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THE DEPENDENCE OF ONE-BOND ^{13}C-^{13}C COUPLING CONSTANTS ON BOND ANGLES - A COMMENT

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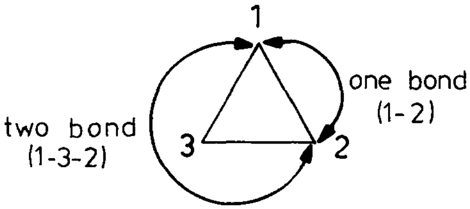
Abstract: The validity of a published relationship between $^1J_{CC}$ and bond angle is questioned on the grounds that the number of coupling-pathways contributing to J is not the same for all of the compounds considered.

In early 1982 Mislow and coworkers[1] reported a quadratic relationship between one-bond carbon-hydrogen coupling constants and the CCC bond angle in systems with a central CH_2 group. Recent work by Pomerantz and Bittner[2] has produced a similar quadratic relating one-bond carbon-carbon coupling constants in C-CH_2-C systems to the CCC angle,θ (eqn. 1).

$$^1J_{CC} = -49.04 + 1.337\theta - 0.005662\theta^2 \qquad \text{(eqn. 1)}$$

The major difference between the systems studied by Mislow and those of Pomerantz is that, while only one pathway is possible for one-bond C-H coupling, two different electronic coupling-paths are possible between adjacent carbons in cyclic molecules and, as Marshall and coworkers have shown[3], the observed coupling constant approximates closely to the sum of the expected values for each pathway (as obtained from model compounds). The contribution to $^1J_{CC}$ from the longer pathway in alicyclic molecules would be expected to be significant only when that pathway is two or at the most three bonds long since four-bond coupling constants in non-conjugated molecules are very small[4], hence limiting the effect to cyclopropanes and cyclobutanes. Thus for 1-methylcyclopropane and similar compounds both one-bond and two-bond pathways will contribute to the observed C(1)-C(2) coupling constant.



An approximate value of between -10 and -15Hz for the two-bond contribution to J_{CC} in cyclopropanes is expected from comparison of the observed carbon-carbon coupling constants for cyclopropanes with those for epoxides (allowing for substituent effects) and from the negative values of J_{CC} observed for the central bond of bicyclobutane derivatives[4]. Hence the one-bond contribution to $^1J_{CC}$ in a hydrocarbon with a 60° bond angle would be expected to be appreciably larger than the observed coupling constants in cyclopropanes.

If the cyclopropane points are excluded from the data of Pomerantz and Bittner (Table 1) and the numbers are replotted (Figure 1), a linear relationship between $^1J_{CC}$ and CCC bond angle, θ, can be obtained (eqn. 2).

Table 1. $^1J_{CC}$ and internuclear angles. (data taken from ref. 2)

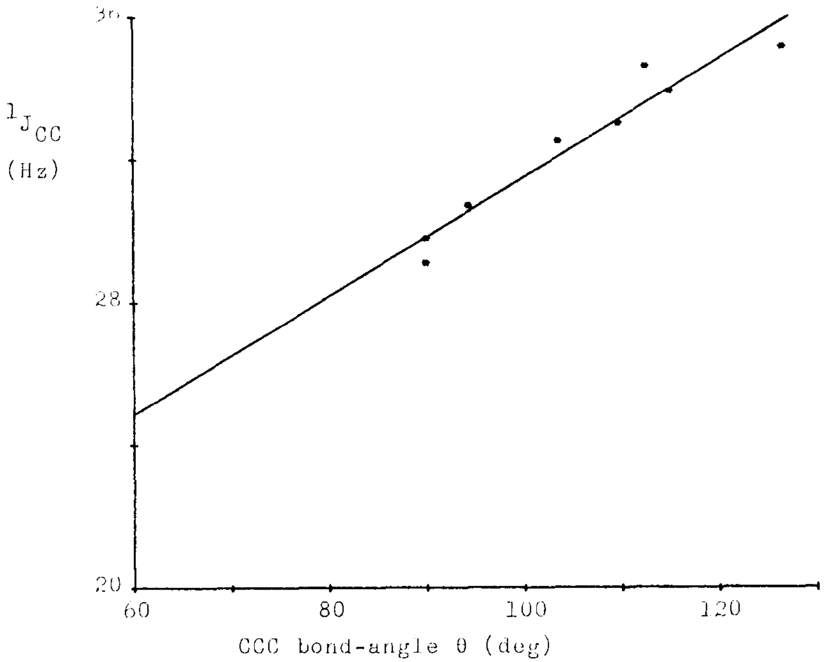
Compound	$^1J_{CC}$,Hz (bond)	θ,deg (angle)
1-methylcyclopropane	13.3 (1-2)	60 (1-2-3)
1,1-dimethylcyclopropane	12.9 (1-2)	60 (1-2-3)
1,1,3,3-tetramethylcyclobutane	29.8 (1-2)	90 (1-2-3)
1-methylcyclobutane	29.1 (1-2)	90 (1-2-3)
norbornane	30.7 (1-7)	94.4 (1-7-4)
"	32.5 (1-2)	103.5 (1-2-3)
bicyclo 2.2.2 octane	33.0 (1-2)	109.7 (1-2-3)
pentane	34.6 (2-3)	112.5 (2-3-4)
1,1-dimethylcyclohexane	33.9 (1-2)	115.0 (1-2-3)
di-tert-butylmethane	35.14 (2-3)	126.5 (2-3-4)

$$^1J_{CC} = 14.91 + 0.166\theta \qquad \text{(eqn. 2)}$$

The correlation coefficient is 0.97 and the standard deviation is 0.55Hz. Extrapolation of this line to θ=60° gives an estimated value for the one-bond contribution to J_{CC} in cyclopropanes of 24.85Hz, and by subtraction a two-bond contribution of -11 to -12Hz, in good agreement with Hansen's predicted value[4].

Since similar arguments can also be applied to the three-bond contribution to $^1J_{CC}$ in cyclobutane derivatives, this analysis can be improved further, although at present the signs and magnitudes of such three-bond contributions are not known.

Figure 1.



In conclusion, while Mislow's quadratic relationship between one-bond carbon-hydrogen coupling constants and CCC bond angle is valid since the same coupling-pathway is involved in every case, the angle-dependence of one-bond carbon-carbon coupling constants is complicated in small-ring molecules by the existence of additional coupling-pathways involving more than one bond and the sizeable contributions these can make to the observed coupling constant,J. Hence it is dangerous to draw conclusions about the relationship between $^1J_{CC}$ and bond-angles based on data obtained from molecules in which different numbers of pathways are contributing to the overall coupling constant.

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