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CORRELATION OF ${}^{13}C$–${}^{1}H$ SPIN-SPIN COUPLING CONSTANTS AND THE SUM OF INTERNUCLEAR ANGLE DISTORTIONS IN SATURATED HYDROCARBONS

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Abstract—An empirical relationship between one bond carbon-hydrogen spin-spin coupling constants, ${}^1J_{CH}$ and the sum of internuclear angle distortions, $\Sigma\Delta\Theta$ has been found. The proposed formula gives ${}^1J_{CH}$ values with a 3.22 Hz average deviation from the experimental values (30 data points, s.d. = 2.74) and useable for both the methylene and methine carbons of saturated hydrocarbons.

The effect of valence angles on hybridization and thereby on the ${}^{13}C$–${}^{1}H$ coupling constants is well known.[1] Using a relatively small data set of mixed cyclic compounds, Foote proposed[2] a linear relationship between the one bond ${}^{13}C$–${}^{1}H$ coupling constant, ${}^1J_{CH}$ and the internuclear bond angle, Θ_n. In a semi-empirical approach for carbons having local c_{2v} symmetry on the NMR time-scale Mislow presented[3] a formula by assuming a linear relationship between the interorbital and internuclear angles. Although in the proposed equation ${}^1J_{CH}$ is a nonlinear function of Θ_n, the curvature of the plot of J vs Θ_n was so slight that it approximated well Foote's empirical straight line relationship and therefore gave satisfactory results for Foote's data set. However, as it turned out later, this formula failed to give correct coupling constants in the case of expanded bond angles, such as the central bond (C–C–C) of di-terc-butylmethane.[4] To overcome this problem Mislow fitted[5] a polynomial to experimental values for ${}^1J_{CH}$ and Θ_n in a set of nine hydrocarbons. Two compounds with expanded bond angles have been added to and the two unsaturated compounds were removed from Foote's original data set. The obtained empirical quadratic equation gives good results for methylene carbons possessing local c_{2v} symmetry, but useless in many other cases, e.g. in the case of methine carbons (missing c_{3v} symmetry) which are of special interest. For the general case of three substituents R_a, R_b, R_c attached to a methine carbon Mislow used an extended semi-empirical treatment[6] which seems to work well, although the calculated ${}^1J_{CH}$ values are somewhat lower than the experimental ones. The interorbital angles, $\Theta_{ij} = \Theta_{ij}$ are calculated from Θ_n (see Ref. 5), the mixing coefficients from the set of equation $\lambda_i\lambda_j \cos\Theta_{ij} = -1$. The fractional s-character, p of carbon a.o.'s from which the four bonds are formed are related to the λ-s by the expression $p_i = 1/1 + \lambda_i^2$ and sum to unity. ${}^1J_{CH} = 500p_H = 500[1 - (p_a + p_b + p_c)]$.

In an effort to find a general solution for the problem, we found that an empirical correlation exists between the ${}^1J_{CH}$ values and the sum of the valence bond distortions, $\Sigma\Delta\Theta$. In this paper the idea and the results obtained by the new formula are reported. Our starting point was rather simple, we thought that we should take into account at least three bonds of the central carbon atom because any distortion in any of them can affect the hybridization state of C–H bond in question. (In our approach we gave equal weight to the C–H and C–C bonds, which is a rough approximation, nevertheless, it has been justified by the results.) We characterized the distortions with the difference of the methane internuclear angle (109.5°) and the internuclear angle of the actual bond ($\Delta\Theta = 109.5° - \Theta_n$). In highly strained structure $\Delta\Theta$ can be a large positive number and in the case of expanded angles it's value is negative. As it is well known[1] that angles smaller than 109.5° increase ${}^1J_{CH}$ (${}^1J_{CH} = 125.0$ Hz) and angles larger than this value have the opposite effect,[7] the summation of these positive and negative distortions seemed to be reasonable. Examples for the calculation of $\Sigma\Delta\Theta$ are given in Fig. 1. Our basis data set consisted of 30 data points, all hydrocarbons (see Table 1).

The ${}^1J_{CH}$ vs $\Sigma\Delta\Theta$ relationship was best approximated by a quadratic expression (see Fig. 2 also), the coefficients of eqn (1) were obtained by fitting a polynomial to experimental values for ${}^1J_{CH}$ and $\Sigma\Delta\Theta$.

$${}^1J_{CH} = 129.09 + 0.5354\Sigma\Delta\Theta + 0.001094(\Sigma\Delta\Theta)^2. \quad (1)$$

The calculated and experimental values are given in Table 1. As it can be seen the proposed equation gives satisfactory agreement with the experimental data and it's validity isn't restricted to certain symmetry classes. The two remarkable exceptions are the H8 proton of nortricyclane and the proton of cubane (see Table 1 and also Fig. 2). In the case of nortricyclane an effect similar to that one observed in cyclopropane (see later) has been assumed, but no explanation was found for the unexpectedly low coupling of cubane. The average deviation between the experimental and calculated values was 3.22 Hz (s.d. = 2.74). One way to reduce further this figure would be the use of more exact internuclear angles. In many cases we calculated these angles by the molecular mechanistic method,[25] although in general, the agreement between the experimental and calculated angles is rather good (especially for hydrocarbons), sometimes the deviations are substantial. On the other side the experimental data show the same kind of deviations.

In comparison with Mislow's semi-empirical treatment[6] of the methine protons and also with his quadratic equation[5] for the methylene protons with c_{2v} symmetry,

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Table 1. Internuclear angles, calculated and experimental $^1J_{CH}$ values for the studied hydrocarbon data set

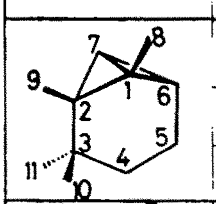
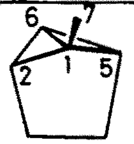
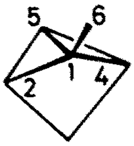
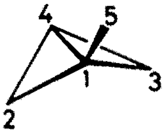
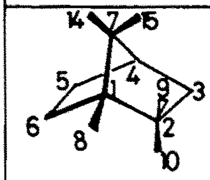
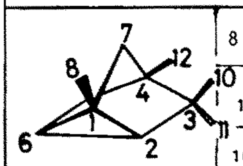
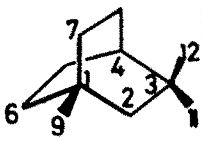
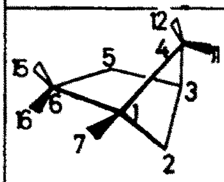
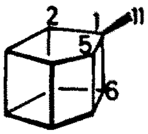
Compound	H	θ_n,deg	Ref.	Calculated $^1J_{CH}$ [Hz]	Experimental $^1J_{CH}$ [Hz]	Ref.
	8	2-1-6=99.5 6-1-7=61.5 2-1-7=58.6		200.4	200.3	9
	9	1-2-3=116.3 1-2-7=58.3 3-2-7=117.7	8	149.8	154.2	9
	10	2-3-4=112.4 2-3-11=109.1 4-3-11=108.8		128.1	126.2	9
	7	2-1-6=60.5 5-1-6=60.5 2-1-5=92.3	8	205.3	206.0	9
	6	4-1-2=80.66 5-1-2=60.0 5-1-4=60.0	11	215.4	212.0	9
	5	1-2-3=102.0 4-2-3=60.54 4-2-1=60.54	8	197.7	205.0	10
	8	7-1-2=102.2 7-1-6=102.1 2-1-6=109.2		137.4	140.1	
	15	1-7-4=92.53 1-7-14=113.4 4-7-14=113.4	8, 15	134.6	131.3	13
	10	1-2-3=102.8 1-2-9=112.0 3-2-9=112.8		129.6	130.3	
	8	6-1-2=60.0 7-1-2=107.0 7-1-6=107.0		161.5	174.0	
	12	3-4-5-101.5 3-4-7=101.5 5-4-7=101.5	12	142.6	148.0	14
	10	2-3-4=96.9 2-3-11=110. 4-3-11=110.		135.4	133.0	
	9	6-1-2=108.9 7-1-2=108.9 7-1-6=108.9	8	130.1	134.7	13
	11	1-2-3=109.7 1-2-12=109.6 3-2-12=110.4		128.4	125.7	
	7	6-1-2=102.0 4-1-6=102.0 4-1-2=88.2		150.0	150.5	
	11	1-4-3=93.1 1-4-12=113.6 3-4-12=113.6	15	134.5	135.1	13
	16	1-6-5=98.2 1-6-15=112.7 5-6-15=115.6		132.2	132.5	
	11	5-1-2=108.0 6-1-2=90.0 6-1-5=90.0		152.6	148.1	16

Table 1. (*Contd*)

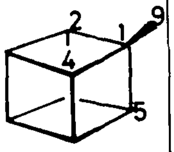
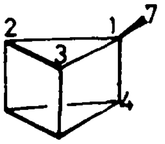
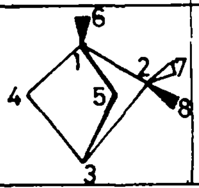
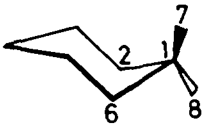
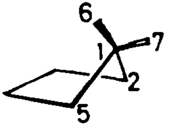
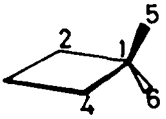
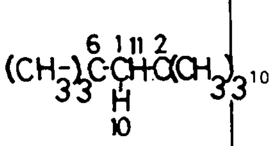
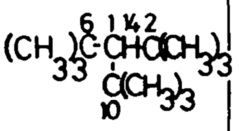
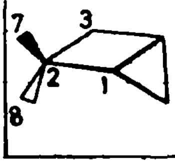
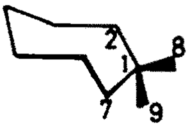
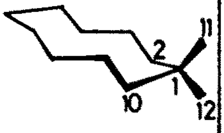
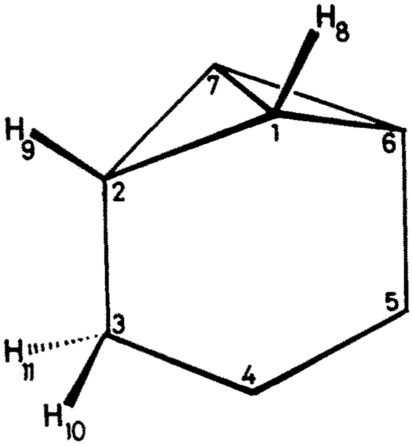
	9	4-1-2=90.0 5-1-2=90.0 5-1-4=90.0		164.1	155.0	13
	7	2-1-3=60.0 4-1-2=90.0 4-1-3=90.0		185.0	180.0	17
	6	4-1-2=89.3 5-1-2=89.3 5-1-4=89.3	25a	165.6	164.0	18
	8	1-2-3=71.5 1-2-7=116.0 3-2-7=116.0	25a	143.2	144.0	
	7	2-1-6=111.3 2-1-8=110.0 6-1-8=110.0	5	127.6	125.1	19
	6	5-1-2=104.5 5-1-7=111.0 2-1-7=111.0	5	130.1	128.5	19
	5	2-1-4=90.0 2-1-6=114.1 4-1-6=114.1	8	134.9	133.6	19
 $(CH_3)_3C{-}\underset{H}{CH}{-}C(CH_3)_3$	10	6-1-2=125.0 6-1-11=112.1 2-1-11=112.1	5	118.5	122.0	5
 $(CH_3)_3C{-}\underset{C(CH_3)_3}{CH}{-}C(CH_3)_3$	14	6-1-10=116.0 6-1-2=116.0 2-1-10=116.	20	119.1	124.0	20
	7	3-2-1=90.0. 3-2-8=111.0 1-2-8=118.0	21	134.5	134.7	22

Table 1 (*Contd.*)

	8	2-1-7=114.9 2-1-9=109.5 7-1-9=109.5	23	126.2	123.6	19
	11	2-1-10=116.1 2-1-12=108.9 10-1-12=108.9	24	126.4	124.4	5

* Calculated by equation (1).



H	INTERNUCLEAR ANGLE [°]	$\Delta\Theta$ [°]*	$\Sigma\Delta\Theta$
8	2-1-6 = 99.5	+10.0	+108.9
	6-1-7 = 61.5	+48.0	
	2-1-7 = 58.6	+50.9	
9	1-2-3 = 116.3	-6.8	+36.1
	1-2-7 = 58.35	+51.1	
	7-2-3 = 117.7	-8.2	
10	2-3-4 = 112.4	-2.9	-1.9
	2-3-11 = 109.15	+0.3	
	4-3-11 = 108.8	+0.7	

* $\Delta\Theta = 109.5° - \Theta_n$

$\Theta_{n(CH_4)} = 109.5°$

Fig. 1. Method for calculating the sum of internuclear angle distortions.

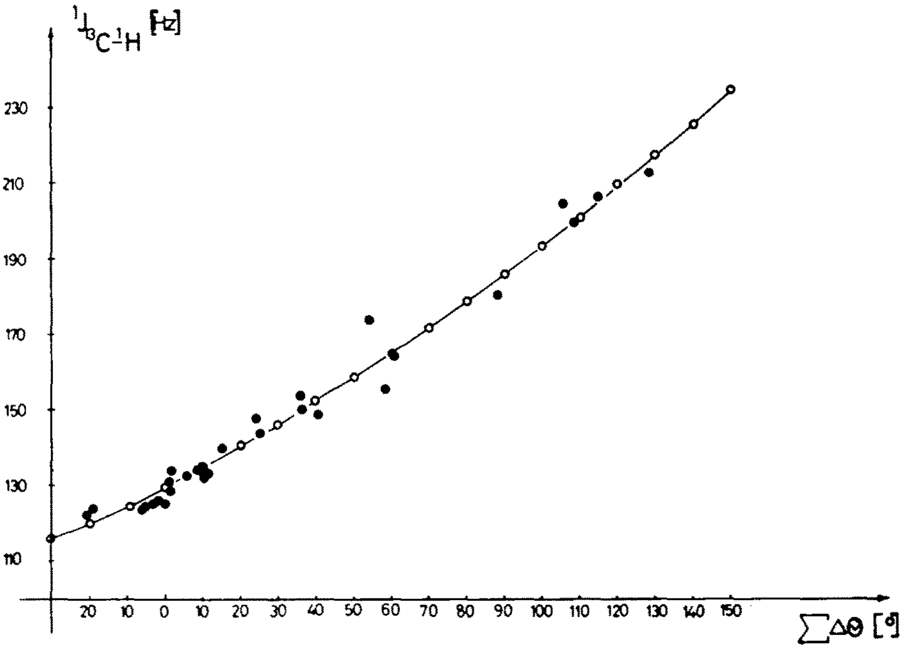
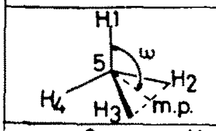
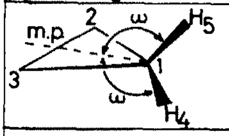
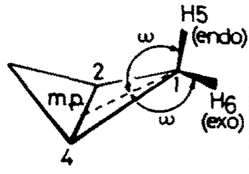


Fig. 2. The plot of the $^1J_{CH}$ vs $\Sigma\Delta\Theta$ relationship ●. Experimental data; ○. values calculated by eqn (1).

our results are surprisingly similar. Although it is obvious that there is a roughly linear relationship between the $\Delta\Theta$ values and s-character of corresponding bond (p_a, p_b, p_c values in the footnote), we failed to rationalize the deeper reasons for the observed similar results of the different approaches. For 14 data points Mislow's treatment[6] gave an average deviation of 7.42 Hz with a s.d. of 3.58 for the $^1J_{CH}$ values which is about two times higher than the same figure of eqn (1) (obtained for 30 data points).

Using eqn (1) it's possible to predict coupling constant for any known structure, e.g. we expect about 145 Hz and 232 Hz for the hexaprismane and tetrahedrane, respectively. The methylene protons of cyclopropane (C_{2v} local symmetry) and those of the bicyclobutane (lacking C_{2v} symmetry) seem to represent a special case (see Table 2). In addition, the $^1J_{CH}$ value of the cyclopropane is of particular interest because this value (161 Hz) served as a basic point for Foote's[2] and Mislow's equations.[5] In the following we argue that the use of this

Table 2. Internuclear and distortion angles (ω), experimental and calculated $^1J_{CH}$ values of cyclopropane and bicyclobutane methylene protons

Compound	θ_n, deg	* Calculated $^1J_{CH}$ [Hz]	ω, deg	Ref.	** $(\Delta\omega)^2$	*** Calculated $^1J_{CH}$ [Hz]	Experiment. $^1J_{CH}$ [Hz]	Ref.
	2-5-3=109.5 3-5-4=109.5 2-5-4=109.5	-	125.25	-	-	-	125.0	5
	H5 3-1-2=60.0 3-1-4=117.6 2-1-4=117.6	148.3	122.25	8	9.0	154.2	161.0	10
	endo 4-1-2=58.9 4-1-6=117.4 2-1-6=117.4	149.2	119.47	8	33.06	170.3	170.0	10
	exo 4-1-2=58.9 4-1-5=118.0 2-1-5=118.0	148.5	125.1	8	0.002	148.5	152.0	10

$$^*\ {}^1J_{CH} = 129.09 + 0.5354\sum\Delta\theta + 0.001094(\sum\Delta\theta)^2$$

$$^{**}\ \Delta\omega = \omega_{CH_4} - \omega$$

$$^{***}\ {}^1J_{CH} = 129.09 + 0.5354(\sum\Delta\Theta + (\Delta\omega)^2) + 0.001094(\sum\Delta\Theta + (\Delta\omega)^2)^2$$

value for the purpose of an equation was not the best choice, because in cyclopropane ring an additional effect, not present in any other member of Foote's data set,[2] exists. The calculated $\Sigma\Delta\Theta$ values for the cyclopropane protons and the endo and exo protons of bicyclobutane are practically identical (33.4, 34.82 and 33.7 respectively) and so, fail to explain both the observed large difference (19 Hz) of the coupling constants of the endo and exo protons and also the definitely off position of cyclopropane (see Table 2).

Looking for possible reasons we found that the only factor left to be considered is the distortion of the C–H bond producing the coupling, itself. In the methane the H1-H2,3 midpoint angle, ω is 125.25. According to our MM2[8] calculations ω equal 125.1° and 119.47° for the exo and endo protons, respectively. In the cyclopropane this angle is 122.25°,[8] which is the mathematical average of the above two. Similarly, but after all not surprisingly, the observed 161 Hz coupling of cyclopropane is also the average of those of the exo and endo protons (161 Hz). Wiberg explained[18] that the two endo-hydrogen is close enough for a repulsive interaction which can lead to a distortion of the bond angles involving these hydrogens. Our MM2 calculations do not support this assumption. Repulsion exists rather between the bridgehead carbons and the corresponding endo hydrogens than between endo hydrogens. But, whatever the reason may be, the exo proton of the bicyclobutane with its 125.1° value represents rather the "normal" case than the protons of the cyclopropane ring, and its 152.0 Hz coupling value coincides sufficiently with the calculated 148.5 Hz (see Table 2). And indeed, by replacing in Mislow's data set[5] the cyclopropane's 161 Hz coupling value by 152 Hz, the average deviation between the calculated and experimental data has been improved from 1.7 Hz to 1.32 Hz. (The modified equation would be: $^{1}J_{CH} = 214.83 - 1.3290\Theta_n + 0.004730\Theta_n^{2}$.)

The observed deviations seemed to be proportional with $(\Delta\omega)^2$, at least by adding $(\Delta\omega)^2$ to the $\Sigma\Delta\Theta$ values, the position of the exo proton remained practically the same, however, the cyclopropane protons and the bicyclobutane endo proton moved up almost to their "correct" positions (see Table 2). It is probable that similar empirical equations could be found in other systems also, e.g. in the case of unsaturated hydrocarbons (the linear term proposed by Laszlo and Schleyer[26] does not seem to have general validity), but in that case contributions from terms other that steric rehybridization, can also be important, what makes the situation more complex.

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REFERENCES

[1] N. Muller and D. E. Pritchard, *J. Chem. Phys.* **31**, 768, 1471 (1959); C. Juan and H. S. Gutowsky, *Ibid.* **37**, 2198 (1962).

[2] C. S. Foote, *Tetrahedron Letters* 579 (1963).

[3] K. Mislow, *Ibid.* 1415 (1964).

[4] L. S. Bartell, W. F. Bradford, *J. Mol. Struct.* **37**, 113 (1977).

[5] M. W. Baum, A. Guenzi, C. A. Johnson and K. Mislow, *Tetrahedron Letters* **23**, 31 (1982).

[6] K. Mislow, private communication.

[7] L. S. Kenneth, W. P. Weber and A. K. Willard, *J. Phys. Chem.* **74**, 3960 (1970).

[8] MM2 program: N. L. Allinger and Y. H. Yuk, *Quantum Chem. Prog. Exchange* **11**, 318 (1980).

[9] G. L. Loss, R. B. Larrabee, *Tetrahedron Letters* 4, 287 (1965).

[10] K. Withrich, S. Meiboom and L. C. Snyder, *J. Chem. Phys.* **52**, 230 (1970).

[11] MNDO program: M. J. S. Dewar and W. Tiel, *J. Am. Chem. Soc.* **99**, 4899 (1977).

[12] R. K. Bohn, K. Mizano, T. Fukuyama and K. Kushitsu, *Bull. Chem. Soc. Japan* **46**, 1395 (1973).

[13] E. W. Della, P. T. Hine and H. K. Patney, *J. Org. Chem.* **42**, 2940 (1977).

[14] G. Olah, *J. Am. Chem. Soc.* **92**, 2544 (1970).

[15] A. Yokozeki, K. Kuchitsu, *Bull. Chem. Soc. Japan* **44**, 2356 (1971).

[16] P. E. Eaton, S. J. Branca, *J. Am. Chem. Soc.* **103**, 2134 (1981).

[17] T. J. Katz, N. J. Acton, *J. Am. Chem. Soc.* **95**, 2738 (1973).

[18] K. W. Wiberg, G. M. Lapman, R. P. Ciula, D. S. Connor, P. Schertler and J. Lavanish, *Tetrahedron* **21**, 2749 (1965).

[19] R. Aydin and H. Gunther, *J. Am. Chem. Soc.* **103**, 1302 (1981).

[20] S. L. Bartell and H. B. Burgi, *J. Am. Chem. Soc.* **94**, 5239 (1072).

[21] P. K. Bohn and Y. H. Tai, *J. Am. Chem. Soc.* **92**, 6447 (1970).

[22] J. M. Lyding, *Diss. Abstr. Int. B.* **39**, 752 (1978).

[23] J. Dillen and H. J. Geise, *J. Chem. Phys.* **70**, 425 (1979).

[24] R. L. Hildebrandt, J. D. Wieser and L. K. Montgomery, *J. Am. Chem. Soc.* **95**, 8598 (1973).

[25] [a] N. L. Allinger, *Adv. Phys. Org. Chem.* **13**, 1 (1976); [b] E. Osawa and H. Musso, *Top. Stereochem.* **13**, 117 (1982).

[26] P. Laszlo and P. R. Schleyer, *J. Am. Chem. Soc.* **86**, 1171 (1964).