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C-C-C BOND ANGLE DEPENDENCE OF ONE BOND ^{13}C-^{13}C COUPLING CONSTANTS

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Abstract: It has been observed that one-bond ^{13}C-^{13}C coupling constants are almost invariant with C-C-C bond angles between tetrahedral and 127° for hydrocarbons where the central atom is a CH_2 group. An empirical quadratic equation is obtained which relates $^{1}J_{CC}$ with the internuclear C-C-C angle, θ.

The recent report of Mislow and coworkers[2] on the dependence of one bond ^{13}C-H coupling constants on C-C-C bond angles has prompted us to now report our findings concerning one bond ^{13}C-^{13}C coupling constants. Mislow has reported that as the C-C-C bond angle, in a system where the central carbon atom is a CH_2 group, becomes larger than tetrahedral, $^{1}J_{CH}$ decreases but much less than expected from previous work. In fact, the value for di-*tert*-butylmethane ($^{1}J_{CH} = 121.7$ Hz) and bis(9-triptycyl)methane ($^{1}J_{CH} = 123.0$ Hz), where the angles are given as 125° and 129° respectively,[2] are not very different from the "normal" value of about 125 Hz for undistorted, tetrahedral species.[3] Indeed, Mislow obtained a quadratic expression (eqn. 1)

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

which relates $^{1}J_{CH}$ to the C-C-C angle, θ_n. As was pointed out, large values of θ_n (115-130°) give rise to an almost invariant one bond C-H coupling constant of about 123-124 Hz.

Our interest in ^{13}C-^{13}C coupling constants in strained systems[4] has led us to also examine systems with large C-C-C bond angles. We now report that a relationship analogous to that reported by Mislow exists between $^{1}J_{CC}$ and the internuclear angle, θ, for systems where the central carbon atom is a CH_2 group. In addition, there is a leveling off of $^{1}J_{CC}$ for angles from tetrahedral to 130°. Thus, for example, we have obtained a value for $^{1}J_{C_2-C_3}$ in 2,2,4,4-tetramethylpentane, di-*tert*-butylmethane (**1**), of 35.14 ±0.04 Hz,[5] not significantly different

$$(CH_3)_3C\text{-}CH_2\text{-}C(CH_3)_3$$

1

from the generally accepted value of about 35 Hz for a tetrahedral carbon atom.[3] This is in spite of the large C_2-C_3-C_4 bond angle of about 126.5°.[6]

Table 1 gives data for $^1J_{CC}$ and the internuclear angle, θ, for systems where the central carbon is a CH_2 group. Figure 1 shows a plot of the one bond ^{13}C-^{13}C coupling constant _vs_. the C-C internuclear angle, θ. The curve drawn through the ten points, which span a range of 66.5° and 22.2 Hz, is the best fit quadratic expression, eqn. 2. The standard deviation is 0.58 Hz.

Table 1. $^1J_{CC}$ and C-C-C Internuclear Angles

Compound	$^1J_{CC}$, Hz (bond)	Ref.	θ, deg (angle)	Ref.
1-methylcyclopropane	13.3 (1-2)	7	60 (1-2-3)	8
1,1-dimethylcyclopropane	12.9 (1-2)	9	60 (1-2-3)	11
1,1,3,3-tetramethylcyclobutane	29.8 (1-2)	10	90 (1-2-3)	12
1-methylcyclobutane	29.1 (1-2)	7	90 (1-2-3)	12
norbornane	30.7 (1-7)	9	94.4 (1-7-4)	13
norbornane	32.5 (1-2)	9	103.5 (1-2-3)	13
bicyclo[2.2.2]octane	33.0 (1-2)	9	109.7 (1-2-3)	14
pentane	34.6 (2-3)	9	112.5 (2-3-4)	16
1,1-dimethylcyclohexane	33.9 (1-2)	9	115.0 (1-2-3)	15
$(CH_3)_3C$-CH_2-$C(CH_3)_3$	35.14 (2-3)	this work	126.5 (2-3-4)	6

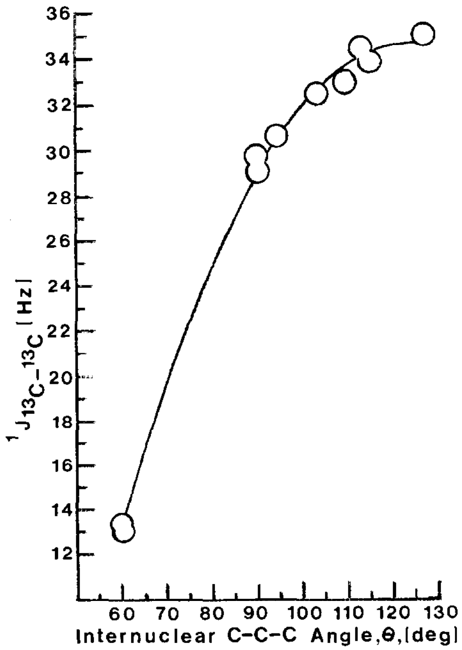
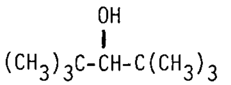


FIGURE 1

$$^{1}J_{CC} = -49.04 + 1.377\,\theta - 0.005662\,\theta^{2} \qquad \text{(eqn. 2)}$$

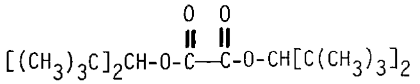
It shows an almost invariant value of $^{1}J_{CC}$ on going from the 109.5° tetrahedral angle [J(calc) = 33.9 Hz] to the highly distorted value of 130° [J(calc) = 34.4 Hz] with the maximum [J(calc) = 34.7 Hz] occurring at 121.6°. It should be noted that eqn. 1 also predicts a maximum at an angle of 127.5°, similar to the 121.6° value found here.

Further evidence for this leveling off of $^{1}J_{CC}$ with large C-C-C bond angles comes from our measurement of $^{1}J_{C_2-C_3}$ in 2,2,4,4-tetramethyl-3-pentanol (2) of 38.3 ± 0.1 Hz.[17] This, value is essentially identical with the corresponding value for $^{1}J_{C_1-C_2}$ in isopropanol of 38.4 Hz[20] and for $^{1}J_{C_2-C_3}$ in 3-pentanol of 37.9 Hz.[10] Because of the lack of structural information for the alcohols of interest, a plot similar to that in Figure 1 cannot be made. Although the structure of 2 has not been reported, it is reasonable to assume that the C_2-C_3-C_4 bond angle is close to the value of 124° reported for the bis-(di-*tert*-butylmethyl) ester of oxalic acid (3) and is quite a bit larger than the 112.3° bond angle reported for isopropanol.[22] Thus the situation here appears to be analogous to that in the hydrocarbons.



$$(CH_3)_3C\text{-}\overset{\displaystyle OH}{\overset{|}{C}}H\text{-}C(CH_3)_3$$

2



$$[(CH_3)_3C]_2CH\text{-}O\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}O\text{-}CH[C(CH_3)_3]_2$$

3

In conclusion, current ideas about the relationship between $^{1}J_{CC}$ and $^{1}J_{CH}$ and bond angles need revision as do the relationships between these coupling constants and hybridization, since hybridization is a function of bond angles, or, more accurately, interorbital angles.

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