}}-\overset{\alpha'}{\underset{1}{CH_3}} \qquad H_3\overset{\beta'}{\underset{5}{C}}-\overset{\alpha'}{\underset{4}{CH_2}}-\underset{3}{\overset{\overset{\alpha'}{CH_3}}{C}}=\underset{2}{\overset{H}{C}}-\overset{\alpha}{\underset{1}{CH_3}}$$

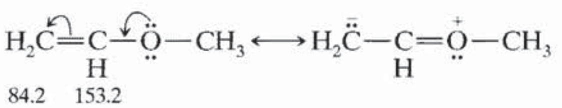
$$\delta_3 = 123.3 + (2 \times 10.6) + (1 \times 7.2) + (1 \times -7.9) - 1.1 = 142.7 \text{ ppm}$$

$$\delta_2 = 123.3 + (1 \times 10.6) + (2 \times -7.9) + (1 \times 1.8) - 1.1 = 115.2 \text{ ppm}$$

The measured values are C-3 = 137.2 and C-2 = 116.8. The agreement is fair.

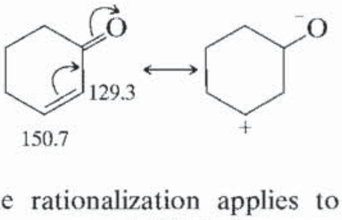
Carbon atoms directly attached to a (*Z*) C=C group are more shielded than those attached to the stereoisomeric (*E*) group by 4–6 ppm (Table 4.9). Alkene carbon atoms in polyenes are treated as though they were alkane carbon substituents on one of the double bonds. Thus, in calculating the shift of C-2 in 1,4-pentadiene, C-4 is treated like a β-sp^3 carbon atom.

Representative alkenes are presented in Table 4.9. There are no simple rules to handle polar substituents on an alkene carbon. The shifts for vinyl ethers can be rationalized on the basis of electron density of the contributor structures



$$\underset{84.2}{H_2C}=\underset{153.2}{\underset{H}{C}}-\ddot{O}-CH_3 \longleftrightarrow H_2\ddot{C}-\underset{H}{C}=\overset{+}{\ddot{O}}-CH_3$$

as can the shifts for α-, β-unsaturated ketones.



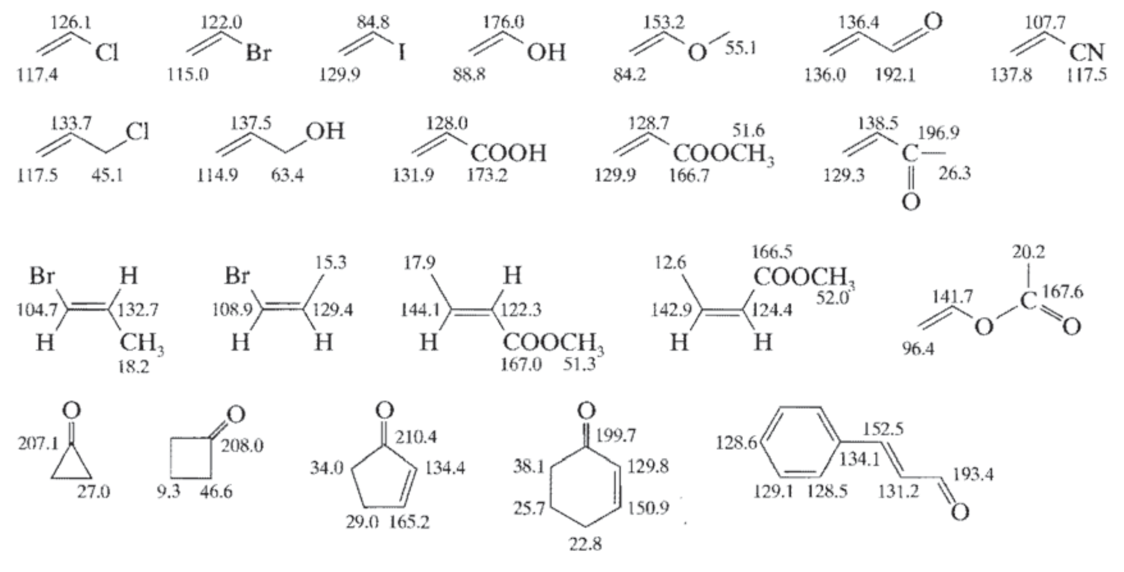
The same rationalization applies to the proton shifts in these compounds. Shifts for several substituted alkenes are presented in Table 4.10.

The central carbon atom (=C=) of alkyl-substituted allenes absorbs in the range of about 200–215 ppm, whereas the terminal atoms (C=C=C) absorb in the range of about 75–97 ppm.

4.7.3 Alkynes

The *sp* carbon atoms of alkynes substituted only by alkyl groups absorb in the range of approximately 65–90 ppm

TABLE 4.10 Chemical Shift of Substituted Alkenes (ppm from TMS)

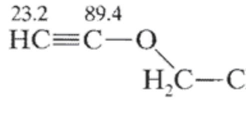


(Table 4.11). The triple bond shifts the sp^3 carbon atoms, directly attached, about 5–15 ppm to the right relative to the corresponding alkane. The terminal ≡CH absorbs further to the right than the internal ≡CR. Alkyne carbon atoms with a polar group directly attached absorb from about 20–95 ppm.

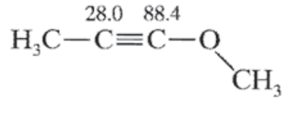
TABLE 4.11 Alkyne Chemical Shifts (ppm)

Compound	C-1	C-2	C-3	C-4	C-5	C-6
1-Butyne	67.0	84.7				
2-Butyne		73.6				
1-Hexyne	68.1	84.5	18.1	30.7	21.9	13.5
2-Hexyne	2.7	73.7	76.9	19.6	21.6	12.1
3-Hexyne	15.4	13.0	80.9			

Polar resonance structures explain these shifts for alkynyl ethers, which are analogous to the shifts for vinyl ethers (Section 3.34).



$HC{\equiv}C{-}O{-}CH_2{-}CH_3$



$H_3C{-}C{\equiv}C{-}O{-}CH_3$

4.7.4 Aromatic Compounds

Benzene carbon atoms absorb at 128.5 ppm, neat or as a solution in $CDCl_3$. Substituents shift the attached aromatic carbon atom as much as ±35 ppm. Fused-ring absorptions are as follows:

Naphthalene: C-1, 128.1; C-2, 125.9; C-4a, 133.7.

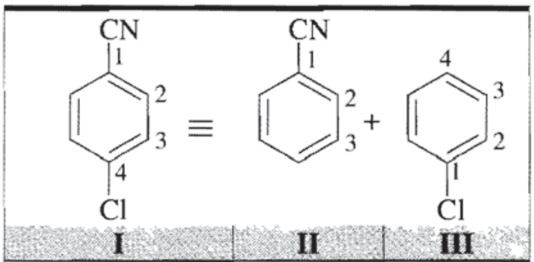
Anthracene: C-1, 130.1; C-2, 125.4; C-4a, 132.2; C-9, 132.6.

Phenanthrene: C-1, 128.3; C-2, 126.3: C-3. 126.3; C-4, 122.2; C-4a, 131.9*; C-9, 126.6; C-10a, 130.1.*

Shifts of the aromatic carbon atom directly attached to the substituent have been correlated with substituent electronegativity after correcting for magnetic anisotropy effects; shifts at the *para* aromatic carbon have been correlated with the Hammett σ constant. *Ortho* shifts are not readily predictable and range over about 15 ppm. *Meta* shifts are generally small-up to several parts per million for a single substituent.

The substituted aromatic carbon atoms can be distinguished from the unsubstituted aromatic carbon atom by its decreased peak height; that is, it lacks a proton and thus suffers from a longer T_1 and a diminished NOE.

Incremental shifts from the carbon atoms of benzene for the aromatic carbon atoms of representative monosubstituted benzene rings (and shifts from TMS



I			II		III	
C #	Cal	Obs	C #	Obs	C #	Obs
1	-18.0	-16.6	1	-16.0	4	-2.0
2	4.6	5.1	2	3.6	3	1.0
3	0.8	1.3	3	0.6	2	0.2
4	10.7	10.8	4	4.3	1	6.4

---

* Assignment uncertain.

of carbon-containing substituents) are given in Table 4.12. Shifts from benzene for polysubstituted benzene ring carbon atoms can be approximated by applying the principle of increment additivity. For example, the shift from benzene for C-2 of the disubstituted compound 4-chlorobenzonitrile is calculated by adding the effect for an *ortho* CN group (+3.6) to that for a *meta* Cl group (+1.0): 128.5 + 3.6 + 1 = 133.1 ppm.

4.7.5 Heteroaromatic Compounds

Complex rationalizations have been offered for the shifts of carbon atoms in heteroaromatic compounds. As a general rule, C-2 of oxygen- and nitrogen-containing rings is further to the left than C-3. Large solvent and pH effects have been recorded. Table 4.13 gives values for neat samples of several five- and six-membered heterocyclic compounds.

4.7.6 Alcohols

Substitution of H in an alkane by an OH group moves the signal to the left by 35–52 ppm for C-1, 5–12 ppm for C-2, and to the right by about 0–6 ppm for C-3. Shifts for several acyclic and alicyclic alcohols are given

TABLE 4.12 Incremental Shifts of the Aromatic Carbon Atoms of Monosubstituted Benzenes (ppm from Benzene at 128.5 ppm). Carbon Atom of Substituents in parts per million from TMS[a]

Substituent	C-1 (Attachment)	C-2	C-3	C-4	C of Substituent (ppm from TMS)
H	0.0	0.0	0.0	0.0	
CH_3	9.3	0.7	−0.1	−2.9	21.3
CH_2CH_3	15.6	−0.5	0.0	−2.6	29.2 (CH_2), 15.8 (CH_3)
$CH(CH_3)_2$	20.1	−2.0	0.0	−2.5	34.4 (CH), 24.1 (CH_3)
$C(CH_3)_3$	22.2	−3.4	−0.4	−3.1	34.5 (C), 31.4 (CH_3)
$CH{=}CH_2$	9.1	−2.4	0.2	−0.5	137.1 (CH), 113.3 (CH_2)
$C{\equiv}CH$	−5.8	6.9	0.1	0.4	84.0 (C), 77.8 (CH)
C_6H_5	12.1	−1.8	−0.1	−1.6	
CH_2OH	13.3	−0.8	−0.6	−0.4	64.5
$CH_2O(C{=}O)CH_3$	7.7	~0.0	~0.0	~0.0	20.7 (CH_3), 66.1 (CH_2), 170.5 (C=O)
OH	26.6	−12.7	1.6	−7.3	
OCH_3	31.4	−14.4	1.0	−7.7	54.1
OC_6H_5	29.0	−9.4	1.6	−5.3	
$O(C{=}O)CH_3$	22.4	−7.1	−0.4	−3.2	23.9 (CH_3), 169.7 (C=O)
(C=O)H	8.2	1.2	0.6	5.8	192
$(C{=}O)CH_3$	7.8	−0.4	−0.4	2.8	24.6 (CH_3), 195.7 (C=O)
$(C{=}O)C_6H_5$	9.1	1.5	−0.2	3.8	196.4 (C=O)
$(C{=}O)F_3$	−5.6	1.8	0.7	6.7	
(C=O)OH	2.9	1.3	0.4	4.3	168
$(C{=}O)OCH_3$	2.0	1.2	−0.1	4.8	51.0 (CH_3), 166.8 (C=O)
(C=O)Cl	4.6	2.9	0.6	7.0	168.5
$(C{=}O)NH_2$	5.0	−1.2	0.0	3.4	
$C{\equiv}N$	−16	3.6	0.6	4.3	119.5
NH_2	19.2	−12.4	1.3	−9.5	
$N(CH_3)_2$	22.4	−15.7	0.8	−11.8	40.3
$NH(C{=}O)CH_3$	11.1	−9.9	0.2	−5.6	
NO_2	19.6	−5.3	0.9	6.0	
N=C=O	5.7	−3.6	1.2	−2.8	129.5
F	35.1	−14.3	0.9	−4.5	
Cl	6.4	0.2	1.0	−2.0	
Br	−5.4	3.4	2.2	−1.0	
I	−32.2	9.9	2.6	−7.3	
CF_3	2.6	−3.1	0.4	3.4	
SH	2.3	0.6	0.2	−3.3	
SCH_3	10.2	−1.8	0.4	−3.6	15.9
SO_2NH_2	15.3	−2.9	0.4	3.3	
$Si(CH_3)_3$	13.4	4.4	−1.1	−1.1	

[a] See Ewing, D.E., (1979). *Org. Magn. Reson.*, **12,** 499, for 709 chemical shifts of monosubstituted benzenes.

TABLE 4.13 Shifts for Carbon Atoms of Heteroaromatics (ppm from neat TMS)

Compound	C-2	C-3	C-4	C-5	C-6	Substituent
Furan	142.7	109.6				
2-Methylfuran	152.2	106.2	110.9	141.2		13.4
Furan-2-carboxaldehyde	153.3	121.7	112.9	148.5		178.2
Methyl 2-furoate	144.8	117.9	111.9	146.4		159.1 (C=O), 51.8 (CH_3)
Pyrrole	118.4	108.0				
2-Methylpyrrole	127.2	105.9	108.1	116.7		12.4
Pyrrole-2-carboxaldehyde	134.0	123.0	112.0	129.0		178.9
Thiophrene	124.4	126.2				
2-Methylthiophene	139.0	124.7	126.4	122.6		14.8
Thiophene-2-carboxaldehyde	143.3	136.4	128.1	134.6		182.8
Thiazole	152.2		142.4	118.5		
Imidazole	136.2		122.3	122.3		
Pyridine	150.2	123.9	135.9			
Pyrimidine	159.5		157.4	122.1	157.4	
Pyrazine	145.6					
2-Methylpyrazine	154.0	141.8[a]	143.8[a]	144.7[a]		21.6

[a] Assignment not certain

in Table 4.14. Acetylation provides a useful diagnostic test for an alcohol: The C-1 absorption moves to the left by about 2.5–4.5 ppm, and the C-2 absorption moves to the right by a similar amount; a 1,3-diaxial interaction may cause a slight (~1 ppm) shift to the left of C-3. Table 4.14 may be used to calculate shifts for alcohols as described earlier.

TABLE 4.14 Chemical Shift of Alcohols (ppm from TMS)

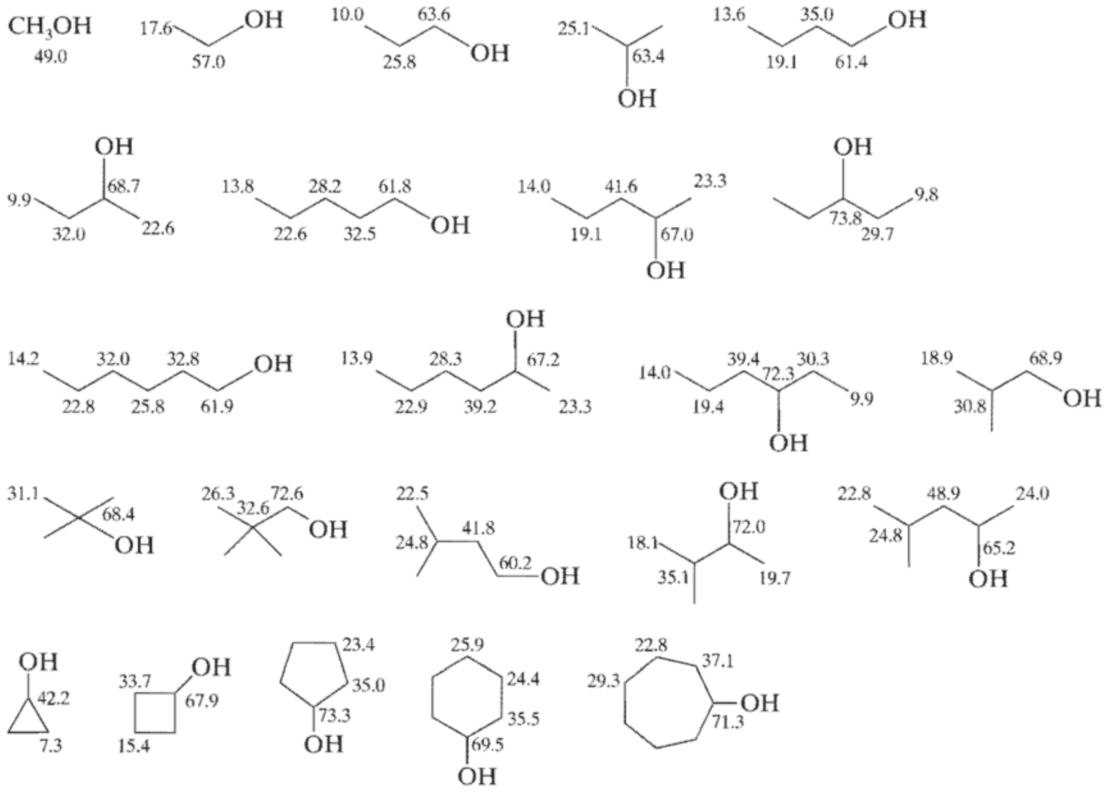
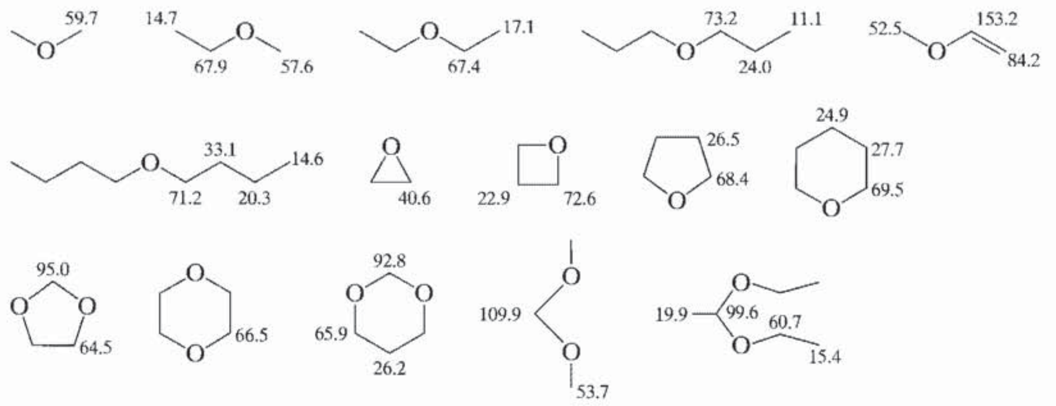
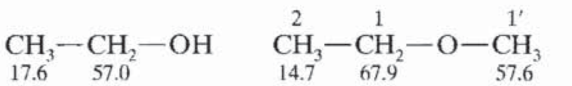


TABLE 4.15 Chemical Shift of Ethers, Acetals, and Epoxides (ppm from TMS)



4.7.7 Ethers, Acetals, and Epoxides

An alkoxy substituent causes a somewhat larger shift to the left at C-1 (~11 ppm larger) than that of a hydroxy substituent. This is attributed to the C-1′ of the alkoxy group having the same effect as a β-C relative to C-1. The O atom is regarded here as an "α-C" to C-1.

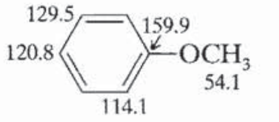


$$\underset{17.6}{CH_3}-\underset{57.0}{CH_2}-OH \qquad \overset{2}{\underset{14.7}{CH_3}}-\overset{1}{\underset{67.9}{CH_2}}-O-\overset{1'}{\underset{57.6}{CH_3}}$$

Note also that the "γ effect" (shift to the right) on C-2 is explainable by similar reasoning. Conversely, the ethoxy group affects the OCH_3 group (compare CH_3OH). Table 4.15 gives shifts of several ethers.

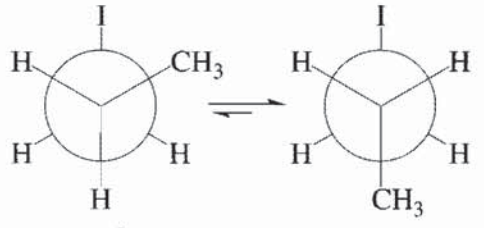
The dioxygenated carbon of acetals absorbs in the range of about 88–112 ppm. Oxirane (an epoxide) absorbs at 40.6 ppm.

The alkyl carbon atoms of arylalkyl ethers have shifts similar to those of dialkyl ethers. Note the large shift to the right of the ring *ortho* carbon resulting from electron delocalization as in the vinyl ethers.



4.7.8 Halides

The effect of halide substitution is complex. A single fluorine atom (in CH_3F) causes a large shift to the left from CH_4 as electronegativity considerations would suggest. Successive geminal substitution by Cl (CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4) results in increasing shifts to the left-again expected on the basis of electronegativity. But with Br and I the "heavy atom effect" supervenes. The carbon shifts of CH_3Br and CH_2Br_2 move progressively to the right. A strong progression to the right for I commences with CH_3I, which is to the right of CH_4. There is a progressive shift to the left at C-2 in the order I > Br > F. Cl and Br show *γ-gauche* shielding at C-3, but I does not, presumably because of the low population of the hindered gauche rotamer. Table 4.16 shows these trends.



gauche *anti*

TABLE 4.16 Shift Position of Alkyl Halides (neat, ppm from TMS)

Compound	C-1	C-2	C-3
CH_4	−2.3		
CH_3F	75.4		
CH_3Cl	24.9		
CH_2Cl_2	54.0		
$CHCl_3$	77.5		
CCl_4	96.5		
CH_3Br	10.0		
CH_2Br_2	21.4		
$CHBr_3$	12.1		
CBr_4	−28.5		
CH_3I	−20.7		
CH_2I_2	−54.0		
CHI_3	−139.9		
CI_4	−292.5		
CH_3CH_2F	79.3	14.6	
CH_3CH_2Cl	39.9	18.7	
CH_3CH_2Br	28.3	20.3	
CH_3CH_2I	−0.2	21.6	
$CH_3CH_2CH_2Cl$	46.7	26.5	11.5
$CH_3CH_2CH_2Br$	35.7	26.8	13.2
$CH_3CH_2CH_2I$	10.0	27.6	16.2

Halides may show large solvent effects; for example, C-1 for iodoethane is at −6.6 in cyclohexane, and at −0.4 in DMF.

4.7.9 Amines

A terminal NH_2 group attached to an alkyl chain causes a shift to the left of about 30 ppm at C-1, a shift to the left of about 11 ppm at C-2, and a shift to the right of about 4.0 ppm at C-3. The NH_3^+ group shows a somewhat smaller effect. *N*-alkylation increases the shift to the left of the NH_2 group at C-1. Shift positions for selected acyclic and alicyclic amines are given in Table 4.17 (see Table 4.8 for heterocyclic amines).

4.7.10 Thiols, Sulfides, and Disulfides

Since the electronegativity of sulfur is considerably less than that of oxygen, sulfur causes a correspondingly smaller chemical shift. Examples of thiols, sulfides, and disulfides are given in Table 4.18.

4.7.11 Functional Groups Containing Carbon

Carbon-13 NMR spectrometry permits direct observation of carbon-containing functional groups; the shift ranges for these are given in Appendix C. With the exception of CH=O, the presence of these groups could not be directly ascertained by ^1H NMR.

TABLE 4.17 Chemical Shift of Acyclic and Alicyclic Amines (in $CDCl_3$, ppm from TMS)

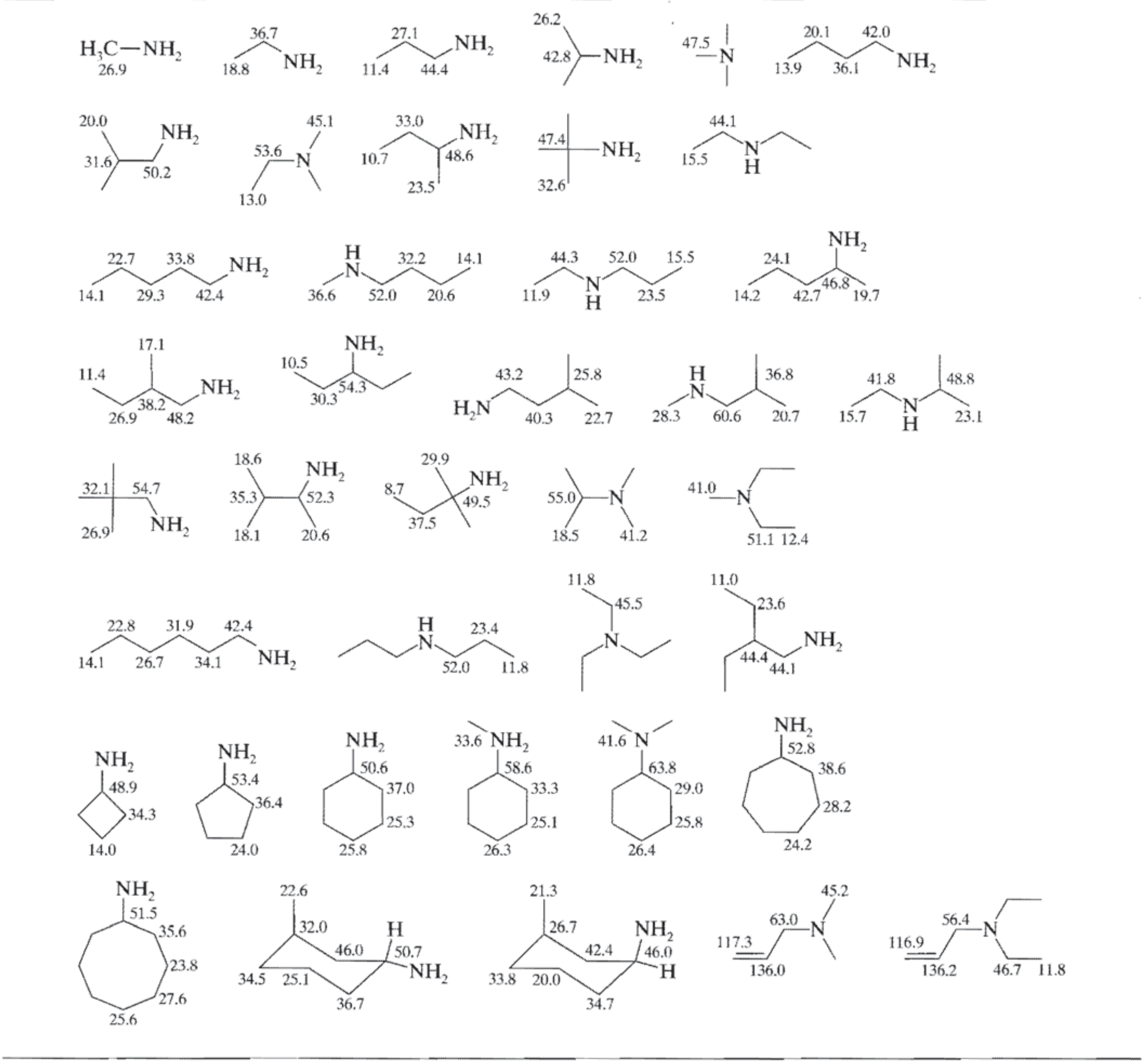


TABLE 4.18 Shift Position of Thiols, Sulfides, and Disulfides (ppm from TMS)

Compound	C-1	C-2	C-3
CH_3SH	6.5		
CH_3CH_2SH	19.8	17.3	
$CH_3CH_2CH_2SH$	26.4	27.6	12.6
$CH_3CH_2CH_2CH_2SH$	23.7	35.7	21.0
$(CH_3)_2S$	19.3		
$(CH_3CH_2)_2S$	25.5	14.8	
$(CH_3CH_2CH_2)_2S$	34.3	23.2	13.7
$(CH_3CH_2CH_2CH_2)_2S$	34.1	31.4	22.0
CH_3SSCH_3	22.0		
$CH_3CH_2SSCH_2CH_3$	32.8	14.5	

4.7.11.1 Ketones and Aldehydes The $R_2C{=}O$ and the $RCH{=}O$ carbon atoms absorb in a characteristic region. Acetone absorbs at 203.3 ppm, and acetaldehyde at 199.3 ppm. Alkyl substitution on the α-carbon causes a shift to the left of the C=O absorption of 2–3 ppm until steric effects supervene. Replacement of the CH_3 of acetone or acetaldehyde by a phenyl group causes a shift to the right of the C=O absorption (acetophenone, 195.7 ppm; benzaldehyde, 190.7 ppm); similarly, α,β-unsaturation causes shifts to the right (acrolein, 192.1 ppm, compared with propionaldehyde, 201.5 ppm). Presumably, charge delocalization by the benzene ring or the double bond makes the carbonyl carbon less electron deficient.

Of the cycloalkanones, cyclopentanone has a pronounced shift to the left. Table 4.19 presents chemical shifts of the C=O group of some ketones and aldehydes. Because of rather large solvent effects, there are differences of several parts per million from different literature sources. Replacement of CH_2 of alkanes by C=O causes a shift to the left at the α-carbon (~10–14 ppm) and a shift to the right at the β-carbon (several ppm in acyclic compounds). In a coupled spectrum, the aldehyde CH=O is a doublet.

4.7.11.2 Carboxylic Acids, Esters, Chlorides, Anhydrides, Amides, and Nitriles The C=O groups of carboxylic acids and derivatives are in the range of 150–185 ppm. Dilution and solvent effects are marked for carboxylic acids; anions appear further to the left. The effects of substituents and electron delocalization are generally similar to those for ketones. Nitriles absorb in the range of 115–125 ppm. Alkyl substituents on the nitrogen of amides cause a small (up to several ppm) shift to the right of the C=O group (see Table 4.20).

4.7.11.3 Oximes The quaternary carbon atom of simple oximes absorb in the range of 145–165 ppm. It is possible to distinguish between *E* and *Z* isomers since the C=O shift is to the right in the sterically more compressed form, and the shift of the more hindered substituent (*syn* to the OH) is farther to the right than the less hindered.

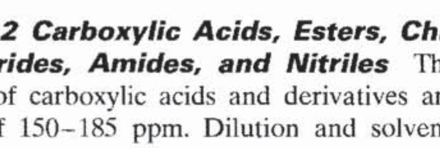


TABLE 4.19 Shift Position of the C=O Group and Other Carbon Atoms of Ketones and Aldehydes (ppm from TMS)

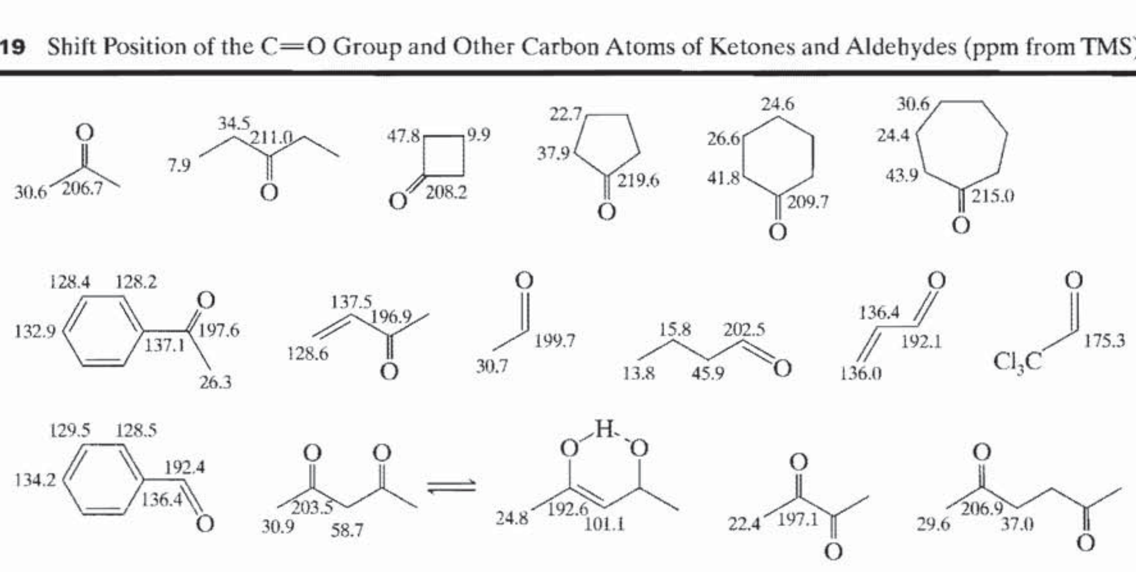
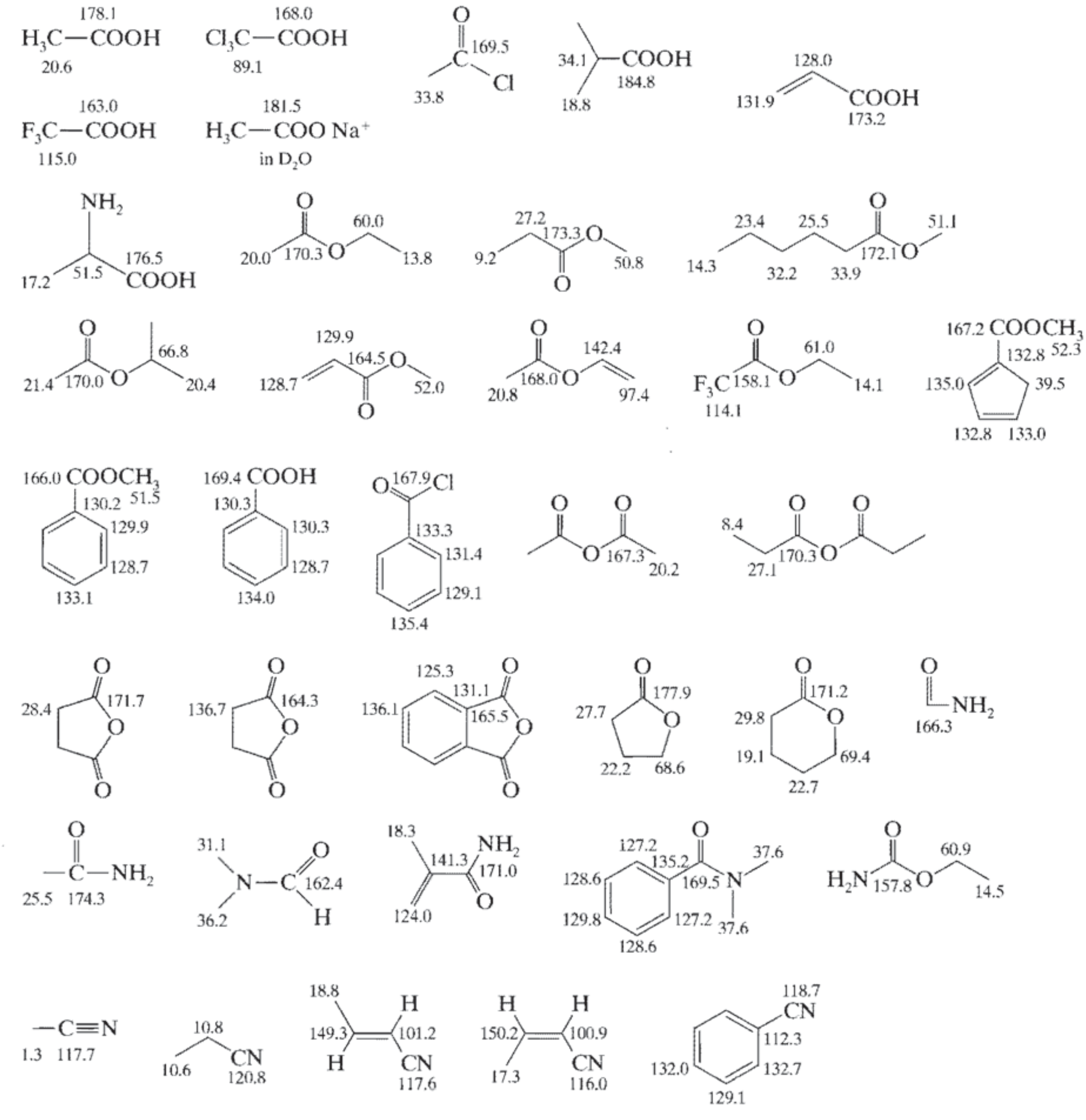


TABLE 4.20 Shift Position of the C=O Group and other Carbon Atoms of Carboxylic Acids. Esters, Lactones, Chlorides Anhydrides, Carbamates, and Nitriles (ppm from TMS)



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