

NMR Tables and Charts

Estimation of ^{13}C chemical shifts in aliphatic chains

$$\delta_{\text{C}} = -2.3 + \sum z + \sum S + \sum K$$

where z is the substituent constant (Table 3.8)

S is a 'steric' correction (Table 3.9)

and K is a conformational increment for γ -substituents (Table 3.10)

Table 3.8 Substituent constants z for Eq. 3.15

	Substituent	z			
		α	β	γ	δ
C	H—	0	0	0	0
	alkyl—	9.1	9.4	-2.5	0.3
	—C=C—	19.5	6.9	-2.1	0.4
	—C≡C—	4.4	5.6	-3.4	-0.6
	Ph—	22.1	9.3	-2.6	0.3
	OHC—	29.9	-0.6	-2.7	0.0
	—CO—	22.5	3.0	-3.0	0.0
	—O ₂ C—	22.6	2.0	-2.8	0.0
	NC—	3.1	2.4	-3.3	-0.5
N	>N—	28.3	11.3	-5.1	0.0
	O ₂ N—	61.6	3.1	-4.6	-1.0
O	—O—	49.0	10.1	-6.2	0.0
	—COO—	56.5	6.5	-6.0	0.0
Hal	F—	70.1	7.8	-6.8	0.0
	Cl—	31.0	10.0	-5.1	-0.5
	Br—	18.9	11.0	-3.8	-0.7
	I—	-7.2	10.9	-1.5	-0.9
Other	—S—	10.6	11.4	-3.6	-0.4
	—SO—	31.1	9.0	-3.5	0.0

Table 3.9 'Steric' correction S for Eq. 3.15

Observed ^{13}C atom	Number of substituents other than H on the atoms directly bonded to the observed $^{13}\text{C}^\dagger$			
	1	2	3	4
Primary	0.0	0.0	-1.1	-3.4
Secondary	0.0	0.0	-2.5	-7.5
Tertiary	0.0	-3.7	-9.5	-15.0
Quaternary	-1.5	-8.4	-15.0	-25.0

† Except that CO₂H, CO₂R, and NO₂ groups are counted as primary (column 1), Ph, CHO, CONH₂, CH₂OH, and CH₂NH₂ groups as secondary (column 2), and COR groups as tertiary (column 3).

Det
observerte
C-atom

Substituering
på nabo-atomene
til det obs. C






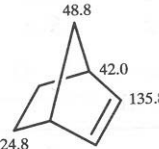
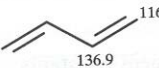
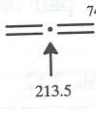
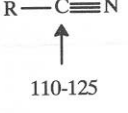

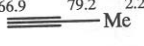


Estimation of ^1H chemical shifts in substituted alkanes

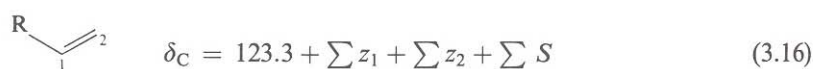
$$\text{R}^1\text{R}^2\text{R}^3\text{CH}, \quad \delta_{\text{H}} = 1.50 + \sum z_i$$

Table 3.20 Substituent constants z for Eq. 3.19

R^i	z	R^i	z	R^i	z
H—	-0.3	$\text{HC}\equiv\text{C}$ —	0.9	MeO—	1.5
Alkyl—	0.0	OHC—	1.2	PhO—	2.3
$\text{CH}_2=\text{CHCH}_2$ —	0.2	MeCO—	1.2	AcO	2.7
MeCOCH ₂ —	0.2	RO ₂ C—	0.8	Cl—	2.0
HOCH ₂ —	0.3	NC—	1.2	Br—	1.9
ClCH ₂ —	0.5	H ₂ N—	1.0	I—	1.4
$\text{CH}_2=\text{CH}$ —	0.8	O ₂ N—	3.0	MeS—	1.0
Ph—	1.3	HO—	1.7	Me ₃ Si—	-0.7

Table 3.11 ^{13}C chemical shifts in some alkenes, alkynes, and nitriles

\equiv 123.3					
					
					

Estimation of ^{13}C chemical shifts in substituted alkenes

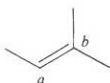
where z_1 and z_2 are the substituent constants (Table 3.12) and S is a 'steric' correction for alkyl substituents:

For each pair of <i>cis</i> substituents	$S = -1.1$
For a pair of geminal substituents on C-1	$S = -4.8$
For a pair of geminal substituents on C-2	$S = 2.5$

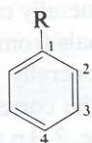
Table 3.12 Substituent constants z for Eq. 3.16

	Substituent R	z_1	z_2
C	H—	0	0
	Me—	10.6	-7.9
	Et—	15.5	-9.7
	Pr ⁿ —	14.0	-8.2
	Pr ⁱ —	20.4	-11.5
	Bu ^t —	25.3	-13.3
	ClCH ₂ —	10.2	-6.0
	HOCH ₂ —	14.2	-8.4
	Me ₃ SiCH ₂ —	12.5	-12.5
	CH ₂ =CH—	13.6	-7.0
	Ph—	12.5	-11.0
	OHC—	13.1	12.7
	RCO—	15.0	5.8
	RO ₂ C—	6.3	7.0
	NC—	-15.1	14.2
	N	RAcN—	6.5
O	RO—	29.0	-39.0
	AcO—	18.4	-26.7
Hal	F—	24.9	-34.3
	Cl—	2.6	-6.1
	Br—	-7.9	-1.4
	I—	-38.1	7.0
Other	Me ₃ Si—	16.9	16.1
	RS—	18.0	-16.0
	Ph ₂ P(=O)—	8.0	11.0

Example, 2-methylbut-2-ene:



<i>a</i>	Base value	123.3	<i>b</i>	Base value	123.3
	1-methyl	10.6		2 × 1-methyl	21.2
	2 × 2-methyl	-15.8		2-methyl	-7.9
	1 <i>cis</i> pair	-1.1		1 <i>cis</i> pair	-1.1
	1 gem pair on C-2	2.5		1 gem pair on C-1	-4.8
	Calculated	119.5		Calculated	130.7
	Observed	118.5		Observed	131.8

Estimation of ^{13}C chemical shifts in substituted benzenes

$$\delta_{\text{C}} = 128.5 + \sum z_i \quad (3.17)$$

Table 3.14 Substituent constants z for Eq. 3.17

Substituent R	z_1	z_2	z_3	z_4
	0	0	0	0
C				
H—	0	0	0	0
Me—	9.3	0.6	0.0	-3.1
Et—	15.7	-0.6	-0.1	-2.8
Pr ⁿ —	14.2	-0.2	-0.2	-2.8
Pr ⁱ —	20.1	-2.0	0.0	-2.5
Bu ^t —	22.1	-3.4	-0.4	-3.1
ClCH ₂ —	9.1	0.0	0.2	-0.2
HOCH ₂ —	13.0	-1.4	0.0	-1.2
CH ₂ =CH—	7.6	-1.8	-1.8	-3.5
Ph—	13.0	-1.1	0.5	-1.0
HC≡C—	-6.1	3.8	0.4	-0.2
OHC—	9.0	1.2	1.2	6.0
MeCO—	9.3	0.2	0.2	4.2
RO ₂ C—	2.1	1.2	0.0	4.4
NC—	-16.0	3.5	0.7	4.3
N				
H ₂ N—	19.2	-12.4	1.3	-9.5
Me ₂ N—	22.4	-15.7	0.8	-11.8
AcNH—	11.1	-16.5	0.5	-9.6
O ₂ N—	19.6	-5.3	0.8	6.0
O				
HO—	26.9	-12.7	1.4	-7.3
MeO—	30.2	-14.7	0.9	-8.1
AcO—	23.0	-6.4	1.3	-2.3
Hal				
F—	35.1	-14.3	0.9	-4.4
Cl—	6.4	0.2	1.0	-2.0
Br—	-5.4	3.3	2.2	-1.0
I—	-32.3	9.9	2.6	-0.4
Other				
Me ₃ Si—	13.4	4.4	-1.1	-1.1
Ph ₂ P—	8.7	5.1	-0.1	0.0
MeS—	9.9	-2.0	0.1	-3.7

Table 3.15 ^{13}C chemical shifts of carbonyl carbons


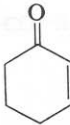
R^1	R^2	δ_{C}	R^1	R^2	δ_{C}
Me—	—H	199.7	Me—	—OH	178.1
Et—	—H	206.0	Et—	—OH	180.4
Pr ⁱ —	—H	204.0	Pr ⁱ —	—OH	184.1
CH ₂ =CH—	—H	192.4	Bu ^t —	—OH	185.9
Ph—	—H	192.0	CH ₂ =CH—	—OH	171.7
			Ph—	—OH	172.6
Me—	—Me	206.0	Me—	—OMe	170.7
Et—	—Me	207.6	Et—	—OMe	173.3
Pr ⁱ —	—Me	211.8	Pr ⁱ —	—OMe	175.7
Bu ^t —	—Me	213.5	Bu ^t —	—OMe	178.9
ClCH ₂ —	—Me	200.7	CH ₂ =CH—	—OMe	165.5
Cl ₂ CH—	—Me	193.6	Ph—	—OMe	166.8
Cl ₃ C—	—Me	186.3	—(CH ₂) ₃ O—		177.9
CH ₂ =CH—	—Me	197.2	—(CH ₂) ₄ O—		175.2
Ph—	—Me	197.6			
—(CH ₂) ₃ —		208.2	Me—	—NH ₂	172.7
—(CH ₂) ₄ —		213.9	CH ₂ =CH—	—NH ₂	168.3
—(CH ₂) ₅ —		208.8	Ph—	—NH ₂	169.7
—(CH ₂) ₆ —		211.7			
		209.0	—(CH ₂) ₃ NH—		179.4
			—(CH ₂) ₄ NH—		173.0
		198.0	Me—	—OAc	167.3
			Ph—	—OAc	162.8
			Me—	—Cl	168.6
			CH ₂ =CH—	—Cl	165.6
			Ph—	—Cl	168.0

Table 3.19 ^1H chemical shifts in methyl, methylene, and methine groups

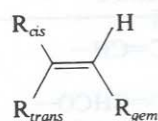
	<i>Methyl protons</i>	δ_{H}	<i>Methylene protons</i>	δ_{H}	<i>Methine protons</i>	δ_{H}	
C	$\text{CH}_3\text{-R}$	0.9	$\text{R-CH}_2\text{-R}$	1.4	>CH-R	1.5	
	$\text{CH}_3\text{-C-C=C}$	1.1	$\text{R-CH}_2\text{-C-C=C}$	1.7			
	$\text{CH}_3\text{-C-O}$	1.3	$\text{R-CH}_2\text{-C-O}$	1.9	>CH-C-O	2.0	
	$\text{CH}_3\text{-C-N}$	1.1	$\text{R-CH}_2\text{-C-N}$	1.4			
	$\text{CH}_3\text{-C-NO}_2$	1.6	$\text{R-CH}_2\text{-C-NO}_2$	2.1			
	$\text{CH}_3\text{-C=C}$	1.6	$\text{R-CH}_2\text{-C=C}$	2.3			
	$\text{CH}_3\text{-Ar}$	2.3	$\text{R-CH}_2\text{-Ar}$	2.7	>CH-Ar	3.0	
	$\text{CH}_3\text{-C=CC=O}$	2.0	$\text{R-CH}_2\text{-C=CC=O}$	2.4			
	$\text{C=C(CH}_3\text{)-C=O}$	1.8	$\text{C=C(CH}_2\text{-R)-C=O}$	2.4			
	$\text{CH}_3\text{-C}\equiv\text{C}$	1.8	$\text{R-CH}_2\text{-C}\equiv\text{C}$	2.2	$\text{>CH-C}\equiv\text{C}$	2.6	
	$\text{CH}_3\text{-CO-R}$	2.2	$\text{R-CH}_2\text{-CO-R}$	2.4	>CH-CO-R	2.7	
	$\text{CH}_3\text{-CO-Ar}$	2.6	$\text{R-CH}_2\text{-CO-Ar}$	2.9	>CH-CO-Ar	3.3	
	$\text{CH}_3\text{-CO-OR}$	2.0	$\text{R-CH}_2\text{-CO-OR}$	2.2	>CH-CO-OR	2.5	
	$\text{CH}_3\text{-CO-OAr}$	2.4					
	$\text{CH}_3\text{-CO-N}$	2.0	$\text{R-CH}_2\text{-CO-N}$	2.2	>CH-CO-N	2.4	
			$\text{R-CH}_2\text{-C}\equiv\text{N}$	2.3	$\text{>CH-C}\equiv\text{N}$	2.7	
	N	$\text{CH}_3\text{-N}$	2.3	$\text{R-CH}_2\text{-N}$	2.5	>CH-N	2.8
		$\text{CH}_3\text{-N-Ar}$	3.0				
		$\text{CH}_3\text{-N-CO-R}$	2.9	$\text{R-CH}_2\text{-N-CO-R}$	3.2	>CH-N-CO-R	4.0
		$\text{CH}_3\text{-N}^+$	3.3	$\text{R-CH}_2\text{-N}^+$	3.3		
O			$\text{R-CH}_2\text{-NO}_2$	4.4	>CH-NO_2	4.7	
			$\text{R-CH}_2\text{-OH}$	3.6	>CH-OH	3.9	
	$\text{CH}_3\text{-OR}$	3.3	$\text{R-CH}_2\text{-OR}$	3.4	>CH-OR	3.7	
	$\text{CH}_3\text{-O-C=C}$	3.8	$\text{R-CH}_2\text{-O-C=C}$	3.7			
	$\text{CH}_3\text{-OAr}$	3.8	$\text{R-CH}_2\text{-OAr}$	4.3	>CH-OAr	4.5	
	$\text{CH}_3\text{-O-CO-R}$	3.7	$\text{R-CH}_2\text{-O-CO-R}$	4.1	>CH-O-CO-R	4.8	
Hal			$\text{RO-CH}_2\text{-OR}$	4.8			
			$\text{R-CH}_2\text{-F}$	4.4			
			$\text{R-CH}_2\text{-Cl}$	3.6	>CH-Cl	4.2	
			$\text{R-CH}_2\text{-Br}$	3.5	>CH-Br	4.3	
Other			$\text{R-CH}_2\text{-I}$	3.2	>CH-I	4.3	
	$\text{CH}_3\text{-Si}$	0.0	$\text{R-CH}_2\text{-Si}$	0.5	>CH-Si	1.2	
	$\text{CH}_3\text{-S}$	2.1	$\text{R-CH}_2\text{-S}$	2.4	>CH-S	3.2	
	$\text{CH}_3\text{-S(O)R}$	2.5					
	$\text{CH}_3\text{-S(O}_2\text{)R}$	2.8	$\text{R-CH}_2\text{-S(O}_2\text{)R}$	2.9			
		$\text{RS-CH}_2\text{-SR}$	4.2				

R = alkyl group. These values will usually be within ± 0.2 p.p.m. unless electronic or anisotropic effects from other groups are strong. An obsolete scale used τ values; these are related to δ values by the simple equation $\tau = 10 - \delta$.

Table 3.22 ^1H chemical shifts of protons attached to multiple bonds

Structure	δ_{H}	Structure	δ_{H}
RCHO	9.4–10.0	>C=CH-	4.5–6.0
ArCHO	9.7–10.5	>C=CHCO-	5.8–6.7
–OCHO	8.0–8.2	–HC=CCO–	6.5–8.0
>NCHO	8.0–8.2	–HC=C–O–	4.0–5.0
–C \equiv CH	1.8–3.1	>C=CH-O-	6.0–8.1
>C=C=CH-	4.0–5.0	–HC=C–N–	3.7–5.0
ArH	6.0–9.0	>C=CH-N-	5.7–8.0

Estimation of ^1H chemical shift in alkenes



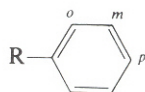
$$\delta_{\text{H}} = 5.25 + z_{\text{gem}} + z_{\text{cis}} + z_{\text{trans}} \quad (3.20)$$

Table 3.23 Substituent constants z for Eq. 3.20

	R	z_{gem}	z_{cis}	z_{trans}
C	H—	0	0	0
	alkyl—	0.45	-0.22	-0.28
	ring-alkyl—	0.69	-0.25	-0.28
	CO—CH ₂ — or NC—CH ₂ —	0.69	-0.08	-0.06
	Ar—CH ₂ —	1.05	-0.29	-0.32
	N—CH ₂ —	0.58	-0.10	-0.08
	O—CH ₂ —	0.64	-0.10	-0.02
	Hal—CH ₂ —	0.70	0.11	-0.04
	S—CH ₂ —	0.71	-0.13	-0.22
	isolated C=C—	1.00	-0.09	-0.23
	conjugated C=C—	1.24	0.02	-0.05
	Ar—	1.38	0.36	-0.07
	OHC—	1.02	0.95	1.17
	isolated RCO—	1.10	1.12	0.87
	conjugated RCO—	1.06	0.91	0.74
	isolated HO ₂ C—	0.97	1.41	0.71
	conjugated HO ₂ C—	0.80	0.98	0.32
	isolated RO ₂ C—	0.80	1.18	0.55
	conjugated RO ₂ C—	0.78	1.01	0.46
	N—CO—	1.37	0.98	0.46
	Cl—CO—	1.11	1.46	1.01
	—C≡C—	0.47	0.38	0.12
N≡C—	0.27	0.75	0.55	
N	alkyl-N—	0.80	-1.26	-1.21
	conjugated alkyl or aryl-N—	1.17	-0.53	-0.99
	—CO—N—	2.08	-0.57	-0.72
	O ₂ N—	1.87	1.30	0.62
O	alkyl-O—	1.22	-1.07	-1.21
	conjugated alkyl or aryl-O—	1.21	-0.60	-1.00
	—CO—O—	2.11	-0.35	-0.64
Hal	F—	1.54	-0.40	-1.02
	Cl—	1.08	0.18	0.13
	Br—	1.07	0.45	0.55
	I—	1.14	0.81	0.88
Other	R ₃ Si—	0.90	0.90	0.60
	RS—	1.11	-0.29	-0.13
	RSO—	1.27	0.67	0.41
	RSO ₂ —	1.55	1.16	0.93

Use the 'conjugated' values when either the substituent or the double bond is further conjugated. Use the 'ring-alkyl' values when the double bond and the alkyl group are part of a five- or six-membered ring.

Estimation of proton chemical shifts in substituted benzenes




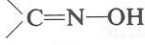
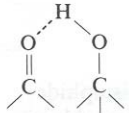
$$\delta_{\text{H}} = 7.27 + \sum z_i \quad (3.21)$$

Table 3.25 Substituent constants for Eq. 3.21

	R	z_{ortho}	z_{meta}	z_{para}
C	H—	0	0	0
	Me—	-0.20	-0.12	-0.22
	Et—	-0.14	-0.06	-0.17
	Pr ⁱ —	-0.13	-0.08	-0.18
	Bu ^t —	0.02	-0.08	-0.21
	H ₂ NCH ₂ — or HOCH ₂ —	-0.07	-0.07	-0.07
	ClCH ₂ —	0.00	0.00	0.00
	F ₃ C—	0.32	0.14	0.20
	Cl ₃ C—	0.64	0.13	0.10
	CH ₂ =CH—	0.06	-0.03	-0.10
	Ph—	0.37	0.20	0.10
	OHC—	0.56	0.22	0.29
	MeCO—	0.62	0.14	0.21
	H ₂ NCO—	0.61	0.10	0.17
	HO ₂ C—	0.85	0.18	0.27
	MeO ₂ C—	0.71	0.1	0.21
	ClCO—	0.84	0.22	0.36
	HC≡C—	0.15	-0.02	-0.01
	N≡C—	0.36	0.18	0.28
	N	H ₂ N—	-0.75	-0.25
Me ₂ N—		-0.66	-0.18	-0.67
AcNH—		0.12	-0.07	-0.28
O ₂ N—		0.95	0.26	0.38
O	HO—	-0.56	-0.12	-0.45
	MeO—	-0.48	-0.09	-0.44
	AcO—	-0.25	0.03	-0.13
Hal	F—	-0.26	0.00	-0.04
	Cl—	0.03	-0.02	-0.09
	Br—	0.18	-0.08	-0.04
	I—	0.39	-0.21	0.00
Other	Me ₃ Si—	0.22	-0.02	-0.02
	(MeO) ₂ P(=O)—	0.48	0.16	0.24
	MeS—	0.37	0.20	0.10

These parameters are simply the shifts measured on the corresponding monosubstituted benzene ring; they are not accurately taken over to polysubstituted benzenes, but the estimation of chemical shift is usually fairly good. Errors are particularly likely to occur when substituents *ortho* to one another interfere with conjugation to the ring.

Table 3.26 ^1H chemical shifts of protons attached to elements other than carbon

	<i>Structure</i>	δ_{H}	<i>Structure</i>	δ_{H}	
NH	RNH_2 and R_2NH	0.5–4.5	OH	monomeric H_2O ~1.5	
	ArNH_2 and ArNHR	3–6		suspended HOD ~4.7	
	RCONH_2 and RCONHR	5–12		ROH 0.5–4.5	
	pyrrole NH	7–12		ArOH 4.5–10	
				RCO_2H 9–15	
SiH		~3.8			9–12
SH	RSH	1–2			7–16
	ArSH	3–4			

These values are very sensitive to temperature, solvent, and concentration: the stronger the hydrogen bonding, the lower field the chemical shift.