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Approximate Self-Consistent Molecular Orbital Theory of Nuclear Spin Coupling. IV. Vicinal Proton–Proton Coupling Constants in Substituted Ethanes and Ethylenes and Related Compounds[1a,b]

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Abstract: The SCF finite perturbation method is applied to the calculation of vicinal proton–proton coupling constants of the $-HC{=}CH-$, $>HC{-}CH<$, $=CH{-}CH<$, and $=CH{-}CH=$ types and in a few planar and six-membered cyclic systems. The calculations were based on the Fermi contact coupling mechanism and were carried out in the INDO molecular orbital approximation. Conformational dependences of the computed couplings are explored and reproduce the well-known trends. Promising agreement is obtained with certain experimental correlations between substituent effects in related molecular frameworks, although unsuccessful predictions of specific substituent effects are found in certain cases.

A great deal of experimental and theoretical attention has been focused on the spin–spin coupling between protons attached to adjacent carbon atoms. The resulting *vicinal* coupling constants (denoted here by $^{3}J_{\mathrm{HH}}$) have been the subject of critical review.[2]

The dependence of $^{3}J_{\mathrm{HH}}$ on the stereochemical relationship between the coupled hydrogens received early attention, both experimentally and theoretically. In substituted ethylenes, the *cis vs. trans* distinction has been clearly demonstrated experimentally,[2–10] and its interpretation by Karplus[11–13] in terms of valence-bond theory was one of the first successful applications of the Ramsey formulation[14] in systems of chemical interest. The dependence of $^{3}J_{\mathrm{HH}}$ upon the dihedral angle between the coupled hydrogens attached to carbons connected by single bonds has also been considered, especially for substituted ethanes. For such compounds the complicating influence of conformational considerations in the interpretation of experimental $^{3}J_{\mathrm{HH}}$ data has been considered formally,[15–22] and attempts have been made to utilize this dependence for

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characterizing the population patterns among conformers.[19–24] The dependence of $^3J_{\mathrm{HH}}$ upon the HCCH dihedral angle in ethane has also been treated by Karplus in the valence bond framework,[11–13] and the results have often been used as guidelines in interpreting the data for substituted ethanes.[13] Similar stereochemical dependences of $^3J_{\mathrm{HH}}$ have also been predicted more recently by modifications of the valence-bond treatment[25–28] and by molecular orbital methods.[29–32] The latter have resulted largely from the MO approximation of the Ramsey formula which was presented by Pople and Santry.[33] A few attempts have been made to account for structural and substituent effects on $^3J_{\mathrm{HH}}$ in terms of either the MO approach[30–32,34–36] or the valence-bond method;[13,25,37] however, the results have indicated only limited promise.

Extensive studies have been carried out on the influence of substituents on $^3J_{\mathrm{HH}}$, especially in substituted ethanes[4,17,38] and ethylenes.[2–10,39–42] In the latter case, comparisons with substituent effects on vicinal couplings on substituted benzenes have raised interesting questions on the nature of the apparently inductive mechanism which seems to dominate these substituent effects.[42–46] These and other comparisons strongly support the view of an overall substituent effect which alternates in sign as it is transmitted down a carbon chain.

The influence of delocalization[32] on $^3J_{\mathrm{HH}}$ and the role of π electrons in mechanisms of vicinal coupling in ethylene have also received attention.[46,47] Recently, Barfield and Karplus have reformulated the valence-bond approach to Fermi contact coupling in terms of Penny–Dirac bond orders, giving rise to a classification of contributions in "direct" and "indirect" categories; this method was applied to ethane-like and ethylene-like fragments.[28]

All previous theories which have been applied to the vicinal proton–proton problems summarized above have relied upon the Ramsey formulation, using either the average excitation energy approximation or the term-by-term second-order sum. The applicability of the former approach is limited by the nature of the basic approximation itself, whereas the latter encounters difficulty in the construction of satisfactory excited-state wave functions and in the serious cancellation problems in the sum.

The theoretical method used in this paper is based on an alternative approach to calculating second-order properties, which has been reported recently from this laboratory.[48–50] This method, which is based on a finite perturbation scheme, was first applied to Fermi contact spin–spin coupling.[50–53] In this application it involves the calculation of an unrestricted SCF MO wave function in the INDO approximation,[54] under the influence of a Fermi contact perturbation, h_{B}, of the form given in eq 1. Within this framework, a

$$h_{\mathrm{B}} = (8\pi/3)\beta\mu_{\mathrm{B}}s_{\mathrm{B}}^{2}(0) \tag{1}$$

proton–proton spin–spin coupling constant is then given by eq 2, where γ_{H} is the magnetogyric ratio of

$$J_{\mathrm{H_AH_B}} = h(4\beta/3)^2\gamma_{\mathrm{H}}^{2}s_{\mathrm{A}}^{2}(0)s_{\mathrm{B}}^{2}(0)\left[\frac{\partial}{\partial h_{\mathrm{B}}}\rho_{s_{\mathrm{A}}s_{\mathrm{A}}}(h_{\mathrm{B}})\right]_{h_{\mathrm{B}}=0} \tag{2}$$

a proton, β is the Bohr magneton, $s_{\mathrm{A}}^{2}(0)$ is the density of the hydrogen 1s orbital of atom A at its nucleus, and $\rho_{s_{\mathrm{A}}s_{\mathrm{A}}}$ is the diagonal spin density matrix element corresponding to that orbital.

The present paper is the fourth in a series devoted to exploring the scope of applicability of the method embodied in eq 2. The first three papers in the series were concerned with directly bonded C–H couplings,[51] directly bonded C–C, C–N, and C–F couplings,[52] and geminal proton–proton coupling constants.[53] The present one reports the calculation of $^3J_{\mathrm{HH}}$ values in several compounds of the general types –HC═CH–, >HC═CH<, ═HC—CH<, and ═HC—CH═, as well as a few planar cyclic compounds. The emphasis here is on structural, conformational, and substituent effects. Such effects in the $^3J_{\mathrm{HH}}$ values of substituted benzenes will be considered in a separate paper.

Results

All calculations reported here were based on eq 2, and were carried out as reported elsewhere.[49,50] Table I summarizes results obtained on substituted ethanes (>HC—CH<), Table II gives results on substituted ethylenes (–HC═CH–), Table III presents results on ═CH—HC< systems, Table IV summarizes ═HC—CH═ results, and Table V is concerned with cyclohexane systems. In all of these cases the chosen geometries were based on the standard geometrical

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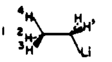
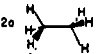
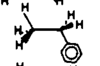
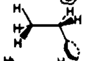
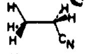
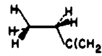
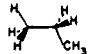
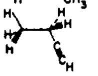
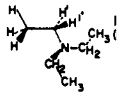
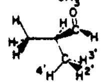
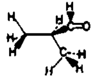
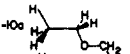
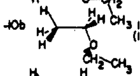
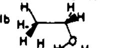
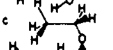
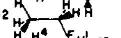
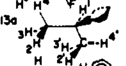
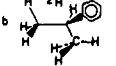
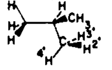
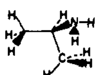
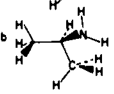
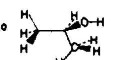
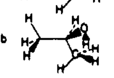
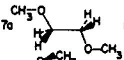
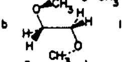
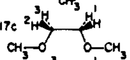
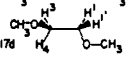
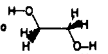
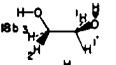
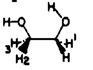
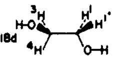
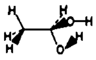
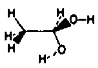
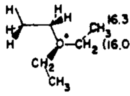
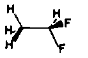
Table I. $^3J_{HH}$ Values in >CH—HC< Compounds[a]

Compound[b]		Calcd $^3J_{12}$	Calcd $^3J_{13}$	Calcd $^3J_{14}$	Calcd $^3J_{av}$[c]	Exptl $^3J_{expt1}$	Exptl Ref
I-1		25.91	2.22	7.91	12.01	8.9	f
-2a		18.62	3.25	3.25	8.37		
-2b		13.00	6.05	6.05	8.38	+8.0	g
-2c		9.60	14.56	0.91	8.36		
-3a		19.00	3.13	3.24	8.46	7.62	h
-3b		18.21	3.17	2.85	8.08		
-4		18.65	3.18	3.49	8.44	+7.60	h
-5		18.66	3.08	2.88	8.21	7.53	h,i
-6		18.34	3.04	3.04	8.14	7.26	j
-7		18.75	3.32	3.15	8.41	7.2	k
-8		18.47 (18.01)[d]	3.04 (3.24)	2.40 (2.24)	7.97 (7.83) [7.90][e]	7.13	h
-9a		18.33 (6.36)	3.45 (13.46)	2.86 (5.51)	8.21 (8.44) [8.32]	7.0	l,m
-9b		18.99 (6.04)	3.66 (12.36)	3.07 (5.91)	8.57 (8.10) [8.33]		
I-10a		17.97	3.30	2.01	7.76	6.97	h
-10b		18.11 (17.91)	3.28 (3.25)	2.19 (2.10)	7.86 (7.75) [7.8]		
-11a		17.89	3.31	2.04	7.75		
-11b		16.88	3.73	1.80	7.47	6.97	m
-11c		17.07	3.49	1.77	7.44		
-12		17.11	3.54	1.59	7.41	6.9	n
-13a		18.65	3.06	2.77	8.16	6.9	l,m
-13b		18.32	3.24	2.91	8.19		
-14		18.44 (5.86)	3.26 (12.32)	2.75 (5.86)	8.15 (8.01) [8.08]	6.8	o
-15a		17.47 (4.64)	2.24 (11.59)	3.04 (6.77)	7.58 (7.67) [7.62]	6.3	l,m
-15b		17.57 (4.61)	2.46 (10.93)	3.18 (7.07)	7.74 (7.54) [7.64]		
-16a		18.03 (4.49)	2.13 (11.35)	3.10 (7.48)	7.75 (7.77) [7.76]	6.2	l,m
-16b		16.63 (3.72)	1.80 (10.35)	3.44 (7.75)	7.29 (7.27) [7.28]		
I-17a		17.88	3.25		10.56	5.3	p
-17b		16.54	3.11		9.82		
-17c		8.35	9.96		6.10		
-17d			9.52 (5.96)	5.96 (3.87)	7.74 (4.91) [6.32]		
-18a		17.69	3.29		10.49	5.27	p
-18b		2.39 (16.24)	1.08 (1.08)		1.74 (8.66) [5.20]		
-18c		8.17	10.05		9.11		
-18d			9.71 (5.83)	5.83 (3.85)	7.77 (4.84) [6.30]		
-19a		16.56	1.97	1.51	6.68	5.26	p
-19b		16.82	1.83	1.82	6.82		
-20		16.32 (16.08)	3.64 (3.66)	1.42 (1.14)	7.13 (6.96) [7.07]	4.7	q
-21		15.04	1.40	1.40	5.95	4.5	r

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[a] Values in Hz. [b] Indexing of hydrogens based upon the scheme in I-1, unless otherwise indicated. [c] Average of $^3J_{HH}$ values between H^1 and other indexed hydrogens. [d] Values in parentheses refer to $^3J_{HH}$ values between $H^{1'}$ and other indexed hydrogens. [e] Values in brackets give the average of $^3J_{HH}$ values between both H^1 and $H^{1'}$ and the other indexed hydrogens, *i.e.*, the average of $^3J_{av}$ for H^1 and $H^{1'}$. [f] G. Fraenkel, D. G. Adams, and J. Williams, *Tetrahedron Lett.*, 767 (1963). [g] D. M. Graham and C. E. Holloway, *Can. J. Chem.*, **41**, 2114 (1963); R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **269**, 385 (1962). [h] Reference 38. [i] G. Slomp, *J. Amer. Chem. Soc.*, **84**, 673 (1962). [j] D. R. Whitman, L. Onsager, M. Saunders, and H. E. Dubb, *J. Chem. Phys.*, **32**, 67 (1960). [k] P. T. Narasimhan and M. T. Rogers, *J. Amer. Chem. Soc.*, **82**, 5983 (1960). [l] J. Ranft, *Ann. Phys. (Leipzig)*, **10**, 1 (1962). [m] A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **25**, 362 (1956). [n] S. L. Stafford and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **83**, 4473 (1961). [o] J. S. Waugh and F. W. Dobbs, *J. Chem. Phys.*, **31**, 1235 (1959). [p] Reference 17. [q] S. Brownstein, B. C. Smith, G. Ehrlich, and A. W. Laubengayer, *J. Amer. Chem. Soc.*, **81**, 3826 (1959). [r] G. W. Flynn and J. D. Baldeschwieler, *J. Chem. Phys.*, **37**, 2907 (1962).

model used previously in this laboratory.[51-55] Table VI presents results on some planar, five- and six-membered ring compounds; except for benzene, which fits the standard model,[55] the geometries for these compounds were chosen on the basis of available structural information on the same or similar compounds.

Calculations on all of the lithium compounds included in this study were based on assumed monomeric structures with carbon-lithium bond distances of 2.1 Å. Actual structures of these solution species are unknown; hence, the calculations reported here must be considered as referring to "hypothetical" lithium compounds. Direct comparison with experimental values must therefore be given only limited significance.

In Tables I and III there are many cases where more than one $^3J_{HH}$ value are defined for a given structure. In such cases the average is given in the table as J_{av}. Also, computations have been carried out on more than one conformation for several of the compounds in each of the tables. In some cases this involves only the conformational relationship of a substituent with respect to a fixed vicinal hydrogen pair; in others it involves the geometrical relationship between the coupled protons. This latter case bears directly upon the important problem of the dependence of $^3J_{HH}$ on the HCCH dihedral angle; the study of this type of dependence is presented in greater detail in Figure 1, which gives results for ethane, propene, and acetaldehyde.

For many of the compounds represented in the tables, the experimental values have been determined without sign. These are assumed to be positive and are listed without explicit sign specification. Those experimental results for which the sign has been determined are so indicated in the tables.

Discussion

1. Overall Trends. Comparisons of calculated and experimental results collected in the tables and figures clearly show that the computational method employed here is able to reproduce the most firmly established aspects of the experimental behaviors of HCCH vicinal couplings, namely, that they are generally positive and

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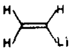
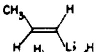
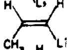
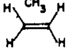
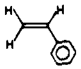
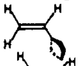
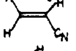
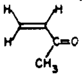
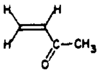
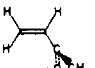
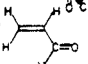
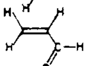
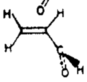
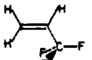
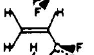
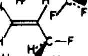
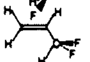
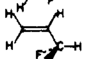
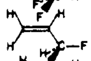
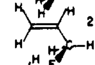
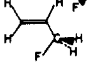
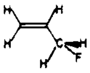
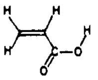
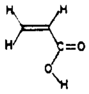
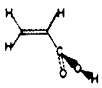
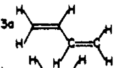
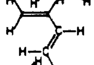
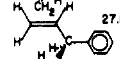
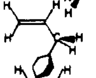
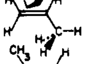
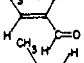
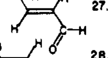
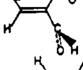
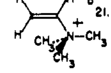
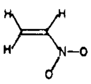
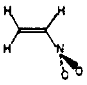
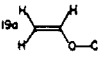
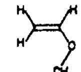
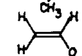
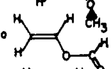
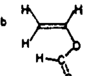
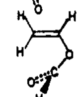
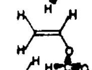
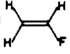
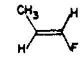
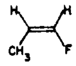
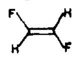
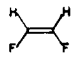
(55) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

Table II. $^3J_{HH}$ Values in ABC=CHX Compounds[a]

Compound	Calcd		Exptl		
	$^3J_{trans}$	$^3J_{cis}$	$^3J_{trans}$	$^3J_{cis}$	Ref
[f] II-1 	43.62	23.03	+23.9	+19.3	c
-2 	47.41		22.2		d
-3 		23.74		17.4	d
-4 	25.15	9.31	+19.1	+11.5	e
-5a 	26.17	9.08	+18.59	+11.48	l
-5b 	26.71	10.26			
-6 	26.05	10.72	+17.92	+11.75	g
-7a 	26.05	9.79			
-7b 	26.61	10.40	+17.80	+10.77	h
-7c 	27.21	11.96			
-8a 	25.69	9.95			
-8b 	26.63	10.68	+17.50	+10.00	i
-8c 	27.00	11.86			
II-9a 	24.99	10.05	+17.49	+11.13	j
-9b 	24.46	9.80			
-10a 	25.41	10.17			
-10b 	24.70	9.42	+17.47	+10.85	j
-10c 	25.43	9.76			
-11a 	25.77	10.19			
-11b 	25.81	9.73	+17.21	+10.66	j
-11c 	25.29	9.98			
-11d 	25.01	9.34			
-12a 	26.53	10.90			
-12b 	25.18	9.72	17.2	10.2	k
-12c 	26.52	11.68			
II-13a 	25.72	9.21			
-13b 	26.53	9.69	+17.05	+10.17	l
-13c 	26.65	10.16			
-14a 	27.15	9.37	+17.00	+10.05	m
-14b 	26.09	9.14			
-15 	25.32	9.21	+16.81	+10.02	n
-16a 	26.89				
-16b 	27.88		15.45		o
-16c 	28.24				
-17 	[b]21.73	5.56	+15.12	+8.18	p
-18a 	21.62	6.93	15.0	7.5	q
-18b 	22.10	8.54			
II-19a 	23.83	6.06			
-19b 	20.94	4.83	+14.4	+6.6	r
-19c 	22.84	5.63			
-20a 	23.40	5.88			
-20b 	21.54	4.78	+13.8	+6.3	s
-20c 	21.16	4.89			
-20d 	22.32	5.47			
-21 	20.73	4.74	+12.75	4.65	t,u
-22 	21.59		+11.1		v
-23 		4.61		+4.5	v
-24 	19.41		+9.5		w
-25 		2.87		+2.0	w,x

[a] Values in Hz. [b] =C—N bond distance taken as the value 1.35 Å reported for analinium ion in L. E. Sutton, Ed., "Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958, p M201. [c] Reference 10. [d] Reference 39. [e] D. M. Graham and C. E. Holloway, *Can. J. Chem.*, **41,** 2114 (1963). [f] E. I. Snyder, *J. Phys. Chem.*, **67,** 2873 (1963). [g] R. T. Hobgood, Jr., R. E. Mayo, and J. H. Goldstein, *J. Chem. Phys.*, **39,** 2501 (1963). [h] S. Castellano and J. S. Waugh, *ibid.*, **37,** 1951 (1962). [i] Reference 41. [j] Reference 2. [k] Y. Arata, H. Shimizu, and S. Fujiwara, *J. Chem. Phys.*, **36,** 1951 (1962). [l] Reference 38. [m] A. A. Bothner-By, C. Naar-Colin, and H. Gunther, *J. Amer. Chem. Soc.*, **84,** 2748 (1962); A. A. Bothner-By and H. Gunther, *Discuss. Faraday Soc.*, **34,** 127 (1963). [n] Reference 9. [o] R. A. Hoffman and S. Gronowitz, *Ark. Kemi*, **16,** 471 (1960). [p] M. Ohtsuru, K. Tori, J. Lehn, and R. Seher, *J. Amer. Chem. Soc.*, **91,** 1187 (1969). [q] Reference 6. [r] J. Feeney, A. Ledwith, and L. H. Sutcliffe, *J. Chem. Soc.*, 2021 (1962). [s] T. Schaefer, *J. Chem. Phys.*, **36,** 2235 (1962). [t] Reference 4. [u] C. N. Banwell and N. Sheppard, *Discuss. Faraday Soc.*, **34,** 115 (1962). [v] R. A. Beaudet and J. D. Baldeschwieler, *J. Mol. Spectrosc.*, **9,** 30 (1962). [w] G. W. Glynn, M. Matsushima, and J. D. Baldeschwieler, *J. Chem. Phys.*, **38,** 2295 (1963). [x] T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *J. Chem. Soc.*, 743 (1961).

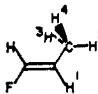
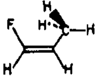
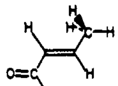
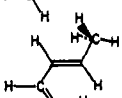
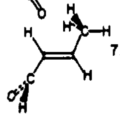
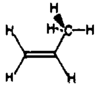
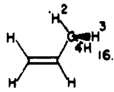
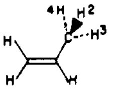
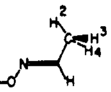
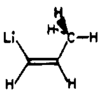
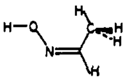
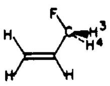
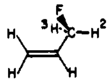
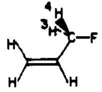
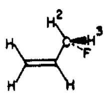
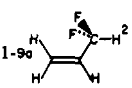
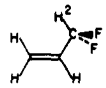
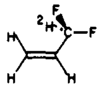
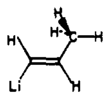
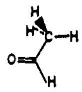
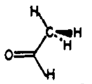
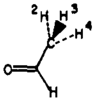
that protons in a *trans* relation have larger coupling constants than those in the corresponding *cis* or *gauche* configurations. Tables I, II, IV, and VI and the figures provide evidence of more subtle aspects of the dependence of $^3J_{HH}$ of HCCH dihedral angle; these details will be discussed in section 2.

The tables also reveal that the established experimental relationships between $^3J_{HH}$ and the coordination or hybridization of the connecting carbons are accommodated by the calculation. Thus, comparison of results for ethane (J_{av}), ethylene (*cis* and *trans* considered individually), and propene (J_{av}) places the four relevant computed values in the correct experimental order for these hydrocarbons, which have linking carbons that can be described approximately as sp^3–sp^3, sp^2–sp^2, and sp^2–sp^3, respectively. Similarly, considering J_{av}, J_{cis}, and J_{trans} for ethyl and vinyl compounds with the same substituents, the correct experimental order is found within each set corresponding to a particular substituent, *e.g.*, I-1 and II-1, I-4 and II-6, I-6 and II-15, I-10 or I-11 and II-19 (OR as the substituent), and I-12 and II-21.

Some other demonstrated experimental trends which to varying degrees are produced in the calculated results are concerned with substituent effects. For example, Tables I and II demonstrate an irregular tendency toward lower computed $^3J_{HH}$ values in ethanes and ethylenes which are substituted by electronegative groups. While direct comparisons are in many cases made difficult because of conformational uncertainties, especially in Table I, some correlations between calculated and experimental trends are in evidence. These are considered in detail in section 4.

The four calculated $^3J_{HH}$ values of compounds V-1 and V-2 (assuming a rapid equilibrium between V-1a and V-1b) provide another example of the overall qualitative agreement of the method with experiment, as these four are in the same order as the experimental numbers. Similarly, the calculated results for all but two of the planar ring systems considered in Table VI show overall agreement with the experimental order, within the relatively small limits that may be associated with experimental error or with conformational choices for the calculations. Even with the two deviating

Table III. ${}^3J_{HH}$ Values for $=$CH—CH$<$ Systems[a]

Compound[b]		Calcd				Exptl	
		${}^3J_{12}$	${}^3J_{13}$	${}^3J_{14}$	${}^3J_{av}$[c]	${}^3J_{HH}$	Ref
III-1		9.21	7.16	7.16	7.84	+7.1	d
-2		9.09	7.15	7.15	7.79	+7.0	d
-3a		7.99	8.31	8.31	8.30		
-3b		7.95	8.10	8.10	8.05	+6.9	e
-3c		7.94	7.15	6.92	7.33		
-4a		8.48	7.00	7.00	7.49		
-4b		16.20	3.20	3.20	7.53	+6.5	f
-4c		2.65	6.61	13.28	7.51		
III-5		15.96	6.67	6.67	9.77	6.2	g
-6		6.82	5.63	5.63	6.03	6.0	h
-7		13.89	6.58	6.58	9.02	5.8	g
-8a			2.14	2.14	2.14		
-8b		6.46	8.34		7.40	5.33	i
-8c			5.44	5.44	5.44		
-8d		15.44	2.70		9.07		
III-9a		4.10			4.10		
-9b		14.41			14.41	5.31	i
-9c		6.49			6.49		
-10		4.74	6.45	6.45	5.88	4.2	h
-11a		4.42	7.40	7.40	6.41		
-11b		14.22	2.51	2.51	6.41	2.83	j
-11c		12.16	3.46	3.62	6.41		

[a] Values in Hz. [b] Indexing of hydrogens based upon the scheme in III-1, unless otherwise indicated. [c] Average of ${}^3J_{HH}$ values between H^1 and other indexed hydrogens. [d] R. A. Beaudet and J. D. Baldeschwieler, *J. Mol. Spectrosc.*, 9, 30 (1962). [e] S. Gronowitz and R. A. Hoffman, *Ark. Kemi*, **16**, 471 (1960). [f] Reference 9. [g] G. J. Karabatsos, R. A. Taller, and F. M. Vane, *J. Amer. Chem. Soc.*, **85**, 2327 (1963). [h] Reference 39. [i] Reference 2. [j] J. G. Powles and J. H. Strange, *Mol. Phys.*, **5**, 329 (1962).

compounds, VI-6 and VI-7, the two couplings for each are in the correct experimental order; the geometries employed in these two cases were based on the assumption of an invariant pyridine framework, which may be responsible for some errors in placing the computed values with respect to those of the other compounds.

Some of the details of these promising comparisons are considered in the following sections.

2. Dependence of ${}^3J_{HH}$ on the HCCH Dihedral Angle. Figure 1 displays the results of ${}^3J_{HH}$ calculations carried out on ethane, propene, and acetaldehyde with a variety of HCCH dihedral angles, θ. Each curve is symmetrical about $\theta = 180°$, and closely resembles the analogous results reported previously based upon either valence-bond[11,25–28] or simple MO approaches.[29–32] It is interesting that the minima of the three curves (especially those of 1c) are displaced somewhat from the 90 and 270° values obtained by Karplus.[11–13] The INDO values of $P^2 s_H s_{H'}$ for the coupled hydrogens were found to follow an angular dependence similar to that given for $J_{HH'}$ in Figure 1a, with a similar displacement of the minima from 90 and 270°. According to the simpler McConnell MO theory,[56] $J_{HH'}$ values are predicted to be proportional to $P^2 s_H s_{H'}$ values. While we do not find a strict proportionality, the similarity of angular dependences suggests a qualitative validity for the early McConnell approach *in this particular case.*

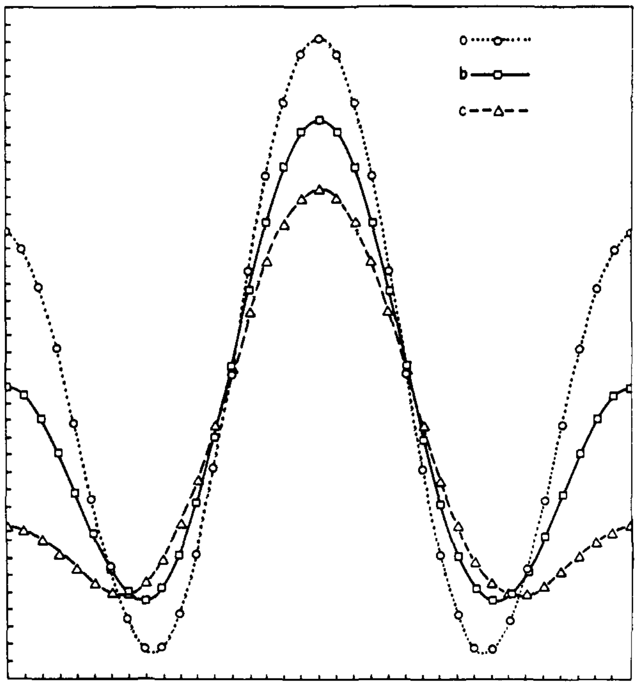
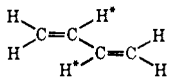
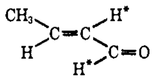
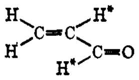
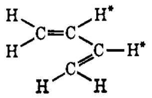
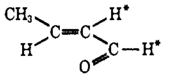
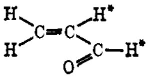
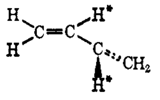
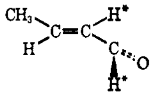
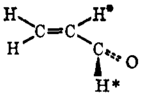


Figure 1. (a) Plot of ${}^3J_{HH}$ *vs.* the HCCH dihedral angle for one proton pair in ethane. (b) Plot of ${}^3J_{H^*H^*}$ *vs.* the H*CCH* dihedral angle for one proton pair in propene, H_2CH^*—$H^*C{=}CH_2$. (c) Plot of ${}^3J_{H^*H^*}$ *vs.* the H*CCH* dihedral angle for one proton pair in acetaldehyde, H_2CH^*—H^*CO.

Although the main features of Figures 1a, 1b, and 1c are similar, there is a general shift of the maxima in the

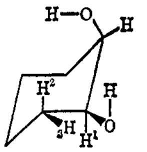
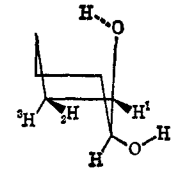
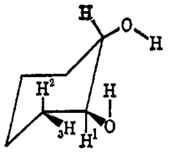
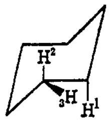
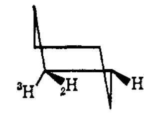
(56) H. M. McConnell, *J. Chem. Phys.*, **24**, 460 (1956).

Table IV. $^3J_{HH}$ Values in =CH—HC= Systems[a]

Compound	Calcd $^3J_{H^*H^*}$	Exptl $^3J_{H^*H^*}$	Ref	Compound	Calcd $^3J_{H^*H^*}$	Exptl $^3J_{H^*H^*}$	Ref	Compound	Calcd $^3J_{H^*H^*}$	Exptl $^3J_{H^*H^*}$	Ref
IV-1a 	17.66			IV-2a 	18.04			IV-3a 	17.69		
IV-1b 	6.78	10.41	*b*	IV-2b 	2.38	7.57	*c*	IV-3b 	2.65	7.40	*c*
IV-1c 	4.32			IV-2c 	6.05			IV-3c 	5.73		

[a] Values in Hz. [b] Reference 40. [c] Reference 41.

Table V. $^3J_{HH}$ Values in Dihydroxycyclohexanes[a]

	Compound	Calcd				Exptl		
		$^3J_{12}$	$^3J_{13}$	$^3J_{12_{res}}$[b]	$^3J_{13_{res}}$[b]	$^3J_{12}$	$^3J_{13}$	Ref
V-1a		16.85	3.53	10.37	2.48	7.1	3.8	*c*
-1b		3.89	1.42					
-2		16.36	3.43			11.0	4.5	*c*
-3a		18.02	2.69	10.56	2.69			
-3b		3.10	2.69					

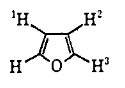
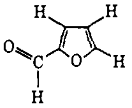
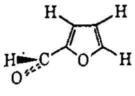
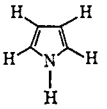
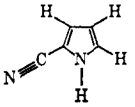
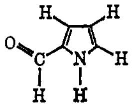
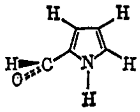
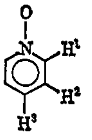
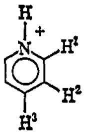
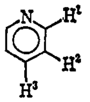
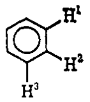
[a] Values in Hz. [b] $^3J_{12_{res}}$ and $^3J_{13_{res}}$ refer to the average of results computed for couplings of two equivalent conformers assumed to be in rapid equilibrium with each other with equal populations. [c] Data taken for deuterated isomers from R. V. Lemieux and J. W. Lown, *Tetrahedron Lett.*, 1229 (1963).

sequence ethane > propene > acetaldehyde, the shift being more pronounced for the maxima at $\theta = 0$. Together with a slight increase in the $^3J_{HH}$ values that correspond to the minima in the sequence ethane < propene < acetaldehyde, this leads to a decrease in the overall variation of $^3J_{HH}$ with θ in the order ethane > propene > acetaldehyde.

Many additional examples of the same type of θ dependence can be found in the tables. In many cases this variation of $^3J_{HH}$ upon θ introduces considerable uncertainty into the direct comparison between computed and experimental values. These uncertainties result from the rather limited knowledge of conformational populations in the experimental systems, and can only be minimized to the extent that limitations on that knowledge can be minimized. Indeed, if a sufficiently decisive demonstration can be made for the reliability of the theory in its present form or in some improved future form, then comparisons of computed and measured $^3J_{HH}$ values may provide the most convenient and reliable access to knowledge of these populations.

The most serious cases in which conformational uncertainties cloud the evaluation of the theoretical

Table VI. ${}^3J_{HH}$ Values in Planar-Ring Systems[a]

Compound		Calcd		Exptl		
		${}^3J_{12}$	${}^3J_{23}$	${}^3J_{12}$	${}^3J_{23}$	Ref
VI-1[b]		2.78	1.25	3.53	1.80	*i*
-2a[c]		2.80	1.26	3.62	1.65	*i*
-2b[d]		2.67	1.21			
-3[d]		3.20	1.79	3.7	2.63	*i*
-4[e]		3.10	1.72	3.74	2.62	*j*
VI-5a[c]		3.15	1.75	3.73	2.68	*i*
-5b[c]		3.03	1.70			
-6[f]		4.55	4.61	6.47	7.65	*k*
-7[g]		5.07	6.29	5.95	7.95	*l*
-8[h]		5.54	8.30	4.84	7.62	*l*
-9		8.15	8.15	7.56	7.56	*m*

[a] Values in Hz. [b] Geometry is based upon data taken from L. E. Sutton, Ed., "Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958, p M162. [c] Geometry based upon that of the parent compound, replacing H with a "standard" formyl group. [d] Geometry based upon data from the reference of footnote *b*, Suppl 1956–1959, 1965, p M108S. [e] Geometry based upon that of parent compound, replacing H with "standard" cyano group. [f] Geometry based upon that of pyridine, with NO distance of 1.30 Å. [g] Geometry based upon that of pyridine with NH distance of 1.00 Å. [h] Geometry based upon data from the reference of footnote *d*, p M120S. [i] R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **37**, 1056 (1959); **39**, 905 (1961). [j] Reference 2. [k] Reference 42. [l] J. B. Merry and J. A. Goldstein, *J. Amer. Chem. Soc.*, **88**, 5560 (1966). [m] J. M. Read, Jr., R. E. Mayo, and J. H. Goldstein, *J. Mol. Spectrosc.*, **21**, 235 (1966).

method occur when the experimental couplings correspond to *individual pairs* of hydrogens, as opposed to averages over more than two couplings (*i.e.*, certain J_{av} values in Tables I and III). Thus, the calculated results of the tables, when viewed in terms of only one pair of hydrogens at a time, reflect qualitatively the expected general type of θ dependence as is depicted in Figure 1. This kind of focusing on an individual pair is reflected in the computed couplings in Table IV and for compound III-9, and the associated θ dependence must be a dominant, determining feature of the corresponding observed ${}^3J_{HH}$ values. A similar situation exists for the calculated J_{av} value in a $CHCH_2$ fragment, where J_{av} is the average of two computed couplings, and an analogous circumstance obtains for the corresponding experimental value J_{exptl}; an example of this is shown in compound III-8. A case with J_{av} and J_{exptl} resulting from three couplings arises in fragments of the type $CHCH_3$; results from Tables I and III show that the conformational influence in this case is not very substantial. Thus, computed results for cases I-2, I-9, I-14, I-15, I-16, III-4, and III-11 are not strongly dependent upon the conformational arrangement of the methyl group with respect to the CH hydrogen.

The results show that the J_{av} and J_{exptl} values which result from averaging of four individual couplings are strongly dependent on the conformational relationship between the two CH_2 groups. This is dramatically illustrated by the computed J_{av} values for the various conformers of compounds I-17 and I-18.

These patterns are summarized in Figure 2, which is derived from Figure 1, and gives the dihedral dependences of computed values of J_{av} obtained from two, three, four, six, and nine ${}^3J_{HH}$ values corresponding to the $CHCH_2$, $CHCH_3$, CH_2CH_2, CH_3CH_2, and CH_3CH_3 moieties of ethane.[57]

3. Influence of Substituent Conformation. Tables I, II, III, V, and VI contain examples in which the conformational relationships between the vicinal systems and substituent groups have been varied. In many cases substantial effects are observed in the computed ${}^3J_{HH}$ values, but in no instance is an effect obtained which is more than about 25% of the coupling constant. The smallest effects of a substituent attached directly to the vicinal CHCH moiety are observed in the calculated J_{av} values for substituted ethanes, as shown in Table I, where such effects are generally less than 7% of the mean J_{av} values of the various conformers for a given molecule. The variation among the individually computed ${}^3J_{HH}$ values, J_{12}, J_{13}, and J_{14}, is somewhat larger.

(57) The J_{av} values given for couplings with CH_2 and/or CH_3 groups in Tables I and III and in Figure 2 bear directly on experimental results only to the extent that they pertain to contributions that the indicated conformations make to the net coupling that results from a rapid averaging process, *e.g.*, rapid rotation.

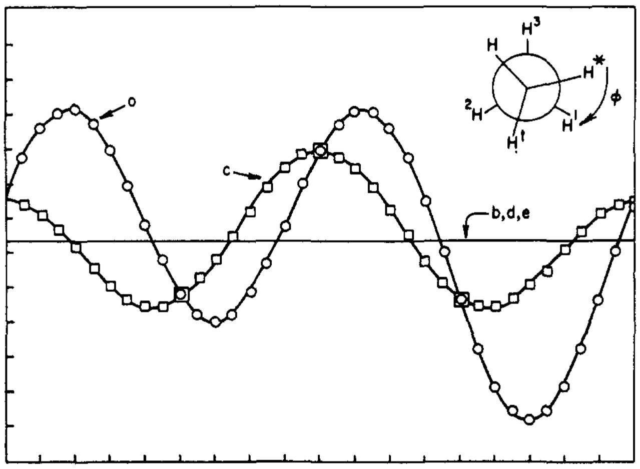


Figure 2. Plots of $^3J_{av}$ *vs.* HCCH dihedral angle for ethane, derived from Figure 1a: (a) $(^3J_{H^*H^1} + {}^3J_{H^*H^2})/2$, *i.e.*, for the CH–CH$_2$ fragment; (b) $^3J_{H^*H^1} + (^3J_{H^*H^2} + {}^3J_{H^*H^3})/3$, *i.e.*, for the CH–CH$_3$ fragment; (c) $(^3J_{H^*H^1} + {}^3J_{H^*H^2} + {}^3J_{H^\dagger H^1} + {}^3J_{H^\dagger H^2})/4$, *i.e.*, for the CH$_2$–CH$_2$ fragment; (d) $(^3J_{H^*H^1} + {}^3J_{H^*H^2} + {}^3J_{H^*H^3} + {}^3J_{H^\dagger H^1} + {}^3J_{H^\dagger H^2} + {}^3J_{H^\dagger H^3})/6$, *i.e.*, for the CH$_2$–CH$_3$ fragment; (e) average of all $^3J_{HH}$ values in CH$_3$–CH$_3$.

In substituted ethylenes some conformationally rather sensitive substituent effects on computed $^3J_{HH}$ values are obtained, especially if the substituent places a conformationally variable, π-bonded atom (or one with a lone pair) directly adjacent to the unsaturated CH carbon. Examples are found in the computed results for compounds II-5, II-7, II-8, II-12, II-13, II-18, II-19, and II-20, where variations due to the conformation of substituents range up to about 25% of the mean couplings computed for a particular vicinal hydrogen pair. It is noted that the $^3J_{HH}$ values computed for hydrogens in the *cis* configuration are more sensitive to the details of substituent conformation than *trans*-related hydrogens. This can be seen in the examples quoted above from Table II, where the effects of substituent conformation are typically in the range of 5–10% of the computed coupling constants for $^3J_{trans}$, but typically in the range of 15–20% for $^3J_{cis}$. From cases II-9, II-10, II-11, and II-14 it is seen that even $^3J_{cis}$ varies by less than 10% with conformational variations of a substituent which has a saturated atom with no lone pairs attached directly to the vicinal CHCH moiety. These results imply an appreciable involvement of π electrons, at least indirectly, in determining substituent effects on the vicinal HCCH coupling mechanism.

4. Substituent Effects. The conformational questions raised above introduce some uncertainties into an evaluation of the present method's ability to handle substituent effects on $^3J_{HH}$ by direct comparison with experimental results. Nevertheless, some conclusions can be drawn in addition to the general ones mentioned in section 1. One experimental pattern which is qualitatively maintained in the calculated results in Tables I and II is the relative sensitivities of $^3J_{HH}$ in substituted ethanes and ethylenes to substituent identities. The experimental order of these sensitivities in terms of the percentage change of the coupling constant throughout a series of compounds is J_{cis} (ethylenes) > J_{trans} (ethylenes) > J_{av} (ethanes). This order was accounted for qualitatively by Karplus from a valence-bond model,[13]

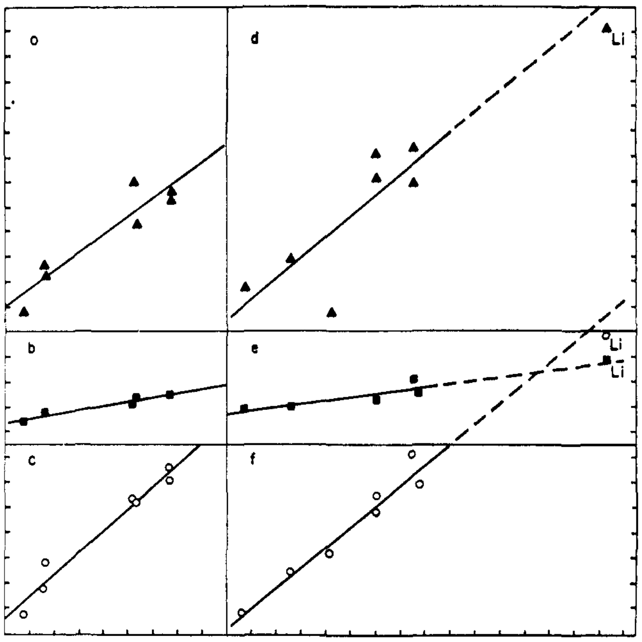


Figure 3. (a) Plot of calculated J_{gem}[53] *vs.* calculated $^3J_{cis}$ for CH$_2$=CHX compounds. (b) Plot of calculated $^3J_{HH}$ (average) for CH$_3$-CH$_2$X compounds *vs.* calculated $^3J_{cis}$ for the corresponding CH$_2$=CHX compounds. (c) Plot of calculated $^3J_{trans}$ *vs.* calculated $^3J_{cis}$ for CH$_2$=CHX compounds. (d) Plot of experimental J_{gem}[53] *vs.* experimental $^3J_{cis}$ for CH$_2$ = CHX compounds. (e) Plot of experimental $^3J_{HH}$ for CH$_3$CH$_2$X compounds *vs.* experimental $^3J_{cis}$ for the corresponding CH$_2$=CHX compounds. (f) Plot of experimental $^3J_{trans}$ *vs.* experimental $^3J_{cis}$ for CH$_2$=CHX compounds.

and is evidenced in the present results. This qualitative conclusion follows from inspection of Figures 3e and 3f with Figures 3b and 3c, which are constructed from the results in Tables I and II and relate these three types of vicinal couplings in a series of compounds with both calculated and experimental results. Plots similar to those in Figures 3d and 3f have been presented previously in representing patterns of experimental data.[3a,4,44] Because monomeric structures were chose- entirely arbitrarily for calculations on the lithium compounds, the resulting values cannot be expected to correspond with experimental results on actual species which may be polymeric. Hence, these results have been excluded from plots 3a, 3b, and 3c. Since the experimental values of $^3J_{cis}$, $^3J_{trans}$, and J_{gem} for vinyllithium all represent the same species, whatever its structure, the corresponding points have been included in Figures 3d and 3e, and have been counted in the least-squares analysis. A lithium point has also been included in Figure 3e; however, it has not been included in the least-squares analysis, since it is not known whether the structures of vinyllithium and ethyllithium are similar. Although the computed $^3J_{HH}$ values themselves are in some cases *not in the correct experimental order*, the correct order of *sensitivities* is indicated from the plots. A noteworthy feature of Figure 3 is that it also shows a qualitative agreement between the calculated and experimental patterns which relate J_{gem} and $^3J_{cis}$ in substituted ethylenes.

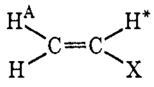
Some apparent failures to account for substituent effects are found in Table I. Some of these can be summarized as difficulties associated with comparing computed results which relate H or CH$_3$ as *substituents*. Related problems are found in analogous calculations on substituted benzenes.[58] Placing ethyl and isopropyl compounds in the same table (Table I) leads to a relatively poor overall correlation. This situation is improved if these categories are separated; in this case, apparent reversals for ethyl compounds are noted only with the substitutuents $-\mathrm{C{\equiv}N}$ and $-\mathrm{C{\equiv}CH}$, and these are of such magnitudes that they could be due to errors in the geometry used in the calculations. For the isopropyl compounds the only obvious difficulty is introduced by the parent compound itself, propane. It is interesting that despite the difficulty of placing ethyl and isopropyl compounds in the same correlation, the $^3J_{\mathrm{av}}$ values computed for $\mathrm{CH_3CH_2X}$ and $\mathrm{(CH_3)_2CHX}$ pairs are in the correct experimental pairwise orders for X taken as H, $\mathrm{CH_3}$, $\mathrm{C_6H_5}$, OH, and $\mathrm{NR_2}$.

There are also some indications in Table II of difficulty in handling $\mathrm{CH_3}$ and H as groups in calculations on ethylenic compounds. Thus, for ethylene itself, the computed $^3J_{trans}$ and $^3J_{cis}$ values both appear to be relatively too low. The computed substituent effect of a methyl group on the values of $^3J_{trans}$ in Table II, as manifested in comparisons of results for pairs of the type $\mathrm{CH_2C{=}CHX}$ and $\mathrm{CH_3HC{=}CHX}$, are all in the wrong sense for the systems available for comparison; *i.e.*, X = Li (II-1 and II-2), X = H (II-4 and II-15), X = CHO (II-8 and II-16), and X = F (II-21 and II-22). Only with X = Li (II-1 and II-3) is the reverse of the experimental order obtained for the three pairs available for this type of comparison with $^3J_{cis}$.

In principle, the origin of these difficulties could lie in at least three possible sources: (a) inadequacies of the "standard geometrical model" to represent properly the molecular geometries with substituents present, (b) inadequacies of the basic theoretical perturbation approach employed here, or (c) deficiencies in the representation of specific substituent effects by the approximate version of the approach employed here. Unquestionably, the computed results are sensitive to chosen bond lengths and bond angles. For example, the values computed for vinyltrimethylammonium ion (II-17) using C–N bond lengths determined for trimethylanalinium ion are closer to correlating with the experimental trend than the values (21.06 and 5.37 Hz) obtained using C–N bond distances appropriate to "standard," saturated $>\!\mathrm{C{-}N}\!<$ groups.

Some indication that (c) should be favored over (b) can be interpreted from the following observations. As pointed out above, the relative sensitivities of $^3J_{\mathrm{av}}$ for substituted ethanes and of $^3J_{cis}$ and $^3J_{trans}$ for substituted ethylenes are in the correct experimental order, even though the *individual* substituent effects are not all accounted for, even qualitatively. Also, the computational method embodied in eq 2 gives strong support for the "alternation effect" of substituents on $^3J_{\mathrm{HH}}$ values, which has been proposed previously based on experimental results.[42,45] Cohen and Schaefer[45] and Castellano and Kostelnik[42] have summarized the data on $^3J_{\mathrm{HH}}$ values in systems of the type $\mathrm{CH^3{-}CH^2{-}CH^1{-}X}$ in ways which demonstrate that the dependence of $^3J_{23}$ upon the electronegativity of X is opposite in sign from that of $^3J_{12}$. Such alternation was not expected on the basis of earlier valence-bond views of inductive mechanisms. In Table VII we have collected results calculated for four types of systems which bear upon this question. There it is demonstrated that $^3J_{12}$ ($J_{\mathrm{H^*A}}$ in the table) indeed varies with substituent in the opposite sense as $^3J_{23}$ ($J_{\mathrm{H^*B}}$, $J_{\mathrm{H^*C}}$, and $J_{\mathrm{H^*D}}$ in the table). Furthermore, the relative sensitivities of the computed $^3J_{12}$ and $^2J_{23}$ to variation of the substituent are seen to be in qualitative agreement with the value $-{}^1/_6$ estimated from experimental data by Castellano and Kostelnik for $(\partial^3J_{23}/\partial\chi_{\mathrm{X}})/(\partial^3J_{12}/\partial\chi_{\mathrm{X}})$, where χ_{X} represents the electronegativity of substituent X. This agreement is seen by comparing the first column of $^3J_{\mathrm{HH}}$ values in Table VII with the last three columns, or by inspection of Figure 4, which is prepared from that table. Points corresponding to X = Li have been excluded from the plots for the above mentioned reasons concerned with structural uncertainties in lithium compounds. Such patterns of qualitative agreement appear to suggest that the present computational method treats the effect of a *particular* substituent on the nuclear spin–spin couplings of a given molecule or in related species in a manner which is consistent with experimental correlations. However, for certain substituent groups, the substituent influence which is being handled in this consistent fashion is not appropriate for the substituent which one is attempting to represent. This could account for the similar appearances of the graphs for calculated and experimental results in Figure 3 in the face of some incorrect orderings within

Table VII. Calculated $^3J_{cis}$ Values[a]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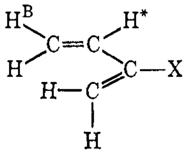
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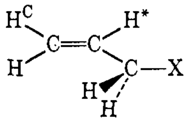
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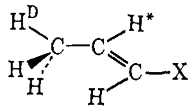
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$-\mathrm{X}^b$	1 $J_{\mathrm{H^*H^A}}$	2 $J_{\mathrm{H^*H^B}}$	3 $J_{\mathrm{H^*H^C}}$	4 $J_{\mathrm{H^*H^D}}$
-Li	23.03	8.24	8.58	4.74
$-\mathrm{CHO}$	10.68	9.21	8.97	7.99
$-\mathrm{CH_3}$	9.21	9.39	9.13	8.11
-H	9.31	9.69	9.21	8.48
$-\mathrm{NH_2}$	7.19	9.97	9.66	8.64
$-\mathrm{OH}$	5.20	10.32	10.06	8.95
-F	4.74	10.56	10.19	9.21

[a] Values in Hz. [b] The $\mathrm{NH_2}$ group is planar in cases A, B, and D, nonplanar in C.

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(58) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, 92, 4506 (1970).

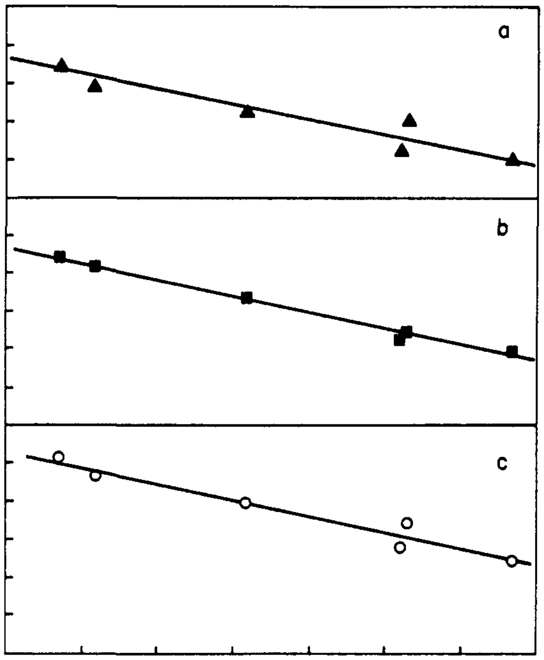
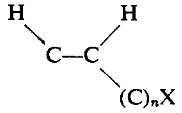


Figure 4. (a) Plot of calculated $J_{\mathrm{H^*D}}$ for type **4** compounds *vs.* calculated $J_{\mathrm{H^*A}}$ for the corresponding compounds. (b) Plot of $J_{\mathrm{H^*HC}}$ for type **3** compounds *vs.* corresponding $J_{\mathrm{H^*HA}}$ values. (c) Plot of $J_{\mathrm{H^*HB}}$ for type **2** compounds *vs.* corresponding $J_{\mathrm{H^*HA}}$ values. (See Table VII for structures **1–4**.)

the calculated values in the tables. A need for additional work in this area is indicated.

Most of the difficulties encountered with calculated substituent effects can be summarized as follows. The calculations generally yield a consistent pattern of results, in terms of the sign of substituent effects, for *cis* hydrogens, in systems which can be symbolized by structure I. In this generalized formula the symbol



I

$(C)_n$ represents a carbon chain of any type containing *n* carbons and connecting a *cis* HCCH moiety to an electronegative atom X (N, O, or F). For all the cases encountered in this study, and in a related study of substituted benzenes,[58] the signs of substituent effects computed for groups which contain these atoms fall into the pattern $n = 0(-)$, $n = 1(+)$, $n = 2(-)$, and $n = 3(+)$. This generalization holds for any of the carbon frameworks tested and is independent of the orientation of the $(C)_nX$ moiety. This suggests that an alternating, σ-inductive effect may be dominating the computed substitutent effects. The fact that the experimental results frequently disagree with the above patterns for $n > 0$ may imply that some important conjugation effects are not being treated adequately in the present calculations.

Summary and Conclusions

The theoretical method applied here is capable of reproducing several important experimental trends. These include the well-studied dependence upon the HCCH dihedral angle and the relationship to hybridization of the connecting carbons, as well as certain correlations between substituent effects in related types of molecules. However, difficulties have been encounted in reproducing experimental substituent effects in certain cases. Uncertainties associated with the molecular geometries employed in the calculations may account for some discrepancies.

Approximate Self-Consistent Molecular Orbital Theory of Nuclear Spin Coupling. V. Proton–Proton Coupling Constants in Substituted Benzenes[1a,b]

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Contribution from the Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. *Received December 1, 1969*

Abstract: The SCF finite perturbation method is applied to the calculation of proton–proton coupling constants in 13 monosubstituted benzenes and 4 disubstituted benzenes. The Fermi contact mechanism is assumed and the INDO molecular orbital approximation is employed. Good agreement with experimental patterns is obtained for benzene and for some correlations of substituent effects in substituted benzenes. Additivity effects and the relationship to vicinal couplings in substituted ethylenes are discussed.

Experimental data on proton–proton constants (J_{HH}) in substituted benzenes abound in the chemical literature.[2,3] Because of the complex spin–spin splitting patterns in the proton spectra of monosubstituted benzenes, most of the earlier results were re-

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(1) (a) Research supported in part by a grant from the National Science Foundation; (b) papers I–IV in this series are given as ref 22–25; (c) Special NIH Fellow, on leave from the University of California, Davis; (d) Postgraduate Scholar of the National Research Council of Canada.

(2) (a) J. A. Pople, W. G. Schneider, and H. J. Berstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, pp 258–265; (b) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1967, pp 770–774.

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