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CORRELATION OF ^{13}C-H SPIN-SPIN COUPLING CONSTANTS AND INTERNUCLEAR ANGLES IN CYCLIC MOLECULES

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A linear function correlates the ^{13}C-H nuclear spin-spin coupling constant J (in c.p.s.) and the fractional s-character (ρ_H) of the carbon a.o. from which the C-H bond is formed[1]:

$$J = 500\ \rho_H \qquad \underline{1}$$

Recently Foote[2] has reported that J in cycloalkanes appears to be related to the internuclear C-C-C bond angle θ_n by a linear function. Similarly, Laszlo and Schleyer[3] have observed a linear relationship between J and the C-C-C internuclear bond angle in C-CH=C systems.

Foote's data are reasonably approximated (Table I) by equation 2:

$$J = 203 - 0.720\ \theta_n \qquad \underline{2}$$

and from 1 and 2 it follows that θ_n is a linear function of ρ_H. This result is surprising since "hybridization would be expected to be more closely connected with interorbital than interatomic angle"[2].

Using normalized and orthogonalized hybrid bonding orbitals[4], the following relationships obtain for the average local C_{2v} symmetry of the central carbon atom in $C-CH_2-C$:

$$2\rho_H + 2\rho_C = 1 \qquad \underline{3}$$

$$\rho_C\,(1 + \lambda^2) = 1 \qquad \underline{4}$$

$$\lambda^2 \cos\theta_o = -1 \qquad \underline{5}$$

where ρ_C is the fractional s-character of the central carbon a.o. from which the C-C bond is formed, λ is the mixing coefficient which determines the p-character of the hybrid ($s+\lambda p$) a.o. bonding to carbon, and θ_o is the interorbital C-C-C bond angle, i.e. the angle subtended by the orbital axes at the central carbon atom. Combining $\underline{1}$, $\underline{3}$, $\underline{4}$ and $\underline{5}$:

$$J = \frac{250\,(1 + \cos\theta_o)}{(1 - \cos\theta_o)} \qquad \underline{6}$$

When θ_n is taken as equal to θ_o, it is found (Table I) that equation $\underline{6}$ does not satisfactorily correlate J and θ_n <u>except</u> for the case of perfect tetrahedral symmetry ($\theta_n = 109.5°$, $J = 125$ c.p.s.). This is the position of minimum angle strain and of maximum overlap where the bonding orbital axes and the internuclear lines coincide, i.e. $\theta_n = \theta_o$ at 109.5°. It has been pointed out[4,5] that any departure from this angle which is introduced by the geometric constraints of ring formation destroys the σ-character of the bond and results in bond "bending".

Let us now postulate (a) that with increasing angle bending, expressed as $\Delta\theta_n = |\theta_n - 109.5°|$, there is a corresponding increase in orbital bending $\Delta\theta_o = |\theta_o - 109.5°|$, where $\Delta\theta_o < \Delta\theta_n$ for a given θ_n (orbital following), and (b) that the correspondence between the two changes may be expressed to a first approximation by a linear relationship, i.e., that $d\Delta\theta_o/d\Delta\theta_n$ is a constant, c ($c \neq 1$). Integration gives:

$$\theta_o = c\theta_n + 109.5\ (1-c) \qquad \underline{7}$$

The constant c may be evaluated by fixing θ_o at 102°52' for $\theta_n = 60°$, the value for cyclopropane[6], whence:

$$\theta_o = 0.1340\ \theta_n + 94.83 \qquad \underline{8}$$

Combination of 6 and 8 gives J as a non-linear function of θ_n. Agreement with found values is good (Table I). Even though the analytical expression is not linear, the curvature of the plot of J vs. θ_n is so slight that the combined function closely approximates Foote's empirical straight line[2].

The present approach may be extended to methine systems R_3CH having local C_{3v} symmetry at the carbon atom bearing the hydrogen. For normalized and orthogonalized orbitals:

$$\rho'_H + 3\rho'_C = 1 \qquad \underline{9}$$

For a given value of θ_n (and thus of θ_o) in the local C_{2v} and C_{3v} systems, $\rho_C = \rho'_C$. Therefore, combining 1, 3 and 9:

$$J' = 3J - 250 \qquad \underline{10}$$

where J' is the J_{C-H} spin-spin coupling constant of the local C_{3v} system. The empirical correlation 2 for C_{2v} thus becomes 11 for C_{3v}, and the analytical expression 6 is converted to 12:

$$J' = 359 - 2.16\,\theta_n \qquad \underline{\underline{11}}$$

$$J' = \frac{500\,(1 + 2\cos\theta_o)}{(1 - \cos\theta_o)} \qquad \underline{\underline{12}}$$

Combination of 12 and 8 then affords J' as a function of θ_n. This treatment gives a J-value for the cubane system which is in satisfactory agreement with the experimental quantity[7] (Table II).

With the appropriate modification[4] of equations 3 - 5 and with a knowledge of the molecular geometry, the present treatment might be extended to systems of lower symmetry than local C_{nv}. For example, in bicyclo[2.2.1] heptadiene, where the bond angles are known[8], the bridgehead carbon has local C_s symmetry and we calculate a J_{C-H} of 145.6 c.p.s. This is in good agreement with the found[9] value of 146 c.p.s.

An extension of the preceding arguments leads to several predictions:

(a) In bicyclo[1.1.1]pentane[10] the θ_n-values of the methine (θ_1, local C_{3v} symmetry) and methylene (θ_2, local C_{2v} symmetry) carbons are correlated by the geometric relationship $2(1-\cos\theta_1) = 3\cos^2\theta_2/2$. It follows that the two values of J_{C-H} should be linked together by equations 2 and 11, or by equations 6, 12 and 8.

(b) Tetrahedrane (C_4H_4), which has local C_{3v} symmetry, should have a J_{C-H} of about 225 c.p.s. (Table II), i.e. lower than that of acetylene[1] (251 c.p.s.) but higher than those of tricyclo[$4.1.0.0^{2,7}$]heptane[11] (200 c.p.s.) and 4,5-diphenyltricyclo[$1.1.1.0^{4,5}$]pentan-2-one[12] (190 c.p.s.).

(c) Prismane or "Ladenburg benzene" (C_6H_6), which has local C_s symmetry, should have a J_{C-H} of about 180 c.p.s.

We note that relationships not unlike those proposed in this paper may also obtain in the ground state triplet methylenes[13]. E.s.r. measurements (^{13}C hyperfine splittings) suggest that bond bending in fluorenylidene involves orbital following similar in magnitude to that given by our equation 8.

Table I

			J_{C-H} (c.p.s.)		
Compound	θ_n^a	Found[a]	[1]	[2]	[3]
Cyclopropane	60.0	161	159.8	750.1	158.9
Cyclobutane	89.3	134	138.7	256.2	138.0
Cyclobutanone	90.0	133.5	138.2	250.0	137.5
Norbornadiene-7	96.7	135.5	133.4	197.7	133.1
Cyclopentane	103.3	128	128.6	156.5	128.8
Cyclohexane	110	123,124	123.8	122.6	124.6
Cycloheptane	112	123	122.4	113.7	123.3
Cycloöctane	112	122	122.4	113.7	123.3
Cyclodecane	116	118	119.5	97.6	121.0
Cyclododecane	112	123	122.4	113.7	123.3

[a] Data from references (1) and (2).

[1] Calcd. from equation 2.

[2] Calcd. from equation 6 assuming $\theta_o = \theta_n$

[3] Calcd. from equations 6 and 8.

Table II

Compound	θ_n	Found	[1]	[2]
Tetrahedrane	60.0	?	229.4	226.7
Cubane	90.0	160 ± 5[a]	164.6	162.5
Adamantane	109.5	(125)	122.4	125.0

[a] Based on dicarbomethoxycubane, ref. 7.

[1] Calcd. from equation 11

[2] Calcd. from equations 12 and 8

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