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Correlations of ^{13}C–H Coupling Constants J_{C-H} and Bond Angles and Bond Force Angles in Strained Organic Molecules†

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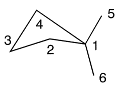
The incorporation of the sum of interatomic angle distortion $\Sigma\Delta\theta$, the sum of bond force angle distortion $\Sigma\Delta\beta$, the C–C–C bond angle θ_{ccc} and the s-character of C–H bonds has improved the prediction of ^{13}C–H coupling constants, J_{CH}, of strained organic molecules to average deviations of less than 2.0 Hz from experimental values.

The theoretical calculation of spin–spin coupling constants is important in the study and interpretation of molecular structure and chemical bonding.[1] Unfortunately, the coupling constants obtained from theoretical calculations deviate greatly from experimental values. Generally, the coupling constants can be empirically evaluated by different structural parameters (such as bond length and angles, *etc.*). The effect of valence bond angles on hybridization and thereby on the ^{13}C–H coupling constants, J_{C-H} has been well studied.[3–5] With a small data set of cyclic compounds, Foote found[3] a linear relationship between J_{C-H} and the C–C–C interatomic angle. Mislow has presented[4,5] some relationships between J_{C-H} and the fractional s-character (ρ_H) of the central carbon atomic orbital and interorbital C–C–C bond angle for some hydrocarbons. Szalontai obtained[6] a quadratic expression between J_{C-H} and the sum of the interatomic angle distortions in saturated hydrocarbons. However, all the calculated J_{C-H} values in three-membered rings differ somewhat from the experimental values, even though the methylene hydrogens of cyclopropane and bicyclobutane were treated separately as special cases.

However, it may be expected that strain-related parameters could be useful in describing J_{C-H} values in strained molecules. Recently, we presented a new approach[7,8] to evaluating the molecular strain and bonding behaviour of strained organic molecules. In this model, the bond force angle (β), defined as the angle subtended at a nucleus by the overlap force vectors to two bonded atoms, is found to be important in quantifying the concept of bond strain. In most strained organic molecules,[7,8] β has a preference for the tetrahedral angle 109.5 °. Thus, it may be regarded as the valence bond angle or interorbital angle. As Foote[3] pointed out, the hybridization would be expected to be more closely connected with the interorbital angle. In an effort to find a general solution for the above-mentioned problems, we found that good correlations exist between the J_{C-H} values and the sum of interatomic angle distortion, $\Sigma\Delta\theta$, and the sum of bond force angle distortion $\Sigma\Delta\beta$ for a wide range of strained organic molecules, including cyclic, bicyclic and polyhedral hydrocarbons. In addition, we have also found excellent correlations between the J_{C-H} values and the C–C–C interatomic angle θ_{CCC} and the s-character in C–H bonds for the local C_{2v} type R_2CH_2.

Table 1 ^{13}C–H coupling constants J_{C-H} (Hz) and sum of bond angles $\Sigma\Delta\theta$ and bond force angles $\Sigma\Delta\beta^a$

	H	$\Sigma\Delta\theta$	$\Sigma\Delta\beta$	J_{C-H} expt. (calcd.)		H	$\Sigma\Delta\theta$	$\Sigma\Delta\beta$	J_{C-H} expt. (calcd.)		H	$\Sigma\Delta\theta$	$\Sigma\Delta\beta$	J_{C-H} expt. (calcd.)
1	5	11.64	2.89	133.6(134.3)	**6**	11	–1.15	0.37	125.7(128.1)	**11**	4	32.08	5.41	161.0(161.6)
2	6	0.86	1.12	128.5(129.5)		7	39.04	11.68	150.5(151.6)	**12**	5	110.86	14.45	205.0(204.8)
3	7	–2.28	–0.49	125.0(126.8)	**7**	10	10.15	3.19	135.1(134.3)		7	36.26	5.97	170.0(163.6)
4	6	10.58	2.36	134.7(133.4)		9	4.78	2.63	132.5(132.3)		8	29.80	7.33	152.0(152.2)
5	8	17.15	7.38	140.1(141.0)	**8**	6	67.92	14.79	164.0(162.5)	**13**	6	32.54	4.69	160.0(164.8)
	9	7.89	3.60	131.3(134.2)		8	20.23	5.34	144.0(139.3)	**14**	6	125.42	16.53	212.0(211.2)
	12	0.69	1.31	130.3(129.7)	**9**	11	40.50	9.38	148.1(149.2)	**15**	7	88.50	14.90	180.0(181.2)
6	9	0.81	1.92	134.7(130.4)	**10**	9	58.50	11.82	155.0(156.6)	**16**	8	115.84	15.30	206.0(206.5)



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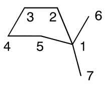

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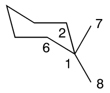

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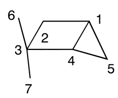

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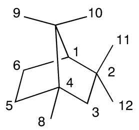

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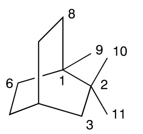

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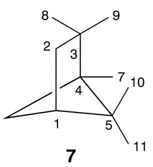

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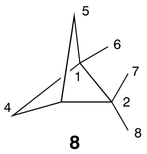

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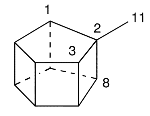

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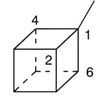

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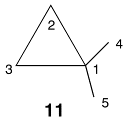

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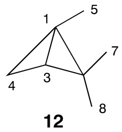

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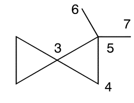

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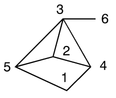

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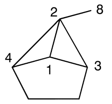

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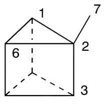

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[a]The coupling constants J_{C-H} were calculated with eqns. (3) and (6) for molecules **1**–**10** and **11**–**16**, respectively. The summations $\Sigma\Delta\theta$ and $\Sigma\Delta\beta$ are summed with θ and β, which are from ref. 8.

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

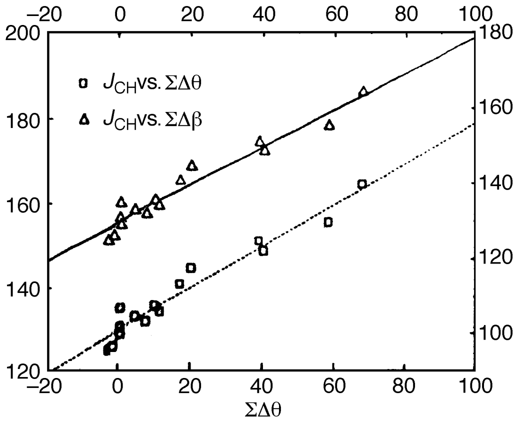

Fig. 1 Plots of J_{C-H} *vs.* $\Sigma\Delta\theta$ and $\Sigma\Delta\beta$

Because any distortion in the valence bond angles can affect the hybridization state of a C–H bond, we should take into account at least three bonds of the central carbon atom. The extent of angle distortion can be characterized by the departure of interatomic and bond force angles from the methane interatomic angle, 109.5 ° ($\Delta\theta = 109.5° - \theta$, $\Delta\beta = 109.5° - \beta$). In highly strained organic molecules, $\Delta\theta$ and $\Delta\beta$ can be large positive or negative numbers.[7,8] As it is well known that J_{C-H} is 125 Hz for the standard angle, 109.5 ° in methane, when the angle is smaller or larger than 109.5 ° J_{C-H} will be increased or decreased. Thus, the summation ($\Sigma\Delta\theta$ and $\Sigma\Delta\beta$) of these positive and negative distortions could be used for the evaluation of J_{C-H} values.

In view of the great degree of bend (with angles ranging from 22 to 33 °)[8] and much higher J_{C-H} values of three-membered rings, the treatments have been performed on the compounds containing three-membered rings (**11**–**16**) and compounds (**1**–**10**) that don't contain three-membered rings.

For compounds (**1**–**10**) with 16 data sets, both J_{C-H} *vis*, $\Sigma\Delta\theta$ and J_{C-H} *vs.* $\Sigma\Delta\beta$ can be best described by linear regression eqns. (1) and (2) (Fig. 1). With both $\Sigma\Delta\theta$ and $\Sigma\Delta\beta$ it is easy to obtain the binary least-square fitting eqn. (3) with a coefficient of 0.981 and mean deviation of 1.68 Hz. For compounds (**11**–**16**), J_{C-H} *vs.* $\Sigma\Delta\theta$ and J_{C-H} *vs.* $\Sigma\Delta\beta$ can also be approximated, by the linear regression eqns. (4) and (5) (Fig. 2). Although the linear relationship between J_{C-H} and $\Sigma\Delta\beta$ of eqn. (5) is not very good, it is of interest to note that J_{C-H} can be best fitted by the binary linear regression given in eqn. (6). The coefficient is as high as 0.992. The mean deviation is only 1.84 Hz.

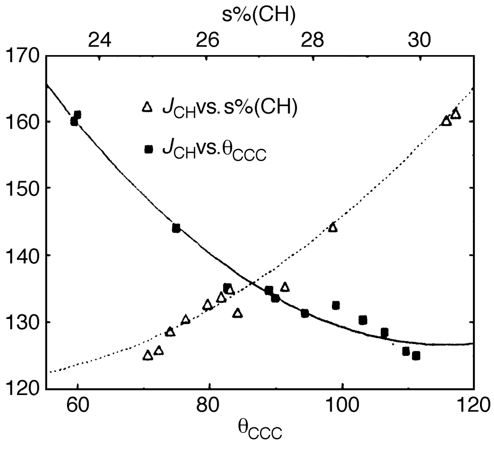

Fig. 2 Plots of J_{C-H} *vs.* θ_{CCC} and s%

Table 2 Fitting equations, average deviation (A.D.), standard deviation (S.D.) and coefficients (R)[a]

No.	Fitting equation	A.D.	S.D.	R
(1)	$J_{C-H} = 129.43 + 0.49\Sigma\Delta\theta$	2.03	2.63	0.974
(2)	$J_{C-H} = 126.77 + 2.33\Sigma\Delta\beta$	1.95	2.64	0.973
(3)	$J_{C-H} = 127.94 + 0.25\Sigma\Delta\theta + 1.18\Sigma\Delta\beta$	1.68	2.32	0.981
(4)	$J_{C-H} = 142.08 + 0.54\Sigma\Delta\theta$	4.06	6.11	0.971
(5)	$J_{C-H} = 137.04 + 4.13\Sigma\Delta\beta$	8.49	11.6	0.890
(6)	$J_{C-H} = 150.49 + 0.98\Sigma\Delta\theta - 3.733\Sigma\Delta\beta$	1.84	3.64	0.992
(7)	$J_{C-H} = 268.97 - 2.46 + 0.011\theta^2$	1.26	1.85	0.990
(8)	$J_{C-H} = 323.71 - 19.27\,S + 0.46\,S^2$	1.34	1.81	0.991

[a] Eqns. (4)–(6) for three-membered rings.

For all the fitting equations, the average deviation (A.D.), standard deviation (S.D.) and correlation coefficients are listed in Table 2. The experimental and calculated J_{C-H} values from eqns. (3) and (6) are shown in Table 1. It can be seen that the proposed equations can produce J_{C-H} values that are in excellent agreement with the experimental data. Their validity is not restricted to certain symmetry classes. They can be applied to any kind of strained organic molecules, such as cyclic, bicyclic, spiro and polyhedral hydrocarbons. Szalontai's treatment[6] gave an average deviation of 3.22 Hz for the J_{C-H} values, which is almost two times higher than the same figure of eqns. (3) and (6). Using eqns. (3) and (6), it is possible to predict J_{C-H} values any known structure, *e.g.* we expect about 142.2, 132.9 and 245.6 Hz for hexaprismane, dodecahedrane and tetrahedrane, respectively.

For structures of the type R_2CH_2 with local C_{2v} symmetry, we have found that the experimental J_{C-H} values have excellent quadratic relationships both with the C–C–C interatomic angle θ_{CCC} and the per cent s-characters in C–H bonds [12 data set, see Fig. 2 and eqns. (7) and (8), respectively, in Table 2]. The coefficients are as high as 0.990 and 0.991 and the mean deviation is as small as 1.26 and 1.34 Hz, respectively. Therefore, the percent s-character in C–H bonds also crucially affects J_{C-H}, which is consistent with previous studies on this kind of relation.[2,4]

In summary, consideration of a strain-related parameter, the bond force angle β, has improved the calculations for ^{13}C–H coupling constants in strained molecules. The best-fit eqns. (3) and (6) can be used to accurately predict J_{C-H} values for the larger rings and three-membered rings, respectively. The other two best-fit equations, eqns. (7) and (8) derived from θ_{CCC} and s%(C–H), can also be used to predict J_{C-H} values for compounds of the type R_2CH_2 with local C_{2v} symmetry. Specifically, the θ-derived eqn. (7) should be recommended to predict J_{C-H} values because θ values are more generally accessible than β values for these species.

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