

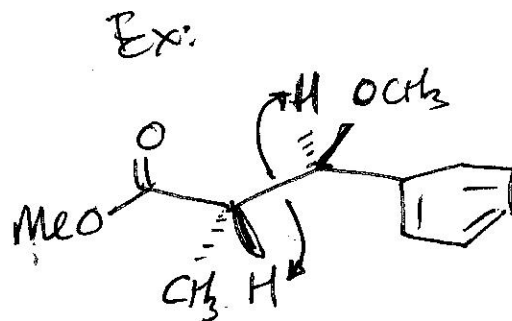
FIGURE 4.51. The vicinal Karplus correlation. Relationship between dihedral angle (ϕ) and coupling constant for vicinal protons.

relationship between dihedral angle and vicinal coupling constant is graphed. Karplus* emphasized that his calculations are approximations and do not take into account such factors as electronegative substituents, the bond angles Θ ($\angle\text{H}-\text{C}-\text{C}'$ and the $\angle\text{C}-\text{C}'-\text{H}'$), and bond lengths. Deductions of dihedral angles from measured coupling constants are safely made only by comparison with closely related compounds. The correlation has been very useful in cyclopentanes, cyclohexanes, carbohydrates, and polycyclic systems. In cyclopentanes, the observed values of about 8 Hz for vicinal cis protons and about 0 Hz for vicinal trans protons are in accord with the corresponding angles of about 0° and about 90° , respectively. In substituted cyclohexane or pyranose rings, the chair is the preferred conformation; the following relations hold and dihedral angles of substituents follow from these 3J proton couplings.

	Dihedral Angle	Calculated J (Hz)	Observed J (Hz)
Axial-axial	180°	9	8-14 (usually 8-10)
Axial-equatorial	60°	1.8	1-7 (usually 2-3)
Equatorial-equatorial	60°	1.8	1-7 (usually 2-3)

Note the near-zero coupling at the 90° dihedral angle. This has been a source of frustration in attempts at fitting proposed structures to the NMR spectra.

* Karplus, M. (1959). *J. Chem. Phys.*, **30**, 11.



A modified Karplus correlation can be applied to vicinal coupling in alkenes. The prediction of a larger trans coupling ($\phi = 180^\circ$) than cis coupling ($\phi = 0^\circ$) is borne out. The cis coupling in unsaturated rings decreases with decreasing ring size (increasing bond angle) as follows: cyclohexenes $^3J = 8.8-10.5$, cyclopentenes $^3J = 5.1-7.0$, cyclobutenes $^3J = 2.5-4.0$, and cyclopropanes $^3J = 0.5-2.0$. Two-bond geminal CH_2 coupling depends on the $\text{H}-\text{C}-\text{H}$ bond angle Θ as shown in Figure 4.52. This relationship is quite susceptible to other influences and should be used with due caution. However, it is useful for characterizing methylene groups in a fused cyclohexane ring (approximately tetrahedral, $^2J \sim 12-18$), methylene groups of a cyclopropane ring ($^2J \sim 5$), or a terminal methylene group, i.e., $=\text{CH}_2$, ($^2J \sim 0-3$). Electronegative substituents reduce the geminal coupling constant, whereas sp^2 or sp hybridized carbon atoms increase it.

Geminal coupling constants are usually negative numbers, but this can be ignored except for calculations.* Note that geminal couplings are seen in routine spectra only when the methylene protons are diastereotopic.

In view of the many factors other than angle dependence that influence coupling constants, it is not surprising that there have been abuses of the Karplus correlation. Direct "reading off" of the angle from the magnitude of the 2J value is risky. The limitations of the Karplus correlations are discussed in Jackman and Sternhell (1969).

* Coupling constants are positive if antiparallel spin states have lower energy than parallel states; the opposite is true for negative coupling constants (see Section 4.1).