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Correlation between C–H and C–C Spin-Spin Coupling Constants and *s* Character of Hybrids Calculated by the Maximum Overlap Method

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For some thirty hydrocarbons the *s* character of hybrids obtained by the application of the maximum overlap method have been correlated with C–H and C–C spin-spin coupling constants. The following relationships were obtained:

$$J_{\mathrm{C}^{13}-\mathrm{H}} = 1079\, a^2_{\mathrm{CH}}/(1+S^2_{\mathrm{CH}}) - 54.9\,,$$

$$J_{\mathrm{C}_1^{13}-\mathrm{C}_2^{13}} = 1020.5\, a^2_{\mathrm{C}_1}\, a^2_{\mathrm{C}_2}/(1+S^2_{\mathrm{CC}}) - 8.2\,.$$

Here the coupling constants are expressed in cps units. In the calculation of the maximum overlap hybrids either the experimental bond lengths or a standard bond lengths were used. For the $J_{\mathrm{C}^{13}-\mathrm{H}}$ and $J_{\mathrm{C}^{13}-\mathrm{C}^{13}}$ coupling constants the standard deviations are 0.9 cps and 1.9 cps respectively. It has been suggested that the large additive constant in the $J_{\mathrm{C}^{13}-\mathrm{H}}$ correlation may be attributed to the ionic character of C–H bonds. A good agreement with the experimental data strongly supports the idea that the Fermi contact term and the hybridization are dominant factors in determining carbon-hydrogen and carbon-carbon spin-spin coupling constants across one bond, at least in hydrocarbons.

Für einige dreißig Kohlenwasserstoffe wurde der mittels der Methode maximaler Überlappung berechnete *s*-Charakter mit den CH- und CC-Spinkopplungskonstanten in Zusammenhang gebracht. Dabei ergeben sich folgende Relationen:

$$J_{\mathrm{C}^{13}-\mathrm{H}} = 1079\, a^2_{\mathrm{CH}}/(1+S^2_{\mathrm{CH}}) - 54{,}9\,,$$

$$J_{\mathrm{C}_1^{13}-\mathrm{C}_2^{13}} = 1020{,}5\, a^2_{\mathrm{C}_1}\, 2\, a^2_{\mathrm{C}_2}/(1+S^2_{\mathrm{CC}}) - 8{,}2\,.$$

(Kopplungskonstanten in cps-Einheiten!)

Im einzelnen basiert die Berechnung des *s*-Charakters entweder auf der experimentellen oder einer Standard-Bindungslänge. Für die CH-Konstanten sind die Standardabweichungen 0,9 und für die entsprechenden CC-Werte 1,9 cps. Die große additive Konstante in der Korrelationsbeziehung der CH-Konstanten wurde auf den teilweisen ionischen Charakter der CH-Bindungen zurückgeführt.

Die gute Übereinstimmung mit den experimentellen Daten weist darauf hin, daß der Fermi-Kontaktterm und die Hybridisierung tatsächlich die dominierenden Faktoren für die CH- und CC-Kopplungskonstanten einer Bindung, zumindest im Fall von Kohlenwasserstoffen, sind.

Le caractère *s* des hybrides à recouvrement maximum obtenus pour une trentaine d'hydrocarbures a été corrélé avec les constantes de couplage spin-spin C–H et C–C. Les relations suivantes ont été obtenues:

$$J_{\mathrm{C}^{13}-\mathrm{H}} = 1079\, a^2_{\mathrm{CH}}/(1+S^2_{\mathrm{CH}}) - 54{,}9\,,$$

$$J_{\mathrm{C}_1^{13}-\mathrm{C}_2^{13}} = 1020{,}5\, a^2_{\mathrm{C}_1}\, a^2_{\mathrm{C}_2}/(1+S^2_{\mathrm{CC}}) - 8{,}2\,.$$

Les constantes de couplage sont experimées en unités cps. Dans le calcul des hybrides on a utilisé soit les longueurs de liaison expérimentales soit des longueurs de liaison standards. Les déviations standards pour les constantes de couplage $J_{\mathrm{C}^{13}-\mathrm{H}}$ et $J_{\mathrm{C}^{13}-\mathrm{C}^{13}}$ sont respectivement de 0,9 cps et

1,9 cps. Il a été suggéré que la grande constante additive présente dans $J_{C^{13}-H}$ peut être attribuée au caractère ionique des liaisons CH. Le bon accord avec les données expérimentales affermit la conception selon laquelle le contact de Fermi et l'hybridation sont les facteurs dominants dans la détermination des constantes de couplage spin-spin CH et CC, du moins en ce qui concerne les hydrocarbures.

Introduction

We consider in this paper the carbon-hydrogen and carbon-carbon spin-spin coupling constants in various hydrocarbons and correlate the experimental values with the theoretical values based on the hybrids calculated by the maximum overlap method. Since the most of molecules considered are relatively large a semiempirical approach and appropriate simplifications in the formula of Ramsey [1] were desirable. It is generally accepted that the Fermi contact interaction, which depends on local properties of electrons near the nuclei, is to a great extent responsible for the magnitudes of the coupling constants. We used the following set of approximations, generally accepted in semiempirical treatments [2—4]: (a) A difference between an excited and the ground state energy appearing in the second order pertubation sums is replaced by the avarage excitation energy. (b) Only the pair of electrons forming the chemical bond between the nuclei in question is responsible for the coupling. In the valence bond formalism the wave function for the pair of electrons making A–B bond is written as:

$$\begin{aligned}\psi_{AB}(1,2) = N_{AB}[\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2) \\ + \lambda_A\, \phi_A(1)\, \phi_A(2) + \lambda_B\, \phi_B(1)\, \phi_B(2)]\,.\end{aligned} \tag{1}$$

Here ϕ is either a hybrid orbital

$$\phi = a(2s) + (1-a^2)^{\frac{1}{2}}(2p) \tag{2}$$

placed on nucleus A or B, or $(1s)$ hydrogen wave function. The coefficients λ_A, λ_B characterize the ionic contributions to the bond. The normalization factor is

$$N_{AB} = [2(1+S_{AB}^2) + \lambda_A^2 + \lambda_B^2 + 2\lambda_A\lambda_B S_{AB}^2 + 4(\lambda_A+\lambda_B)S_{AB}]^{-\frac{1}{2}} \tag{3}$$

and $S_{AB} = \int \phi_A \phi_B d\tau$ is the overlap integral between the functions ϕ_A and ϕ_B. Since the difference in electronegativity between carbon and hydrogen is small we assume in the first approximation that $\lambda_A = \lambda_B = 0$. The Fermi contact term takes then the simple form:

$$J_{AB} = (16\pi\beta\hbar)^2 \gamma_A \gamma_B |(n_A s)_A|^2\, |(n_B s)_B|^2 a_A^2 a_B^2 / 18h\Delta E(1+S_{AB}^2)\,, \tag{4}$$

where $(n_A s)_A$ and $(n_B s)_B$ are the values of spherically symmetrical atomic orbitals on the nuclei A and B respectively. Other constants have their usual meaning. If atoms with a similar electron withdrawing power are involved $|(n_A s)_A|^2$ and $|(n_B s)_B|^2$ are approximately constant and the above expression (4) is further reduced to

$$J_{AB} \sim a_A^2 a_B^2 / (1+S_{AB}^2)\,. \tag{5}$$

The spin-spin coupling constants between directly bonded nuclei are proportional to the product of s characters of the bonding orbitals divided by $(1+S_{AB}^2)$. The derived formula is similar to the well known empirical relationship of Muller and Pritchard [2]

$$J_{C^{13}-H} = 500a^2 . \tag{6}$$

In fact, when the variations of bond overlaps are neglected the above expression (5) is reduced to already mentioned relationship of Muller and Pritchard. For CC bonds Frei and Bernstein [5] derived an analogous relationship between the carbon-carbon coupling constants in various CC bond types and hybrid s character. Again their relationship does not contain the dependence of $J_{C^{13}-C^{13}}$ on the variations of the CC bond overlaps. However, there is accumulated evidence from the maximum overlap calculations of hybridization in large number of hydrocarbons (see later) that the variations of bond overlaps are not negligible. They appear to be about 10% for C–H bonds and exceeding even 15% for C–C bonds. Therefore it seems desirable to re-examine the empirical correlations of Muller and Pritchard and of Frei and Bernstein by considering an explicit inclusion of bond overlaps and their variations in a relationship between spin-spin coupling constants and s character of the relevant hybrids.

In this paper we report results for some thirthy hydrocarbons for relevant CH and CC bonds hybrids and their s character and bond overlap obtained by applying the maximum overlap method. Some of the molecules reported have not been previously considered by the maximum overlap method. A dozen of molecules have been considered before, however the earlier work was based on standard bond lengths, while in this work, whenever available or accurate enough the experimental bond lengths were adopted. Thus for a number of molecules the hybrids were re-evaluated in order to have more reliable correlation. Although the difference between the hybrids and bond overlaps calculated for the experimental geometry and those based on standard CC bond lengths [6] is in the most cases small, by adopting the experimental bond lengths we eliminate a possible systematic deviation due to other sources which make the prediction of exact experimental bond lengths difficult. However, since the difference is small we included in the derivation of the correlation between spin-spin coupling constants and hybrid s character a dozen molecules whose hybrid parameters, in the absence of accurate experimental bond lengths, were calculated assuming standard bond lengths. The maximum overlap hybrids for the most of these molecules have already been published. Finally, for few molecules by using a correlation between bond overlap and bond length [7, 8] an iterative procedure was used. In this way a consistency between the calculated bond overlaps and bond lengths and the assumed bond lengths may be achieved in the process of the calculation. The so obtained results should be slightly superior to those based on the standard bond lengths.

The method of maximum overlap has been described in details in earlier work (see for example Ref. [9, 10]). We assume therefore that the method and the notation is familiar. In the method we search for the optimal hybrid coefficients which will make a suitably weighted sum of bond overlaps maximal. The basic overlap integrals are taken from the available Tables [11].

Results and Discussion

The hybrids obtained by the maximum overlap method, the corresponding s character and bond overlaps for various C–H bonds in the molecules considered are shown in Table 1. We use a shortened notation sp^n for the hybrids, where $n=(1-a^2)/a^2$. Also in Table 1 are listed the computed and the experimental values of $J_{\mathrm{C}^{13}-\mathrm{H}}$ spin-spin coupling constants. The J values computed by using the Muller and Pritchard relationship in several cases show a poor agreement when compared with the corresponding experimental values. These include the following molecules: cyclooctatetraene, cyclopropane, allene, ferrocene, acetylene and methyl acetylene, and one or two CH bonds of the polycyclic hydrocarbons at the end of the table. By using the calculated hybrids and calculated bond overlaps and the experimental $J_{\mathrm{C}^{13}-\mathrm{H}}$ from Table 1 we modified the relationship of Muller and Pritchard by including the bond overlaps and derived the following linear relationship:

$$J_{\mathrm{C}^{13}-\mathrm{H}} = 1079\, a_{\mathrm{CH}}^2/(1+S_{\mathrm{CH}}^2) - 54.9\,. \tag{7}$$

It connects the directly bonded carbon-hydrogen coupling constants with the s character and bond overlaps of the hybrids involved. The linear coefficient and the constant in the expression (7) are determined by applying the least square procedure. The spin-spin coupling constants calculated by the linear relationship (7) are also given in Table 1. By examining the entries in the table we see that the modified relationship leads to a better agreement with the experimental J constants. This is particularly evident in the cases of cyclooctatetraene, allene, ferrocene, acetylene and methyl acetylene, barrelene and nortricyclene for all of which the Muller and Pritchard relationship gives a poor agreement. Perhaps acetylene and methyl acetylene are the most dramatic examples. The maximum overlap method gives for CH and CC bonds in acetylene $sp^{1.25}$ and $sp^{0.80}$ hybrids respectively. Firstly we observe the inadequacy of the usual description of linear carbon bonds with sp hybrids for cases like acetylene when the two bonds are not equivalent. Hybrids involved in short CC bond tend to increase their s character in the process of maximizing the total overlap. The so obtained hybrids fail to give a satisfactory spin-spin coupling constant $J_{\mathrm{C}^{13}-\mathrm{H}}$, however when used in connection with the linear relationship (7) the discrepancy is removed, after the magnitude of the CH bond overlap is taken into account. There are, however, several cases when the both, i.e., Muller and Pritchard relationship and our expression (7), do not give satisfactory results. For example, this is the case of cyclopropane. It indicates that in some molecules, especially in highly strained small ring compounds, certain factors neglected in our treatment and not important in less strained systems may now be of importance. Another example, when the application of the Muller and Pritchard relationship gives considerably better result than the linear relationship including bond overlap, is ethylene. The future work has to account for this anomaly, but it seems that the presence of CC double bonds leads generally to somewhat higher computed values of $J_{\mathrm{C}^{13}-\mathrm{H}}$ and that in the maximum overlap procedure some correction for localized π bonds need to be considered. Nevertheless, even in these cases of poor agreement the differences between the experimental and the computed spin-spin coupling constants do not exceed 10% of the

Table 1. *Hybrids obtained by the maximum overlap method, the corresponding s characters and overlap integrals, and the $J_{C^{13}-H}$ coupling constants calculated using the relationships of Muller and Pritchard and the modified expression introduced in this paper and the experimental $J_{C^{13}-H}$ values*

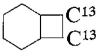
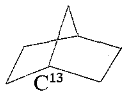
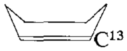
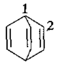
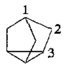
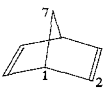
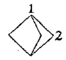
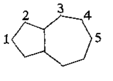
Molecule	Geometry Refs.	CH-hybrids	s %	Bond overlap		$J_{C^{13}-H}$ spin-spin coupling constants			
					Refs.	exp.	Refs.	Muller and Pritchard	This paper[aaa]
Cyclohexane	a	$sp^{2.87}$	25.8	0.722	A	124	aa	129	128.3 cps
Ethane	b	$sp^{2.94}$	25.4	0.718	B	124.9	bb	127	126.0
Methane	b	$sp^{3.00}$	25.0	0.722	A	125	[3]	125	122.4
$H_2C=C[C^{13}H_3]_2$	c	$sp^{2.93}$	25.4	0.721	C	126	[3]	127.2	125.8
Neopentane	d	$sp^{2.93}$	25.4	0.718	A	126	cc	127.2	126.2
$C_6H_5-H_2C^{13}-CH_3$	[14]	$sp^{2.89}$	25.7	0.721	D	127	[6]	128.4	127.4
Cyclopentane	e	$sp^{2.82}$	26.2	0.724	B	128	aa	131	130.5
$HC\equiv CC^{13}H_3$	b	$sp^{3.00}$	25.0	0.717	B	131.4	dd	125.1	123.4
Cyclobutane	e	$sp^{2.65}$	27.4	0.729	B	134 136	[16] ee	136.9	138.0
	f	$sp^{2.68}$	27.2	0.728	E	138	ff	136.0	136.9
	g	$sp^{2.48}$	28.7	0.725	B	139	gg	143.5	148.2
Cyclooctatetraene	h	$sp^{2.32}$	30.1	0.736	[12]	155	hh	150.5	155.8
Ethylene	b	$sp^{2.16}$	31.5	0.740	A	156.4	bb	157.9	165.3
	i	$sp^{2.26}$	30.7	0.737	A	157	ii	153.3	159.5
Benzene	b	$sp^{2.18}$	31.5	0.741	A	159	jj	157.5	164.4
Cubane	ST	$sp^{2.11}$	32.1	0.750	F	160 ± 5	kk	160.7	167.0
Cyclopropane	j	$sp^{2.50}$	28.6	0.733	B	161	ll	143.0	145.9
Allene	k	$sp^{2.20}$	31.2	0.739	A	168.2	mm	156.1	162.3
Ferrocene	a	$sp^{2.00}$	33.3	0.742	A	175	nn	166.7	176.4
$H_3CC\equiv C^{13}-H$	b	$sp^{1.24}$	44.6	0.773	A	247.6	dd	223.2	246.6
Acetylene	b	$sp^{1.25}$	44.5	0.771	B	248.7	bb	222.6	247.8
	ST	1H $sp^{2.64}$	27.5	0.728	G	140 ± 1	oo	137.3	138.5
		2H $sp^{2.02}$	33.1	0.744		176 ± 1		165.7	175.3
	ST	1H $sp^{2.54}$	28.3	0.741	F	148	pp	141.3	141.2
		2H $sp^{2.72}$	26.9	0.738		133		134.4	133.0
		3H $sp^{2.05}$	32.8	0.751		175		164.2	171.5
	g	1H $sp^{2.65}$	27.4	0.726	H	135.5	qq	136.9	138.6
		2H $sp^{2.53}$	28.3	0.728		146		141.5	144.8
		7H $sp^{1.99}$	33.4	0.738		172.5		167.2	178.6
	ST	1H $sp^{2.11}$	32.1	0.750	F	164		160.7	167.0
		2H $sp^{2.46}$	28.9	0.743		144		144.6	146.1

Table 1(continued)

Molecule	Geometry Refs.	CH-hybrids	s %	Bond overlap	Refs.	$J_{C^{13}-H}$ spin-spin coupling constants exp.	Refs.	Muller and Pritchard	This paper[aaa]
	1	1H $sp^{2.06}$	32.7	0.744	A	179	ss	163.3	172.0
		2H $sp^{2.02}$	33.1	0.743		164		165.3	174.5
		3H $sp^{2.32}$	30.1	0.738		154		150.5	155.4
		4H $sp^{2.25}$	30.7	0.739		154		153.6	159.5
		5H $sp^{2.32}$	30.1	0.738		154		150.5	155.4

[aaa] Footnotes of Table 1 are placed at the end of Table 2.

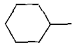
magnitude of $J_{C^{13}-H}$. This is below the upper limit of the dipole-dipole and orbital-dipole interactions [3] neglected in our calculations.

The superiority of here introduced correlation which includes bond overlap variations over the simpler relationship of Muller and Pritchard is illustrated by application to 1,3,5-cycloheptetriene. This molecule was not used in deriving the linear relationship (7) and is therefore more suitable for the comparison. The experimental $J_{C^{13}-H}$ coupling constants for CH bonds at carbon atoms C_1, C_2, and C_3 are 163.5 cps, 132.6 cps, and 177.0 cps respectively. By using the available maximum overlap hybrids [12] the Muller and Pritchard relationship gives 161, 154, and 156 cps respectively [13], while the modified relationship (7) gives for the corresponding J constants the values: 173.4, 125.3 and 190.0. Although the both calculated sets of J values deviate appreciably from the exeprimental values, the constants calculated by the modified relationship do show correctly the relative values of different J, what is not the case for the values based on the $J=500a^2$.

Several trends in the $J_{C^{13}-H}$ coupling constants are evident from Table 1. For instance, the decrease in the $J_{C^{13}-H}$ with the increasing of CCC angle along the series: cyclopropane, cyclobutane, norbornadiene (at C_7), cyclopentane and cyclohexane, discussed by Foote [14], is very well reproduced. There is a decrease in the p character of the ring CC bonds along the series reflecting the tendency of carbon to attain tetrahedral interorbital angles as closely as possible. An analogous angle dependence of the olefinic spin-spin coupling constants found by Laszlo and Schleyer [15] in the series: norbornadiene (olef.), barrelene, cyclohexene, and cyclooctatetraene is similarly reflected by a regular variation of the $s-p$ content of the CH hybrids along the series. The calculated and the experimental coupling constants in the conjugated systems considered: ferrocene, benzene, and azulene show a fairly satisfactory agreement. In azulene is particularly the difference between the J values for the five and the seven membered rings well reproduced, although the agreement for the individual $J_{C^{13}-H}$ values is less satisfactory.

There are no many experimental data on directly bonded carbon-carbon coupling constants in hydrocarbons. Fortunately, the data are available for typical carbon-carbon bonds, which makes it possible to extend the correlation over a wide range of CC bonds. In Table 2 are listed the maximum overlap hybrids

Table 2. *Hybrids obtained by the maximum overlap method, the corresponding s characters and* CC *overlap integrals, and the* $J_{C^{13}-C^{13}}$ *coupling constants calculated using the relationship of Frei and Bernstein and the modified expression introduced in this paper and the experimental* $J_{C^{13}-C^{13}}$ *values*

Molecule	Geometry Refs.	CC-hybrids	*s* %	Bond overlap	Bond overlap Refs.	$J_{C^{13}-C^{13}}$ spin-spin coupling constants Exp.	Exp. Refs.	Frei and Bernstein	This paper
$C_6H_5-H_2C^a-C^bH_3$[bbb]	IT	*ab* $sp^{3.11}$	24.4	0.649	D	34±1	[6]	29.9	33.4 cps
		ba $sp^{3.20}$	23.8						
Ethane	b	$sp^{3.20}$	23.8	0.648	B	36.6±0.3	bb	29.2	32.6
Neopentane	d	*ab* $sp^{3.00}$	25.0	0.651	A	36.9	cc	30.6	34.2
		ba $sp^{3.22}$	23.7						
 $-C^a-C^bH_3$	IT	*ab* $sp^{2.23}$	31.0	0.676	D	44.2±0.3	[6]	39.5	44.1
		ba $sp^{3.15}$	24.1						
$HC\equiv C^aC^bH_3$	b	*ab* $sp^{1.18}$	45.8	0.718	A	67.4	tt	62.3	68.7
		ba $sp^{3.01}$	24.9						
Ethylene	b	$sp^{1.72}$	36.8	0.764	A	67.6±0.1	bb	74.6	79.1
$C_6H_5-C\equiv C^a-C^bH_3$	IT	*ab* $sp^{1.18}$	45.8	0.718	D	68.6	[6]	61.9	68.3
		ba $sp^{3.04}$	24.8						
$C_6H_5-HC^a=C^bH_2$	IT	*ab* $sp^{1.71}$	37.0	0.765	D	70±3	[6]	74.9	79.4
Acetylene	b	$sp^{0.80}$	55.5	0.858	B	171.5±0.2		173.7	172.8
$C_6H_5-C^a\equiv C^bH$	IT	*ab* $sp^{0.86}$	53.6	0.856	D	175.9±0.3	[6]	167.8	167.1

[bbb] The pair of carbon atoms for which $C^{13}-C^{13}$ spin-spin coupling constants are calculated are marked with superscripts *a* and *b*.

Bond lengths:

[ST] Standard bond lengths, as suggested in Ref. [6].
[IT] Bond lengths calculated by iterative procedure described in Ref. [7].
[a] Tables of interatomic distances, L. E. Sutton ed., Chem. Soc. Special Publ. No. 11, 1958.
[b] Costain, C. C., Stoicheff, B. P.: J. chem. Physics **30**, 777 (1959).
[c] Laurie, V. W.: J. chem. Physics **34**, 1516 (1961).
[d] Zeil, W., Haase, J., Dakkouri, M.: Z. Naturforsch. **22**a, 1644 (1967).
[e] Almeningen, A., Bastiansen, O., Skancke, P. N.: Acta chem. scand. **15**, 711 (1961).
[f] Lawrence, J. L., MacDonald, S. G. G.: Acta crystallogr. B **25**, 978 (1969).
[g] Morino, Y., Kuchitsu, K., Yokozeki, A.: Bull. chem. Soc. Japan **40**, 1552 (1967).
[h] Bastiansen, O., Hedberg, L., Hedberg, K.: J. chem. Physics **27**, 1311 (1957).
[i] Naumov, V. A., Bezubov, V. M.: Zhur. Strukt. Khim. **8**, 530 (1967).
[j] Bastiansen, O., Fritsch, F. N., Hedberg, K.: Acta crystallogr. **17**, 538 (1964).
[k] Maki, A. G., Toth, R. A.: J. molecular Spectroscopy **17**, 136 (1965).
[l] Hanson, A. W., as cited by Bastiansen, O., Derrisen, J. L.: Acta chem. scand. **20**, 1319 (1966).

Coupling constants:

[aa] Jackman, L. M., Sternhell, S.: Application of the NMR spectroscopy in organic chemistry, 2nd ed., p. 346. Oxford: Pergamon Press 1969.
[bb] Lynden-Bell, R. M., Sheppard, N.: Proc. Roy. Soc. (London) A **269**, 385 (1962).
[cc] Litchmann, W. M., Grant, D. M.: J. Amer. chem. Soc. **89**, 6775 (1967).
[dd] Schoolery, J. N., Johnson, L. F., Anderson, W. A.: J. molecular Spectroscopy **5**, 110 (1960).
[ee] Burke, J. J., Lauterbur, P. C.: J. Amer. chem. Soc. **86**, 1870 (1964).

involved in various CC bonds of the several selected hydrocarbons, together with the corresponding CC bond overlaps and the experimental carbon-carbon $J_{C^{13}-C^{13}}$ spin-spin coupling constants. By applying the least square procedure the following correlation expression, assuming a linear dependence, is obtained:

$$J_{C^{13}-C^{13}} = 1020.5\, a_1^2 a_2^2/(1 + S_{CC}^2) - 8.2\,. \tag{8}$$

The above expression may be considered as an extension of the relationship introduced by Frei and Bernstein [5]:

$$J_{C^{13}-C^{13}} = 575.5\, \mathrm{a}_1^2 \mathrm{a}_2^2 - 3.44 \tag{9}$$

who have ignored the dependence of J on variations of CC bond overlaps. The overall agreement between the calculated, using the relationship (8), and the experimental J values is fairly good. In several cases the calculated spin-spin coupling constant is somewhat better than the one obtained by using the relationship of Frei and Bernstein.

Before concluding this section we should comment on the relatively large constant term in the linear relationship for $J_{C^{13}-H}$ (Eq. (7)). Since the additive constant in the $J_{C^{13}-C^{13}}$ correlation (Eq. (8)) is small it seems plausible to assume that the constant term originates from the ionic character fo CH bonds. A simple calculation for ethane and acetylene shows that by including as little as 1.2% of ionic VB function describing the charge flow from hydrogen towards carbon the additive constant −54.9 cps would be eliminated.

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Concluding Remarks

The $J_{C^{13}-H}$ coupling constants are the most thoroughly investigated spin-spin coupling constants. However, their theoretical investigation and interpretation have been the subject of controversy. Muller and Pritchard [2] and Schoolery [16] proposed a linear dependance of $J_{C^{13}-H}$ on the s character of the carbon hybrid participating in the CC bond. This has been supported by a VB treatment of Gutowsky and Juan [17]. Musher [18] argued that the influence of the hybridization would be of minor importance if other factors, tacitly assumed to be constant, like the dependence of $J_{C^{13}-H}$ on the effective carbon charge, are taken into account. Duijneveldt, Gil, and Murrell [19] suggested that the avarage energy approximation and a localized bond concept are not justified and that the success of localized bond models is accidental. Even more divers opinions persist on the theoretical explanation of the Malinowski additivity rules [20]. Goldtsein and Hobgood [21] used a simple orbital overlap argument in rationalizing the increases of the $J_{C^{13}-H}$ coupling constants of adjacent CH bonds by a substitution of a more electronegative nucleus. Considine [22] correlated $J_{C^{13}-H}$ of substituted methanes with the orbital electronegativities and found a good linear dependence. Grant and Litchman [23] have shown that the substitutent effects could be explained by changes in the effective nuclear charge of the carbon atom in question. On the other hand, Cyr and Cyr [24] invoked the variation of the lowest excitation energy of substituted methanes and found a good agreement with the experimental data. Brown and Puckett [25] investigated the correlation between CC stretching force constant and $J_{C^{13}-H}$ and concluded that J is influenced by bond polarity but not by hybridization. Undoubtedly, all these factors contribute to the coupling constants of a directly bonded nuclei and in many instances it has been difficult to separate the individual contributions. This is especially true for systems having atoms of very different electron withdrawing power. In hydrocarbons some of the above mentioned factors are expected not to vary sharply from molecule to molecule. Therefore, inspite of the drastic approximations involved, the linear correlation presented in this paper may well contain all the essential factors of importance when considering hydrocarbons. The good agreement between the experimental and the calculated $J_{C^{13}-H}$ and $J_{C^{13}-C^{13}}$ coupling constants shows that the hybridization is the dominant factor in determining and influencing the variations of the direct spin-spin coupling constants, at least in the large family of hydrocarbons. This confirms that the Fermi contact mechanism is responsible for the magnitude of the coupling of the bonded nuclei. Also some superiority of the relationships which take into account the variations of bond overlaps has been demonstrated. The improvement obtained by the inclusion of the overlap integral in the expression (5) is not unexpected, since it is equivalent to some measure to the inclusion of the correlation between the electrons with different spins [26]. The calculated coupling constants are generally quite sensitive on the magnitude of bond lengths and bond angles employed in the calculation. The use of additional and more accurate data may alter somewhat the correlation parameters appearing in Eqs. (7) and (8), but will not, we expect, change our main conclusions.

The present correlation of J and s character, the correlation of the chemical shifts with the exponent n of sp^n hybrids [27], the correlation of CC and CH bond overlaps with bond lengths [7, 8], the possibility of the prediction of molecular angles [9, 12, 28, 29], the correlation of bond energies [30, 31] and thermodynamic proton acidities [32], all these amply show that the hybrids obtained by the suitably scaled maximum overlap method offer a good and useful approximate description or, at least, hydrocarbon molecules.

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