another indication of how the inclusion of 3d orbitals introduces the characteristic features of a π bond.

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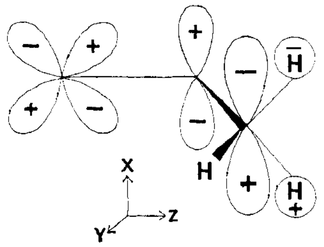
(12) The character of the highest occupied MO of **5** is similar to that of butadiene. The conformational preference of **5**



(with 3d orbitals) can be understood in terms of the pseudo-π orbital of the methyl group preferring a position of minimum overlap with the P=C π orbital. Similar rationalizations have been applied to the conformational preferences of polyenes; see R. Hoffmann and R. A. Olofson, *J. Amer. Chem. Soc.*, **88**, 943 (1966). J. P. Lowe, *ibid.*, **92**, 3799 (1970), has applied similar hyperconjugative arguments to the structural properties of ethane and propylene with apparent success [see, however, I. R. Epstein and W. N. Lipscomb, *ibid.*, **92**, 6094 (1970)].

Conformation and Substituent Dependence of Long-Range H–H Coupling over Four Bonds

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Abstract: A theoretical study of the conformation and substituent dependence of long-range coupling constants between protons separated by four bonds is presented in terms of self-consistent perturbation theory in the semiempirical INDO (intermediate neglect of differential overlap) approximation of molecular orbital theory. Calculated results are reported for propane and propene and their monosubstituted fluoro and cyano derivatives, which are taken as representative of inductive and hyperconjugative substituents, respectively. It is predicted that the long-range coupling constants for the monosubstituted derivatives of propane should be more positive than the propane value. Hyperconjugative substituents at the terminal carbons would be an exception, as negative shifts are noted in these cases. Similar trends in the long-range coupling constants for the various monosubstituted derivatives of propene are consistent with the experimental data. The calculated results also show that the orientation of the coupled protons with respect to the substituent is an important factor.

A large number of experimental values of long-range coupling constants between protons separated by four bonds, ${}^4J_{HH'}$, have been reported.[1,2] The physical situation which gives rise to this type of coupling is complex and existing theoretical studies[3-7] have not been completely successful in correlating the experimental data.

In unsaturated molecules the π-electron mechanism is often the most important factor for coupling over four bonds.[3,5-7] However, in saturated molecules and in certain conformations of unsaturated molecules the σ-electron mechanism is dominant.[2,4] Coupling constants between nuclei separated by four bonds are strongly conformation and substituent dependent and can be either positive or negative in sign. Because of the unavailability of experimental data for unstrained and unsubstituted hydrocarbons, the problem of elucidating the conformational dependencies are inextricably associated with uncertainties in the nature of substituent effects.

Existing theoretical descriptions[3-7] of long-range H–H coupling constants over four bonds have been based on molecular fragments, the assumption that the σ- and π-electron systems can be treated independently, and neglect of substituent effects. Because integral parameters were determined semiempirically, questions of the importance of direct *vs.* indirect mechanisms[8] are unresolved. There have been no previous systematic theoretical investigations of substituent effects on ${}^4J_{HH'}$, but some crude, qualitative MO descriptions[2,9] appeared to be reasonably consistent with the experimental results.

In the present study some of the difficulties mentioned above are overcome by means of calculations based on self-consistent perturbation theory[10] in the semiempirical INDO (intermediate neglect of differential overlap) approximation[11] of self-consistent-field molecular orbital (SCF-MO) theory. This method permits all valence-electron calculations on hydrocarbons of variable geometry with substituents in the second row of the periodic table.

I. Theoretical Formulation

Calculations of H–H coupling constants are based on approximate molecular orbital wave functions[10]

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(1) S. Sternhell, *Pure Appl. Chem.*, **14**, 15 (1964).
(2) M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969).
(3) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).
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(9) D. J. Sardella, *J. Mol. Spectrosc.*, **31**, 70 (1969).
(10) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960, 2965 (1968).
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which are self-consistent to the presence of the contact interaction between the electronic and nuclear spins. In this method a perturbation of magnitude

$$\eta_{\mathrm{N}} = (8\pi/3)\beta\mu_{\mathrm{N}}\phi_{\mathrm{s}}^{2}(\mathrm{N}) \qquad (1)$$

is added to the diagonal element for the s orbital of atom N in the core Hamiltonian corresponding to electrons of α spin and is subtracted from the corresponding element of the core Hamiltonian for electrons of β spin. In eq 1 β is the Bohr magneton, μ_{N} is the magnetic moment of nucleus N, and $\phi_{\mathrm{s}}^{2}(\mathrm{N})$ denotes the s-orbital density at nucleus N. With the perturbation specified in eq 1 the coupling constant between nucleus N and N′ is given by

$$J_{\mathrm{NN}'} = h(4\beta)^{2}\gamma_{\mathrm{N}}\gamma_{\mathrm{N}'}\phi_{\mathrm{s}}^{2}(\mathrm{N})\phi_{\mathrm{s}'}^{2}(\mathrm{N}')\frac{\partial}{\partial\eta_{\mathrm{N}}}[\rho_{\mathrm{s}}(\eta_{\mathrm{N}})]_{\eta_{\mathrm{N}}=0} \qquad (2)$$

where γ_{N} denotes the magnetogyric ratio of nucleus N and $\rho_{\mathrm{s}'}(\eta_{\mathrm{N}})$ is the diagonal element of the spin-density matrix in the s′ orbital centered on nucleus N′ due to the perturbation, η_{N}, at nucleus N. Equation 2 is simplified by the method of finite differences[10] to the result

$$J_{\mathrm{NN}'} = h(4\beta)^{2}\gamma_{\mathrm{N}}\gamma_{\mathrm{N}'}\phi_{\mathrm{s}}^{2}(\mathrm{N})\phi_{\mathrm{s}'}^{2}(\mathrm{N}')[\rho_{\mathrm{s}'}(\eta_{\mathrm{N}})/\eta_{\mathrm{N}}] \qquad (3)$$

The relationship of the self-consistent perturbation method to earlier work is established since the derivative in eq 2 has been related to the mutual atom–atom polarizability[12]

$$\pi_{\mathrm{s,s}'} = -4\sum_{\substack{i,\ \mathrm{occ}\\ j,\ \mathrm{unocc}}}(\epsilon_j - \epsilon_i)^{-1}c_{is}c_{js}c_{is'}c_{js'} \qquad (4)$$

where ϵ_j and ϵ_i are the energies of the unoccupied and occupied molecular orbitals, respectively, and the *c*'s are the coefficients of the valence s orbitals in the MO's.

Previous qualitative discussions[2,9] of substituent effects on ${}^{4}J_{\mathrm{HH}'}$ were based on eq 4 and fragments of the propane molecule. It was suggested[2] that both inductive and hyperconjugative substituents at the C_2 carbon atom should produce positive shifts in the values of ${}^{4}J_{\mathrm{HH}'}$. With even less justification it was proposed that both types of substituents at a terminal carbon atom should lead to negative shifts in the values of ${}^{4}J_{\mathrm{HH}'}$. The available experimental data[2,9] appeared to be reasonably consistent with these predictions.

Molecular orbital wave functions which were used in the present study were based on finite perturbation theory in the INDO approximation.[11,13] The major advantage of this method over the widely used CNDO (complete neglect of differential overlap)[14] method is the inclusion of the one-center interaction integrals. In these all-valence-electron methods[11-13] atomic matrix elements are based on atomic ionization potentials and electron affinities. Electron repulsion integrals are obtained theoretically from valence s orbitals. Bonding parameters are determined empirically to give the best fit to accurate LCAO–SCF functions for diatomic molecules. The INDO approximation, which includes semiempirical one-center electron-interaction integrals, leads to reasonable calculated results for geometries, bond angles, stretching force constants, hyperfine coupling constants, and nuclear spin–spin coupling constants.[10] Valence s-orbital densities are semiempirical ones from ref 10.

For simplicity in the calculations which are to be reported and consistency with the semiempirical parameterization scheme, only tetrahedral and trigonal bond angles were used in these calculations. Bond lengths, which are representative values from the compilations of Sutton,[15] are entered in Table I.

Table I. Bond Lengths (Å) Used in the Calculations[a]

–C—C–	1.540	–C—H	1.090
–C—C=	1.510	=C—H	1.080
–C—C≡	1.464	–C—C≡N	1.157
=C—C≡	1.426	=C—C≡N	1.164
–C=C–	1.337	–C—F	1.3836
		=C—F	1.333

[a] Reference 15.

Since the spin-density matrices must be known quite accurately to calculate coupling constants by means of eq 3, it is necessary to modify the usual energy criterion for convergence of the SCF procedure. The one proposed by Pople, McIver, and Ostlund[10] was adopted here. This requirement for termination of the SCF procedure is that the root-mean-square difference between two successive ($N \times N$) density matrices

$$\sqrt{\sum_{i,j}(\rho_{ij} - \rho_{ij}')^{2}/N}$$

be less than 10^{-9}. Computations on molecular systems containing the cyano function converged very slowly under this criterion. However, it was found that 25 cycles in the SCF procedure were sufficient to give results which were accurate to two significant figures in the long-range H–H coupling constants. All computations were performed on a Control Data Corp. 6400 digital computer.

II. Results and Discussion

A. Conformational Dependence of Propanic Coupling. Calculations of ${}^{4}J_{\mathrm{HH}'}$ by the methods described in section I were based on the 20 atomic orbitals in the valence shell of the propane molecule. The calculated results for 60° intervals of the dihedral angles ϕ and ϕ' are entered in Table II. The dihedral angles are both measured clockwise from the C_1–C_2–C_3 plane as depicted in Figure 1. The occurrence of the absolute maximum in the calculated values, which corresponds to the all-trans or "W" arrangement ($\phi = \phi' = 180°$) of the coupled protons, is in accord with previous results based on VB (valence bond) wave functions and a large amount of experimental data.[1,2,4] The experimental results show that coupling in this conformation is positive in sign, and in unstrained molecules is in the range 1–2 Hz. However, in contrast to the semiempirical VB results, the positive values of ${}^{4}J_{\mathrm{HH}'}$ in Table II occur for only a narrow range of dihedral angles near the all-trans orientation of the coupled protons.

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(12) C. A. Coulson and H. C. Longuet-Higgens, *Proc. Roy. Soc., Ser. A*, **191**, 39 (1947).

(13) Program 141, Quantum Chemistry Program Exchange, Bloomington, Ind.

(14) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, 136 (1965); **44**, 3289 (1966).

(15) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. **11**, S1–S19 (1958); No. **18**, S1–S23 (1965).

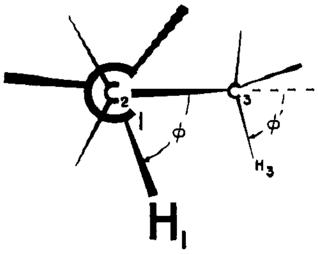

Figure 1. Specification of the dihedral angles ϕ and ϕ' in propane.

An unambiguous comparison of theoretical and experimental data as a function of conformation is not possible because in unstrained molecules of known geometry the experimental results are sensitive to nearby substituents. However, the calculated results can be compared with conformational trends[2] in a wide range of substituted cyclic molecules. For example, experimental values of ${}^4J_{HH'}$ between axial and equatorial protons (ϕ = 60°, ϕ' = 180°) in a large number of cyclic molecules have magnitudes in the range 0.4–0.8 Hz. Values of −0.5 and −0.4 Hz have been obtained[16] for two highly substituted pyranose derivatives, whereas both positive and negative values have been inferred[17] for the two types of axial–equatorial couplings which occur in a series of conduritol derivatives. The negative sign for this type of coupling (−0.49 Hz) in Table II appears to be in better agreement with the experimental data than previous results (+0.65 Hz) which were based on a VB formulation.[2,4]

Table II. Calculated INDO Results for ${}^4J_{HH'}$ in Propane[a]

ϕ, deg	ϕ', deg	${}^4J_{HH'}$, Hz	ϕ, deg	ϕ', deg	${}^4J_{HH'}$, Hz
0	0	−1.04	120	120	−0.12
	60	−0.58		180	0.45
	120	−0.25		240	−0.29
	180	−0.29		300	−0.62
	240	−0.25			
	300	−0.58	180	180	1.44
				240	0.45
60	60	−0.71		300	−0.49
	120	−0.46			
	180	−0.49	240	240	−0.12
	240	−0.62		300	−0.46
	300	−0.32	300	300	−0.71

[a] The dihedral angles ϕ and ϕ' are measured from the C_1–C_2–C_3 plane as depicted in Figure 1.

Even fewer experimental data are available for coupling between axial protons (ϕ = ϕ' = 60°) in cyclic molecules. On the basis of a few experimental values, it has been concluded that this type of coupling is negative in sign.[2] However, there is disagreement over the experimental evidence for abnormally large values in this arrangement.[18] Experimental values in the range 0.3–0.9 Hz are consistent with the calculated INDO result of −0.71 Hz in Table II as well as the value obtained in VB calculations.[2,4]

A large number of experimental data are also available for cases in which one of the protons can assume all of the orientations of a methyl group. In these cases trans and gauche coupling constant results are usually obtained by assuming an average over staggered equilibrium conformations

$$ {}^4J_{HH'}{}^{\text{trans}} = (1/3)[{}^4J_{HH'}(180°,180°) + 2\,{}^4J_{HH'}(60°,180°)] \quad (5) $$

$$ {}^4J_{HH'}{}^{\text{gauche}} = (1/3)[{}^4J_{HH'}(60°,180°) + {}^4J_{HH'}(60°,60°) + {}^4J_{HH'}(60°,300°)] \quad (6) $$

Substituting the calculated values from Table II into eq 5 and 6, it is found that ${}^4J_{HH'}{}^{\text{trans}}$ = 0.17 Hz and ${}^4J_{HH'}{}^{\text{gauche}}$ = −0.50 Hz. The respective experimental values are 0.3 to 1.0 and −0.15 to −0.50 Hz.[19] The VB results[2,4] for these cases appear to be in somewhat better agreement with the experimental data.

In the propane molecule itself, for which both of the coupled protons can assume all of the equilibrium orientations for the completely staggered conformation, a calculated value of −0.28 Hz is obtained on averaging the nine appropriate values from Table II. The experimental magnitude for propane is less than 0.3 Hz,[20] and by analogy with the signs for several tetramethyl compounds[21] it appears that the sign of ${}^4J_{HH'}$ should be positive. This would imply a major discrepancy between calculated and experimental results.

To test the sensitivity of the calculated long-range coupling constants in propane to conformational factors other than dihedral angles, the C_1–C_2–C_3 angle was increased to 120°. Calculated values for representative dihedral angles are ${}^4J_{HH'}(180°,180°)$ = 0.48 Hz, ${}^4J_{HH'}(60°,180°)$ = −0.60 Hz, ${}^4J_{HH'}(60°,60°)$ = −0.70 Hz, ${}^4J_{HH'}(60°,300°)$ = −0.30 Hz. Comparison with the data in Table II indicates that the only major change is a decrease by a factor of 3 of the value for the all-trans arrangement of the coupled protons. Long-range coupling constants involving the out-of-plane hydrogen atoms are only slightly affected by the increase in the distance between the C_1 and the C_3 carbon atoms. These results lend strong support to the hypothesis[8,22,23] that the large positive values which occur in the all-trans or "W" arrangement of the coupled protons can be attributed to a *direct* interaction between the bonds associated with the coupled nuclei. This interaction was originally envisioned[22] as arising from significant overlap of the carbon hybrid "rear lobes." However, such interactions were not explicitly considered in previous VB calculations,[4] which offers an alternative description of the angular dependence of long-range H–H coupling constants. The problem is further complicated because attempts to sort out the relevant mechanisms for long-range coupling in propane by means of *ab initio* SCF–MO calculations have been unsuccessful.[24]

[16] L. D. Hall, J. F. Manville and A. Tracey, *Carbohyd. Res.*, **4**, 514 (1967).

[17] R. J. Abraham, H. Gottshalck, H. Paulsen, and W. A. Thomas, *J. Chem. Soc.*, 6268 (1965).

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[23] A. Padwa, E. Shefter, and E. Alexander, *ibid.*, **90**, 3717 (1968).

[24] J. J. Reed, Ph.D. Thesis, University of Arizona, 1970.

Table III. Calculated Long-Range H–H Coupling Constants in Propane and Monosubstituted Propanes

		Coupling constant, Hz						
				$CH_3CH_2CH_2F$			$CH_3CH_2CH_2CN$	
ϕ, deg	ϕ', deg	$CH_3CH_2CH_3$	CH_3CHFCH_3	Trans	Gauche	$CH_3CHCNCH_3$	Trans	Gauche
60	60	−0.71	−0.48	−0.63	−0.62	−0.21	−0.75	−0.74
60	180	−0.49	−0.49		−0.44	−0.45		−0.52
60	300	−0.32	−0.16	−0.26		−0.27	−0.33	
180	60	−0.49	−0.49	−0.40	−0.48	−0.45	−0.53	−0.53
180	180	1.44	1.83		1.47	1.43		1.29
180	300	−0.49	−0.29	−0.40		−0.47	−0.53	
300	60	−0.32	−0.16	−0.26	−0.24	−0.27	−0.33	−0.33
300	180	−0.49	−0.29		−0.41	−0.47		−0.48
300	300	−0.71	−0.66	−0.63		−0.67	−0.75	
$\langle {}^4J_{HH'} \rangle_{av}$		−0.28	−0.13	−0.22		−0.20	−0.32	

B. Substituent Dependencies of Propanic Coupling. Previous theoretical discussions[2,9] of substituent effects on long-range H–H coupling constants were based on eq 4 and crude, qualitative arguments. In particular, it was suggested[2] that either inductive or hyperconjugative substituents at the C_2 carbon atom in Figure 1 would produce shifts to more positive values of ${}^4J_{HH'}$. On the basis of even more speculative considerations, it was suggested[2] that both types of substituents at the C_1 or C_3 carbon atoms would produce negative shifts. These qualitative suggestions seemed to be consistent with the available experimental data.[2]

In an attempt to examine these substituent effects on a more quantitative basis, calculated results for some monosubstituted propanes were obtained by the theoretical methods outlined in section I. Fluoro and cyano substituents were assumed to be representative of inductive and hyperconjugative substituents, respectively. Calculated results for the monosubstituted propane derivatives at the C_2 and C_3 carbon atoms for the staggered conformations are entered in Table III along with the corresponding results for propane from Table II. The position of the substituent R at the C_2 carbon atom is depicted in Figure 2a. At the C_3 carbon atom the substituent can be either trans or gauche to the C_1 carbon atom as depicted in Figures 2b and 2c, respectively.

In almost all of the cases in Table III the effect of introducing a substituent is to produce a *positive shift* in the values of ${}^4J_{HH'}$ relative to the propane values. The exception is for substitution of a cyano function at the C_3 carbon, a case for which the shift is toward negative values for all conformations. Perhaps the most interesting result exhibited by the data in Table III is the strong steric dependencies of the shifts in the value of ${}^4J_{HH'}$ due to substituents. The greatest shifts in the values of the long-range coupling constants occur for fluorine substitution at the C_2 carbon for the cases in which the coupled protons are both trans ($\phi = \phi' = 180°$) or both gauche ($\phi = \phi' = 60°$) to the fluorine atom. Steric dependencies of substituent effects are also known for directly bonded,[25] geminal,[26] and vicinal H–H coupling constants.[27]

Average values of ${}^4J_{HH'}$ for propane and the monosubstituted propanes are entered at the bottom of Table III. These values are based on the very crude assumption that the introduction of a substituent does not modify the equality of the rotamer populations. Unfortunately there have been no systematic experimental investigations of these very small long-range coupling constants in the substituted propanes to permit comparison with the data in Table III. Furthermore, in molecules with structural rigidity the complexity of the substituent and conformational factors at the present time only allow the conclusion that substituent effects do play an important role.[2,9] Fortunately, the data for allylic coupling constants, which are to be discussed in the subsequent sections, are less ambiguous.

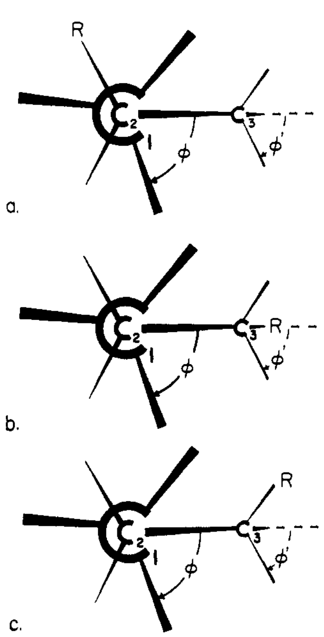

Figure 2. (a) Position of substitution at the C_2 carbon atom of propane. (b) The substituent R is trans to the C_1 carbon atom. (c) The substituent R is gauche to the C_1 carbon atom.

C. Conformational Dependence of Allylic Coupling. A large number of experimental data for long-range H–H coupling over one double and three single bonds have been reported.[1,2,28] The gross features of the angular dependence of allylic coupling were explained in terms of a π-electron mechanism, which necessarily leads to coupling constants of negative sign.[3] On including a σ-electron mechanism, for which the largest

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(28) E. W. Garbisch, *J. Amer. Chem. Soc.*, **86**, 5561 (1964).

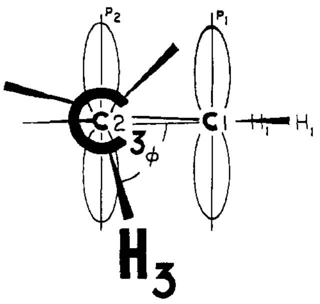

Figure 3. Specification of the dihedral angle ϕ in propene. The C_3 atom eclipses the C_2 carbon atom, and the cisoid proton H_1 eclipses the transoid proton H_1'.

(positive) contributions occur for the all-trans arrangement, it follows that J(transoid) > J(cisoid).[2,4] There are, however, well-documented examples in which the reverse is true.[29,30]

Calculated values of transoid and cisoid allylic coupling constants for propene (18 orbitals in the valence shell) are entered in Table IV for 30° intervals of the dihedral angle ϕ. The dihedral angle is measured from the C_1–C_2–C_3 plane as depicted in Figure 3. The calculated results in Table IV differ in two important ways from previous results based on VB wave functions.[2,4] In Table IV the calculated values of $^4J_{HH'}$ are positive only for transoid coupling constants between protons in which the dihedral angle is near 180°. In addition, there is a slight crossing of the cisoid and transoid coupling constants for dihedral angles between about 60 and 90°.

Table IV. Calculated INDO Results for Cisoid and Transoid Coupling Constants in Propene

ϕ,[a] deg	$^4J_{HH'}$(transoid), Hz	$^4J_{HH'}$ (cisoid), Hz
0	−0.54	−1.15
30	−1.32	−1.67
60	−2.83	−2.72
90	−3.20	−3.18
120	−1.52	−2.50
150	0.89	−1.33
180	2.01	−0.76

[a] Dihedral angle ϕ is measured from the C_1–C_2–C_3 plane as depicted in Figure 3.

In propene itself, the protons on the C_3 carbon atom can assume all of the equilibrium positions available to a methyl group, and so the allylic coupling constants are obtained from the formula

$$\langle {}^4J_{HH'}\rangle_{av} = (1/3)[{}^4J_{HH'}(0°) + {}^4J_{HH'}(120°) + {}^4J_{HH'}(240°)] \quad (7)$$

Substitution of the appropriate values from Table IV into eq 7 yields calculated values of −1.19 and −2.05 Hz for the transoid and cisoid coupling constants, respectively. Experimental values are −1.33 and −1.75 Hz, respectively.[31]

Although the calculated data in Table IV are strictly only applicable to the propene molecule itself, it should be instructive to compare the results with experimental data for molecules of more or less rigid geometry. Although a comparison of this type ignores substituent factors, it should provide some information about the reliability of the general conformational factors. In Figure 4 experimental data for transoid allylic coupling constants[32] are plotted as a function of the dihedral angle ϕ. The solid line in Figure 4 is a plot of the data from Table IV. For convenience in plotting the experimental data, nominal errors of ±0.2 Hz were assumed for the coupling constants and ±10° in the dihedral angles. The overall agreement between the calculated and experimental results appears to be somewhat better than previous results based on VB wave functions. In particular, the agreement appears to be better for dihedral angles smaller than about 45°. The few available experimental results[29] for cisoid allylic coupling constants in rigid molecules are larger than the calculated values in Table IV.

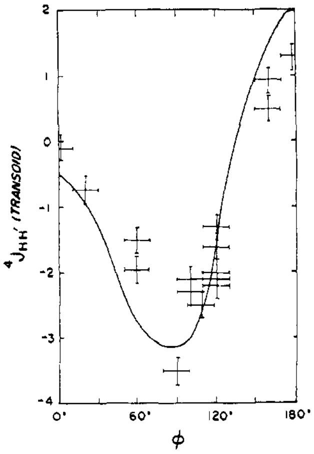

Figure 4. Comparison of calculated and experimental values of transoid allylic coupling. The solid line is a plot of the data from Table IV. The crosses denote experimental values taken from Table VI of ref 2.

D. Substituent Dependence of the Allylic Coupling Constants. In contrast to the substituted propanes, a large number of long-range coupling-constant data are available for the monosubstituted propenes.[2] Calculations in this series were again based on fluoro and cyano substituents, taken to be representative of inductive and hyperconjugative groups, respectively. In the case of propene it is necessary to consider substitution at all three carbon atoms. The calculated results for propene and the 1-, 2-, and 3-monosubstituted fluoro and cyanopropenes are entered in Table V along with the corresponding experimental values.

To compare the theoretical and experimental results, it is necessary to perform rotational averages. With the assumption of equality of the populations of the rotational isomers in the 1- and 2-monosubstituted propenes, average values of the cisoid and transoid allylic coupling constants, $\langle {}^4J_{HH'}\rangle_{av}$, were calculated from eq 7 and entered in Table V. For the 3-substituted propenes, rotamer populations, in general, will be unequal, and it is necessary to calculate the average values from the equation

$$\langle {}^4J_{HH'}\rangle_{av} = p_a{}^4J_{HH'}(120°) + [(1 - p_a)/2][{}^4J_{HH'}(0°) + {}^4J_{HH'}(240°)] \quad (8)$$

where p_a denotes the population of the rotational isomer in which the substituent eclipses the double bond. The population of the other two rotamers is therefore

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(32) Reference 2, Table VI.

Table V. Comparison of Calculated and Experimental Long-Range H–H Coupling Constants in Representative Monosubstituted Propenes

	Cisoid coupling constant, Hz				Transoid coupling constant, Hz			
Molecule	$^4J_{HH'}$ (0°)	$^4J_{HH'}$ (120°)	$\langle ^4J_{HH'} \rangle_{av}$	$^4J_{HH'}$ (exptl)	$^4J_{HH'}$ (0°)	$^4J_{HH'}$ (120°)	$\langle ^4J_{HH'} \rangle_{av}$	$^4J_{HH'}$ (exptl)
Propene	-1.15	-2.50	-2.05^{a}	-1.75^{b}	-0.54	-1.52	-1.19^{a}	-1.33^{b}
1-Fluoropropene	-0.68	-2.58	-1.94^{a}	-1.8^{c}	-0.23	-1.73	-1.23^{a}	-1.6^{c}
2-Fluoropropene	-0.79	-2.21	-1.73^{a}	-1.0^{c}	-0.28	-1.09	-0.63^{a}	-0.4^{c}
3-Fluoropropene	-0.99^{d}	-1.85^{d}	-2.05^{e}	-1.63^{f}	-0.69^{d}	-0.29^{d}	-1.16^{e}	-1.27^{f}
		-2.42^{g}				-1.73^{g}		
1-Cyanopropene	-1.26	-2.76	-2.26^{a}	-1.5^{h}	-0.71	-1.80	-1.43^{a}	-1.4^{h}
2-Cyanopropene	-0.49	-2.58	-1.88^{a}	-1.7^{h}	-0.59	-1.75	-1.36^{a}	-1.2^{h}
3-Cyanopropene	-1.16^{d}	-2.63^{d}	-2.31^{e}	-1.9^{i}	-0.58^{d}	-1.84^{d}	-1.53^{e}	-1.68^{i}
		-2.63^{g}				-1.79^{g}		

[a] Coupling constant was calculated from eq 7. [b] See ref 31. [c] M. Y. DeWolf and J. D. Baldeschwieler, *J. Mol. Spectrosc.*, **13**, 344 (1964). [d] These values were obtained for the case in which the substituent at the C_3 carbon atom had a dihedral angle of 240°. [e] Coupling constant obtained from eq 8. [f] See ref 34. [g] The substituent at the C_3 carbon atom had a dihedral angle of 0°. [h] G. S. Reddy, J. H. Goldstein, and L. Mandell, *J. Amer. Chem. Soc.*, **83**, 1300 (1961). [i] R. C. Hirst, Ph.D. Thesis, University of Utah, 1963.

$(1 - p_a)/2$, and in eq 8 the two coupling constants in brackets are those obtained for the rotamer which has the substituent 120° from the C_1–C_2–C_3 plane as depicted in Figure 2c. With rotamer population data from the work of Bothner-By and coworkers,[33,34] average values of the allylic coupling constants in 3-fluoropropene and 3-cyanopropene were calculated from eq 8 and entered in Table V.

Although there are some significant discrepancies between the calculated results and experimental data in Table V, the substituent trends are satisfactorily reproduced. Particularly gratifying is the duplication of the large positive shift which is noted for cisoid allylic coupling in 2-fluoropropene. In contrast to the data for the monosubstituted propanes, a cyano substituent at any one of the carbon atoms gives calculated long-range coupling constants which are more negative than the propane value. For the cisoid coupling constants this is only experimentally verified for the 3-cyanopropene. The inadequacy of the calculated results in these cases may be related to an overestimation of substituent effects,[10] which is implicit in the parameterization in the INDO scheme. This disparity may be greatest when the chain has its greatest extension. This would have the effect of giving poorer overall agreement for cisoid than for transoid allylic coupling constants. At least qualitatively, the data in Table V reproduce the trends which are observed[2] in rigid molecules toward more positive cisoid but more negative transoid allylic H–H coupling constants with substitution at the C_1 carbon atom.

III. Conclusions

Finite perturbation theory in the semiempirical INDO approximation of molecular orbital theory provides a satisfactory description of long-range H–H coupling in propane, propene, and their monosubstituted derivatives. The calculated conformational dependencies of $^4J_{HH'}$ in the unsubstituted derivatives is in somewhat better agreement with the experimental results than previous VB calculations. The superiority of the INDO method is probably attributable to the inclusion of *direct* as well as *indirect* mechanisms in the integral parameterization. However, it appears that the calculated *magnitudes* are not generally in as good agreement with the experimental values. For example, the negative sign which is predicted for $^4J_{HH'}$ in propane is probably incorrect.

Although the calculated numerical results are not in as good agreement as might be hoped, the shifts in the calculated long-range coupling constants from the propene value owing to inductive and hyperconjugative substituents are generally in the right direction. Comparable experimental data are not available for the monosubstituted propanes. In this case it is predicted that inductive substituents at either the C_1 or C_2 carbon should produce positive shifts. This should also be true for hyperconjugative substituents at the C_2 carbon atom. It is predicted that a hyperconjugative substituent at a terminal carbon should give a small negative shift from the propane value.

The calculated long-range H–H coupling constants are found to be quite sensitive to the orientation of the coupled protons relative to the substituent. This effect appears to be most pronounced for strongly electronegative substituents such as fluorine. In rigid molecules the absence of good experimental data for the unstrained and unsubstituted hydrocarbons does not yet permit an adequate test of these predictions.

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(33) A. A. Bothner-By, unpublished work cited in footnote 32 of ref 26a.

(34) A. A. Bothner-By, S. Castellano, and H. Günther, *J. Amer. Chem. Soc.*, 87, 2439 (1965).