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THE EFFECT OF BOND ANGLE ON HYBRIDIZATION

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THE discovery that the C^{13}-H nuclear spin-spin coupling constant appears to be a linear function of the amount of s-character in the carbon orbital from which a C-H bond is formed[1] has made direct estimation of hybridization possible for the first time. In cyclopropane[1a] and certain cyclopropenes[2] the C-H bonds are found by this technique to contain an unusually large amount of s-character, a reflection of increased p-character in the internal bonds which are forced by the geometry of the system to maintain abnormally small angles with one another.

Because angle strain effects are known to be extremely important in determining reactivities and other properties of strained systems,[3] it is important to know whether or not changes in hybridization also occur where deviations from normal angle are less extreme than those in three-membered rings. As a means of answering this question, we have measured $J_{C^{13}\text{-}H}$ in several cyclic compounds in which C-C-C bond angles vary over a wide range.

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[1] a N. Muller and D. E. Pritchard, J. Chem. Phys. 31, 768, 1471 (1959); b J. N. Shoolery, ibid. 31, 1427 (1959); c C. Juan and H. S. Gutowsky, J. Chem. Phys. 37, 2198 (1962).

[2] G. L. Closs, Proc. Chem. Soc. 152 (1962).

[3] See the recent review by Ya. I. Gol'dfarb and L. I. Belen'kii Russian Chemical Reviews 29, 214 (1960).

Unfortunately, the satellite peaks are very broad in the simple cyclanes[4] as a consequence of virtual coupling,[5] and high accuracy of measurement is not possible; nevertheless, the observed variations in the coupling constant are considerably larger than the experimental error (estimated at ± 1-2 cps).

The measured coupling constants are listed in the accompanying table, along with the per cent s-character in the C-H bonds (calculated from the data by means of the reported[1] relationship) and the C-C-C interatomic angles, either experimental or computed. Detectable changes in hybridization do in fact appear to occur in these systems, even with rather small deviations from the tetrahedral angle. A steady decrease in the amount of s-character in the external bonds (which must reflect a corresponding increase in the s-character of the C-C-C bonds) occurs in the series cyclopropane-cyclodecane, closely paralleling the increase in bond angles. Cyclododecane, in which the average bond angle is only slightly larger than normal, has a hybridization close to that of cyclohexane.

In the accompanying figure the coupling constants are plotted against C-C-C interatomic angle. In spite of the fact that hybridization would be expected to be more closely connected with <u>interorbital</u> than interatomic angle (if the bonds are bent[6]), a straight line fits the data well, except that the points for cyclobutane and cyclobutanone fall somewhat too low. This correlation permits immediate estimation of C-C-C interatomic angles if $J_{C^{13}-H}$ is measurable, although there is as yet insufficient data

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[4] For example, in cyclooctane the peak width at half height is roughly 7 cps; all measurements were made on neat liquids at 60 mc with a Varian A-60 spectrometer.

[5] J. I. Musher and E. J. Corey, Tetrahedron **18**, 791 (1962).

[6] as they must be, at least in cyclopropane, if orthogonal orbitals are used: see C. A. Coulson and T. H. Goodwin, J. Chem. Soc. 2851 (1962) and references therein; but cf. G. S. Handler and J. H. Anderson, Tetrahedron **2**, 345 (1958).

Table 1

Compound	$J_{C^{13}\text{-}H}$ (cps)	% s-Character in C-H Bond[1a]	C-C-C Interatomic Angle
1. cyclopropane	161[1a]	32	60°
2. cyclobutane	134	27	89.3°[7]
3. cyclopentane	128; 128[1a]	26	103.3°[8]
4. cyclohexane	124; 123[1a]	25	109.5°[8b]
5. cycloheptane	123	25	112°[9]
6. cyclooctane	122	24	112°[10]
7. cyclodecane	118	24	116°[11]
8. cyclododecane	123	25	112°[12]
9. cyclobutanone-α	131 (lower satellite)		
-β	136 (upper satellite)		
average	133.5	27	90°
10. norbornadiene-7	135	27	96.7°[13]

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[7] calculated, assuming 160° dihedral: J. D. Dunitz and V. Schomaker, J. Chem. Phys. **20**, 1703 (1952).

[8] a K. S. Pitzer and W. E. Donath, J. Amer. Chem. Soc. **81**, 3213 (1959); b J. B. Hendrickson, ibid, **83**, 4537 (1961).

[9] J. B. Hendrickson, ibid, **84**, 3355 (1962).

[10] J. B. Hendrickson, private communication.

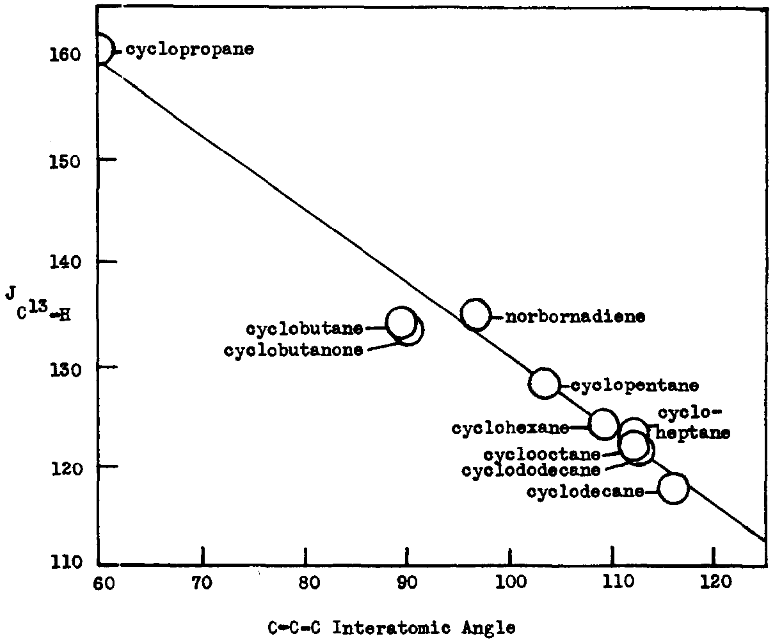
[11] average value for cis and trans-1,6-diaminocyclodecane dihydrochlorides: J. D. Dunitz and K. Venkatesan, Helv. Chim. Acta **44**, 2033 (1961); E. Huber-Buser and J. D. Dunitz, ibid. **44**, 2027 (1961).

[12] average value: J. D. Dunitz and H. M. M. Shearer, ibid. **43**, 18 (1960).

[13] a W. C. Hamilton, Ph. D. Thesis, California Institute of Technology, 1954; b W. G. Woods, R. A. Carboni, and J. D. Roberts, J. Amer. Chem. Soc. **78**, 5653 (1956).

to predict the accuracy of such a calculation.

Fig. 1



The apparent changes in hybridization provide a rationalization for many of the unusual properties of strained systems. Streitwieser has suggested that the unreactivity of cyclopropyl halides in solvolysis is a consequence of the increased difficulty of localizing a p-orbital on an atom in which more than the usual amount of p-character is used in the C-C bonds.[14] Such an explanation can be extended to account for the unreactivity of saturated 7-norbornyl derivatives in solvolysis[13b,15] and for the high

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[14] A. Streitwieser, Chem. Revs. 56, 573 (1956).

[15] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, J. Amer. Chem. Soc. 77, 4183 (1955). The 7-angle of norbornane (96.3°) is nearly identical to that in norbornadiene: see C-h. Wong and A. F. Berndt, Ph. D. Theses, California Institute of Technology, 1957.

reactivity of cyclononyl and cyclodecyl tosylates.[16] It should be observed, however, that the hybridization arguments are probably equivalent to the more conventional ones based on strain differences in the ground and transition states ("I" strain[17]).[18]

A recent study of the rates of base-catalyzed enolization of cyclanones strongly suggested that the acidity of the α-hydrogens decreases regularly from cyclobutanone to cycloheptanone;[19] this acidity sequence parallels the decrease in s-character in the C-H bonds of the corresponding cyclanes, as it should if hybridization controls acidity.[20]

Ketone and lactone carbonyl stretching frequencies in the infrared are well known to increase with decreasing ring size; the trend is again consistent with an increase in s-character of the carbonyl σ-bond with a decrease in ring size.

That hybridization and bond angle must be closely related appears to be demonstrated; further experimentation is needed to establish the generality of the observed linear correlation between $J_{C^{13}-H}$ and bond angle.

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[16] [a] R. Heck and V. Prelog, *Helv. Chim. Acta* **38**, 1541 (1955); [b] H. C. Brown and G. Ham, *J. Amer. Chem. Soc.* **78**, 2735 (1956).

[17] H. C. Brown, *J. Chem. Soc.* 1248 (1956).

[18] P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.* **83**, 183 (1961).

[19] H. Shechter, M. J. Collis, R. Dessy, Y. Okuzumi, and A. Chen, *ibid.* **84**, 2905 (1962).

[20] An almost simultaneous study, however, found that cycloheptanone and cyclooctanone reacted *faster* than cyclohexanone, and pointed out the importance of the angle between the C-H bond and the ketone group: A. Schriesheim, R. J. Muller, and C. A. Rowe, Jr., *ibid.* **84**, 3164 (1962). The reason for disagreement in relative rates is unclear.

[21] [a] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, second ed. (1958), p. 148, 185; [b] K. B. Wiberg and B. J. Nist, *J. Amer. Chem. Soc.* **83**, 1226 (1961); [c] C. A. Coulson and W. A. Moffitt, *Phil. Mag.* **40**, 1 (1949).