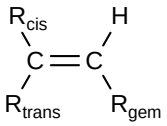
9.61 Parameters for Calculating Vinyl Chemical Shifts



$$\delta_{C=CH} = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$$

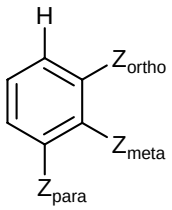
Substituent R	Zi for R (ppm) Zgem	Zcis	Ztrans
H	0.0	0.0	0.0
Alkyl	0.45	-0.22	-0.28
Alkyl (cyclic)	0.69	-0.25	-0.28
CH_2OH	0.64	-0.01	-0.02
CH_2SH	0.71	-0.13	-0.22
CH_2X (X = F, Cl, Br)	0.70	0.11	-0.04
CH_2NR_2	0.58	-0.10	-0.08
CF_3	0.66	0.61	0.32
$C=CR_2$ (isolated)	1.00	-0.09	-0.23
$C=CR_2$ (conjugated)	1.24	0.02	-0.05
C≡C-R	0.47	0.38	0.12
C≡N	0.27	0.75	0.55
COOH (isolated)	0.97	1.41	0.71
COOH (conjugated)	0.80	0.98	0.32
COOR (isolated)	0.80	1.18	0.55
COOR (conjugated)	0.78	1.01	0.46
C(O)H	1.02	0.95	1.17
$C(O)NR_2$	1.37	0.98	0.46
C(O)Cl	1.11	1.46	1.01
C=O (isolated)	1.10	1.12	0.87
C=O (conjugated)	1.06	0.91	0.74
CH_2-C(O)R; CH_2-CN	0.69	-0.08	-0.06
CH_2Ar	1.05	-0.29	-0.32
Ar	1.38	0.36	-0.07
Ar (o-subs)	1.65	0.19	0.09

Substituent R	Zi for R (ppm) Zgem	Zcis	Ztrans
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
OR (R, aliphatic)	1.22	-1.07	-1.21
OR (R, conjugated)	1.21	-0.60	-1.00
O-C(O)-R	2.11	-0.35	-0.64
$O\text{-}P(O)(OEt)_2$	0.66	0.88	0.67
SR	1.11	-0.29	-0.13
S(O)R	1.27	0.67	0.41
$S(O)_2R$	1.55	1.16	0.93
S-C N	0.80	1.17	1.11
SF_5	1.68	0.61	0.49
SePh (5)	1.36	0.17	0.24
Se(O)Ph (1)	1.86	0.97	0.63
$Se(O_2)Ph$ (1)	1.76	1.49	1.21
NR_2 (R, aliphatic)	0.80	-1.26	-1.21
NR_2 (R, conjugated)	1.17	-0.53	-0.99
N=N-Ph	2.39	1.11	0.67
NO_2	1.87	1.30	0.62
N-C(O)R	2.08	-0.57	-0.72
N_3	1.21	-0.35	-0.71[2]
$P(O)(OEt)_2$	0.66	0.88	0.67
$SiMe_3$ (1)	0.77	0.37	0.62
$GeMe_3$ (1)	1.28	0.35	0.67

The increments 'R conjugated' are to be used instead of 'R isolated' when either the substituent or the double bond is conjugated with further substituents. The increment alkyl (cyclic) is to be used when both the substituent and the double bond form part of a ring. (Data for compounds containing 3- and 4-membered rings have not been considered.) Numbers in parentheses represent the number of examples used to calculate the parameters.

[1] Pascual, C. *Helv. Chem. Acta* **1966**, *49*, 164.
[2] L'Abbe, G. *Chem. & Ind. (London)* **1971**, 278

9.62 Parameters for Calculating Benzene Chemical Shifts



$$\delta_{Ar\text{-}H} = 7.36 + Z_{ortho} + Z_{meta} + Z_{para}$$

Zi for R (ppm)			
Substituent R	**Zortho**	**Zmeta**	**Zpara**
H	0.0	0.0	0.0
CH_3[a]	-0.18	-0.11	-0.21
$C(CH_3)_3$	0.02	-0.08	-0.21
CH_2Cl	0.02	-0.01	-0.04
CH_2OH	-0.07	-0.07	-0.07
CF_3	0.32	0.14	0.20
CCl_3	0.64	0.13	0.10
$CH=CH_2$	0.04	-0.04	-0.12
CH=CHCOOH[a]	0.19	0.04	0.05
C C-H	0.15	-0.02	-0.01
C C-Ph[a]	0.17	-0.02	-0.03
Ph[a]	0.23	0.07	-0.02
COOH[a]	0.77	0.11	0.25
$C(O)OCH_3$[a]	0.68	0.08	0.19
C(O)OPh[a]	0.85	0.14	0.27
$C(O)NH_2$[a]	0.46	0.09	0.17
C(O)Cl[a]	0.76	0.16	0.33
$C(O)CH_3$[a]	0.60	0.10	0.20
$C(O)C(CH_3)_3$	0.44	0.05	0.05
C(O)H[a]	0.53	0.18	0.28
C(NPh)H	0.6	0.2	0.2
C(O)Ph[a]	0.45	0.12	0.23
C(O)C(O)Ph[a]	0.62	0.15	0.30
CN[a]	0.29	0.12	0.25
F	-0.29	-0.02	-0.23
Cl[a]	-0.02	-0.07	-0.13
Br[a]	0.13	-0.13	-0.08
I	0.39	-0.21	0.00
OH[a]	-0.53	-0.14	-0.43
OCH_3[a]	-0.45	-0.07	-0.41

Zi for R (ppm)			
Substituent R	**Zortho**	**Zmet[a]**	**Zpara**
OPh[a]	-0.36	-0.04	-0.28
$O\text{-}C(O)CH_3$[a]	-0.27	-0.02	-0.13
O-C(O)Ph[a]	-0.14	0.07	-0.09
$O\text{-}SO_2Me$	-0.05	0.07	-0.01
SH	-0.08	-0.16	-0.22
SMe	-0.08	-0.10	-0.24
SPh	0.06	-0.09	-0.15
SO_2Cl	0.76	0.35	0.45
NH_2[a]	-0.71	-0.22	-0.62
NMe_2	-0.66	-0.18	-0.67
NEt_2[a]	-0.68	-0.15	-0.73
NMe_3+I-	0.69	0.36	0.31
$NHC(O)CH_3$[a]	0.14	-0.07	-0.27
$NH\text{-}NH_2$	-0.60	-0.08	-0.55
N=N-Ph	0.67	0.20	0.20
N=O	0.58	0.31	0.37
NO_2[a]	0.87	0.20	0.35
$P(O)(OMe)_2$	0.48	0.16	0.24
$SiMe_3$	0.22	-0.02	-0.02
BPh_3^-	-0.16	-0.42	-0.56

[a]Data in dilute $CDCl_3$ by Paul Schatz, University of Wisconsin, Madison. Original data from *J. Am. Chem. Soc.* **1956**, *78*, 3043 at 30 MHz with 50% solutions in cyclohexane.