Karplus Relationships

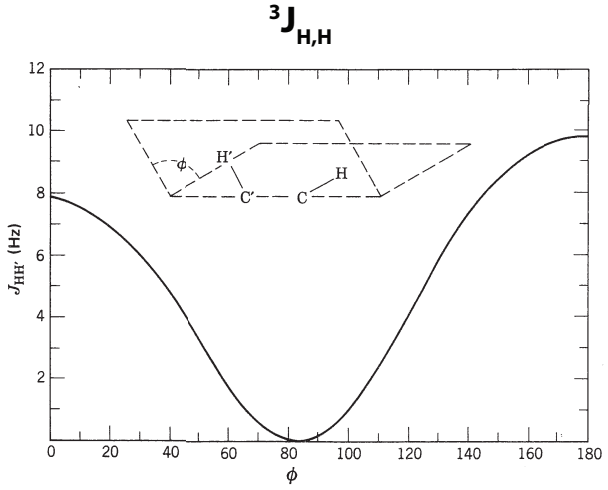


FIGURE 3.57 The vicinal Karplus correlation. Relationship between dihedral angle (ϕ) and coupling constant for vicinal protons.

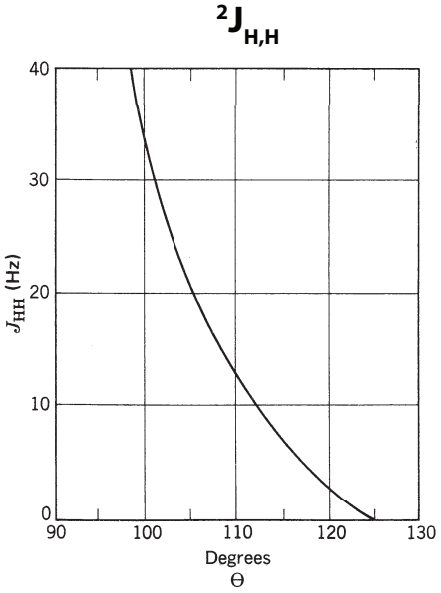


FIGURE 3.58 The geminal Karplus correlation. J_{HH} for CH_2 groups as a function of >H—C—H. Note the zero coupling at about 125°.

Silverstein, R., et. al. (2005). "Spectrometric Identification of Organic Compounds," 7th Ed. New York: Wiley.

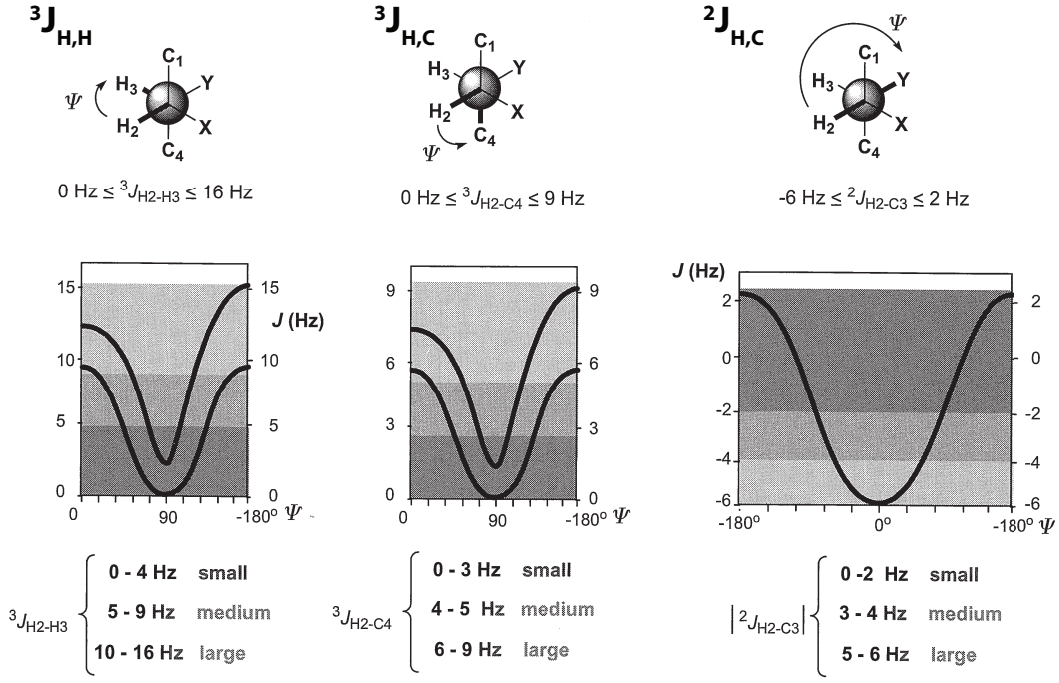


FIGURE **4.7** Relationship between coupling constants (^3J, ^2J) and dihedral angle ψ. Upper curves represent original Karplus equation, lower curves are the Altona equation for heteroatom-substituted carbon chains.

Crews, P., et. al. (2010). "Organic Structure Analysis," 2nd Ed. New York: Oxford.

TABLE 4.1 Some $^1J_{CH}$ Values

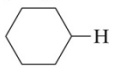
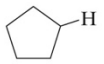
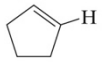
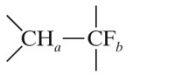
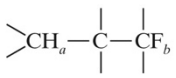
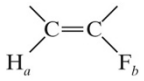
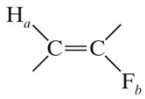
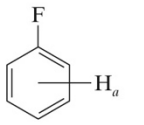
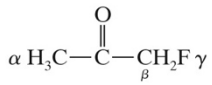
Compound	*J*(Hz)
sp^3	
CH_4	125.0
CH_3CH_3	124.9
$CH_3\underline{C}H_2CH_3$	119.2
$(CH_3)_3CH$	114.2
	123.0
	128.0
$PhCH_3$	129.0
CH_3NH_2	133.0
	134.0
$ROCH_3$	140.0
CH_3OH	141.0
CH_3Cl	150.0
CH_3Br	151.0
	161.0
$(CH_3O)_2\underline{C}H_2$	162.0
CH_2Cl_2	178.0
	180.0
	205.0
$CHCl_3$	209.0
sp^2	
$CH_3\underline{C}H{=}C(CH_3)_2$	148.4
$CH_2{=}CH_2$	156.2
C_6H_6	159.0
	160.0
$C{=}C{=}C{-}H$	168.0
	170.0
$CH_3\underline{C}H{=}O$	172.4
	178.0
$NH_2\underline{C}H{=}O$	188.3
$=COH(OR)$	195.0
$CH_3\underline{C}HX$, X=halogen	198.0
	238.0
sp	
$CH{\equiv}CH$	249.0
$C_6H_5C{\equiv}CH$	251.0
$HC{\equiv}N$	269.0

TABLE 4.2 Some $^2J_{CH}$ Values

Compound	*J*(Hz)
sp^3	
$C\underline{H}_3CH_3$	−4.5
$C\underline{H}_3CCl_3$	5.9
$R\underline{C}(=O)C\underline{H}_3$	6.0
$\underline{C}H_3C\underline{H}{=}O$	26.7
sp^2	
$*C_6H_6$	1.0
$C\underline{H}_2{=}C\underline{H}_2$	2.4
$C{=}C(\underline{C}H_3)\underline{H}$	5.0
$(C\underline{H}_3)_2\underline{C}{=}O$	5.5
$CH_2{=}\underline{C}HC\underline{H}{=}O$	26.9
sp	
$C\underline{H}{\equiv}\underline{C}H$	49.3
$C_6H_5O\underline{C}{\equiv}C\underline{H}$	61.0

* ^3J = 7.6 Hz ($>^2 J$).

Proton–Fluorine

	44–81
	3–25
	0–4
	1–8
	12–40
	*o* 6–10 *m* 5–6 *p* 2
	αγ 4.3 βγ 48

Proton–Phosphorus

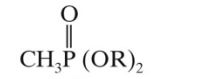
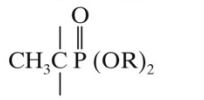
	630–707
$(CH_3)_3P$	2.7
$(CH_3)_3P{=}0$	13.4
$(CH_3CH_2)_3P$	0.5 (HCCP) 13.7 (HCP)
$(CH_3CH_2)_3P{=}0$	11.9 (HCCP) 16.3 (HCP)
	10–13
	15–20
$CH_3OP(OR)_2$	10.5–12
$P[N(CH_3)_2]_3$	8.8
$O{=}P[N(CH_3)_2]_3$	9.5

TABLE 4.3 Coupling Constants for ^{19}F, ^{31}P, D Coupled to ^{13}C

Compound	^1J(Hz)	^2J(Hz)	^3J(Hz)	^4J(Hz)
CH_3CF_3	271			
CF_2H_2	235			
CF_3CO_2H	284	43.7		
C_6H_5F	245	21.0	7.7	3.3
$(C_4H_9)_3P$	10.9	11.7	12.5	
$(CH_3CH_2)_4P^+Br^-$	49.0	4.3		
$(C_6H_5)_3P^+CH_3I^-$	88.0	10.9		
	^1J(Hz) of CH_3 = 52			
$C_2H_5(P{=}O)(OC_2H_5)_2$	143	7.1 (J_{COP})	6.9 (J_{CCOP})	
$(C_6H_5)_3P$	12.4	19.6	6.7	
$CDCl_3$	31.5			
$CD_3(C{=}O)CD_3$	19.5			
$(CD_3)_2SO$	22.0			
C_6D_6	25.5			