The Karplus Equation

The Karplus equation (equations?) describes an approximate relation between the observed vicinal coupling constant (H-C-C-H, $3J$) and the dihedral angle between the coupled protons ($\phi$, see the Newmann projection). The equation published in Karplus’s original paper$^1$ is:

$$3J_{HH'} = A + B \cos \phi + C \cos 2\phi$$

where $A = 4.22$, $B = -0.5$ and $C = 4.5$ Hz. In developing the equation, Karplus considered the effect of bond lengths and ionic substitutions in addition to the bond angles. There are many variations of the Karplus equation, however in a simplified form, the equation is expressed as follows:$^2$

$$3J = 8.5 \cos^2 \phi - 0.28 \text{ for } 0^\circ < \phi < 90^\circ$$

$$3J = 9.5 \cos^2 \phi - 0.28 \text{ for } 90^\circ < \phi < 180^\circ.$$

It can be seen that for dihedral angles of $0^\circ$ or $180^\circ$, $\cos^2 \phi = 1$, and the observed coupling constant should be large (8–10 Hz). Conversely, for dihedral angles around $90^\circ$, $\cos^2 \phi$ is close to zero, and the observed coupling constant is small (and probably unobservable) or zero. The curve in figure 1 shows this graphically.

To use the equation to predict coupling constants, it is necessary to make a physical model of the compound in question and observe the bond angles from the model. The Karplus equation works best for systems with hindered rotation (such as bicyclic systems).

It should be noted that the Karplus equation contains inherent limitations in its derivation, and should not be used to justify bond angles to within a few degrees. The nature of the equation may also be perturbed by effects such as the electronegativity of a substituent (electronegative groups reduce the coupling constant, electropositive groups increase the coupling constant), the orientation of the substituent, the hybridization of the carbon atoms, the bond lengths and the bond angles (other than $\phi$).

References


© Peter Marrs, University of Victoria Chemistry 363 NMR Notes, September 2014