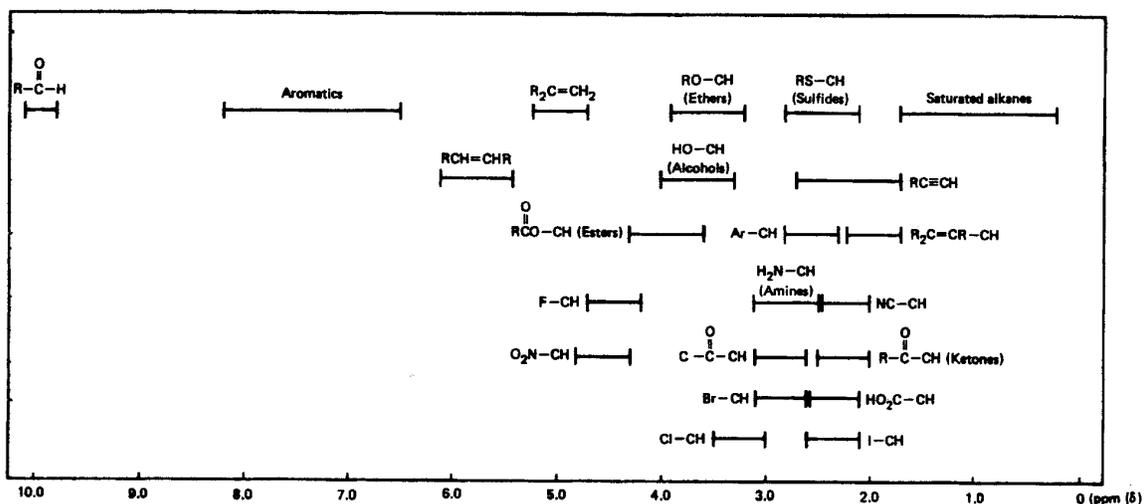# Chemical Shift

Analysis of the Chemical Shift as a Structural Tool

^{1}H Chemical Shifts

The figure below from the Lambert text charts the ^{1}H chemical shift ranges of some of the more common chemical moieties:

The correlation between a particular chemical environment and the corresponding chemical shift is very high, and are the fundamental to the use of NMR as a structural tool.

Rule based approaches express the empirical correlations between structure and chemical shift as a parameterized equation.

Alkane Systems

One of the earliest such systems was developed for substituted methane molecules has been named Shoolery's Rules.

These rules enable the prediction of chemical shifts of ^{1}H resonances in simple CH_2XY or $CHXYZ$ type molecules.

Shoolery, who worked for many years at Varian Associates, was interested in investigating the second-order effects of substituent groups, i.e., whether the additivity of effects of the substituent groups could be accurately predicted (Shoolery, J.H. (1959) *Technical Information Bulletin* **2**, Varian Associates, Palo Alto, CA).

Shoolery's Rules begin with the ^{1}H chemical shift of methane (0.23 ppm) and adds an empirically derived value for substituent groups:

$$\delta = 0.23 + \sum_i \Delta_i$$

$$= 0.23 + \Delta_X + \Delta_Y + \Delta_Z$$

## Substituent Parameters for Shoolery's Rule (R = H or Alkyl)

Substituent	Δ_i	Substituent	Δ_i
CH_3	0.47	C_6H_5	1.83
$CR{=}CR_2$	1.32	Br	2.33
$C{\equiv}CR$	1.44	OR	2.36
NR_2	1.57	Cl	2.53
SR	1.64	OH	2.56
CN	1.70	O(CO)R	3.01
CO—R	1.70	NO_2	3.36
I	1.82	F	4.00

Shooler's Rules are accurate to approximately 0.3 ppm for CH_2XY groups, and decrease somewhat in accuracy for methine systems.

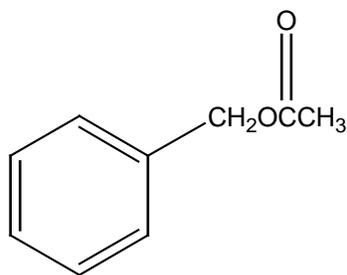**Comparison of Shoolery's Rules Calculation and experimental ^{1}H NMR data.**

$Cl - CH_2 - Cl$

$\delta = 0.23 + (2 \times 2.53) = 5.29$ ppm vs. 5.30 obs.
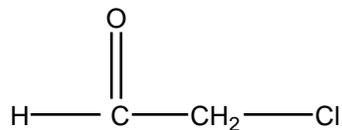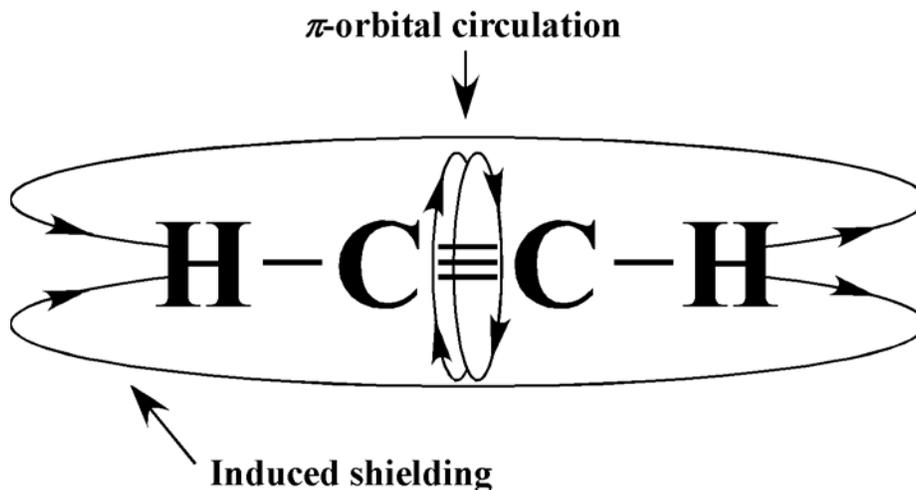

$\delta = 0.23 + 1.70 + 2.53 = 4.46$ ppm vs. 4.55 obs.

$\delta = 0.23 + 1.83 + 3.01 = 5.07$ ppm vs. 5.0 obs.

Unsaturated Aliphatic Systems

Alkynes

The carbon-carbon triple bond (sp-hybridized) of the alkynes (with its associated linearity) generates a substantial shielding anisotropy.

The chemical shift of acetylene is 2.88 ppm and the range of substituted alkynes is from approximately 1.8 ppm to 2.9 ppm.

Alkenes

The carbon-carbon double bond (sp^2 hybridization) exhibits increased electronegativity and lower anisotropy that the triple bond.

The range of alkene ^{1}H chemical shifts, i.e., of the protons directly bonded to carnons atoms involved in the double bonds, is relatively large, 4.5 ppm to 7 ppm.

The observed ^{1}H chemical shift depends upon the detailed chemistry of the carbons involved in the double bond.

The chemistry of alkenes is common, and empirical rules have been developed to predict ^{1}H chemical shifts for these systems.

Pascual, C., Meier, J. and Simon, W. (1966) Rule for the Estimation of the Chemical Proton Shift in Double Bonds. *Helv. Chim. Acta* **49**, 164-168.

Tobey, S.W. (1969) Structural Assignments in Polysubstituted Ethylenes by Nuclear Magnetic Resonance. *J. Org. Chem.* **34**, 1281-1298.

The chemical shift of ethene, C_2H_4, is 5.28 ppm. The empirical rules for predicting ^1H chemical shifts for protons that are directly bonded to carbon atoms that are participate in a double bond are based on the following relation

$$\delta = 5.28 + \sum_i Z_i$$

$$= 5.28 + Z_{gem} + Z_{cis} + Z_{trans}$$

wherein the empirical Z_i are tabulated below

Substituent Parameters for the Tobey-Simon Rule

Substituent	Z_{gem}	Z_{cis}	Z_{trans}
H	0.0	0.0	0.0
Alkyl	0.44	−0.26	−0.29
CH_2O, CH_2I	0.67	−0.02	−0.07
CH_2S	0.53	−0.15	−0.15
CH_2Cl, CH_2Br	0.72	0.12	0.07
CH_2N	0.66	−0.05	−0.23
C=C	0.50	0.35	0.10
C≡N	0.23	0.78	0.58
C=C (isolated)	0.98	−0.04	−0.21
C=C (conjugated)	1.26	0.08	−0.01
C=O (isolated)	1.10	1.13	0.81
C=O (conjugated)	1.06	1.01	0.95
CO_2H (isolated)	1.00	1.35	0.74
CO_2R (isolated)	0.84	1.15	0.56
CHO	1.03	0.97	1.21
OR (R aliphatic)	1.18	−1.06	−1.28
OCOR	2.09	−0.40	−0.67
Aromatic	1.35	0.37	−0.10
Cl	1.00	0.19	0.03
Br	1.04	0.40	0.55
NR_2 (R aliphatic)	0.69	−1.19	−1.31
SR	1.00	−0.24	−0.04

Aldehydes

The ^1H resonances of aldehyde resonate are relatively low field due to inductive (presence of carbon double bond and oxygen) and deshielding (π-orbital) influences

The ^1H chemical shift of acetaldehyde is 9.8 ppm. The chemical shift range of ^1H resonances in substituted aldehydes is 10 ppm ± 0.3 ppm.

Aromatic Systems

Delocalized electrons in the aromatic ring systems (sp^2 hybridized carbon atoms) give rise to large diamagnetic shielding.

As expected, the substituent effects on ^1H chemical shifts are similar to those of the alkenes.

The ^1H chemical shift of the protons in benzene, C_6H_6, is 7.27 and the empirical relation may be written as follows:

$$\delta = 7.27 + \sum_i S_i$$

wherein the S_i are given ion the following table

Substituent Parameters for Aromatic Proton Shifts

Substituent	S_{ortho}	S_{meta}	S_{para}
CH_3	−0.17	−0.09	−0.18
CH_2CH_3	−0.15	−0.06	−0.18
NO_2	0.95	0.17	0.33
Cl	0.02	−0.06	−0.04
Br	0.22	−0.13	−0.03
I	0.40	−0.26	−0.03
CHO	0.58	0.21	0.27
OH	−0.50	−0.14	−0.40
NH_2	−0.75	−0.24	−0.63
CN	0.27	0.11	0.30
CO_2H	0.80	0.14	0.20
CO_2CH_3	0.74	0.07	0.20
$COCH_3$	0.64	0.09	0.30
OCH_3	−0.43	−0.09	−0.37
$OCOCH_3$	−0.21	−0.02	−0.13
$N(CH_3)_2$	−0.60	−0.10	−0.62
SCH_3	0.37	0.20	0.10

^{13}C Chemical Shifts

The figure below from the Lambert text charts the ^{13}C chemical shift ranges of some of the more common chemical moieties:
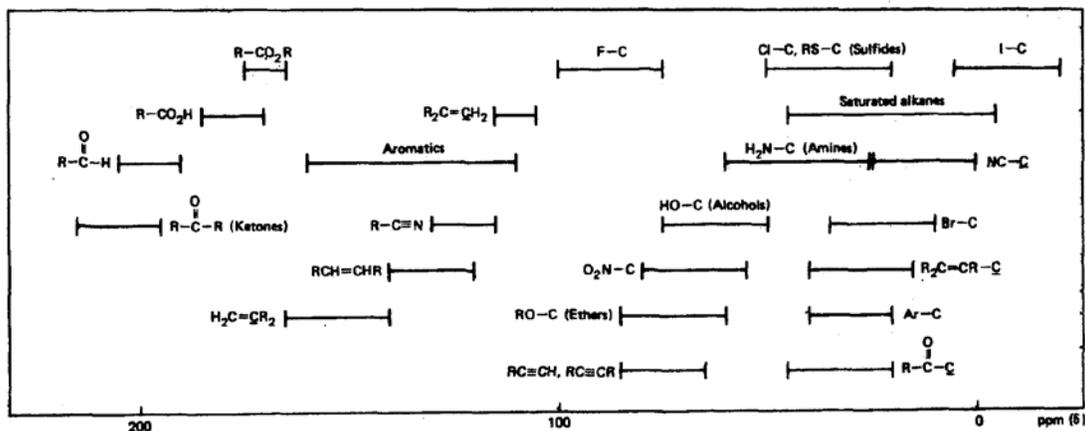
Saturated Aliphatics

The chemical shifts of ^{13}C nuclei are an extremely powerful structural tool.

The large relative chemical shift range (usually) allows resolution of most or all of the ^{13}C resonances.

For saturated straight-chain hydrocarbons, Prof. David Grant (of our dept!) has developed the following empirical expression:

$$\delta = -2.5 + \sum_i A_i n_i$$

wherein $i = \alpha$ (9.1), β (9.4), γ (-2.5), δ (0.3) and ε (0.1)

Thus the ^{13}C chemical shifts of the methyl carbons in pentane may be calculated as follows:

$\underline{C}H_3CH_2CH_2CH_2CH_3$ $\delta = -2.5 + 9.1 + 9.4 - 2.5 + 0.3 = 13.8$ ppm vs. 13.9 obs.

$CH_3\underline{C}H_2CH_2CH_2CH_3$ $\delta = -2.5 + (2 \times 9.1) + 9.4 - 2.5 = 22.6$ ppm vs. 22.8 obs.

$CH_3CH_2\underline{C}H_2CH_2CH_3$ $\delta = -2.5 + (2 \times 9.1) + (2 \times 9.4) = 34.5$ ppm vs. 34.7 obs.

7

For branched chains, things get a little more complicated, but the following adjustments extend Grant's rules to these important systems:

$^{13}CH_3$ group in the presence of 3° carbon (CH), subtract 1.1 ppm

$^{13}CH_3$ group in the presence of a 4° carbon, subtract 3.4 ppm

$-^{13}CH_2-$ group in the presence of 3° carbon, subtract 2.5 ppm

$-^{13}CH_2-$ group in the presence of 4° carbon, subtract 7.2 ppm

$-^{13}CH-$ group in the presence of 2° carbon, subtract 3.7 ppm

$-^{13}CH-$ group in the presence of 3° carbon, subtract 9.5 ppm

$-^{13}CH-$ group in the presence of 4° carbon, subtract 1.5 ppm

$-^{13}C-$ group in the presence of 1° carbon, subtract 1.5 ppm

$-^{13}C-$ group in the presence of 2° carbon, subtract 8.4 ppm

Cyclic Alkanes

The ^{13}C resonances of cyclopropane, C_3H_6, are remarkably low at -2.6 ppm. The chemical shift of butane is substantially higher at 23.3 ppm and the other cyclic alkanes resonate at 27.7 ppm $\pm$ 2 ppm.

Substituent influences are challenging to estimate in the general sense due to the constrained geometries, but the methyl substituent parameters for cyclohexane, C_6H_{12} are tabulated below

Substituent Parameters for Methyl Substitution on Cyclohexane

Stereochemistry	α	β	γ	δ
Equatorial	5.6	8.9	0.0	−0.3
Axial	1.1	5.2	−5.4	−0.1

Alkane Derivatives

The substituent effects of heteroatoms and/or unsaturated carbon moieties on the ^{13}C chemical shifts of alkanes may be estimated by adding the substituent parameter value(s) to the chemical shift of the simple source hydrocarbon molecule.

The substituent parameter value depends in this case upon whether the substituent is internal or terminal with respect to the carbon chain.
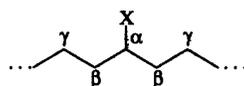
The expression for derivatized alkanes may be written as:

$$\delta = \delta_{C_nH_{2n+2}} + \sum_i X_i$$

wherein the X_i are given in the following table:
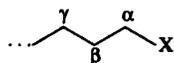
Terminal

3-23

Internal

3-24

Carbon Substituent Parameters for Functional Groups*

X	Terminal X (3-23)			Internal X (3-24)		
	α	β	γ	α	β	γ
F	68	9	−4	63	6	−4
Cl	31	11	−4	32	10	−4
Br	20	11	−3	25	10	−3
I	−6	11	−1	4	12	−1
OH	48	10	−5	41	8	−5
OR	58	8	−4	51	5	−4
OAc	51	6	−3	45	5	−3
NH_2	29	11	−5	24	10	−5
NR_2	42	6	−3			−3
CN	4	3	−3	1	3	−3
NO_2	63	4		57	4	
$CH{=}CH_2$	20	6	−0.5			−0.5
C_6H_5	23	9	−2	17	7	−2
$C{\equiv}CH$	4.5	5.5	−3.5			−3.5
(C=O)R	30	1	−2	24	1	−2
(C=O)OH	21	3	−2	16	2	−2
(C=O)OR	20	3	−2	17	2	−2
$(C{=}O)NH_2$	22		−0.5	2.5		−0.5

*From F.W. Wehrli, A.P. Marchand, and S. Wehrli, *Interpretation of Carbon-13 NMR Spectra*, 2nd ed., John Wiley & Sons Ltd., Chichester, UK, 1988.

Sample Calculations:

1,3-dichloropropane

Cl – $\underline{C}H_2CH_2CH_2$ – Cl

The ^{13}C chemical shift of the propane methyl resonance is 16 ppm as shown below:

$\underline{C}H_3CH_2CH_3$ $\qquad\qquad$ $\delta = -2.5 + 9.1 + 9.4 = 16$ ppm
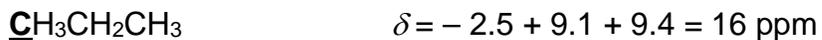
The Cl atom in the 1-position is terminal and α and thus adds 31 ppm.

The Cl atom in the 3-position is terminal and γ and thus adds -4 ppm.

Summing the parameters, we obtain

$$\delta = 16 + 31 - 4 = 43 \text{ ppm vs. } 42 \text{ ppm obs.}$$

3-methylpentane

$$
\begin{array}{c}
\overset{\displaystyle \overset{6}{CH_3}}{\underset{\displaystyle H_3C\!-\!\overset{2}{CH_2}\!-\!\underset{3}{CH}\!-\!\overset{4}{CH_2}\!-\!\underset{5}{CH_3}}{|}}
\end{array}
$$

$\delta_1 : \alpha, \beta, 2\gamma, \delta\square$

$\delta_1 = -2.5 + 9.1 + 9.4 + (2 \times -2.5) + 0.3 = 11.3$ ppm vs. 11.3 obs.

$\delta_2 : 2\alpha, 2\beta, \gamma\square$; C_2 is 2° with an attached 3° carbon (-2.5)

$\delta_2 = -2.5 + (2 \times 9.1) + (2 \times 9.4) - 2.5 = 29.5$ ppm vs. 29.3 obs.

$\delta_3 : 3\alpha, 2\beta$; C_3 is 3° with two 2° carbons attached (2×-3.7)

$\delta_3 = -2.5 + (3 \times 9.1) + (2 \times 9.4) + (2 \times -3.7) = 36.2$ ppm vs. 36.7 obs.

$\delta_6 : \alpha, \beta, 2\gamma\square$; C_6 is 1° with and attached 3° carbon (-1.1)

$(= -2.5 + 9.1 + (2 \times 9.4) + (2 \times -2.5) - 1.1 = 29.5$ ppm vs. 29.3 obs.

$$
\begin{array}{c}
19.3\;\overset{6}{CH_3} \\
(18.6) \\
| \\
H_3C\!-\!\overset{2}{CH_2}\!-\!\underset{3}{CH}\!-\!\overset{4}{CH_2}\!-\!\underset{5}{CH_3} \\
11.3 \quad 29.5 \quad 36.2 \\
(11.3) \quad (29.3) \quad (36.7)
\end{array}
$$