JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 92, NUMBER 14 JULY 15, 1970

Physical and Inorganic Chemistry

Approximate Self-Consistent Molecular Orbital Theory of Nuclear Spin Coupling. III. Geminal Proton–Proton Coupling Constants[1a,b]

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Abstract: The SCF finite perturbation method is applied to the calculation of geminal proton–proton coupling constants in 19 compounds with saturated $>CH_2$ groups, and 22 compounds with unsaturated $=CH_2$ groups. The calculations were based on the Fermi contact mechanism and the INDO molecular orbital approximation. Generally good agreement is obtained with experimental trends of substituent effects. The results are discussed in terms of the more qualitative Pople–Bothner-By theory, with which good agreement is obtained. Angular and conformational dependences of the computed couplings are explored.

The chemical literature of the past 10 years contains a large body of experimental and theoretical work on correlating the signs and magnitudes of proton–proton coupling constants with molecular structure. Much attention has focused upon coupling between protons bonded to the same carbon atom. These *geminal* proton–proton coupling constants (denoted here by $^2J_{HH}$) have been the subject of frequent studies and critical review.[2]

Early valence-bond calculations generally provided qualitatively correct predictions on the dependences of the *magnitude* of $^2J_{HH}$ on the HCH angle and on the conformations of adjacent conjugating groups.[3,4] However, these apparent early correlations required reexamination[5–7] when the assumed positive sign for $^2J_{HH}$ was later shown to be incorrect for many systems. These valence-bond calculations were based upon developments from Ramsey's[8] second-order perturbation formula for the Fermi contact term, using the average ΔE approximation.

An independent-electron, molecular orbital (MO) approach of Pople and Bothner-By[9] provided successful qualitative predictions on the consequences to $^2J_{HH}$ of inductive and hyperconjugative effects due to neighboring groups. It was based on the Pople–Santry[10] MO treatment of the Ramsey formula, which avoids the average ΔE approximation. This application to $^2J_{HH}$ took the form of a four-electron model of a CH_2 fragment. It provided useful qualitative insight into the nature of substituent effects, but was not directly applicable to calculations on actual molecules. Applications of the Pople–Santry formula to the calculation of $^2J_{HH}$ for molecules using various approximate molecular orbital schemes have had some limited success.[11–14] There are serious difficulties associated

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(1) (a) Research supported in part by a grant from the National Science Foundation; (b) papers I and II in the series are given in ref 24 and 25; (c) Special NIH Fellow, on leave from the University of California, Davis; (d) Postgraduate Scholar of the National Research Council of Canada.

(2) A. A. Bothner-By, *Advan. Magn. Resonance*, **1**, 195 (1965).

(3) H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959).

(4) (a) M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, **83**, 4726, (1961); (b) *J. Chem. Phys.*, **36**, 2054 (1962).

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

(6) E. L. Allred, D. M. Grant, and W. Goodlett, *ibid.*, **87**, 673 (1965).

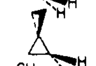
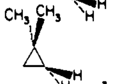
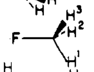
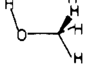
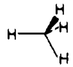
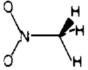
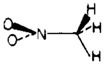
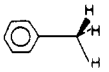
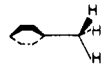
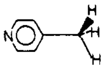
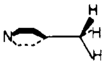
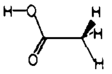
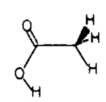
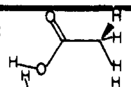
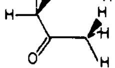
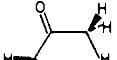
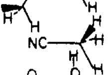
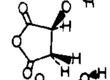
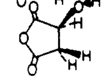
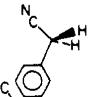
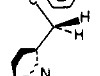
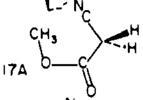
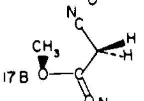
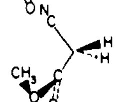
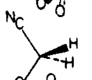
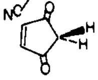
(7) M. Barfield and D. M. Grant, *Advan. Magn. Resonance*, **1**, 149 (1965).

(8) N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953).

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

(10) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1963).

Table I. Calculated and Experimental J_{HH} Values for Geminal Hydrogens Attached to Saturated Carbons[a]

	Compound		Calculated[b]				Experimental	
			J_{12}	J_{13}	J_{23}	J_{av}[c]	$J_{obs.}$[d]	Ref.[e]
1		f	8.80				+5.53	t
2		g	8.35				+5.5	u,v
3		h	8.31				(+)2.0	u
4		i	2.50				-3.9	w
5		j	2.15				-4.5	w
6			-1.85	-1.85	-1.85	-1.85	(-)9.6	x
7			-2.38	-2.38	-1.60	-2.12	-10.8	y,z
8			-6.13	-6.13	-6.13	-6.13	(-)12.4	3,4,5
9A			-5.05	-5.05	-7.05	-5.72	(-)13.2	3
9B		k	-6.41	-6.41	-4.34	-5.72		
10A			-4.64	-4.64	-7.45	-5.58	(-)14.4	3,4,5
10B		l	-6.35	-6.35	-4.02	-5.58		
11A			-4.70	-4.70	-8.83	-6.08	(-)14.5	*
11B		l	-7.11	-7.11	-3.99	-6.07		
12A			-5.81	-5.81	-9.84	-7.15	(-)14.6	3,4,5
12B			-5.84	-5.84	-10.09	-7.26		
12C			-6.28	-6.28	-9.89	-7.38		
12D		m	-8.08	-8.45	-5.57	-7.37		
13A			-5.62	-5.62	-11.82	-7.69	(-)14.9	3,4,5
13B			-5.61	-5.61	-12.47	-7.89		
14			-7.73	-7.73	-7.73	-7.73	(-)16.9	3,4,5
15A		n	-10.44				(-)18.2	5
15B		o	-10.46					
16A			-9.13				(-)18.5	3,4,5
16B		p	-5.70					
17A			-11.69				(-)18.7	3,4,5
17B		q	-11.90					
17C		r	-6.47					
18			-9.11				(-)20.4	3,4,5
19		s	-12.22				-21.5	3,4,5

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[a] Values in Hz. [b] Calculations based on standard geometries with the indicated conformations, unless specifically noted otherwise. Numbering of hydrogens as noted for the representative arrangements in compounds 1 and 6. [c] $^2J_{HH}$ is taken as simply the average of all J_{gem} values obtained for the given CH_2 or CH_3 fragment in its indicated conformation, each value counted the appropriate number of times. [d] J_{obs} is simply the experimentally observed $^2J_{HH}$ value, which may be the result of averaging over various contributing conformations. Assumed signs are in parentheses. [e] Numbers refer to reference numbers in the text. Asterisk refers to D. P. Biddiscombe, E. F. G. Herington, I. J. Lawrenson, and J. F. Martin, *J. Chem. Soc.*, 444 (1963). [f] Geometry based on that of compound 2, with a "standard" CN group replacing a hydrogen. [g] Geometry based on data given in L. E. Sutton, Ed., "Interatomic Distances," The Chemical Society, London, Supplement 1956–1959, 1965, p M82S. [h] Geometry based on data given in L. E. Sutton, Ed., "Interatomic Distances," The Chemical Society, London, 1958, p M134. [i] Geometry based on data given in L. E. Sutton, Ed., "Interatomic Distances," The Chemical Society, London, 1958, pp M182, M98S. [j] Geometry based on that of cyclopropane (see *i*), with two "standard" methyl groups replacing two geminal hydrogens. [k] Conformation with the plane of the NO_2 group perpendicular to that of NCH^1 fragment. [l] Conformation with the plane of the aromatic ring perpendicular to that of the CCH^1 fragment. [m] Conformation with the plane of the carbonyl group perpendicular to the CCH^1 fragment. [n] Geometry based on planar ring, with C—C, CC(O), C=O, C(O)O, CO, CH, and OH bond distances of 1.540, 1.480, 1.230, 1.265, 1.430, 1.080, and 0.960 Å, respectively, and COC, OCO, OCC, CCC, HCH, HCO, and COH angles of 99.0°, 119.0°, 123.2°, 97.5°, 111.4°, and 109.5°, respectively. [o] Same geometry as described in *n* except that the COH plane is perpendicular to that of the ring. [p] Conformation with the NCCC plane perpendicular to the plane of the ring. [q] Conformation with the COC plane perpendicular to the NCCC(O)O plane. [r] Conformation with COCO plane perpendicular to the NCCC plane. [s] Geometry based on a planar ring with C=C, C—C(O), C(O)—C(H_2), C=O, CH, and CH distances of 1.340, 1.450, 1.520, 1.230, 1.080, and 1.090 Å, respectively, and C(O)CC(O),H′ CC(O)C, C(O)CC, CCO, and HCH angles of 95.0, 114.8, 108.2, 122.6 and 111.4°, respectively. [t] C. A. Reilly and J. Swalen, *J. Chem. Phys.*, **32**, 1378 (1960). [u] F. S. Mortimer, *J. Mol. Spectrosc.*, **5**, 199 (1960). [v] N. Sheppard and J. J. Turner, *Proc. Roy. Soc.*, **A252**, 506 (1959). [w] D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3218 (1963). [x] F. K. Kaplan and J. D. Roberts, *ibid.*, **83**, 4666 (1961). [y] J. F. Bagli, P. E. Marand, and R. Gaudry, *J. Org. Chem.*, **28**, 1207 (1963). [z] B. Bak, J. T. Nielson, J. Rastrup-Andersen, and M. Schottlander, *Spectrochim. Acta*, **18**, 741 (1962).

with these applications and in the analogous valence bond treatment which avoids the average ΔE approximation.[15] These are due to the problem of con-

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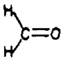
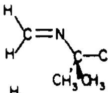
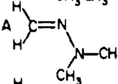
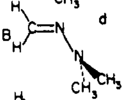
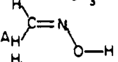
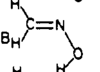
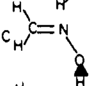
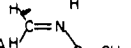
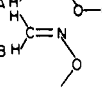
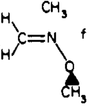
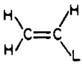
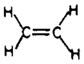
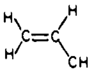
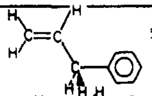
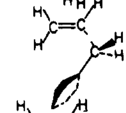
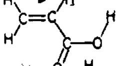
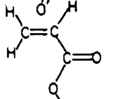
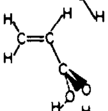
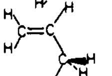
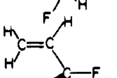
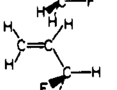
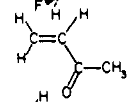
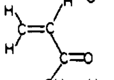
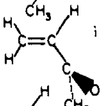
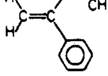
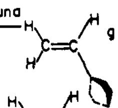
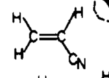
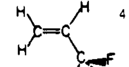
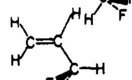
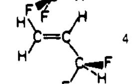
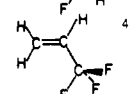
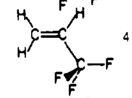
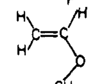
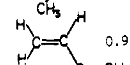
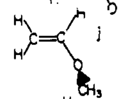
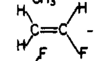
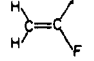
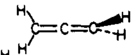
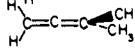
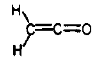
(11) R. C. Fahey, G. C. Graham, and R. L. Piccioni, *J. Amer. Chem. Soc.*, **88**, 193 (1966).
(12) J. N. Murrell and V. M. S. Gil, *Theor. Chim. Acta*, **4**, 114 (1966).
(13) S. Polezzo, P. Cremaschi, and M. Simonetta, *Chem. Phys. Lett.*, **1**, 357 (1967).
(14) P. Loeve and L. Salem, *J. Chem. Phys.*, **43**, 3402 (1965).
(15) M. Barfield, *ibid.*, **48**, 4458, 4463 (1968).

Table II. Calculated and Experimental J_{HH} Values for Geminal Hydrogens Attached to Unsaturated Carbons[a]

Compound	Calculated J_{HH}	Experimental $J_{obs.}$[b]	Ref.[c]
20 	31.82	40.2 to 42.4	1,k
21 	16.58	(+)16.1 to 16.5	l
22A 	8.96	(+)10.3 to 12.0	l
22B  [d]	9.81		
23A 	4.76	(+)7.6 to 10.0	l,m
23B 	5.00		
23C  [e]	5.37		
24A 	4.81	(+)7.0 to 9.2	l,m
24B 	7.72		
24C  [f]	5.26		
25 	13.80	7.1	n
26 	3.24	2.3	o
27 	5.00	2.08	p
28A 	5.03	1.96	q
28B  [g]	4.72		
29A 	4.34	1.7	r
29B 	4.97		
29C  [h]	5.16		
30A 	4.43	1.54	1
30B 	4.62		
30C 	4.[illegible]		
31A 	4.33	1.10	s
31B 	4.95		
31C  [i]	5.24		
32A 	5.00	1.08	t
32B  [g]	5.12		
33 	4.59	0.91	u
34A 	4.87	0.67	1
34B 	4.58		
34C 	4.53		
35A 	4.44	-0.15	1
35B 	4.43		
36A 	2.32	-2.1	v,w
36B 	0.95		
36C  [j]	1.19		
37 	-0.18	-3.2	x,y
38 	-1.68	-4.8	z
39 	-7.63		
40 	-8.65	(-)9.0	6
41 	-11.92	(-)15.8	6

[a] Values in Hz. [b] J_{obs} is simply the experimentally observed $^2J_{HH}$ value, which is generally the average result of various contributing conformations. Assumed signs are given in parentheses. [c] Numbers refer to reference numbers in the text. [d] Geometry based on a conformation with the plane of the two methyl carbons and the attached nitrogen normal to the plane of the H_2CNN fragment. [e] Geometry based on a conformation with the dihedral CNOH angle equal to 90°. [f] Geometry based on a conformation with the dihedral CNOC angle equal to 90°. [g] Geometry based on a conformation with the "phenyl plane" normal to the "vinyl plane." [h] Geometry based on a conformation with the OCO plane normal to the "vinyl plane". [i] Geometry based on a conformation with the CCO plane normal to the "vinyl plane". [j] Geometry based on a conformation with the COC plane normal to the "vinyl plane". [k] B. L. Shapiro, R. M. Kopchik, and S. J. Ebersole, *J. Chem. Phys.*, **39**, 3154 (1963). [l] B. L. Shapiro, S. J. Ebersole, G. J. Karabatsos, F. M. Vane, and S. L. Manatt, *J. Amer. Chem. Soc.*, **85**, 4041 (1963). [m] B. L. Shapiro, S. J. Ebersole, and R. M. Kopchik, *J. Mol. Spectrosc.*, **11**, 200 (1963). [n] C. S. Johnson, M. A. Weiner, J. S. Waugh, and D. Seyferth, *J. Amer. Chem. Soc.*, **83**, 1306 (1961). [o] D. M. Graham and C. E. Holloway, *Can. J. Chem.*, **41**, 2114 (1963). [p] A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, **83**, 231 (1961). [q] A. A. Bothner-By, C. Naar-Colin, and H. Gunther, *ibid.*, **84**, 2748 (1962). [r] Y. Arata, H. Shimizu, and S. Fujiwara, *J. Chem. Phys.*, **36**, 1951 (1962). [s] S. Castellano and J. S. Waugh, *ibid.*, **37**, 1951 (1962). [t] E. I. Snyder, *J. Phys. Chem.*, **67**, 2873 (1963). [u] R. T. Hobgood, Jr., R. E. Mayo, and J. H. Goldstein, *J. Chem. Phys.*, **39**, 2501 (1963). [v] J. Feeney, A. Leadwith, and L. H. Sutcliffe, *J. Chem. Soc.*, 2021 (1962). [w] R. T. Hobgood, Jr., G. S. Reddy, and J. H. Goldstein, *J. Phys. Chem.*, **67**, 110 (1963). [x] C. N. Banwell and N. Sheppard, *Discuss. Faraday Soc.*, **34**, 115 (1962). [y] C. N. Banwell, N. Sheppard, and J. J. Turner, *Spectrochim. Acta*, **16**, 794 (1960). [z] G. W. Flynn, M. Matsushima, and J. D. Baldeschwieler, *J. Chem. Phys.*, **38**, 2295 (1963).

structing satisfactory excited-state wave functions and to the serious cancellation effects in the second-order perturbation sum.

Barfield[16] has given a molecular orbital treatment of spin-spin coupling in terms of the density matrix formalism and the average ΔE approximation. In applying this method to geminal coupling in a four-electron fragment, he concludes that reasonable choices of the pivotal parameter lead to negative $^2J_{HH}$ values in saturated hydrocarbons.

Recently, an alternative theoretical approach for calculating second-order properties has been reported from this laboratory.[17-19] Using finite perturbation

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(16) M. Barfield, *J. Chem. Phys.*, **44**, 1836 (1966).

(17) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *Chem. Phys. Lett.*, **1**, 465 (1967).

(18) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960 (1968).

(19) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *ibid.*, **49**, 2965 (1968).

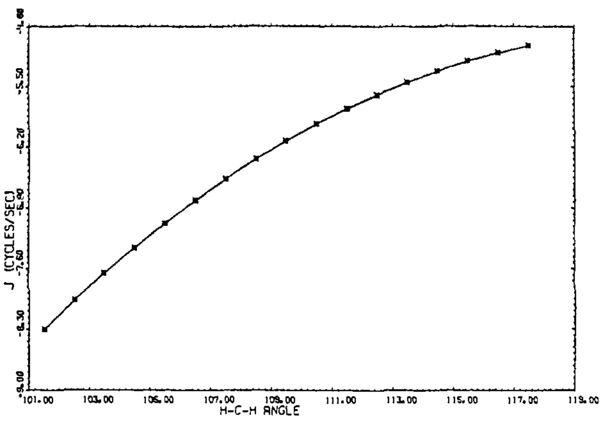

Figure 1. Plot of ${}^2J_{12}$ *vs.* the H^1CH^2 angle, θ, for methane.

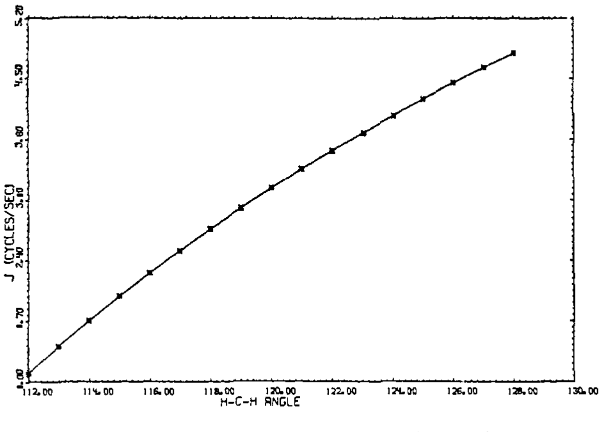

Figure 2. Plot of ${}^2J_{12}$ *vs.* the H^1CH^2 angle, θ, for ethylene.

techniques, it avoids explicit consideration of excited states without invoking the average ΔE approximation. Its initial application involved INDO (Intermediate Neglect of Differential Overlap) MO wave functions[20] in an approximate SCF framework for calculating the Fermi contact spin-coupling interaction.[17-19] In this application it requires the calculation of an unrestricted INDO MO wave function in the presence of a contact perturbation due to the presence of a finite nuclear moment μ_B. It has been shown that at this level of approximation the method leads to an expression for the reduced coupling constant K_{AB} given by eq 1, where β is the Bohr magneton, $s_A^2(0)$ is the valence-shell s-orbital density of atom A at its nucleus, and K_{AB}

$$K_{AB} = (8\pi/3)^2\beta^2 s_A^2(0) s_B^2(0)\left\{\frac{\partial}{\partial h_B}\rho_{s_As_A}(h_B)\right\}_{h_B=0} \qquad (1)$$

is defined as $2\pi J_{AB}/h\gamma_A\gamma_B$. The term in braces is the derivative of the diagonal spin density matrix element corresponding to that orbital.

The present paper, devoted to geminal proton–proton couplings, is the third in a series designed to explore the applicability of this new method to the calculation of a variety of spin–spin coupling constants. Preliminary results[17-19] for ${}^2J_{HH}$ showed considerable promise; here we explore in some detail the influence of molecular structure, substituents, and conformational effects on the ${}^2J_{HH}$ values computed by this method.

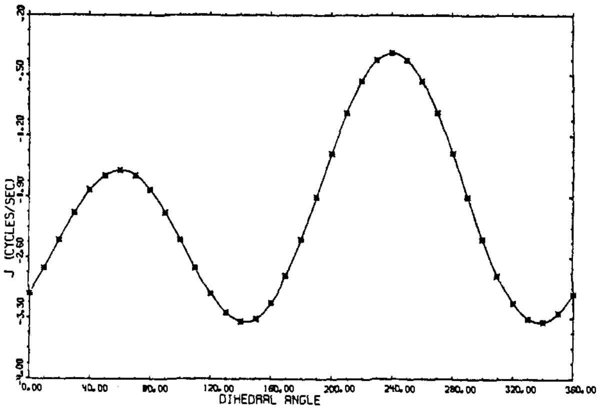

Figure 3. Plot of ${}^2J_{12}$ *vs.* the dihedral H^1COH angle, ϕ, for methanol.

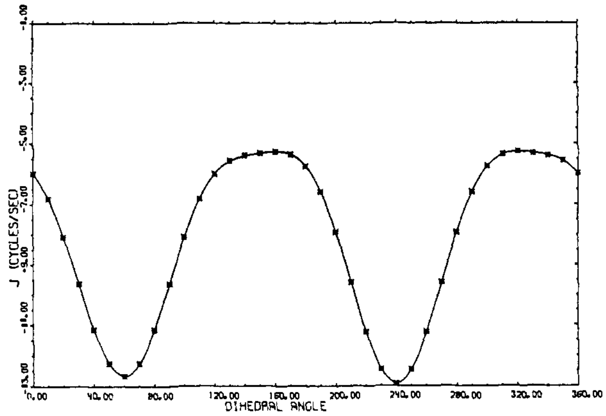

Figure 4. Plot of ${}^2J_{12}$ *vs.* the dihedral H^1CCH angle, ϕ, for acetaldehyde.

Results

All calculations reported here were based on eq 1. Computational details are described elsewhere in some detail.[18,19] Except for the ring-containing compounds included in Table I, all calculations were based on the standard geometrical model used previously in this laboratory.[18-21] For the ring compounds, geometries were chosen on the basis of available structural information on the same or similar compounds. These choices are noted in Table I, which contains calculated and experimental values of ${}^2J_{HH}$ for hydrogens attached to saturated carbon atoms. Table II collects the calculated and experimental ${}^2J_{HH}$ values for hydrogens attached to unsaturated carbons. Both tables contain some entries for which calculations were performed for more than one conformation of a substituent group. Where methyl groups are involved, the weighted average of the three independent computed ${}^2J_{HH}$ values for *each conformation* is also given in Table I.

Figures 1–4 summarize the results of calculations in which molecular geometry was varied systematically. In the first two, the dependence of calculated values of ${}^2J_{HH}$ on the HCH angle is presented. The latter two figures demonstrate the sensitivity of calculated ${}^2J_{HH}$ values to the conformational relationship between the HCH fragment and an attached group with 2p electrons

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(20) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

(21) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

available for conjugative interaction with the fragment.

Discussion

Overall Trends. Tables I and II reveal overall trends of general qualitative agreement between calculated and experimental $^2J_{HH}$ values within each table. In some cases geometrical or conformational questions render direct comparisons impossible. However, the general pattern of trends is satisfactorily established by the less questionable cases, and indicates that the degree of fit into an established trend may provide a criterion by which conformational uncertainties can be settled in some cases. The trends will be considered in greater detail below.

Tables I and II show that the calculation reproduces the experimentally known negative sign of $^2J_{HH}$ for saturated hydrocarbons, the positive sign for $H_2C=$ groups in olefinic hydrocarbons, as well as the intermediate $^2J_{HH}$ values for cyclopropyl CH_2 groups. The dependence of $^2J_{HH}$ on HCH angle and carbon hybridization have been discussed previously; the earlier VB treatments gave incorrect signs.[3,4] Figures 1 and 2 provide some additional information on this point. The former gives values of $^2J_{12}$ computed for various H^1CH^2 angles in methane, with the H^3CH^4 angle and all bond lengths maintained at their tetrahedral-methane values. Figure 2 provides the same type of information for $^2J_{HH}$ in deformed ethylene, where only the HCH group containing the coupled protons is deformed. In both figures it is seen that the computed $^2J_{HH}$ values increase algebraically with the HCH angle.

The computed results in Tables I and II also reflect other aspects of known experimental trends as summarized by Pople and Bothner-By.[9]

(a) For both sp^2 and sp^3 CH_2 groups, substitution of an electronegative atom in an α position leads to a positive shift in $^2J_{HH}$. Agreement with this is evident by comparing fluoromethane (case 6) and methanol (case 7) with methane (case 8) and by comparing formaldehyde (case 20) and the imines (cases 21–24) with ethylene (case 26).

(b) Substitution of an electronegative atom in a position β to the CH_2 groups introduces a negative shift in $^2J_{HH}$. This is especially evident in comparisons of the fluoroethylenes (cases 37 and 38) and methoxyethylene (case 36) with ethylene. An additional example is found within the imines; *i.e.*, comparing case 21, in which an alkyl carbon occupies the β position, with cases 22, 23, and 24, in which a nitrogen or oxygen atom occupies that position. Additional possible examples of this relationship may be found in both tables, but their interpretation is complicated by possible domination of another influence (c).

(c) A π-electron system adjacent to a CH_2 group generally leads to a negative $^2J_{HH}$ shift. Evidence that the present method maintains this trend can be seen in the last three entries of Table II. For sp^3 groups, it is seen that the only entries in Table I for which computed $^2J_{HH}$ values are more negative than that of methane are for compounds which have adjacent π systems; furthermore all but two compounds (or three, depending on the inclusion of a correction given later) of this structural type in the table have computed $^2J_{HH}$ values lower than the methane value.

Comparison with the Rules of Pople and Bothner-By. Tables I and II provide substantial support for the general trends stated by Pople and Bothner-By on the basis of their MO treatment of geminal proton coupling.[9] Of crucial importance in that treatment was the concept of the "local symmetry" of CH_2 group molecular orbitals; this symmetry was defined with respect to the relative signs of the corresponding atomic orbital coefficients for the coupled hydrogens in the LCAO MO. Using a four-electron CH_2 fragment and the independent electron spin coupling formalism developed earlier by Pople and Santry,[10] they arrived at a description of substituent effects on $^2J_{HH}$ which can be summarized in two general rules.

"I. Withdrawal of electrons from orbitals *symmetric* between hydrogen atoms (generally inductive effects) should lead to a positive change in the coupling constant.

II. Withdrawal of electrons from orbitals *antisymmetric* between hydrogen atoms (generally hyperconjugative effects) should lead to a *negative* change in the coupling constant."

Consistent with I and II are the predictions of effects of opposite sign for electron donation into the CH_2 group. Thus, electron donation into the symmetric CH_2 orbitals should give a negative change in $^2J_{HH}$, and donation into antisymmetric orbitals should lead to a positive change.

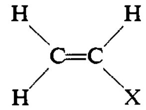
Rule II is similar to a conclusion reached by Barfield and Grant from experimental work and valence-bond treatments.[5] These rules are, of course, closely related to the experimental trends summarized as a, b, and c above.

$=CH_2$ Groups. In discussing the present results in terms of rules I and II we begin with Table II, for which fewer questions arise in relation to conformational uncertainties than in Table I.

Ample evidence for rule I can be seen by comparing results for cases 26–41, in which a carbon atom is attached directly to the H_2C carbon, with cases 21–24, in which a more electronegative atom (O or N) is bonded directly to the H_2C carbon. An inductive withdrawal of electrons from the H_2C group by the O or N-R moiety is expected on intuitive chemical grounds and is confirmed by inspection of the density matrix; Table II shows that a positive influence on the computed $^2J_{HH}$ values accompanies this inductive withdrawal, in agreement with rule I and with experimental data. As pointed out by Pople and Bothner-By,[9] a concomitant effect which operates in these systems is a back-donation from the lone-pair orbitals on N or O into the antisymmetric H_2C group orbitals. According to rule II, this effect should also give a positive change in $^2J_{HH}$.

The most apparent consequences of agreement with rule II in Table II are constituted by the last three entries. The INDO density matrices indicate strong hyperconjugation in which electron density from the antisymmetric H_2C orbitals is transferred into the $C=CR_2$ or $C=O$ π bond. According to rule II this should lead to a substantial negative shift in $^2J_{HH}$, which is observed in the computed values for cases 39–41 in comparison with ethylene. These predictions are in qualitative agreement with the experimental results on dimethyl allene and ketene, reported by Allred, Grant, and Goodlett;[6] these authors also presented a valence-bond theory which related the reduction in $^2J_{\mathrm{HH}}$ to hyperconjugation in a manner analogous to what was described above.

According to the theory of Pople and Bothner-By, replacement of one hydrogen in ethylene by a more electronegative atom or group, X, to give a vinyl compound, I, should be accompanied by decrease in $^2J_{\mathrm{HH}}$ from the ethylene value. This was based on rule II and the observation that MO theory predicts a general electron withdrawal from the antisymmetric H_2C group orbital. Agreement with this prediction is clear from Table II in comparisons of both computed and experimental values for cases in which X is F or O-R (cases 36, 37, and 38) with the ethylene value. A similar relationship can be displayed for $H_2C{=}NX$ systems: both the calculated and experimental ranges of values of $^2J_{\mathrm{HH}}$ for compounds 23 and 24, in which an oxygen atom is attached to the imine nitrogen, are in turn lower than the $^2J_{\mathrm{HH}}$ values given for compound 21, in which X is a *t*-butyl group. Case 25 appears to constitute an example of an effect of the same type, but of the opposite sign, *i.e.*, a donation from the C–Li bond into the antisymmetric H_2C orbital. However, the calculation appears to overemphasize this effect, in that the computed $^2J_{\mathrm{HH}}$ value is much too high to fit into the experimental trend. On the other hand, the calculation was based on an assumed structure and geometry, whereas the nature of vinyllithium in solution is not well established.



I

The theoretical method gives an incorrect prediction (relative to ethylene) if the substituent X in I is CH_3 (case 27). For the series $H_2C{=}CH{-}CY$, represented by cases 27–35, the experimental variation of $^2J_{\mathrm{HH}}$ with substituent Y may be reflected to a considerable extent in the calculated values. However, in making a comparison there are substantial conformational uncertainties and the values span only a small range.

$>CH_2$ Groups. Examples can be cited in Table I in support of inductive withdrawal according to rule I, although in each case the interpretation is complicated somewhat by a concomitant back-donation into the antisymmetric H_2C orbital, as discussed by Pople and Bothner-By.[9] Fluoromethane (6) and methanol (7), considered in relation to methane (8) are examples, as are cyanoethylene oxide (1), ethylene oxide (2), and ethylenimine (3), considered in comparison to the cyclopropane hydrocarbons (4 and 5). In each case the compound containing an electronegative atom directly adjacent to the H_2C group leads to computed and experimental $^2J_{\mathrm{HH}}$ values which are higher than the values for the corresponding "parent" hydrocarbon. Another example is nitromethane (9), although it is only evident if care is taken to account for hyperconjugation effects. In case 9A, such effects can influence $^2J_{23}$ but not $^2J_{12}$ or $^2J_{13}$ because of symmetry restrictions. Therefore, the latter two should be dominated by the inductive effect, and, indeed, these values are higher than the methane value. In this manner the hyperconjugative withdrawal effect responsible for the low value of $^2J_{23}$ according to II can be estimated as roughly -2 Hz. Similar considerations applied to methanol can be used to estimate the effect of back-donation into the antisymmetric H_2C orbital. By symmetry, such an influence can operate on a CH^2H^3 fragment but not on a CH^1H^2 or CH^1H^3 fragment. Hence, the inductive effect of the OH group, with methane as reference, can be identified with $^2J_{12}$ and $^2J_{13}$, *i.e.*, about 3.7 Hz. The back-donation effect in this configuration can then be estimated as roughly the difference $^2J_{23} - {}^2J_{12}$, about 0.8 Hz. This has the correct sign according to rule II. A more accurate account of these effects in methanol is given in Figure 3, in which $^2J_{12}$ is plotted *vs.* the dihedral H^1COH angle ϕ between H^1 and the hydroxyl hydrogen. As expected from the discussion of Pople and Bothner-By on the geometry of antisymmetric influences, the maxima in $^2J_{12}$ values occur at the angles 60° and 240°, when the COH plane bisects the H^1CH^2 angle, and the hydroxyl hydrogen is *trans* and *cis*, respectively, to H^3. The latter conformation leads to the higher maximum. Of interest are the positions of the minima in the curve, at about 145° and 335°. These do not correspond to the configurations in which either of the coupled protons lies in the COH plane, *i.e.*, 0, 120, 180, and 300°. It is these latter configurations for which the positive contributions due to antisymmetric back-donation would be absent in the simplest application of the model of Pople and Bothner-By. However, for ϕ in the regions of 150° and 330°, the oxygen p atomic orbital holding the nonbonded electron pair is properly positioned for back-donation into the *symmetric* CH^1H^2 group orbital; according to rule II, this should give a negative contribution to $^2J_{12}$. The form of Figure 3 indicates that this interaction may be significant.

Cases 9–19 constitute examples which support the predicted effects of hyperconjugative withdrawal as described in rule II. For all of these compounds the experimental $^2J_{\mathrm{HH}}$ values are more negative than that of methane. For most of the conformations covered in cases 9–19, the average of $^2J_{12}$, $^2J_{13}$, and $^2J_{23}$ is also lower than the methane value. However in *all* cases, those conformations containing the H_2C group in the optimum conformation for hyperconjugative electron withdrawal yield computed $^2J_{\mathrm{HH}}$ values for the corresponding HH pair which are substantially below the methane value. Thus, while the average computed $^2J_{\mathrm{HH}}$ values for nitromethane (9), toluene (10), and 4-methylpyridine (11) are *less* negative than the methane value, the computed $^2J_{23}$ values for cases 9A, 10A, and 11A are substantially more negative. The conformational dependence of the hyperconjugative influence on $^2J_{\mathrm{HH}}$ was discussed by Pople and Bothner-By within the framework of their localized MO model,[9] and by Barfield and Grant *via* a valence-bond treatment.[5] Qualitatively similar conformational relationships are contained in the calculated results for compounds 9–19. Malic anhydride (case 15) and cyclopentene-3,5-dione (case 19) are examples in which the rigid geometry of a ring system ensure that the C—C=O plane will bisect (at least approximately) the HCH angle; this type of configuration should, according to II, lead to substantial reductions in $^2J_{\mathrm{HH}}$ for these compounds. In the latter case, the combination of two conjugating carbonyl groups leads to very low calculated and experimental values of $^2J_{\mathrm{HH}}$. Although the computed value is not as low as one might expect by comparison with the trends, it is quite sensitive to the chosen geometry, which is not given by the standard geometrical model employed in the other calculations. The calculations on the five-membered ring compounds 15 and 19 used the same bond lengths and bond angle for the CH_2 fragment; comparison of the two computed results shows a substantial effect of the second neighboring carbonyl group, about -2 Hz.

The detailed dependence of computed $^2J_{HH}$ values on the assumed orientation of a conjugating group is shown in Figure 4, where calculated values of $^2J_{12}$ for acetaldehyde are plotted against the dihedral H^1CCH angle, ϕ, which relates H^1 and the formyl hydrogen. As expected from the reasoning upon which rule II was based, the largest negative hyperconjugative effects on $^2J_{12}$ are obtained when the CCO plane bisects the H^1CH^2 angle, *i.e.*, when ϕ is 60 or 240°. Of interest is the fact that the computed maxima do not occur at the dihedral angles 0, 120, 180, and 300°, which would correspond to the configurations for which the conjugative electron withdrawal from the CH^1H^2 group orbital would be absent in the model of Pople and Bothner-By. However, as they pointed out, an electron withdrawal from the symmetric CH^1H^2 orbital, leading to a positive contribution to $^2J_{12}$, would be expected in the configurations corresponding to ϕ values of 150 and 330°. These angles are close to the values corresponding to the maxima of Figure 4. Furthermore, these maxima occur at $^2J_{12}$ values significantly higher than the methane value, which is close to the $^2J_{12}$ values computed for ϕ equal to 0, 120, 180, and 300°, *i.e.*, where interactions with the π system of the carbonyl group should be absent. Hence, a significant positive contribution due to a symmetric withdrawal into the carbonyl π system seems indicated at the positions of the maxima in Figure 4. This angular dependence for acetaldehyde is entirely analogous to the methanol case of Figure 3, except that the direction of electron transfer due to the interaction with a neighboring π system is opposite, and so is the sign of the effect on $^2J_{12}$.

One apparent difficulty with the present calculation occurs in connection with the predicted substituent effect of the CN group (cases 14, 16, 17, and 18). Although the predictions place the various compounds in approximately the experimentally observed order (depending upon assumptions on substituent conformations), the negative contribution associated with a CN group may be underestimated in the calculations. Thus, the experimental results show that the substituent effect on $^2J_{HH}$ of a neighboring CN group in acetonitrile (14) is almost twice that of a neighboring carbonyl group in acetone (13). This was rationalized by the simple MO and VB treatments[5,9] in terms of hyperconjugation for both πx and πy electrons with a CN group (assigning the z direction as that of the C–C axis).[5,9] However, the computed results in Table I indicate –CN and –CO– substituent effects of roughly comparable size in these compounds and malononitrile (18). For other cases in Table I the relative contributions of –CN and –CO– substituent effects cannot be discussed with confidence in terms of the level of agreement with experimental results, because of uncertainties associated with conformations of s substituent groups.

The Factor $s_A{}^2(0)s_B{}^2(0)$. A possible source of difficulty in the calculations described above is the assumed constancy of the factor $s_A{}^2(0)s_B{}^2(0)$ in eq 1. Grant and Litchman[22] suggested that variations in this factor may play a dominant role in the dependence of J_{CH} on substituent effects in substituted methanes. Employing the Slater[23] screening concept of effective nuclear charge in the manner of Grant and Litchman, we have investigated[24,25] their approach as a qualitative guideline for judging the possible importance of such variations in determining the variations of J_{CH} and J_{CC} in a variety of compounds. This suggested that variation in $s_A{}^2(0)$-$s_B{}^2(0)$ could be significant, while not dominant.

For $^2J_{HH}$ coupling constants, we have tested the analogous adjustment given in

$$J_{adj} = [(1.0 - 0.30q_A)(1.0 - 0.30q_B)]^3 J_{unadj} \quad (2)$$

where J_{unadj} represents the value computed directly according to eq 1 and q_A is the excess local electron density on hydrogen atom A (total A density $= -1.0$). The effects of this adjustment are small and relatively unimportant. Changes are generally less than 0.5 Hz, and do not lead to much improvement in correlation with experimental results.

Summary and Conclusions

In the INDO approximation, the application of SCF finite perturbation theory to Fermi contact spin coupling gives $^2J_{HH}$ values for substituted methanes and ethylenes which generally show the experimentally correct trends for substituent and structural effects. Less success is realized in providing actual values for some cases than in accounting for trends. Questions of molecular conformations introduce uncertainties in comparing experimental results for some cases. The more qualitative predictions of the earlier, independent-electron MO approach of Pople and Bothner-By are born out in the present work. Results on the conformational aspects of conjugative effects on $^2J_{HH}$ should prove useful in work on structure determination.

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