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A Theoretical Interpretation of Substituent Effects on the H–H and ^{13}C–H Spin Coupling Constants for CH_3X, $(CH_2)_2X$, and $CH_2{=}CHX$ Derivatives[1]

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An attempt has been made to explain the experimental trend of H–H and ^{13}C–H nuclear spin coupling constants for CH_3X, $(CH_2)_2X$, and $CH_2{=}CHX$ systems on the basis of the Pople and Santry expression for the contact term. The calculated magnitudes of the coupling constants are parallel with the observed values, but are uniformly lower by a factor of between 1.5 and 2. The variation in the calculated coupling constants with the electronegativity (E_x) of the substituent, X, follows the well-acknowledged observed tendency for directly-bonded ^{13}C–H, geminal H–H, and vicinal *cis* and *trans* H–H coupling constants. Theoretical calculations also predict the E_x dependency of the directly-bonded ^{13}C–H coupling constants for two geminal C–H bonds in the $^{13}CH_2{=}CHX$ fragment. The difference between two geminal ^{13}C–C–H coupling constants in the $CH_2{=}^{13}CHX$ system is also obtained by calculation. Discussions of the factors which dominate the couplings are also presented.

The theory of nuclear spin-coupling based on delocalized molecular orbitals presented by Pople and Santry[3] has been used, with a good deal of success, to estimate numerical values for a large number of couplings. Pople and Santry themselves applied[4] the theory to H–H, ^{13}C–H, and ^{13}C–^{13}C couplings in ethane, ethylene, and acetylene; Murrell *et al.*[5] also carried out similar calculations. Fahey *et al.*[6] calculated the H–H and ^{13}C–H coupling constants for various hydrocarbons using the extended Hückel theory. The present authors[2] also calculated the H–H couplings for saturated and unsaturated simple hydrocarbons, aldehydes, and small strained ring compounds by using a modified Hückel MO theory. In addition to these calculations of coupling constants, the couplings involving other nuclei, ^{19}F, ^{31}P, and ^{29}Si, have been investigated theoretically with fair success.[7,8]

There have, however, been only a few investigations of theoretical interpretations of the substituent effects on the signs and magnitudes of the nuclear spin coupling constants. As is well known,[9] the signs and magnitudes of geminal and vicinal H–H couplings, particularly of the geminal coupling, $J^{gem}_{H\text{-}H}$, depend sensitively on the nature of the substituent, X, for CH_3X, $(CH_2)_2X$, and $CH_2{=}CHX$ systems. Pople and Bothner-By[10] gave a satisfactory interpretation of the substituent effects of geminal H–H coupling with the aid of simple MO formalism, distinguishing the electronic effects into inductive and hyperconjugative electron transfer.

However, the substituent effects on the ^{13}C–H and vicinal H–H couplings are still open to further investigation. The substituent effect on the directly-bonded ^{13}C–H couplings has been attributed to the change in the hybridization[11] of the carbon atom in the C–H bond, in the C–H bond distances,[12] or in the $1s(H)$–$2s(C)$ partial bond order.[13] However, there have been no systematic studies of the substituent effect on the directly bonded ^{13}C–H and

1) Part II of "Molecular Orbital Calculations of Nuclear Spin Coupling Constants." Part I, the previous paper, Ref. 2.

2) T. Yonezawa, I. Morishima, M. Fujii and H. Kato, This Bulletin, **40**, 487 (1967).

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

4) J. A. Pople and D. P. Santry, *ibid.*, **9**, 311 (1965).

5) F. B. Van Dnijnveldt, V. M. S. Gil and J. N. Murrell, *Theoret. Chim. Acta*, **4**, 85 (1966); R. Ditchfield and J. N. Murell, *Mol. Phys.*, **14**, 481 (1968).

6) R. C. Fahey, G. C. Graham and R. L. Piccioni, *J. Am. Chem. Soc.*, **88**, 193 (1966).

7) J. N. Murrell, P. E. Stevenson and G. T. Jones, *Mol. Phys.*, **12**, 265 (1967).

8) A. H. Cowley, W. D. White and S. L. Manatt, *J. Am. Chem. Soc.*, **89**, 6433 (1967).

9) J. W. Emsley, J. Feeney and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford (1966).

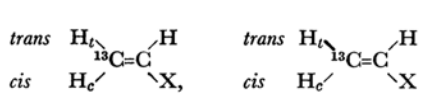
10) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

11) N. Müller and D. E. Pritchard, *ibid.*, **31**, 768, 1471 (1959); C. Juan and H. S. Gutowsky, *ibid.*, **37**, 2198 (1962).

12) N. Müller, *ibid.*, **36**, 359 (1962).

13) T. Yonezawa, I. Morishima and M. Fujii, This Bulletin, **38**, 1224 (1965); *ibid.*, **39**, 2110 (1966).

^{13}C–C–H couplings through the geminal two bonds, such as J_{C-H_t} and J_{C-H_c}, and J_{C-C-H_t} and J_{C-C-H_c}, specified as follows:



In the present study, we attempt to gain a comprehensive theoretical understanding of the substituent effect on the signs and magnitudes of directly-bonded ^{13}C–H, geminal H–H, and ^{13}C–H, and of vicinal H–H coupling constants for CH_3X, $(CH_2)_2X$, and CH_2=CHX systems.

Method of Calculation

For most of the couplings studied to date, particularly those involving only carbon and hydrogen atoms, it has been found that the Fermi contact term is most dominant.[3] All of our calculations are carried out, therefore, by neglecting the other two terms, the orbital and dipolar terms. In the LCAO approximation, the molecular orbital expression for the contact contribution to the spin-spin coupling constant between the A and B nuclei is given by:[3]

$$J_{AB} = -h\gamma_A\gamma_B\left(\frac{8\beta}{3}\right)^2 \sum_{i}^{occ}\sum_{j}^{unocc}({}^3\Delta E_{i\to j})^{-1} \times \sum_{\lambda\mu\gamma\sigma} C_{i\lambda}C_{j\mu}C_{j\gamma}C_{i\sigma}(\phi_\lambda|\delta(\gamma_A)|\phi_\mu) \times (\phi_\gamma|\delta(r_B)|\phi_\sigma) \quad (1)$$

The notations in Eq. (1) are the same as in Ref. 3. In the approximation which retains only one-center integrals involving valence s orbitals on the atoms A and B and in the one-electron independent MO approximation, Eq. (1) becomes:[3]

$$J_{AB} = \frac{16}{9}\beta^2\gamma_A\gamma_B h(S_A|\delta(r_A)|S_A)(S_B|\delta(r_B)|S_B)\pi_{S_A,S_B} = \frac{16}{9}\beta^2 h\gamma_A\gamma_B S_A^2(0)S_B^2(0)\pi_{S_A,S_B} \quad (2)$$

$S_A^2(0)$ and $S_B^2(0)$ denote the spin densities at the A and B nuclei of the valence s orbitals, and $\pi_{S_AS_B}$ is the mutual polarizability of the s valence orbital belonging to the atoms A and B. It is written as:

$$\pi_{S_A,S_B} = 4\sum_{i}^{occ}\sum_{j}^{unocc}(\varepsilon_i-\varepsilon_j)^{-1}C_{iS_A}C_{jS_A}C_{jS_B}C_{iS_A} \quad (3)$$

The values of $S_A^2(0)$ for the $1s$ and $2s$ valence orbitals for the H and C atoms were obtained using the Slater AO with an orbital exponent of 1.2 for H and using the SCF AO for the carbon atom.[14] With the appropriate constants, the H–H and ^{13}C–H spin coupling constants are given by the equations:

$$J_{H-H} = 6.235\times10^3\pi_{H-H}(\text{Hz}) \quad (4)$$

$$J_{C-H} = 7.885\times10^3\pi_{C-H}(\text{Hz}) \quad (5)$$

when π_{H-H} are π_{C-H} are given in units of $(\text{eV})^{-1}$.

In the present calculation, three types of molecular orbitals are employed for most of the molecules.

One-electron MO functions and energies were obtained by the extended Hückel method[15] (method A) and by two modified methods with a zero overlap approximation (methods B and C). The secular equations and parameters adopted in these three methods are summarized in Table 1. To construct a molecular orbital, Slater atomic orbitals were used as the basis set. The atomic coordinates for the evaluation of an overlap matrix, $S_{\mu\nu}$, were calculated from the pertienent bond distances and bond angles.[16] The valence-state ionization potentials (I_μ) used for the diagonal element of the H matrix are given in Table 2, together with the calculated values of $-0.5(I_\mu+A_\mu)$, where A_μ denotes an electron affinity. In method A, all the overlaps are included. In methods B and C, however, all the overlap integrals, $S_{\mu\nu}$, in the secular equations are replaced by $\delta_{\mu\nu}$ (=1 for $\mu=\nu$ and=0 for $\mu=\nu$). The method B was adopted in one of our previous paper,[2] where it was shown to have an advantage over method A. In the method C, the evaluation of $H_{\mu\mu}$ is slightly modified, as may be seen in Table 1. Pople and Segal[17] used this type of $H_{\mu\mu}$ parametrization for the starting

Table 1. Summary of the methods of the one-electron MO calculation

	Method A (EHMO)	Method B	Method C
$H_{\mu\nu}$	$0.5S_{\mu\nu}(H_{\mu\mu}+H_{\nu\nu})K$	$0.5S_{\mu\nu}(H_{\mu\mu}+H_{\nu\nu})K$	$0.5S_{\mu\nu}(H_{\mu\mu}+H_{\nu\nu})K$
Secular Eq.	$\lvert H_{\mu\nu}-\varepsilon S_{\mu\nu}\rvert=0$	$\lvert H_{\mu\nu}-\varepsilon\delta_{\mu\nu}\rvert=0$	$\lvert H_{\mu\nu}-\varepsilon\delta_{\mu\nu}\rvert=0$
$H_{\mu\mu}$	$-I_\mu$	$-I_\mu$	$-0.5\ (I_\mu+A_\mu)$
K	1.75	1.0	1.0

14) J. R. Morton, J. R. Rowlands and D. H. Whiffen, National Physical Laboratory Report BPR, 13 (1962).
15) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).
16) Data taken from "Tables of Interatomic Distances and Configurations in Molecules and Ions," L. E. Sutton, ed., Special Publication No. 11 and 18, The Chemical Society, London (1958 and 1965).
17) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

TABLE 2. THE VALUE OF DIAGONAL MATRIX ELEMENT $H_{\mu\mu}$ (eV)[a]

Atom	Methods A and B Valence AO					Method C Valence AO				
	1s	2s	2p	3s	3p	1s	2s	2p	3s	3p
H	−13.60					−7.17				
C		−21.34	−11.42				−15.34	−6.00		
N		−27.50	−14.49				−20.64	−8.35		
O		−35.30	−17.76				−27.57	−11.30		
F		−38.24	−20.86				−31.30	−12.18		
Cl				−24.02	−15.03				−19.23	−9.38

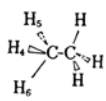
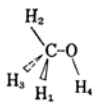
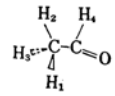
a) The values of the ionization popotential and the electron affinity were taken from Pritchard and Skinner, *Chem. Revs.*, **55**, 745 (1955).

MO functions in their semi-empirical SCF MO-(CNDO) theory. Compared with method B, method C gives slightly smaller ionization potentials and coupling constants which are in better agreement with the experimental results.

Results

The calculated and observed coupling constants are compared in Tables 3 to 7. In Figs. 1 to 4, the variation in the observed and calculated H–H and ^{13}C–H coupling constants is plotted against the electronegativity, E_x, of the substituent, X. The values of E_x are tentatively taken from those of Cavanaugh and Daily,[18] which were derived empirically from the internal chemical shifts, as is summarized in Table 8. The empirical linear correlation between the observed nuclear spin-coupling constants and their E_x values has been established by many workers.[9] For the saturated CH_3X system, the calculation by the method A gives somewhat unfavorable*1 values of the geminal

TABLE 3. CALCULATED AND OBSERVED VALUE OF J_{HH} FOR CH_3X DERIVATIVES

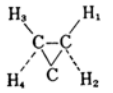
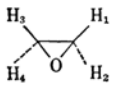
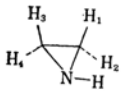
Molecule	J_{AB}	Calculated J_{H-H}, Hz Method A	Method B	Method C	Observed J, Hz	Ref.
CH_4	$^2J_{HH}$ (*gem*)	−20.9	−3.9	− 4.9	−12.4	a, b
	$^2J_{HH}$ (*gem*)	−24.4	−4.8	− 5.9	−12.4	a, b
	$^3J_{H_2H_4}$ (*gauche*)	+ 0.0	+0.7	+ 0.2	+ 8.3[c]	b
	$^3J_{H_2H_6}$ (*trans*)	+ 8.0	+8.2	+19.2		
CH_3Cl	$^2J_{HH}$ (*gem*)	—	−4.2	− 3.1	−10.8	d
	$^2J_{H_1H_2}$ (*gem*)	−28.1	−4.9	− 3.9	−10.8[c]	d
	$^2J_{H_1H_3}$ (*gem*)	−27.8	−4.8	− 3.6		
	$^3J_{H_1H_4}$	− 1.4	−0.2	+ 0.1	—	
	$^3J_{H_2H_4}$	+ 1.4	+0.5	+ 0.5	—	
CH_3F	$^2J_{HH}$ (*gem*)	—	−4.3	− 1.6	− 9.6	d
	$^2J_{H_1H_2}$	—	−6.1	−11.1	−12.0[c]	e
	$^2J_{H_2H_3}$	—	−6.4	−12.3		
	$^2J_{H_1H_3}$	—	−2.6	− 0.6		
	$^3J_{H_1H_4}$	—	+5.1	+12.3	+ 2.8[c]	
	$^3J_{H_2H_4}$	—	+0.3	+ 2.5		
	$^3J_{H_3H_4}$	—	+0.7	− 0.6		
$CH_3C{\equiv}N$	$^2J_{HH}$	−23.7	−5.9	− 9.9	−16.9	a
$CH_3C{\equiv}CH$	$^2J_{HH}$	−24.5	−5.8	− 8.7	—	

a) M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **82**, 4276 (1961); *J. Chem. Phys.*, **36**, 2054 (1962); *J. Am. Chem. Soc.*, **85**, 1901 (1963).
b) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc. (London)*, **A269**, 385 (1962).
c) Average
d) H. J. Bernstein and N. Sheppard, *J. Chem. Phys.*, **37**, 3012 (1962).
e) E. Sackmann and H. Dreeskamp, *Spectrochim. Acta*, **21**, 2005 (1965).

18) J. R. Cavanaugh and B. P. Daily, *ibid.*, **34**, 1099 (1961).

*1 The calculated coupling constants obtained by three methods differ to some extent each other. The major concern in this work is the theoretical interpretation of the observed trend of E_x dependency and the sign of the coupling constants, with rather crude approximation. Therefore we reserve the quantitative discussion on the absolute value of the coupling constants.

TABLE 4. CALCULATED AND OBSERVED VALUES OF J_{HH} FOR $(CH_2)_2X$ DERIVATIVES

Molecule		Method A	Method B	Method C	Observed J, Hz		Ref.
	$^2J_{H_1H_2}$ (*gem*)	−30.0	−3.0	+ 2.0	−4.5		a
	$^3J_{H_1H_3}$ (*cis*)	+ 0.9	+1.8	+ 1.5	+9.2		a
	$^3J_{H_1H_4}$ (*trans*)	+ 4.2	+3.8	+10.0	+5.4		a
	$^2J_{H_1H_2}$ (*gem*)	−35.3	−5.1	− 1.9	+5.5		b
	$^3J_{H_1H_3}$ (*cis*)	0.0	+1.6	+ 1.2	+4.5		b
	$^3J_{H_1H_4}$ (*trans*)	+ 4.3	+4.7	+12.5	+3.1		b
	$^2J_{H_1H_2}$ (*gem*)	−32.9	−2.8	+ 5.1	+2.0		c
	$^3J_{H_1H_3}$ (*cis*)	+ 0.5	+1.7	+ 1.7	+6.3[c]	+7.2[d]	
	$^3J_{H_2H_4}$ (*cis*)	+ 1.0	+2.0	+ 2.5		+5.5[d]	
	$^3J_{H_1H_4}$ (*trans*)	+ 5.3	+5.3	+12.6	+3.8		c

a) D. J. Patel, M. E. H. Howden and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963).
b) N. Sheppard and J. J. Turner, *Proc. Roy. Soc. (London)*, **A252**, 506 (1959).
c) F. S. Mortimer, *J. Mol. Spectry.*, **5**, 199 (1962).
d) T. Yonezawa and I. Morishima, *ibid.*, **27**, 210 (1968).

TABLE 5. CALCULATED AND OBSERVED VALUES OF J_{HH} FOR CH_2=CHX DERIVATIVES

Molecule X	J	Calculated J, Hz Method A	Method B	Method C	Observed J, Hz	Ref.
H	$^2J_{HH}$ (*gem*)	−31.8	− 2.0	+ 5.2	+ 2.5	a, b, c
	$^3J_{HH}$ (*cis*)	+ 2.2	+ 3.8	+ 2.9	+11.6	a, c, b
	$^3J_{HH}$ (*trans*)	+13.5	+13.5	+34.0	+19.1	a, b, c
CN	$^2J_{HH}$ (*gem*)	−31.3	− 1.6	+ 1.6	+ 0.9	d
	$^3J_{HH}$ (*cis*)	+ 3.2	+ 5.1	+ 3.8	+11.8	d
	$^3J_{HH}$ (*trans*)	+13.5	+12.7	+29.6	+17.9	d
CH_3	$^2J_{HH}$ (*gem*)	—	− 2.4	+ 4.1	+ 2.1	e
	$^3J_{HH}$ (*cis*)	—	+ 2.9	+ 1.4	+10.0	e
	$^3J_{HH}$ (*trans*)	—	+12.8	+32.0	+16.8	e
CO_2H	$^2J_{HH}$ (*gem*)	−31.7	− 2.0	+ 4.0	+ 1.7	f
	$^3J_{HH}$ (*cis*)	+ 1.5	+ 2.8	− 0.4	+10.2	f
	$^3J_{HH}$ (*trans*)	+12.2	+11.6	+26.9	+17.2	f
COH	$^2J_{HH}$ (*gem*)	−31.5	− 1.6	+ 6.3	− 1.7	g
	$^3J_{HH}$ (*cis*)	+ 1.7	+ 3.1	+ 1.3	+ 6.3	g
	$^3J_{HH}$ (*trans*)	+12.7	+12.9	+32.2	+13.8	g
Cl	$^2J_{HH}$ (*gem*)	−32.2	− 3.0	+ 1.8	− 1.4	h
	$^3J_{HH}$ (*cis*)	+ 0.6	+ 1.4	− 1.1	+ 7.3	h
	$^3J_{HH}$ (*trans*)	+ 9.7	+ 9.9	+24.4	+14.6	h
OCH_3	$^2J_{HH}$ (*gem*)	—	− 3.9	− 0.7	− 2.0	i
	$^3J_{HH}$ (*cis*)	—	+ 0.4	− 1.2	+ 7.0	i
	$^3J_{HH}$ (*trans*)	—	+ 9.0	+22.2	+14.1	i
F	$^2J_{HH}$ (*gem*)	—	− 4.4	− 1.9	− 3.2	h
	$^3J_{HH}$ (*cis*)	—	0.0	− 0.8	+ 4.7	h
	$^3J_{HH}$ (*trans*)	—	+ 7.9	+20.7	+12.8	h

a) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc. (London)*, **A269**, 385 (1962).
b) G. S. Reddy and J. H. Goldstein, *J. Mol. Spectry.*, **8**, 475 (1962).
c) D. M. Graham and C. E. Halloway, *Can. J. Chem.*, **41**, 2114 (1963).
d) R. T. Hobgood, Jr., R. E. Mayo and J. H. Goldstein, *J. Chem. Phys.*, **39**, 2501 (1963).
e) A. A. Bothenr-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961).
f) S. Castellano and J. S. Waugh, *J. Chem. Phys.*, **34**, 295 (1961).
g) T. Schaefer, *ibid.*, **36**, 2235 (1962).
h) C. N. Banwell and N. Sheppard, *Discussions Faraday Soc.*, **34**, 115 (1962).
i) R. T. Hobgood, Jr., G. S. Reddy and J. H. Goldstein, *J. Phys. Chem.*, **67**, 110 (1963).

TABLE 6. CALCULATED AND OBSERVED VALUES OF J_{CH} FOR CH_3X AND $(CH_2)_2X$ DERIVATIVES

Molecule	Calculated J_{CH}, Hz Method A	Method B	Method C	Observed J_{CH}, Hz	Ref.
CH_3X					
X=H	+56.8	+48.7	+ 76.0	+125	a
CH_3	+64.1	+50.9	+ 77.9	+126	a
Cl	+60.5	+50.5	+100.3	+150	a
OH	+73.3	+63.0	+103.7	+141	a
F	+68.1	+68.1	+108.5	+149	a
CHO	—	+50.4	+ 79.4	+127	a
CN	+59.3	+53.1	+ 88.1	+136	a
C≡CH	+58.6	+51.2	+ 83.4	+132	a
$(CH_2)_2X$					
X=CH_2	+91.5	+75.4	+114.5	+161	a
O	+95.0	+79.7	+125.7	+176	b
NH	+94.8	+80.3	+127.4	+168	b
	+92.3	+78.1	+125.2		

a) N. Müller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).
b) F. S. Mortimer, *J. Mol. Spectry.*, **5**, 199 (1950).

H–H coupling; they are too negative, particularly for molecules with electronegative substituents such as X=O, N, F. The method B also gives improper results, as is depicted in Fig. 1; the substituent effect of the calculated values is opposite to that of the observed values. The results calculated by method C are the most acceptable, though the magnitudes are uniformly lower than those of the experiments by a factor of 1.5 (Fig. 1).

The linear dependence of the directly-bonded J_{CH} on E_x is also satisfactorily provided for by the method C than by the method B (Fig. 3). Thus, for the following discussion, the results obtained by method C are adopted for CH_3X systems.

For three-membered ring systems, $(CH_2)_2X$, none of the methods of calculation predict the observed trend of the H–H and C–H couplings. The most striking discrepancy between the cal-

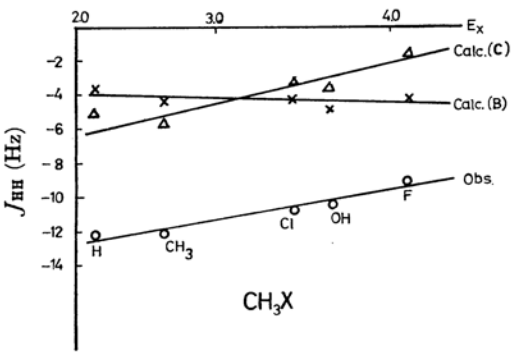


Fig. 1. The calculated and observed geminal coupling constants, J_{HH}, in CH_3X systems are ploted *versus* the electronegativity of the substituent, X (E_x).

TABLE 7. CALCULATED AND OBSERVED VALUES OF J_{CH} AND J_{C-C-H} FOR CH_2=CHX DERIVATIVES

Molecule X		Calculated J_{CH} and J_{CCH}, Hz Method B	Method C	Observed J_{CH} and J_{CCH}, Hz
H	$^1J_{CH}$ (*trans*)	+72.6	+108.7	+156.4[a]
	$^1J_{CH}$ (*cis*)			
	$^2J_{CCH}$ (*trans*)	− 0.1	+ 3.5	− 2.4[a]
	$^2J_{CCH}$ (*cis*)			
CN	$^1J_{CH}$ (*trans*)	+77.9	+122.5	—
	$^1J_{CH}$ (*cis*)	+72.6	+107.9	—
	$^2J_{CCH}$ (*trans*)	+ 0.4	+ 8.1	—
	$^2J_{CCH}$ (*cis*)	− 0.4	+ 1.7	—
CH_3	$^1J_{CH}$ (*trans*)	+75.0	+113.4	+162[b]
	$^1J_{CH}$ (*cis*)	+69.7	+102.3	+156[b]
	$^2J_{CCH}$ (*trans*)	+ 0.2	+ 4.4	—
	$^2J_{CCH}$ (*cis*)	− 0.3	+ 2.2	—
CO_2H	$^1J_{CH}$ (*trans*)	+74.7	+115.3	—
	$^1J_{CH}$ (*cis*)	+73.0	+106.7	—
	$^2J_{CCH}$ (*trans*)	+ 0.2	+ 7.8	—
	$^2J_{CCH}$ (*cis*)	− 0.3	+ 1.2	—
CHO	$^1J_{CH}$ (*trans*)	+76.3	+118.9	—
	$^1J_{CH}$ (*cis*)	+71.9	+104.3	—
	$^2J_{CCH}$ (*trans*)	+ 0.1	+ 5.6	—
	$^2J_{CCH}$ (*cis*)	− 0.04	+ 2.3	—
Cl	$^1J_{CH}$ (*trans*)	+78.1	+123.0	+161[c]
	$^1J_{CH}$ (*cis*)	+69.8	+100.9	+160[c]
	$^2J_{CCH}$ (*trans*)	+ 2.5	+ 14.7	—
	$^2J_{CCH}$ (*cis*)	− 0.9	+ 0.3	—
OCH_3	$^1J_{CH}$ (*trans*)	+84.2	+135.0	—
	$^1J_{CH}$ (*cis*)	+64.2	+ 91.1	—
	$^2J_{CCH}$ (*trans*)	+ 7.2	+ 24.4	—
	$^2J_{CCH}$ (*cis*)	− 0.9	− 0.5	—
F	$^1J_{CH}$ (*trans*)	+82.6	+133.1	—
	$^1J_{CH}$ (*cis*)	+66.6	+ 96.5	—
	$^2J_{CCH}$ (*trans*)	+ 8.6	+ 25.1	—
H, Cl>C=C<Cl, H	$^1J_{CH}$(*cis*)	+88.7	+151.2	+199.1[a]
	$^2J_{CCH}$(*cis*)	− 0.6	+ 6.1	0[a]
H, Cl>C=C<H, Cl	$^1J_{CH}$(*trans*)	+96.3	+168.6	+198.3[a]
	$^2J_{CCH}$(*trans*)	+4.1	+ 21.8	+ 15.7[a]

a) N. Müller, *J. Chem. Phys.*, **37**, 2329 (1962).
b) Taken from the values for styrene.
c) E. B. Wipple, W. E. Stewart, G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, **34**, 2136 (1961).

TABLE 8. ELECTRONEGATIVITY (E_x) OF ATOM AND FUNCTIONAL GROUP[a]

Atom and Group	E_x	Atom and Gorup	E_x
H	2.10	C_6H_5	2.75
CN	2.49	Cl	3.25
CH_3	2.50	–O–	3.31
CO_2H	2.60	OH	3.46
CHO	2.69	F	3.90

a) Taken from Ref. 18.

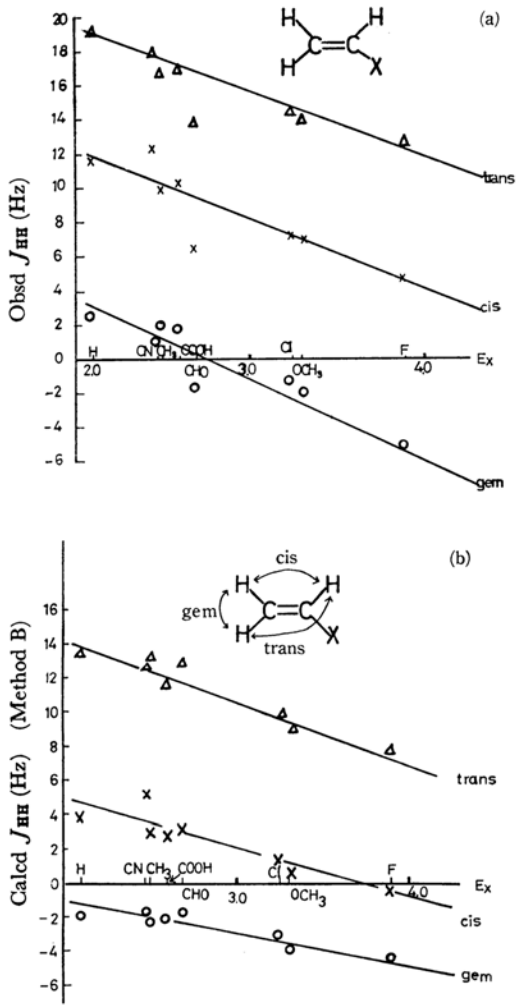


Fig. 2. The geminal, vicinal *cis*, and vicinal *trans* coupling constants in mono-substituted vinyl compounds are plotted *versus* the electronegativity of the substituent, X (E_x); (a): calculated values, (b) experimental values.

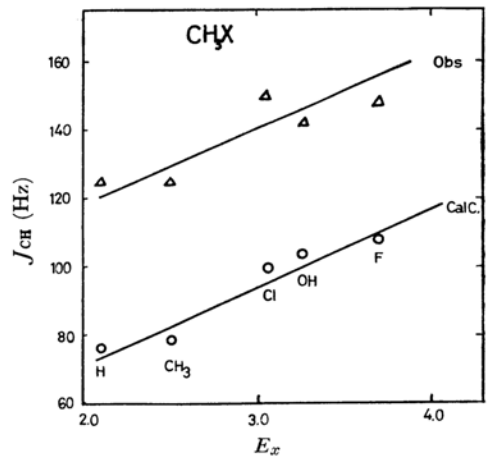


Fig. 3. The calculated and experimental ^{13}C–H coupling constants, J_{CH}, in CH_3X systems are plotted *versus* the electronegativity of the substituent, X (E_x).

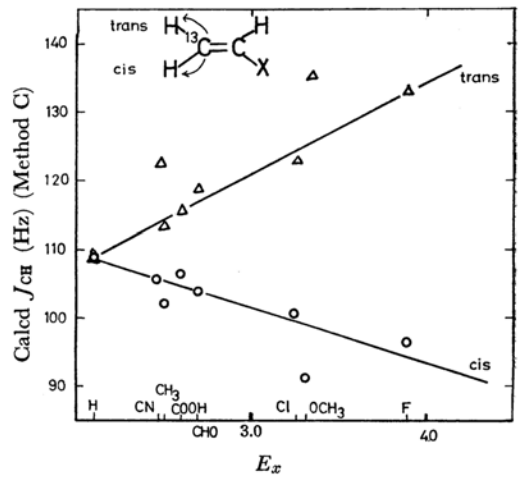


Fig. 4. The calculated ^{13}C–H coupling constants for directly bonded ^{13}C–H (*cis*) and ^{13}C–H (*trans*) in $^{13}CH_2$=CHX systems are plotted *versus* the electronegativity of the substituent, X (E_x).

culated and experimental coupling constants is in the vicinal H–H coupling constants. The greater value of the vicinal *cis* H–H coupling than that of the *trans* coupling is not reproduced by calculations.

For vinyl derivatives the geminal and vicinal *cis* and *trans* H–H coupling constants calculated by method B decrease linearly as E_x increases and are in agreement with the observed results (Fig. 2), but their magnitudes are lower than those of the experiments by a factor of about 1.5. Method C gives a poorer agreement with the experimental results in the present case because: (i) the *trans* H–H couplings are too positive, (ii) the *cis* coupling is more negative than the geminal coupling, behavior which contradicts the observed tendency, and (iii) the linear dependency of J_{H-H} on E_x disagrees with the observed feature.*2 Table 7 gives the ^{13}C–H couplings through one bond, J_{C-H}, and through two bonds, J_{C-C-H}. Because of the lack of experimental data, no comparison between calculated and observed values is yet possible. The calculated values of directly bonded ^{13}C–H coupling constants are somewhat different for ^{13}C–H_t and ^{13}C–H_c bonds, which are located respectively *cis* and *trans*, with respect to the substituent, X.

The variation in the calculated J_{C-H} values is

*2 The method C is adopted to improve the overestimated polarization due to heteroatoms in method B. However, this may cause improper sequence of σ and π orbitals in the vinyl compounds. So this may lead to a poor agreement with experiments.

plotted against E_x in Fig. 4. The J_{C-H_t} value increases as E_x increases, while the J_{C-H_c} value decreases. As may easily be seen from Table 7 and Fig. 4, the J_{C-H_c} value is generally greater than J_{C-H_t}. This definite trend of the J_{C-H} dependency on E_x has not been found experimentally. This prediction has, however, been partly confirmed experimentally by the present authors;[19] our results will be published elsewhere. However, the trend of J_{C-H_c} is also supported here by limited examples of the observed data (Table 7). Table 7 and Fig. 5 also reveal that the calculated values of

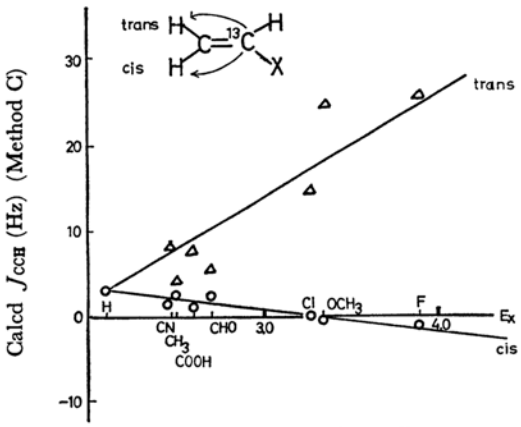


Fig. 5. The calculated ^{13}C–C–H coupling constants for *cis* and *trans* protons in $CH_2=^{13}CHX$ systems are plotted *versus* the electronegativity of the substituent, X (E_x).

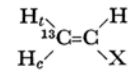
J_{C-C-H_t} are more positive than J_{C-C-H_c}. Figure 5 also reveals the opposite trend of J_{C-C-H_t} and J_{C-C-H_c}, a trend which is similar to the case with the directly-bonded ^{13}C–H coupling constants, J_{C-H_t} and J_{C-H_c}. The observed ^{13}C–C–H coupling constant for 1,2-dichloroethylene may serve as the only example of a compound with different *cis*- and *trans*-type ^{13}C–C–H coupling constants. Calculations by methods B and C reproduce the trend of the experimental value.

Discussion

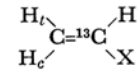
Before entering into our discussion, it should be pointed out that the present calculations do not include the contributions of the π-electrons to the coupling. The neglect of σ-π-interaction in the present study fails to account for π-electron contribution. Semiempirical methods for estimating π-electron coupling have been developed by McConnell[20] and Karplus.[21] They have shown that, for ethylene, the π-contribution is 1.8 Hz for the vicinal H–H coupling. This correction, however, is insufficient to cover the difference between the calculated coupling constants and the observed values. Since a major concern of this study is to give a theoretical interpretation of the experimental trend of the nuclear spin coupling constants, apart from the magnitude and sign of the calculated coupling constants, the substituent effect on the J value will be discussed without taking any account of the π-electron contirubition.

In general, the magnitudes of the coupling constants, as calculated on the basis of the contact term, reproduce the trend of the experimental values, but they are lower by a factor of between 1.5 to 2 (Figs. 1—3). Of the three types of calculations employed here, methods B and C are generally more satisfactory for the molecules containing heteroatoms. For hydrocarbons, the extended Hückel method (method A) is promising[6,8] except for the calculation of the J_{H-H} value for geminal protons. The most unfavorable aspect of method A is the too negative values for the geminal H–H coupling constants of most compounds, particularly for a geminal coupling in the CH_2 group adjacent to the heteroatom. This shortcoming is imporved by methods B and C, as has been discussed in a previous paper.[2] For example, the geminal H–H and directly-bonded ^{13}C–H coupling constants for formaldehyde are calculated to be -39.8 Hz and $+105.6$ Hz by method A, $+2.1$ Hz and $+99.1$ Hz by method B, and $+23.7$ Hz and $+161.7$ Hz by method C. The last set is comparable with the observed values of $+40.2$ and $+172$ Hz.

Let us now discuss our theoretical predictions of a general trend of the J_{C-H} and J_{C-C-H} values in vinyl derivatives. The directly-bonded ^{13}C–H coupling constants, J_{C-H_t} and J_{C-H_c}, increase and decrease respectively, with the increase in the electronegativity, E_x, in the vinyl compound (Fig. 4):



The same situation is also obtained for the geminal ^{13}C–C–H coupling constants, J_{C-C-H_t} and J_{C-C-H_c}, in:



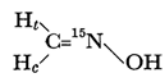
(Figs. 4 and 5). It is well accepted that a linear relationship exists between the *s* character in the bonding carbon orbital and the directly-bonded J_{C-H}. The positive trend of the geminal H–H coupling constants, J_{H-H}, with an increase in the *s* character of the C–H bond has also been observed for geminal ^{13}C–C–H coupling constants, J_{C-C-H}, in ethane (-4.5 Hz), ethylene (-2.4 Hz), and

19) T. Yonezawa and I. Morishima, unpublished work.
20) H. M. McConnell, *J. Mol. Spectry.*, **1**, 11 (1957).
21) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

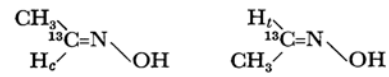
acetylene (+49.2 Hz).[22] Hence, an increase or decrease in the coupling constants can be expected in both cases as the *s* character of the carbon atom in the C–H bond increases or decreases. Therefore, it seems a reasonable prediction by calculation that the general trend of J_{C-H} is similar to that of J_{C-C-H}. It can also be said that the positive or negative trend of J_{C-C-H_t} and J_{C-C-H_c} depends mainly on the increase or decrease in the *s* character of the carbon atom in the C–H_t and C–H_c bonds.

In their theory of nuclear spin-coupling between geminal hydrogens, Pople and Bothner-By[10] have given elegant explanations of the general trend of J_{H-H} in terms of inductive and hyperconjugative electron withdrawal or donation of an adjacent substituent. Their theory can be qualitatively extended to the case of the ^{13}C–C–H geminal coupling in the ^{13}C–CX–H system, as has been done by McLauchlan and Shaefer.[23] However, the general features of J_{C-C-H} in H–C–^{13}C–X system can not be explained by the theory of Pople and Bothner-By.

The experimental values of J_{C-H} and J_{C-C-H} are completely lacking. The only instance of an experimental J_{C-C-H} value has been obtained for vinyl bromide,[24] $J_{C-C-H_t}=+7.5$ Hz, while $J_{C-C-H_c}=-8.5$ Hz, the calculation for which is not performed in the present study. A similar situation may hold for other substituted compounds. In fact, the values of $J_{C-C-H}=0$ in *trans*-dichloroethylene and $J_{C-C-H}=+15.7$ Hz (assumed positive) in *cis*-dichloroethylene are consistent with this assumption. Although calculation yields too positive values for J_{C-C-H_t} and J_{C-C-H_c}, the relative magnitudes of these two couplings may be reliable. The validity of the above predictions that $J_{C-H_t} > J_{C-H_c}$ and $J_{C-C-H_t} > J_{C-C-H_c}$ in the $H_2{}^{13}C{=}CHX$ and $H_2C{-}{}^{13}CHX$ systems respectively should be examined by further experiments. A similar relation, $J_{^{15}N-H_t} > J_{^{15}N-H_c}$, also holds for:



Lehn *et al.*[25] have obtained values of $J_{^{15}N-C-H_t}=-13.88$Hz and $J_{^{15}N-C-H_c}=+2.68$ Hz. Since the gyromagnetic ratio of the ^{15}N nucleus has the minus sign, the large minus coupling constant for $J_{^{15}N-C-H_t}$ is related to the large positive coupling for $J_{^{13}C-C-H_t}$ in the $H_2{}^{13}C{=}CHX$ system. Also, in this case the present calculation gives the values of −11.53 Hz and −3.09 Hz (method B) for $J_{^{15}N-C-H_t}$ and $J_{^{15}N-C-H_c}$ respectively. The large difference between these two geminal coupling constants is again reproduced by the calculation. Similar behavior is also seen in directly-bonded ^{13}C–H coupling constants of propionaldoxime:[26]



Observed:[26] $J_{C-H_c}=161$Hz $J_{C-H_t}=171$Hz

Calculated:[27] (method C) $J_{C-H_c}=131$Hz $J_{C-H_t}=141$Hz

The ^{13}C–H coupling constant for the *trans* C–H bond with respect to the substituent OH is much larger than the *cis* one; this trend is also reproduced by the present calculation. This is also the case for formaldoxime ($J_{C-H_t}=141$ Hz and $J_{C-H_t}=129$ Hz). However, these differences in the coupling constants may possibly be considered to be due to the effect of lone-pair orientation.[26-28]

Because of the delocalized nature of the MO wave functions, and of the many different terms involved in Eq. (1), it does not seem to be easy to isolate the factors which dominate the coupling. In a previous work[2] we found a definite rule for finding the dominant contribution of the excitations which are specified by the orbital symmetry. Below we will discuss briefly the substituent effects on the coupling constant by considering how the dominant excitations vary with the substituent, X.

As we demonstrated previously,[2] a dominant contribution to the geminal H–H′ coupling constant for the CH_3X system is the excitation from the highest occupied (HO) MO, *a* (antisymmetric with respect to the two 1*s* atomic orbitals, *h* and *h*′), to the lowest or second lowest vacant (LV) MO, *a**. As the substituent, X, becomes more electronegative, the antisymmetric orbital energy is lowered, but the LV *a** orbital energy remains almost unchanged, resulting in an increase in the excitation energy ($\varepsilon_j-\varepsilon_i$). The effect of the substituent, X, on the numerator of Eq. (3) is somewhat difficult to analyse. Let us now tentatively consider the value of $2C_{i\mathrm{H}}C_{i\mathrm{H}}$, for an occupied *a* orbital which contributes dominantly to $J_{H-H'}$. This value is now designated as the "partial bond order" between *h* and *h*′ 1*s* orbitals. The partial bond order for the HO *a* orbital increases in its absolute value with an increase in the electronegativity, E_x. This enhancement of the antibonding character between H and H′ decreases the absolute value of the geminal H–H′ coupling constant. These two effects, the lowering of the HO *a* orbital energy and the increas-

22) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc. London, Ser. A*, **269** 385 (1962).
23) K. A. McLauchlan and T. Schaefer, *Can. J. Chem.*, **44**, 32 (1966).
24) R. M. Lynden-Bell, *Mol. Phys.*, **6**, 537 (1963).
25) J. M. Lehn, private communication.
26) T. Yonezawa and I. Morishima, *J. Mol. Spectry.*, **27**, 210 (1968).
27) T. Yonezawa and I. Morishima, *ibid.*, in press.
28) J. P. Kintzinger and J. M. Lehn, *Chem. Commun.*, **1967**, 660.

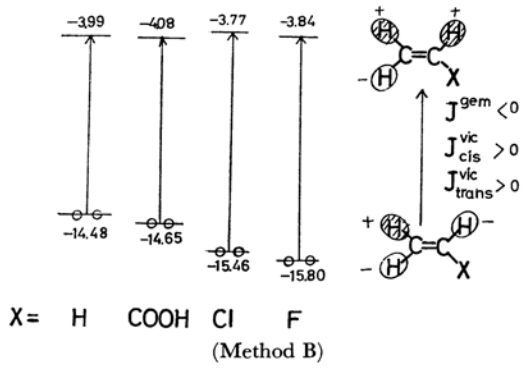


Fig. 6. HO and LV molecular orbital energies (eV) and signs of the orbital coefficients for monosubstituted vinyl compounds.

ing of the atomic orbital coefficient in the HO *a* orbital, contribute dominantly to the increase in the geminal H–H′ couplings in CH_3X systems.

It is well-known that the replacement of X by hyperconjugative groups, such as –C≡CH, –C≡N, and CH_3, increases the negative geminal coupling constant.[29,30] These experimental results are well reproduced by the present calculations, as may be seen in Table 3. The dominant contribution to the geminal and vicinal H–H coupling for vinyl derivatives is made by the excitation from the highest occupied to the lowest unoccupied orbitals, whose orbital symmetry are shown in Fig. 6. These electronic excitations lead to negative and positive H–H coupling constants for geminal and vicinal couplings respectively. The energy difference between these orbitals increases as the electronegative group is replaced. This is illustrated in Fig. 6. Although, of course, the atomic orbital coefficients change, the increases in the excitation energy may play a dominant role in the decrease of the geminal and vicinal coupling constants.

Further progress in the calculation of the signs and magnitudes of nuclear spin coupling constants will come from improvements in the MO energies and LCAO coefficients. Some promise in this regard is shown by the approach using a semi-empirical SCF-MO calculation developed in our laboratory.[31] We got a value of +12.3 Hz for the geminal proton-proton coupling constant of formaldehyde, for instance, by this method. The ^{13}C–H coupling constant is even more improved. The details[32] will be given in the near future.

29) M. Barfield and D. M. Grant, *J. Chem. Phys.*, **36**, 2054 (1962).

30) M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1899 (1963).

31) T. Yonezawa, K. Yamaguchi and H. Kato, This Bulltin, **40**, 536 (1967); H. Kato, H. Konishi and T. Yonezawa, *ibid.*, **40**, 1017 (1967).

32) T. Yonezawa, I. Morishima, H. Konishi and H. Kato, unpublished work.