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THE DEPENDENCE OF ^{13}C-^{1}H COUPLING CONSTANTS ON C-C-C BOND ANGLES

Mary W. Baum, Alberto Guenzi, Constance A. Johnson,
and Kurt Mislow

Department of Chemistry, Princeton University,
Princeton, New Jersey 08544

Summary: The relationship between one-bond ^{13}C-^{1}H coupling constants and internuclear C-C-C bond angles (θ_n) in hydrocarbons of the type R_2CH_2 is best approximated by a quadratic expression.

Some years ago, Foote[1] obtained a linear relationship between one-bond ^{13}C-^{1}H nuclear spin-spin coupling constants ($^1\underline{J}$) and internuclear C-C-C bond angles (θ_n) in cycloalkanes. It was subsequently postulated[2] that $^1\underline{J}$ could be expressed as a non-linear function of the interorbital angle (θ_o) and that a linear relationship existed between θ_n and θ_o. However, neither function satisfactorily accounts for the unexpectedly high $^1\underline{J}$ values of compounds with greatly expanded bond angles, such as di-tert-butylmethane[3] and tri-tert-butylmethane.[4] We now report the salient results of a new study, whose major conclusion is that the relationship between $^1\underline{J}$ and θ_n is approximated by a quadratic expression which differs significantly from the previously described relationships,[1,2] and which necessitates a revision of the postulate[2] that θ_o is a linear function of θ_n. The coefficients in the quadratic expression were evaluated by fitting a polynomial to experimental values for $^1\underline{J}$ and θ_n in a set of nine hydrocarbons of the type R_2CH_2 (Table 1).[5-17] The central bond angles in this set range from 60 to 129°, and the C-CH_2-C fragments have local $\underline{C}_{2v}$ symmetry on the NMR timescale. A plot of the empirical relationship (eq. 1) is shown in Figure 1.

$$^1\underline{J} = 256.05 - 2.0917\,\theta_n + 0.008202\,\theta_n^2 \qquad \text{(eq. 1)}$$

TABLE 1

Compound	^1J (Hz)	Ref.	θ_n (deg)	Ref.
cyclopropane	160.3 ± 0.9	5	60.0	
cyclobutane	133.6 ± 0.9	5	89.3	6
norbornane, C-7	131.3 ± 0.6	7	94.4 ± 1.5	8
cyclopentane	128.5 ± 0.6	5	104.5	9
cyclohexane	125.1 ± 0.6	5	111.3 ± 0.3	10
cycloheptane	123.6 ± 0.6	5	114.9 ± 0.7	11
cyclodecane	124.4 ± 0.5	12	116.1 ± 1.1	13
di-*tert*-butylmethane	121.7 ± 0.5	12	125	14
bis(9-triptycyl)methane	123.0 ± 0.5	12	129.0	16

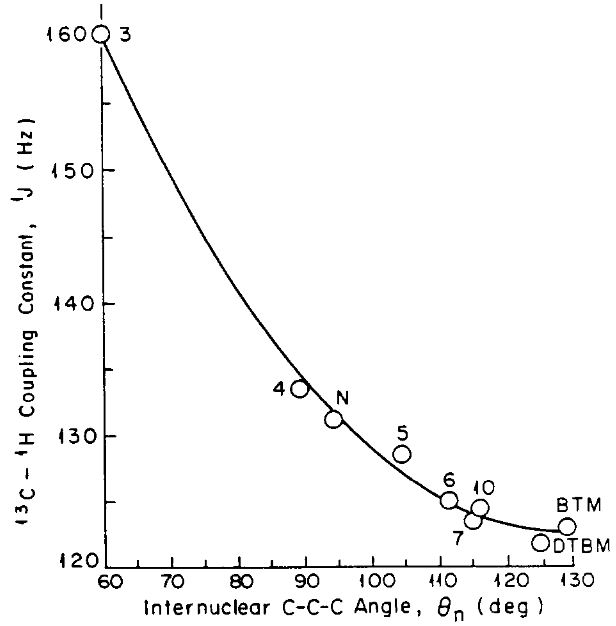

FIGURE 1

^1J as a function (eq. 1) of internuclear C-C-C angle (data from Table 1). Numerals refer to the ring sizes of the corresponding cycloalkanes, and letters to C-7 in norbornane (N) and to the central bond angles in di-*tert*-butylmethane (DTBM) and bis(9-triptycyl)methane (BTM).

The curvature of this function correlates well with the observed invariance of ^{1}J at 123-124 Hz for values of $130^{\circ} > \theta_n > 115^{\circ}$. This invariance is predictable even when di-*tert*-butylmethane and bis(9-triptycyl)methane are removed from the basis set and a polynomial is fitted to the values of ^{1}J and θ_n in the remaining set of seven cyclic hydrocarbons. The quadratic relationship thus obtained[18] yields values of 123.7 and 123.9 Hz for di-*tert*-butylmethane and bis(9-triptycyl)methane, respectively, in good agreement with the found values.

For local C_{2v} symmetry, θ_o's may be calculated from the experimental ^{1}J's according to eq. 2.[2] Combining these values with the corresponding θ_n's yields an empirical expression for orbital following (eq. 3)[19] which may prove useful in providing estimates of ^{1}J values from bond angles for hydrocarbons of the type R_3CH, $R_2R'CH$, and $RR'R''CH$ with local C_{3v}, C_s, and C_1 symmetry at the methine carbon, respectively.[2]

$$^{1}J = 250(1 + \cos\theta_o)/(1 - \cos\theta_o) \qquad \text{(eq. 2)}$$

$$\theta_o = 84.82 + 0.3853\,\theta_n - 0.001473\,\theta_n^2 \qquad \text{(eq. 3)}$$

Thus, for example, $^{1}J = 121.9$ Hz calculated[20] for tri-*tert*-butylmethane is comparable to the experimental value of 124 ± 1 Hz.[21] Of course, the limitations inherent in eq. 1 restrict application to systems with $\theta_n <$ ca. 130°.

That the present findings can be extended to systems other than hydrocarbons is suggested by a preliminary study of cyclic ethers[22] and dialkylcarbinols,[23] whose behavior parallels that of the hydrocarbons in Figure 1, most notably in the insensitivity of ^{1}J to changes in θ_n for large values of θ_n. The present findings may also serve a heuristic function in the development of more sophisticated theoretical models for ^{13}C-^{1}H spin-spin coupling.[24]

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