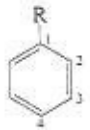
Estimation of ^{13}C chemical shifts in substituted benzenes



$$\delta_C = 128.5 + \sum z_i \qquad (3.17)$$

Table 3.14 Substituent constants z for Eq. 3.17

	Substituent R	z_1	z_2	z_3	z_4
	H—	0	0	0	0
C	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_2C—	2.1	1.2	0.0	4.4
	NC—	−16.0	3.5	0.7	4.3
N	H_2N—	19.2	−12.4	1.3	−9.5
	Me_2N—	22.4	−15.7	0.8	−11.8
	AcNH—	11.1	−16.5	0.5	−9.6
	O_2N—	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_3Si—	13.4	4.4	−1.1	−1.1
	Ph_2P—	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

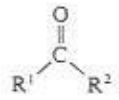
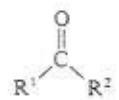
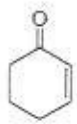
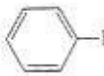
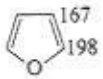
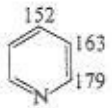
		δ_C			δ_C
Me—	—H	199.7	Me—	—OH	178.1
Et—	—H	206.0	Et—	—OH	180.4
Pr^i—	—H	204.0	Pr^i—	—OH	184.1
CH_2=CH—	—H	192.4	Bu^t—	—OH	185.9
Ph—	—H	192.0	CH_2=CH—	—OH	171.7
			Ph—	—OH	172.6
Me—	—Me	206.0			
Et—	—Me	207.6	Me—	—OMe	170.7
Pr^i—	—Me	211.8	Et—	—OMe	173.3
Bu^t—	—Me	213.5	Pr^i—	—OMe	175.7
$ClCH_2$—	—Me	200.7	Bu^t—	—OMe	178.9
Cl_2CH—	—Me	193.6	CH_2=CH—	—OMe	165.5
Cl_3C—	—Me	186.3	Ph—	—OMe	166.8
CH_2=CH—	—Me	197.2	$-(CH_2)_3O-$		177.9
Ph—	—Me	197.6	$-(CH_2)_4O-$		175.2
$-(CH_2)_3-$		208.2			
$-(CH_2)_4-$		213.9	Me—	$—NH_2$	172.7
$-(CH_2)_5-$		208.8	CH_2=CH—	$—NH_2$	168.3
$-(CH_2)_6-$		211.7	Ph—	$—NH_2$	169.7
		209.0	$-(CH_2)_3NH-$		179.4
			$-(CH_2)_4NH-$		173.0
			Me—	—OAc	167.3
			Ph—	—OAc	162.8
		198.0	Me—	—Cl	168.6
			CH_2=CH—	—Cl	165.6
			Ph—	—Cl	168.0

Table 3.16 ^{13}C–^{1}H coupling constants

$^1J_{CH}$ CH_4 125 $CH_2{=}CH_2$ 156  159 $HC{\equiv}CH$ 249

 161  134  128  123





Estimation of $^1J_{CH}$ in alkanes

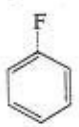
For $R^1R^2R^3CH$, $$^1J_{CH} = 125 + \sum z_i \qquad (3.18)$$

Table 3.17 Substituent constants for Eq. 3.18

	Substituent R	*z*		*Substituent R*	*z*
	H—	0	N	H_2N—	8
C	Me—	1	O	HO—	18
	Bu^t—	−3	Hal	F—	24
	$ClCH_2$—	3		Cl—	27
	$HC{\equiv}C$—	7		Br—	27
	Ph—	1		I—	26
	OHC—	2			
	MeO_2C—	−1			
	NC—	11			

Table 3.18 ^{13}C–F coupling constants

$RCH_2CH_2CH_2F$ $^1J_{CF}$ 165 $^2J_{CF}$ 18 $^3J_{CF}$ 6 Hz



$^1J_{CF}$ 245 $^2J_{CF}$ 21 $^3J_{CF}$ 8 $^4J_{CF}$ 3 Hz

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

	Methyl protons	δ_H	*Methylene protons*	δ_H	*Methine protons*	δ_H
C	CH_3—R	0.9	R—CH_2—R	1.4	>CH—R	1.5
	CH_3—C—C=C	1.1	R—CH_2—C—C=C	1.7		
	CH_3—C—O	1.3	R—CH_2—C—O	1.9	>CH—C—O	2.0
	CH_3—C—N	1.1	R—CH_2—C—N	1.4		
	CH_3—C—NO_2	1.6	R—CH_2—C—NO_2	2.1		
	CH_3—C=C	1.6	R—CH_2—C=C	2.3		
	CH_3—Ar	2.3	R—CH_2—Ar	2.7	>CH—Ar	3.0
	CH_3—C=CC=O	2.0	R—CH_2—C=CC=O	2.4		
	C=C(CH_3)—C=O	1.8	C=C(CH_2—R)—C=O	2.4		
	CH_3—C≡C	1.8	R—CH_2—C≡C	2.2	>CH—C≡C	2.6
	CH_3—CO—R	2.2	R—CH_2—CO—R	2.4	>CH—CO—R	2.7
	CH_3—CO—Ar	2.6	R—CH_2—CO—Ar	2.9	>CH—CO—Ar	3.3
	CH_3—CO—OR	2.0	R—CH_2—CO—OR	2.2	>CH—CO—OR	2.5
	CH_3—CO—OAr	2.4				
	CH_3—CO—N	2.0	R—CH_2—CO—N	2.2	>CH—CO—N	2.4
			R—CH_2—C≡N	2.3	>CH—C≡N	2.7
N	CH_3—N	2.3	R—CH_2—N	2.5	>CH—N	2.8
	CH_3—N—Ar	3.0				
	CH_3—N—CO—R	2.9	R—CH_2—N—CO—R	3.2	>CH—N—CO—R	4.0
	CH_3—N^+	3.3	R—CH_2—N^+	3.3		
			R—CH_2—NO_2	4.4	>CH—NO_2	4.7
O			R—CH_2—OH	3.6	>CH—OH	3.9
	CH_3—OR	3.3	R—CH_2—OR	3.4	>CH—OR	3.7
	CH_3—O—C=C	3.8	R—CH_2—O—C=C	3.7		
	CH_3—OAr	3.8	R—CH_2—OAr	4.3	>CH—OAr	4.5
	CH_3—O—CO—R	3.7	R—CH_2—O—CO—R	4.1	>CH—O—CO—R	4.8
			RO—CH_2—OR	4.8		
Hal			R—CH_2—F	4.4		
			R—CH_2—Cl	3.6	>CH—Cl	4.2
			R—CH_2—Br	3.5	>CH—Br	4.3
			R—CH_2—I	3.2	>CH—I	4.3
Other	CH_3—Si	0.0	R—CH_2—Si	0.5	>CH—Si	1.2
	CH_3—S	2.1	R—CH_2—S	2.4	>CH—S	3.2
	CH_3—S(O)R	2.5				
	CH_3—$S(O_2)$R	2.8	R—CH_2—$S(O_2)$R	2.9		
			RS—CH_2—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 $\tau = 10 - \delta$.

Estimation of ^{1}H chemical shifts in substituted alkanes

$$R^1R^2R^3CH, \qquad \delta_H = 1.50 + \sum z_i \tag{3.19}$$

Table 3.20 Substituent constants z for Eq. 3.19

R^i	z	R^i	z	R^i	z
H—	−0.3	HC≡C—	0.9	MeO—	1.5
Alkyl—	0.0	OHC—	1.2	PhO—	2.3
CH_2=$CHCH_2$—	0.2	MeCO—	1.2	AcO	2.7
$MeCOCH_2$—	0.2	RO_2C—	0.8	Cl—	2.0
$HOCH_2$—	0.3	NC—	1.2	Br—	1.9
$ClCH_2$—	0.5	H_2N—	1.0	I—	1.4
CH_2=CH—	0.8	O_2N—	3.0	MeS—	1.0
Ph—	1.3	HO—	1.7	Me_3Si—	−0.7

Table 3.21 ^{1}H chemical shifts of methylene groups in some cyclic compounds

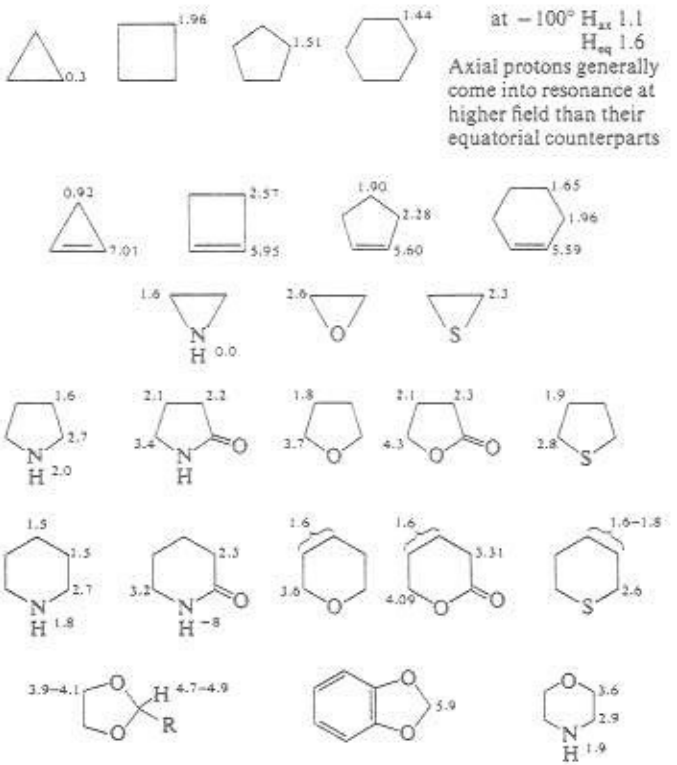


Table 3.22 ^{1}H chemical shifts of protons attached to multiple bonds

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≡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