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A Molecular Orbital Treatment of ^{13}C–H Spin-Spin Coupling Constants

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A molecular orbital interpretation of the directly-bonded ^{13}C–H spin-spin coupling constant without the concept of hybridization is presented. The observed values of J_{C-H} for some saturated and conjugated compounds are shown to be proportional to the square of the bond order between the 1S atomic orbital of the hydrogen atom and the 2S atomic orbital of the carbon atom, P^2, which is calculated using the extended Hückel molecular orbital method.

In a preliminary communication,[1] we pointed out that a molecular orbital method is successful in interpreting the ^{13}C–H spin-spin coupling constants of some aliphatic cyclic and unsaturated compounds. In the present paper, the full details of an MO treatment of ^{13}C–H spin-spin coupling constants will be presented.

Several investigators have directed their attention towards the elucidation of the factors affecting proton-^{13}C spin-spin coupling. Especially, the directly-bonded proton-^{13}C coupling constant, J_{C-H}, has been studied extensively.[2-7] These investigations have led to the conclusions that the Fermi contact term may play an essential role in the coupling, and that J_{C-H} depends solely upon the fractional S-character of the carbon hybrid atomic orbital.

The relation between J_{C-H} and the fractional S-character, ρ_{C-H}, of the carbon hybrid orbital used in the C–H bond may be expressed as Eq. 1 on the basis of semiempirical studies.[2,6]

$$J_{C-H} = 500\ \rho_{C-H}\ \text{c.p.s.} \qquad (1)$$

The additivity relation of substituent effects on J_{C-H} in substituted methanes and formyl compounds has been discussed by the aid of Eq. 1. Besides this relation, the relations between J_{C-H} and the C–C–C internuclear bond angle in the C–CH–C systems,[8,9] the C–H bond distances[2] and the electronegativity of the substituent have been investigated by several authors. Goldstein and Hobgood[7] and Veillard and Del Re[10] have calculated the fractional S-character, ρ_{C-H}, by the maximum overlap orbital method; they found that the ρ_{C-H} so obtained paralleled that estimated from the experimental J_{C-H} value obtained with Eq. 1.

In this paper, an attempt will be made to calculate the J_{C-H} values *ab initio* using the extended Hückel MO[11] method in which the parameters affecting the J_{C-H} value, that is, the bond distance, the bond angle and the electronegativity, are involved.

Theoretical

A molecular orbital treatment of spin-spin coupling was presented by McConnell[12] for proton-proton spin systems; this treatment gave a positive value for every J_{H-H} value, and was found to be less valuable than a valence bond treatment. Recently, Pople and Santry[13] have extended the MO theory of spin-spin coupling and have pointed out that the coupling constants calculated by an MO theory are not always positive. In fact, they obtained a negative J_{H-F} coupling constant in hydrogen fluoride without the introduction of an "average triplet excitation energy," ΔE. It has also been shown recently[14] that the geminal proton-proton coupling constnats in various systems can be interpreted well by this molecular orbital theory. However, since the J_{C-H} value for directly-bonded C–H is believed to be positive in sign, McConnell's procedure, as simplified by adopting an average excitation energy, ΔE, may be used.*

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[1] T. Yonezawa, I. Morishima, M. Fujii and K. Fukui, This Bulletin, **38**, 1224 (1965).

[2] N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).

[3] M. Karplus and D. M. Grant, *Proc. Natl. Acad. Sci.* (U. S.), **45**, 1269 (1959).

[4] N. Muller, *J. Chem. Phys.*, **36**, 359 (1962).

[5] H. Dreeskamp and E. Sackmann, *Z. Physik. Chem.*, **34**, 273 (1962).

[6] C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).

[7] J. H. Goldstein and R. T. Hobgood, Jr., ibid., **40**, 3592 (1964).

[8] S. S. Foote, *Tetrahedron Letters*, No. 9, 579 (1963).

[9] K. Mislow, ibid., No. 22, 1415 (1964).

[10] A. Veillard and G. Del Re, *Theoret. Chim. Acta.*, **2**, 55 (1964).

[11] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); K. Morokuma, H. Kato, T. Yonezawa and K. Fukui, This Bulletin, **38**, 1263 (1965).

[12] H. M. McConnell, *J. Chem, Phys.*, **24**, 460 (1956).

[13] J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

[14] J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

* This point will be checked in the final section of the present paper.

TABLE I. COULOMB INTEGRAL OF VARIOUS ATOMIC ORBITALS (eV.)

Atom	Orbital				
	1S	2S	2P	3S	3P
Hydrogen	−13.60	—	—	—	—
Carbon	—	−21.43	−11.42	—	—
Oxygen	—	−35.30	−17.76	—	—
Nitrogen	—	−27.50	−14.49	—	—
Chlorine	—	—	—	−25.26	−15.09

In a molecular orbital treatment of the C^{13}–H spin-spin coupling proposed by Muller2) or Pople and Santry13), they used a two-center molecular orbital localized in the C–H bond. On the other hand, in order to take into account the effect of neighboring atoms, (the bond distance, the valence angle, and so on,) on the electronic structure of the C–H bond, we used a delocalized molecular orbital obtained by a linear combination of the valence atomic orbitals of all the atoms in the molecule.

When we assume that $J_{\mathrm{C-H}}$ is exclusively determined by the Fermi contact term, it may be expressed by the equation12):

$$J_{\mathrm{C-H}} = (1/h)(2\beta h)^2\gamma_{\mathrm{C}}\gamma_{\mathrm{H}}(1/\varDelta E)(2\pi^2/3)P^2 \times(2S_{\mathrm{C}}|\delta|2S_{\mathrm{C}})(1S_{\mathrm{H}}|\delta|1S_{\mathrm{H}}) \tag{2}$$

where $P=2\sum_{i}^{occ} a_{1\mathrm{S_H}} b^i{}_{2\mathrm{S_C}}$ and $a^i{}_{1\mathrm{S_H}}$ and $b^i{}_{2\mathrm{S_C}}$ are coefficients of the hydrogen 1S and the carbon 2S orbitals in the *i*th molecular orbital respectively.** $\varDelta E$ is the mean excitation energy, which is assumed to be constant throughout this treatment. Then Eq. 2 may then be simply written as:

$$J_{\mathrm{C-H}} = AP^2 \tag{3}$$

where A is a constant. It may be seen that $J_{\mathrm{C-H}}$ is proportional to the square of the bond order, P^2. In the present method, a molecular orbital is represented by a linear combination of valence atomic orbitals, that is, the 1S orbital of the hydrogen atom, the 2S, $2P_x$, $2P_y$ and $2P_z$ orbitals of the carbon, oxygen, nitrogen atoms and so on.11) The orbital energy is given by solving the secular equation:

$$\det|H_{rs} - \varepsilon S_{rs}| = 0 \tag{4}$$

where H_{rs} is a matrix element and S_{rs} is the overlap integral between the *r*th and the *s*th atomic orbitals. The Coulomb integral, H_{rr}, of an atomic orbital is the negative value of the ionization potential15) of the valence state of the neutral atom, which is tablulated in Table I, the resonance integral, H_{rs}, is expressed as:

TABLE II. CALCULATED VALUES OF p^2 AND OBSERVED $J_{^{13}\mathrm{C-H}}$

No.	Compound	P^2	$J_{\mathrm{C-H}}$ c. p. s.	Ref.
No.	Group a	Cycloalkanes and some other heterocylic compounds		
1	Ethylene oxide	0.0810	175	a
2	Ethyleneimine	0.0693	168	b
3	Cyclopropane	0.0677	161	c
4	Cyclobutane	0.0600	134	d
5	Cyclobutanone β	0.0585	136	d
6	α	0.0525	131	d
7	Norbornadiene-7i)	0.0548	135.5	e
8	Cyclopentane	0.0524	128	c
9	Cyclohexane	0.0515	124	c
	Group b	Halmothanes and ethane		
1	Chloroform	0.0605	209	a
2	Dichloromethane	0.0517	178	a
3	Monochloromethane	0.0447	150	a
4	Ethane	0.0441	126	a
5	Methane	0.0380	125	a
	Group c	Unsaturated compounds		
1	Acetylene	0.0942	248	a
2	Norbornadienei)	0.0763	172	e
3	Norbornenej)	0.0745	166	e
4	Benzene	0.0671	159	a
5	Ethylene	0.0620	157	a
6	Allene	0.0508	166	f
	Group d	$-^{13}$CHO Compounds		
1	Formic acid	0.1156	215	g
2	Formate ion	0.1123	195	h
3	Formamide	0.0855	192	g
4	Benzaldehyde	0.0841	174	g
5	Acetaldehyde	0.0835	172	g

a) F. C. Nachod and W. D. Phillips, "Determination of Organic Structures by Physical Methods," Vol. 2, Academic Press, New York (1962).

b) F. S. Mortier, *J. Mol. Spectry.*, **5**, 199 (1960).

c) Ref. 2.

d) Ref. 8.

e) K. Tori, R. Muneyuki and H. Tanida, *Can. J. Chem.*, **41**, 3142 (1963).

f) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc.*, **A 269**, 385 (1962).

g) Ref. 4.

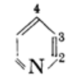
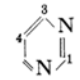
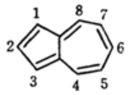
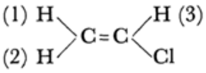
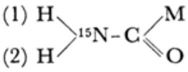
h) R. M. Hammaker, *J. Mol. Spectry.*, **15**, 506 (1965).

i), j) Bond distances and bond angles are referred to C. F. Wilcox, *J. Am. Chem. Soc.*, **82**, 414 (1960).

** The bond order, P, used in Eq. 2 is related to that between the 1S atomic orbital of the hydrogen atom and the 2S atomic orbital of the carbon atom and so should be referred to as the "partial bond order."

15) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

TABLE III. CALCULATED VALUES OF P^2 AND OBSERVED $J_{^{13}C-H}$

Compounds	Position		P_2	J_{C-H}, (c. p. s.)	Ref.
Group a Aromatic compound					
Nitrobenzene	*o*		0.0610	170	a
	m		0.0655	164	a
	p		0.0650	162	a
Pyridine	2		0.0660	179	b
	3		0.0691	163	b
	4		0.0685	152	b
Pyrrole	2		0.0840	182	c
	3		0.0703	169	c
Pyrimidine	1		0.0740	206	d
	3		0.0625	182	d
	4		0.0652	168	d
		(I)[h]	(II)[i]		
Azulene	1, 3	0.0718	0.0558	165	e
	2	0.0708	0.0875	183	e
	4, 8	0.0615	0.0580	158	e
	5, 7	0.0630	0.0674	161	e
	6	0.0630	0.0560	158	e
Group b					
Vinyl chloride	1		0.0620	161	f
 ${}^{(1)\,H}_{(2)\,H}\!>\!C{=}C\!<\!{}^{H\,(3)}_{Cl}$	2		0.0581	160	f
	3		0.0734	195	f
Group c				$\lvert J_{^{15}N-H} \rvert$, c. p. s.	
Formamide	1		0.0492	92	g
 ${}^{(1)\,H}_{(2)\,H}\!>\!{}^{15}N{-}C\!<\!{}^{M}_{O}$	2		0.0420	88	g

a) P. C. Lauterbur, *J. Chem. Phys.*, **38**, 1432 (1963).
b) L. Z. Malinowski, L. Z. Pollara and J. P. Larmann, *J. Am. Chem. Soc.*, **84**, 2649 (1962).
c) K. Tori and T. Nakagawa, *J. Phys. Chem.*, **68**, 3163 (1964).
d) G. S. Reddy, R. T. Hobgood and J. H. Goldstein, *J. Am. Chem. Soc.*, **84**, 336 (1962).
e) H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, No. 14, 468 (1961).
f) G. J. Karabatsos and C. E. Orzech, Jr., *J. Am. Chem. Soc.*, **86**, 3574 (1964).
g) G. Brinsch, J. B. Lambert, B. W. Roberts and J. D. Roberts, ibid., **86**, 5564 (1964).
h) Calculated assuming regular pentagon and heptagon R(C-C)=1.40 Å, R(C-H)=1.10Å
i) $\angle C_3$-C_2-C_1=95°, $R(C_9$-$C_{10})$ bond distance=1.48 Å, R(C-H)=1.10 Å other R(C-C)=1.40 Å

$$H_{rs} = 0.5K(H_{rr} + H_{ss})S_{rs} \qquad (5)$$

where the value of K is taken as 1.75 as in a paper reported by Hoffmann,[11] and the values of S_{rs} are obtained by Mulliken's Table.[16] The interatomic distances and bond angles of several compounds required for the calculation were referred to Sutton's compilation.[17] For the other compounds, references are cited in the footnote of Tables II and III.

Results

The values of the calculated P^2 values and the observed J_{C-H} values are cited in Tables II and III. In Table II, the compounds are classified systematically in four groups, a to d. In group a, saturated cyclic compounds are listed. Since cyclobutane is non-planar and has two groups of nonequivalent C–H bonds, the mean value of these two bond orders is indicated in the table. For the sake of simplicity, the calculation of J_{C-H} is carried out with respect to only one configuration, the chair form, for cyclohexane and the staggered form for ethane. In each group, a, b, c,

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[16] R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).
[17] L. E. Sutton, "Interatomic Distances," The Chemical Socieyt, London (1958).

and d, one can find a linear relation between the calculated valued of P^2 and the observed J_{C-H} values, with a few discrepancies as to acetylene and allene in group c. These linear relations are exemplified in Fig. 1 and Fig. 2 for group a and group b respectively. We find also some discrepancies between different groups. For example, the nearly constant values of J_{C-H}/P^2 in group a and group b, the average values of which are obtained from Figs. 1 and 2, are not equal. The values of J_{C-H}/P^2, which is equal to the A constant, are estimated to be 2200 (c. p. s.) and 3600 (c. p. s.) for group a and group b in Table II respectively. The A value of group b is exceptionally large. It might be attributed to the parametrization of H_{rr}, H_{rs} or to the assumption of a constant excitation energy, ΔE; this question will be discussed in a later part.

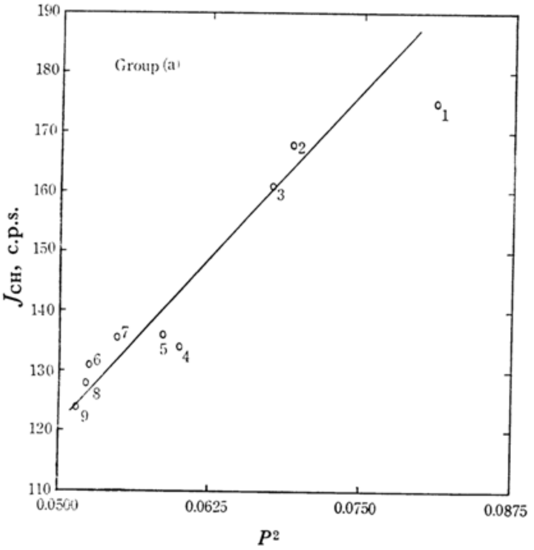

Fig. 1. A plot of the calculated values of P^2 versus observed J_{CH} for compounds of group a in Table II.

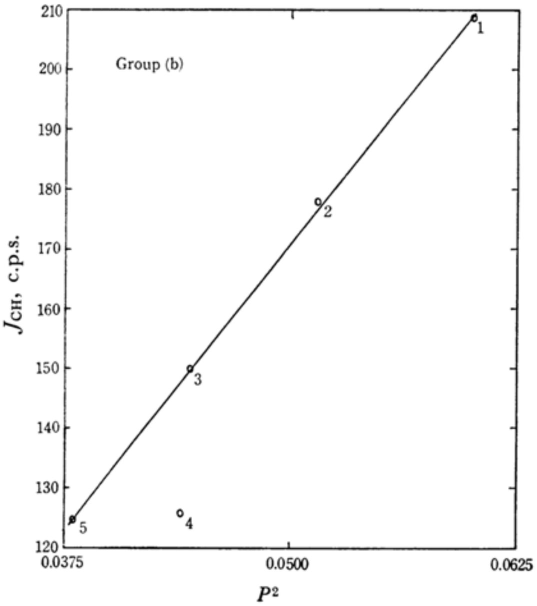

Fig. 2. A plot of the calculated values of P^2 versus observed J_{CH} for compounds of group b in Table II.

In Table III, in order to compare the J_{C-H} values, at the different positions in a molecule, we present the calculated P^2 values and the observed J_{C-H} values of aromatic compounds in group a and vinyl chloride compound in group b. In each compound, there seems to be a linear relation between P^2 and J_{C-H}. However, the interpretation of J_{C-H} for the C–H bond adjacent to the heteroatom is difficult by the present treatment. For example, the J_{C-H} for the ortho position of nitrobenzene, the $J_{C(2)-H}$ for pyridine, and the $J_{C(3)-H}$ for pyrimidine are all too large for the calculated P^2 value. In azulene, calculation is done in two ways. In Calculation I, the molecular shape for the azulene is assumed to be a regular pentagon and heptagon with the bond distances of R(C–C)=1.40 Å and R(C–H)=1.10 Å, while in Calculation II, we assume that the bond distances for $R(C_9–C_{10})$, other R(C–C) and R(C–H) are 1.48 Å, 1.40 Å, and 1.10 Å respectively, and that the $C_3–C_2–C_1$ bond angle is 95°. An exceptionally large J_{C-H} value at position 2 can be interpreted by the method of Calculation II, in which the bond angle at the carbon 2 is more acute than in Calculation I. On the contrary, for other positions the results by Calculation I seem to be better than those of Calculation II. Therefore, a more satisfactory agreement may be expected when the calculation is carried out assuming that the $C_3–C_2–C_1$ bond angle at position 2 is slightly more obtuse than 95°. At any rate, however, the molecular shape of azulene has not been definitely determined; the validity of the present results should be examined by future experiments.

Vinyl chloride in group b of Table III is given as an example to show the difference between the $J_{C-H(2)}$ value *cis* and the $J_{C-H(1)}$ value *trans* to the chlorine atom. In group c, we applied the present treatment to formamide-^{15}N in order to explain the difference between $J_{N-H(1)}$ and $J_{N-H(2)}$. Assuming that the magnitude of the coupling between nitrogen-15 and directly-bonded hydrogen is determined by the contact interaction, as in the case of ^{13}C–H coupling, the ^{15}N–H coupling constnat should be expressed by a relation similar to Eq. 2. The constant A in Eq. 3 for nitrogen–15 and hydrogen coupling no doubt differs from that for ^{13}C–H, since the product of the gyromagnetic ratios and the mean triplet excitation energy are different for each coupling case.

Discussion

In the present treatment, only one coupling mechanism, the Fermi term, and the approximation of the mean excitation energy are assumed. Nuclear spin-spin interactions have been proposed to proceed by three different mechanisms, mechanisms which arise from: (1) the Fermi contact interaction, (2) the nuclear spin-electron orbital interaction, and (3) the electron-nuclear dipole-dipole interaction. It has been shown that[13] the coupling of protons with other directly-bonded nuclei derives principally from the contact term. In a molecular orbital treatment,[12,13] the contact term may be further divided into one- and two-electron contributions; the former has been commonly neglected.[12,13] However, the deviations from the linear relationship expressed by Eq. 1 have been observed, and the validity of the S-character calculated from the experimental $J_{\mathrm{C-H}}$ value with Eq. 1 has been criticized by Karabatsos.[18] This deviation may be attributed to the breakdown of one or more assumptions involved in Eq. 1 or to the neglect of another coupling mechanisms, such as the dipole-dipole interaction and the spin-orbital term.[18,19] The deviations from the linear correlation represented by Eq. 3 which are found in compounds of group c and group a in Table II might be partly due to this.

The second assumption, the mean excitation energy, ΔE, was taken only for the sake of simplicity in our work. Recently, this point has been reexamined by Pople and Santry[13] for proton-proton coupling[13] and F–H coupling; they showed that an MO treatment is successful in interpreting the sign of the coupling constant for each case. For C–H coupling, we also examined the sign of the $\pi_{\mathrm{SA,SB}}$ term in Pople's equation[15] instead of $P^2/\Delta E$, where $\pi_{\mathrm{SA,SB}}$ is written as:

$$\pi_{\mathrm{SA,SB}}=4\sum_{i}^{occ}\sum_{j}^{unocc}(E_i-E_j)^{-1}C_{i\mathrm{SA}}C_{i\mathrm{SB}}C_{j\mathrm{SA}}C_{j\mathrm{SB}}$$

For a directly-bonded C–H spin-spin system, the sign of the calculated value of $\pi_{\mathrm{SC,SH}}$ is positive for most compounds,* this leads to the positive value of $J_{\mathrm{C-H}}$. From these considerations, the approximation of the mean exictation energy, ΔE, in the present treatment is rather crude, but it is qualitatively valid so far as the sign of $J_{\mathrm{C-H}}$ is concerned. These points should be investigated in future studies.

A few discrepancies found in Tables II and III may also be attributed partly to this assumption of the constant mean excitation energy. Namely, in Table II the fact that the $J_{\mathrm{C-H}}/P^2$ for group b is larger than that for groups a, c and especially d means that the mean excitation energy of the compounds in groups a, c and d should decrease. Finally, the disagreement as to heterocyclic compounds in Table III may be partly attributed to the parametrization of Hoffmann's extended Hückel molecular orbital.

The calculations were carried out on the IBM 7090 at Japan IBM Co., with the permission of the UNICON Committee, whose help we hereby acknowledge.

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18) G. J. Karabatsos, *J. Am. Chem. Soc.*, **86**, 3574 (1964).

19) N. Muller, *J. Chem. Phys.*, **42**, 4309 (1965).

* Details of this point will be published in the near future.