Conformational Dependence and Mechanisms for Long-Range H–H Coupling Constants over Four Bonds

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Abstract: An experimental and theoretical study is presented of the conformational dependence and mechanisms for coupling over four bonds in propanic and allylic systems. A separation of the propanic coupling into direct and indirect contributions is performed by means of self-consistent perturbation theory in the INDO approximation. Direct contributions assume greatest importance for the planar arrangements of the H-C-C-C-H moiety, assuming maximum positive values for the "W" orientation. The "through-space" contribution, which arises when the coupled nuclei are close spatially, is negative in sign. Making use of the relationship of nuclear spin-spin coupling constants to hyperfine coupling constants from ESR spectroscopy, coupling mechanisms are discussed in terms of electron-transfer and exchange-polarization mechanisms. Extended Hückel molecular-orbital and valence-bond results, which are assumed to be indicative of the importance of these respective mechanisms, are summed. In comparing these results with the experimental data, several difficulties with previous theoretical treatments are removed. Of particular importance, in this regard, is the improvement for coupling over four bonds involving a methyl group and the planar arrangement for cisoid and transoid allylic coupling constants. From the point of view of structural determination, significant long-range coupling across four single bonds involving a methyl group can be considered diagnostic of an antiperiplanar arrangement, while the dependence of the allylic coupling constants on dihedral angle ϕ is adequately represented by two theoretical treatments.

A very large amount of experimental and theoretical work has been concerned with the problem of long-range H–H coupling over four bonds in saturated and unsaturated hydrocarbons.[2,3] Since the relevant experimental data are usually obtained in complex molecules, which are multicyclic and/or highly substituted, the major experimental problem has been one of attempting to separate the conformational dependence from substituent and hybridization effects. Theoretical studies of long-range H–H coupling in saturated hydrocarbons have been based on valence-bond (VB)[4] and molecular-orbital (MO)[5,6] formulations. Because the physical situation giving rise to this type of coupling is quite complicated, none of these treatments has been completely successful in reproducing the experimental trends.

In the present study, a new formulation is presented which analyzes the various mechanisms involved, including the conformational dependencies of these mechanisms. Making use of the fact that certain MO and VB approximations represent mutually exclusive contributions, the summed results provide a better description of H–H coupling over four bonds than previous results based on one or the other semiempirical methods.

I. Theoretical Formulation

Most theoretical descriptions of nuclear spin–spin coupling have been based on the second-order perturbation formulation of Ramsey[7] and the assumption that the Fermi contact term is adequate for describing coupling between protons. The mathematical details are given in two reviews.[8,9] and in the literature references cited in this section.

In the various computational schemes based on second-order perturbation theory, the contact contribution to the coupling between nuclei N and N′ is of the form

$$J_{\mathrm{NN'}} = -(2h)^{-1}(16\pi\beta\hbar/3)^2\gamma_{\mathrm{N}}\gamma_{\mathrm{N'}}\phi_r^{\,2}(\mathrm{N})\phi_s^{\,2}(\mathrm{N'})\mathfrak{F}(r,s) \quad (1)$$

where γ_{N} and $\gamma_{\mathrm{N'}}$ are the magnetogyric ratios of nuclei N and N′, $\phi_r^2(\mathrm{N})$ and $\phi_s^2(\mathrm{N'})$ are the densities of *s*-type orbitals, *r* and *s*, which are centered on N and N′, respectively, and $\mathfrak{F}(r,s)$ is a *spin-coupling function* with a mathematical form which is dependent on the approximations which are used in the molecular wavefunctions. For example, in the VB approximation and the assumption of the so-called "average energy approximation," $\mathfrak{F}(r,s)$ assumes a particularly simple form[10]

$$\mathfrak{F}(r,s) = (\Delta E)^{-1}p(r,s) \quad (2)$$

where ΔE is the "average excitation energy" and $p(r,s)$ is the Penney-Dirac bond order.[11] The Penney–Dirac bond order is related to the exchange contribution to the binding energy, such that for completely localized systems, it assumes the value unity for atoms that are bonded and zero for nonbonded atoms. In actual systems for which there are deviations from perfect pairing, the bond order can be related to nonlocal bond orders for four electron fragments. It was suggested that terms in the coupling constant which are of first order in these bond orders be called "direct" contributions, and that terms of second order and higher be termed "indirect".[10] "Through-bond" and "through-space" mechanisms correspond to special cases of indirect and direct mechanisms, respectively.

In the MO scheme of Pople and Santry,[12] the spin-coupling function is proportional to the mutual atom–atom polarizability, π_{rs}

$$\mathfrak{F}(r,s) = (1/2)\pi_{rs} = 2\sum_{i,j}[\epsilon_i - \epsilon_j]^{-1}c_{ir}c_{is}c_{jr}c_{js} \quad (3)$$

where c_{ir} and c_{jr} denote the coefficients of the *r*th atomic orbital in the *i*th occupied and in the *j*th unoccupied MO's with energies ϵ_i and ϵ_j, respectively. Even though exchange integrals are not ordinarily used in the simple MO schemes which are used to evaluate the coefficients and energies in eq 3, the mutual atom–atom polarizabilities, in general, are nonvanishing, and all of the magnetic moments will be coupled to some extent.

By means of a double perturbation formulation, Hiroike[13] argued that those parts of the coupling constant calculated via eq 2 and 3 are mutually exclusive and correspond to successive terms in a more general expansion of the coupling-constant expression. Certain difficulties with such an analysis are obvious when dealing with approximate methods. The most obvious objections are the empirical choice of a value for ΔE in eq 2 and, since the parameters in the semiempirical VB and MO methods are determined from experimental criteria, it is not at all clear that in each case one "overcompensates" for the neglect of the other.

A more recent version[14] of the VB method includes an explicit sum over VB triplet states (VB–SOT) in the second-order perturbation sum. The spin-coupling function is given by

$$\mathfrak{F}(r, s) = \sum_{\kappa}[{}^3E_{\kappa} - {}^1E_0]^{-1} \sum_{jklm} (\tfrac{1}{2})^{2n-i_{jl}-i_{km}} c_j c_{\kappa l} c_k c_{\kappa m} f^r{}_{jl} f^s{}_{km} \quad (4)$$

where the first summation is over triplet structures arising as linear combinations of the $3[(2n)!/(n + 2)!(n - 1)!]$ linearly independent VB canonical structures for a system of $2n$ electrons. The coefficients c_j and c_k of the singlet canonical structures occur in the ground state VB wavefunction, whereas the $c_{\kappa l}$ are the coefficients of the triplet canonical structures in the κth triplet level. The quantities such as i_{jl} and $f^r{}_{jl}$ are determined from the superposition diagrams of the singlet and triplet canonical structures.[14] Equation 4 includes the effects of deviations from perfect pairing in the triplet states, whereas eq 2 corresponds to the assumption of localized triplets.[10] Since the effects of deviations from perfect pairing in the VB scheme involve nonvanishing interbond exchange integrals, which are not implicit in the MO schemes used to calculate coupling constants from eq 3, it follows that eq 3 and 4 represent mutually exclusive contributions. Because of the objections of the previous paragraph, it will be necessary to present an heuristic argument to justify this procedure for the systems of interest.

Recent calculations of coupling constants by MO methods have been greatly improved by the introduction of self-consistent-field (SCF) procedures. In particular, the finite perturbation method[15] (FPT) in the CNDO[16] and INDO[17] (complete and intermediate neglect of differential overlap, respectively) approximations of unrestricted SCF–MO theory. The INDO scheme is an improvement on the CNDO method for spin-coupling problems, because it includes the one-center exchange integrals, and these are essential for providing an adequate description of π-electron mechanisms.[15] In saturated systems, the inclusion of the one-center exchange integrals has a significant effect on coupling between nuclei separated by two bonds, but for coupling in the σ-electron framework with nuclei separated by more than three bonds, they are of negligible importance.[18] The mathematical details of the INDO–FPT method for coupling constants have been discussed in so many recent papers, that it would be superfluous to reproduce them here. The procedure is quite simple. The Fermi contact interaction associated with one of the coupled nuclei is *added* to the diagonal element for the s orbital centered on the nucleus in the Fock matrix for electrons of α spin, and it is *subtracted* from the corresponding element of the Fock matrix for electrons of β spin. This has the effect of inducing a very small spin density throughout the molecular electronic system. After self-consistency is achieved, the nuclear spin–spin coupling constant is proportional to the value of the spin density at the second nucleus.

The term "exchange integral" is used in both MO and VB descriptions, but it does not always refer to the same integral. In the VB terminology,[19,20] the two-center exchange integral between atomic orbitals s and t, separated by a distance R_{st} is given by eq 5 and 6, where S_{st} denotes the overlap integral, J_{st} is a one-electron exchange attraction integral, and A_{st} is the two-center, two-electron exchange integral of MO theory. Three- and four-center integrals are seldom used in semiempirical schemes. If orbitals s and t are on the same center, the overlap integral vanishes, and the VB and MO exchange integrals are identical, $K(s,t) = A_{st}$.

$$K(s, t) = e^2 \int\int s(1)t(2)[-(1/r_{1t}) - (1/r_{2s}) + (1/r_{12}) + (1/R_{st})]s(2)t(1)d\tau_1 d\tau_2 \quad (5)$$

$$= 2S_{st}J_{st} + A_{st} + S_{st}{}^2/R_{st} \quad (6)$$

As noted previously, an heuristic justification for summing the MO and VB results from eq 3 and 4 can be based on the relationships of the nuclear spin–spin coupling constants to hyperfine coupling constants from the ESR spectra of organic radicals in solution.[10,21-27] The latter are proportional to the unpaired spin densities at the nuclear sites. Although a large number of mechanisms have been proposed to explain the factors responsible for the transmission of spin density in organic free radicals, it appears that only two are required to provide an adequate description.[28] *Exchange polarization* denotes those mechanisms which arise in the simple VB methods which include only nonpolar structures in the basis set. In radicals in which σ–π terms are dominant[29] or in aliphatic fragments,[30] spin-polarization mechanisms appear to make minor contributions to hyperfine coupling. Even though *electron-transfer* mechanisms are absent in the VB methods without ionic structures, good results are attributable to the empirical adjustment of integral parameters.[28] Simple MO schemes, such as the extended Hückel (EHMO) method, neglect all types of exchange integrals and configuration interaction. As a consequence, these methods only include spin-delocalization mechanisms by electron transfer and completely ignore exchange polarization.[31] Because of the neglect of exchange polarization, negative spin densities are not implicit in the simple Hückel methods.

From the preceding arguments, it is reasonable, therefore, to use eq 1 and 3 in the extended Hückel approximation to provide an estimate of the contribution of electron-transfer terms to the nuclear spin–spin coupling. The use of eq 1 and 4 to provide an estimate of the spin-polarization contribution will depend on judicious choices of the exchange-integral parameters. In fact, theoretical values would eliminate the possibility of any type of "calibration." To avoid any prejudice in this investigation, no new parameters were introduced. Semiempirical parameters in the MO scheme were based on those of Pople et al.[17] Valence-bond parameters were from previous work.[14] The INDO–FPT method includes both electron-transfer and spin-polarization mechanisms. The latter arise because of the inclusion of only the one-center exchange integrals, and the SCF procedure corresponds to the mixing of singly excited configurations.[32] These results provide an interesting basis for comparison with other calculated results and for qualitatively sorting out the importance of direct and indirect mechanisms for coupling in saturated systems. In sections II–IV, it will be shown that the two-center exchange integrals are also important for long-range nuclear spin–spin coupling.

II. Propanic Coupling

Within the simple VB scheme, a large number of spin-polarization mechanisms for coupling over four bonds in propane can be envisioned. Consider the situation depicted in **1**. The bonds containing the coupled nuclei are labeled 1 and 3, and the bonds to the C_2 carbon atom are 2,2′, 2″, 2‴. Previous VB results included four indirect mechanisms:

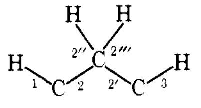

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Table I. Long-Range H–H Coupling Constants in Propane Calculated in Various Approximations within the INDO–FPT Scheme

Dihedral angles		INDO–FPT		
ϕ	ϕ'	i[a]	ii[b]	iii[c]
0	0	−1.06	1.09	0.35
	60	−0.61	0.30	−0.12
	120	−0.22	−0.70	−0.64
	180	−0.13	−0.92	−0.68
	240	−0.22	−0.70	−0.64
	300	−0.61	0.30	−0.12
60	60	−0.76	0.35	−0.47
	120	−0.45	−0.43	−0.54
	180	−0.47	−0.39	−0.47
	240	−0.62	−0.45	−0.53
	300	−0.32	−0.37	−0.38
120	120	−0.13	−0.71	−0.76
	180	0.56	−0.34	−0.59
	240	−0.30	0.06	−0.27
	300	−0.62	−0.45	−0.53
180	180	2.09	−0.60	−0.90
	240	0.56	−0.34	−0.59
	300	−0.47	−0.39	−0.47
240	240	−0.13	−0.71	−0.76
	300	−0.45	−0.43	−0.54
300	300	−0.76	0.35	−0.47

[a] These are results from the unmodified INDO–FPT program; all coupling constants in hertz. [b] All overlap integrals between valence atomic orbitals on the C_1 and C_3 carbon atoms were set equal to zero. [c] In addition to the approximation of footnote b, all overlap integrals between the hydrogen atoms on C_1 and the hydrogen atoms and valence atomic orbitals on C_3 were set equal to zero. Also, the overlap integrals between the hydrogen atoms on C_3 and the hydrogen atoms and valence atomic orbitals on C_1 were set equal to zero.

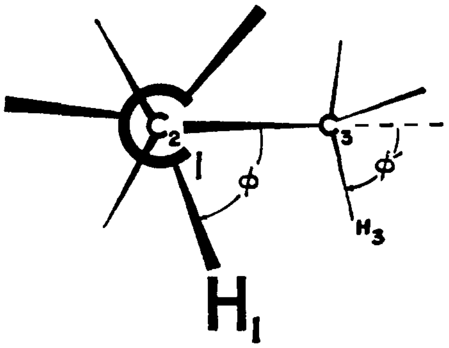


Figure 1. Specification of the dihedral angles ϕ and ϕ' in propane.

the two possible geminal–vicinal interactions (1 → 2 → 3 and 1 → 2′ → 3) and the two possible vicinal–vicinal interactions (1 → 2″ → 3 and 1 → 2‴ → 3).[2,4] There was no experimental evidence which indicated that direct interaction between bonds 1 and 3 was an important factor. As the only unknown was the value for the angularly independent geminal (1 → 2 and 2′ → 3) interaction, an empirical value gave maximum, positive coupling in the "W" conformation, and the other angular dependencies seemed to be consistent with the experimental data.

More recent calculations based on the INDO–FPT approximation indicate that direct mechanisms are important for coupling between protons separated by four and even five bonds.[6,33-35] The importance of the direct and indirect mechanisms for coupling over four bonds in propane is demonstrated by means of a series of INDO–FPT computations. These results are summarized in Table I as functions of the dihedral angles ϕ and ϕ', which are measured in the same sense from the C_1–C_2–C_3 plane as depicted in Figure 1. The three sets of calculated results were based on the following considerations.

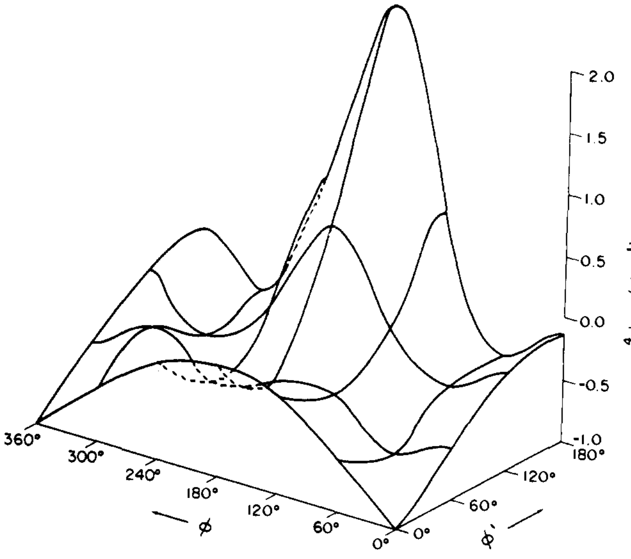
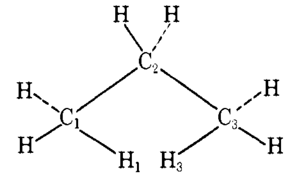


Figure 2. A plot of the INDO–FPT results for propane as a function of the dihedral angles ϕ and ϕ'.

i. Entered in the third column of Table I are the coupling constants from the unmodified INDO–FPT computer program.[36] These results are also depicted schematically in Figure 2 as a function of the two dihedral angles. Prominent features in the plots are the absolute maximum for the "W" conformation **1** for which $\phi = \phi' = 180°$. The absolute minimum in these calculations occurs for the conformation **2** in which H_1 and H_3 are proximate ($\phi = \phi' = 0°$).



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ii. In the second set of calculations with results in Table I, all overlap integrals between valence atomic orbitals on the C_1 and C_3 carbon atoms were set equal to zero. The changes in the coupling constants between the two sets of calculations are remarkable. In particular, coupling in the "W" arrangement **1** is negative instead of positive, and the coupling in the arrangement **2** has also changed sign. These results indicate that the orbitals on the carbon atoms, which are bonded to the coupled protons, have a substantial effect on coupling over four bonds. Furthermore, the "rear-lobe" hypothesis[37] which was invoked to explain the large magnitudes of coupling in the "W" arrangement would appear to be substantiated.

iii. In the third set of calculations, overlap integrals between the hydrogen atoms attached to C_1 and those attached to C_3 were set equal to zero. Because of the proportionality of resonance integrals to overlap integrals in these schemes, the resonance integrals also go to zero in the computation of the elements of the Fock matrices. In addition, overlap integrals between hydrogen atoms on C_1 (and on C_3) and all valence atomic orbitals on C_3 (and on C_1) were set equal to zero. As a consequence, the results in the last column of Table I provide a measure of the importance of indirect mechanisms to propanic coupling. The difference between the results of set I and set III is, therefore, a measure of the importance of the direct mechanism within this approximate scheme. Except for dihedral angles near $\phi = \phi' = 0°$, in which the coupled protons are close together, there is very little difference in the results in the last two

Table II. Long-Range H–H Coupling Constants[a] in Propane Calculated by Several Semiempirical Methods

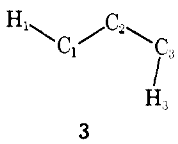
Dihedral angles ϕ	Dihedral angles ϕ'	INDO–FPT A	EHMO B	VB–SOT C	B + C D
0	0	−1.06	−0.15	−0.06	−0.21
	60	−0.61	−0.01	−0.13	−0.14
	120	−0.22	0.22	−0.13	0.09
	180	−0.13	0.52	−0.04	0.48
	240	−0.22	0.22	−0.13	0.09
	300	−0.61	−0.01	−0.13	−0.14
60	60	−0.76	−0.03	−0.46	−0.49
	120	−0.45	0.01	−0.18	−0.17
	180	−0.47	0.07	−0.09	−0.02
	240	−0.62	−0.05	−0.41	−0.46
	300	−0.32	−0.01	−0.15	−0.16
120	120	−0.13	0.09	−0.38	−0.29
	180	0.56	0.57	−0.08	0.49
	240	−0.30	0.06	−0.20	−0.14
	300	−0.62	−0.05	−0.41	−0.46
180	180	2.09	1.54	−0.02	1.52
	240	0.56	0.57	−0.08	0.49
	300	−0.47	0.07	−0.09	−0.02
240	240	−0.13	0.09	−0.38	−0.29
	300	−0.45	0.01	−0.18	−0.17
300	300	−0.76	−0.03	−0.46	−0.49

[a] In hertz.

columns of Table I. Therefore, on the basis of these calculations, it must be concluded that there are two major types of direct mechanisms for propanic coupling; there is a "through-space" mechanism associated with proximate orientations of the coupled nuclei, *but the most important direct interaction is that associated with the orbitals on the carbons to which the coupled protons are attached.*

The coupling constants based on the INDO–FPT method include contributions from both spin-polarization and electron-transfer mechanisms. In extended π-electron systems in which the spin-polarization mechanism is dominant,[28] the INDO–FPT and VB results[38] are in agreement. To separate the spin-polarization and electron-transfer mechanisms, it will be useful to use a non-SCF scheme such as an extended Hückel (EH) method[39] to provide a measure of the importance of electron-transfer mechanisms.

Coupling constants for propane in the extended Hückel approximation are entered in column B of Table II. Calculated values of $^4J_{HH'}$ were based on eq 3 with MO wavefunctions and energies from the EH scheme which is used to assemble the Fock matrices for the SCF procedure in the CNDO approximation.[16] For comparison, the INDO–FPT results from Table I are also included in Table II. Except for conformations close to **1**, there is very little agreement between the two sets of results. In particular, it should be noted that for the "dipper" conformation **3**, the results are of opposite sign, and for the nonplanar conformations, the coupling constants are close to zero in the EH approximation.



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Previous VB calculations[4] of $^4J_{HH'}$ for propane were based on the assumption that direct mechanisms were unimportant. As a consequence, it was necessary to make an empirical choice of the interaction parameter. From the preceding discussion, this can no longer be justified. To obtain information about the importance of spin-polarization mechanisms, the VB calculations were repeated and the results entered in column C of Table II. The VB results were based on eq 1 and 4 and a formulation[40] in terms of group functions with intergroup configuration interaction. Results were obtained for an eight-electron moiety consisting of the two bonds containing the coupled nuclei and the two C–H bonds on the C_2 carbon atom. As a consequence, the tabulated results correspond to indirect mechanisms associated with the two types of vicinal–vicinal interactions ($1 \rightarrow 2'' \rightarrow 3$ and $1 \rightarrow 2''' \rightarrow 3$ in **1**). The two-center VB exchange integrals for the vicinal interactions are those given by Karplus.[41] Additional indirect spin-polarization mechanisms are to be expected from the two types of geminal–vicinal interactions ($1 \rightarrow 2 \rightarrow 3$ and $1 \rightarrow 2' \rightarrow 3$ in **1**) considered previously.[4] However, the large uncertainties associated with the exchange integrals between geminal bonds[2,8,42] suggest that it would be safer to omit interactions of this type and see how the results compare with the experimental.

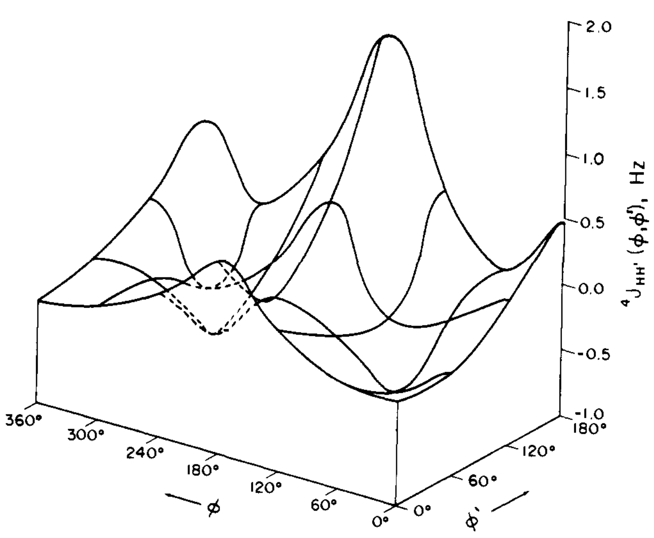


Figure 3. Calculated results for propane, based on the sum of the EHMO and VB–SOT results in Table II, plotted as a function of the dihedral angles ϕ and ϕ'.

The EHMO and VB–SOT results in columns B and C of Table II were summed, and the total was entered in column D of the table. They are also plotted as a function of the two dihedral angles in Figure 3. The major effect of the introduction of the spin-polarization mechanisms, implied by the VB results, is to put nonnegligible minima in the $^4J_{HH'}$ coupling-constant surface at $\phi = \phi' = 60°$ and at $\phi = 300°$, $\phi' = 120°$. Furthermore, this is in marked contrast to the FPT–INDO results for which the absolute minimum occurs for $\phi = \phi' = 0°$ in Figure 2.

Representative experimental results for coupling over four bonds in saturated, cyclic molecules have been tabulated in several reviews.[2,3] Because the data were obtained in highly substituted compounds, there are some ambiguities in the experimental results which make a precise comparison impossible. The trends in the experimental data were summarized as follows.

i. Coupling constants between equatorial protons ($\phi = \phi' = 180°$) are always positive in sign and in the range 1–2 Hz.

ii. Coupling over four bonds between axial and equatorial protons ($\phi = 60°$ and $\phi' = 180°$, respectively) are in the range 0.4–0.8 Hz and are probably negative in sign from studies of pyranose derivatives.[43,44]

iii. Long-range H-H coupling between axial protons ($\phi = \phi' = 60°$) are in the range −0.3 to −0.9 Hz.

It may be significant that the *larger* values for coupling constants between axial and equatorial protons and between axial protons refer to six-membered oxygen heterocycles. Unlike some earlier examples of apparently significant

Table III. Calculated Long-Range H–H Coupling Constants[a] over Four Bonds in the Case in Which One of the C–H Bonds Is Associated with a Methyl Group

Dihedral angle	INDO–FPT A	EHMO B	VB–SOT C	MO + VB D
0	−0.45	0.17	−0.10	0.07
60	−0.52	0.01	−0.23	−0.22
120	−0.17	0.17	−0.22	−0.05
180	0.38	0.56	−0.07	0.49

[a] In hertz.

"non-W" long-range coupling,[45] these interactions have been well established in careful recent studies[46-51] but are notably absent in cyclohexane derivatives which have been subject to detailed NMR studies[52,53] and in adamantane derivatives,[54] thus underlining the ambiguities mentioned above.

From the preceding discussion, it appears that the INDO–FPT results are in somewhat better agreement with experimental data, particularly for the axial–equatorial coupling. However, the −1.06-Hz coupling predicted by the INDO–FPT method seems inconsistent with experimental data for cases in which the protons are in proximate orientations.[2] Furthermore, better justification for the results in column D of Table II is to be found in comparing the calculated and experimental results for coupling over four bonds in those cases in which a methyl group is involved, and also for the case of allylic coupling to be discussed in subsequent sections.

III. Coupling over Four Single Bonds Involving a Methyl Group

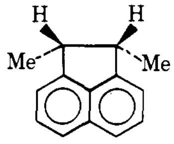
The impetus for the theoretical work developed in section II stemmed from the disparity between our experimental data (see below) and existing VB[4] and MO[6] results for coupling over four bonds in those cases in which one of the coupled protons is part of a C–H bond of a methyl group. In this case, only a single dihedral angle is involved, and the coupling constants are based on the formula

$$
{}^4J_{\mathrm{HH'}}(\phi) = (1/3)[{}^4J_{\mathrm{HH'}}(\phi, 60°) + {}^4J_{\mathrm{HH'}}(\phi, 180°) + {}^4J_{\mathrm{HH'}}(\phi, 300°)] \quad (7)
$$

which assumes that the rotamer populations, corresponding to the staggered arrangement, are equivalent, and that it is not necessary to include a weighting over the intermediate rotational states. Calculated results from eq 7 and several approximations in Table II are tabulated in Table III for several values of the dihedral angle ϕ.

It has been generally observed[3] that interactions across four single bonds involving methyl groups are appreciable when $\phi = 180°$ (${}^4J_{\mathrm{HH'}} = 0.7$–$1.0$ Hz) and are much weaker when $\phi = 60°$ (${}^4J_{\mathrm{HH'}} =$ ca. -0.3 Hz).

In the view of the imperfect agreement between the above experimental trends and the predictions based on the VB[4] and MO[5,6] treatments, we have synthesized a number of substances (**4–11**) of reasonably well-defined geometry and analyzed their NMR spectra (see Experimental Section) in an attempt to determine empirically the dependence of ${}^4J_{\mathrm{Me\text{-}C\text{-}C\text{-}H}}$ on the dihedral angle ϕ. It can be seen that these values range from −0.17 to +0.15 Hz for $\phi =$ ca. 0° and from −0.36 to −0.13 Hz for $\phi =$ ca. 120°. The data for compounds **4–9** could have been of questionable generality because of the possibility of special effects due to angle strain, but this was ruled out when identical trends were observed in the strainless series **10–11**. However, results for propylene oxide[55] **12** and the bicyclobutane **13**[56] show that extreme angular strain may be associated with atypical values of ${}^4J_{\mathrm{Me\text{-}C\text{-}C\text{-}H'}}$ especially for the region near $\phi = 0°$. Interestingly, the data for 1-methylbenzocyclobutene (**14**),[57] which may not be ideally planar, fall closer to the "normal" range.



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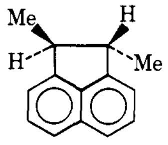
(${}^4J^{128°} = -0.26$ Hz)



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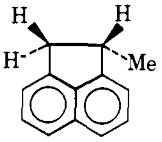
(${}^4J^{0°} = -0.08$ Hz)



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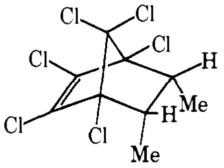
(${}^4J^{128°} = -0.15$, ${}^4J^{0°} = +0.01$ Hz)



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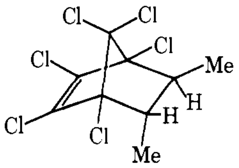
(${}^4J^{120°} = -0.32$ Hz)



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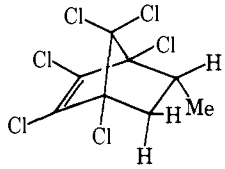
(${}^4J^{0°} = +0.15, -0.10$ Hz)



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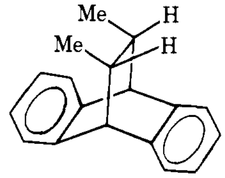
(${}^4J^{120°} = -0.13$, ${}^4J^{0°} = -0.17$ Hz)



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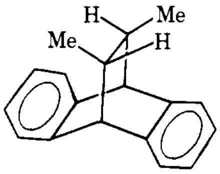
(${}^4J_{\mathrm{Me,H}} = -0.36$ Hz)



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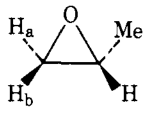
(${}^4J_{\mathrm{Me,H}} = -0.02$ Hz)



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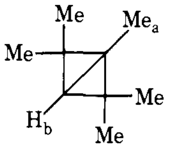
(${}^4J_{\mathrm{Me,a}} = -0.36$, ${}^4J_{\mathrm{Me,b}} = +0.52$ Hz)



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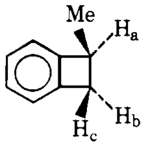
(${}^4J_{\mathrm{Me_a,H_b}} = 0.7$ Hz)



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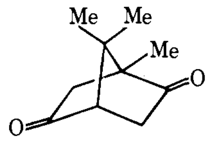
(${}^4J_{\mathrm{Me,b}} = -0.06$,
${}^4J_{\mathrm{Me,c}} = -0.05$,
${}^3J_{\mathrm{a,b}} = +5.10$,
${}^3J_{\mathrm{a,c}} = +2.36$ Hz)



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In addition, published data for several camphor derivatives[58,59] and our results for camphor-1,5-dione (**15**) show that ${}^4J_{\mathrm{Me\text{-}C\text{-}C\text{-}H}}$ for $\phi = 80°$ lies in the range of $|0.1|$–$|0.2|$ Hz. In view of the fact that the results obtained from the series **7–9** showed no anomalies attributable to strain in the bicyclic system, these results are probably of general significance, but the negative signs attributed to these small interactions by us (Figure 4) are based only on the interpolation between the data for $\phi = 60$ and 120°.

The above experimental results are shown in Figure 4 in the form of oblong areas representing the ranges quoted above with some allowance for error in determining bond angles. It can be seen that these areas deviate markedly from the INDO–FPT results (dashed line in Figure 4), especially for dihedral angles less than about 100 and more than 120°. The summed results (solid line in Figure 4) seem to be consistent with the experimental results for angles less than 120° but do not go all the way up to about 1 Hz for

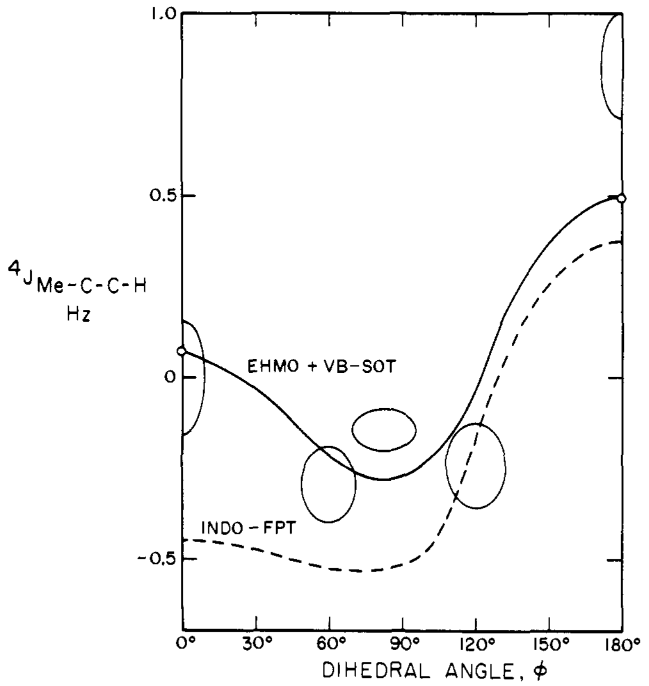


Figure 4. Comparison of the calculated INDO-FPT and EHMO + VB-SOT results with experimental values for the case of coupling over four single bonds involving a methyl group as a function of the dihedral angle ϕ.

angles near 180°. This inadequacy may simply be related to the failure of the VB method to include spin-polarization mechanisms corresponding to the direct mechanism. This could be corrected by inclusion of the exchange integral between the hybrid orbitals on C_1 and C_3 and directed toward H_1 and H_3.

From the structural point of view, the empirical relationship summarized in Figure 4 is very fortunate; it appears that with the exception of highly strained systems appreciable values of $^4J_{\mathrm{Me-C-C-H}}$ are confined to geometries where ϕ approaches 180°, thus making the interpretation of such data straightforward.

In the case in which both of the coupled protons can assume all of the orientations available to a methyl group, i.e., in propane, itself, it is necessary to average over the nine values for the staggered conformation. The calculated values corresponding to approximations A–D in Tables II and III are −0.22, 0.19, −0.18, and 0.02 Hz, respectively. The experimental value for propane has been estimated to be less than 0.2 Hz,[60] and in analogy with signs measured in several related molecules,[61] the sign is probably positive.

Considerably larger values[62-65] (up to 0.65 Hz)[62] have been reported for acetonides, and this is clearly a case of a very substantial substituent effect[2,66-68] on the magnitude of $^4J_{\mathrm{Me-C-Me}}$.

IV. Allylic Coupling

Allylic coupling corresponds to the special case of coupling over four bonds in which there is a C–C double bond in the path connecting the coupled nuclei. The most pronounced features of this type of coupling were first rationalized in terms of a π-electron mechanism,[22] which assumes its maximum (negative) value when the proton on the C_3 carbon atom eclipses the $2p$ atomic orbital on the C_2 carbon atom. This corresponds to the case in which the dihedral angle ϕ, measured from the C_1–C_2–C_3 plane in Figure 5, is 90°. The larger absolute values for the cisoid [$^4J(H_1$–$H_3)$ in Figure 5] than the transoid [$^4J(H_1'$–$H_3)$ in Figure 5] coupling constants were attributable[2-4] to a cancellation between the negative π-electron contribution and the σ-electron contribution, which assumes its maximum positive value in the planar, transoid ("W") arrangement. The INDO–FPT results[6] provided a reasonable description of conformational and substituent effects on allylic coupling constants.

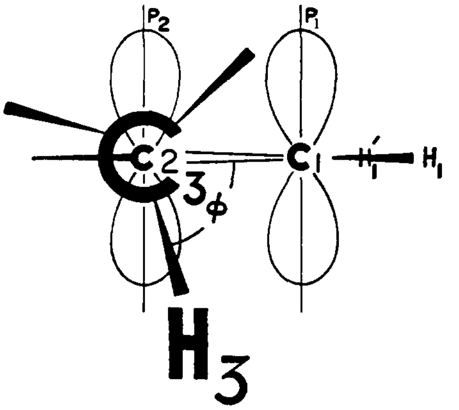


Figure 5. Specification of the dihedral angle ϕ in propene. The C_3 carbon atom eclipses the C_2 carbon atom, and the cisoid proton H_1 eclipses the transoid proton H_1'.

Table IV. Calculated Values of the Transoid Allylic Coupling Constants[a] in Propene at 15° Intervals of the Dihedral Angle ϕ

Dihedral angle ϕ, deg	INDO–FPT A	EHMO B	VB–SOT C	B + C D
0	−0.54	0.34	−0.38	−0.04
15	−0.75	0.31	−0.53	−0.22
30	−1.31	0.22	−0.92	−0.70
45	−2.09	0.11	−1.45	−1.34
60	−2.84	0.01	−1.99	−1.98
75	−3.27	−0.02	−2.38	−2.40
80	−3.31	−0.01	−2.46	−2.47
85	−3.28	0.02	−2.51	−2.49
90	−3.20	0.06	−2.53	−2.47
105	−2.58	0.26	−2.39	−2.13
120	−1.53	0.56	−2.01	−1.45
135	−0.29	0.89	−1.48	−0.59
150	0.88	1.18	−0.96	0.22
165	1.71	1.38	−0.58	0.80
180	2.01	1.45	−0.44	1.01

[a] In hertz.

Recent experimental studies[69-72] of allylic coupling have shown that some additional factors are involved. For example, the usual trend toward larger magnitudes for cisoid than transoid coupling constants is reversed for certain valus of the dihedral angles. Furthermore, both types of coupling assume very small magnitudes for dihedral angles near 0°.

Calculated values of the transoid and cisoid allylic coupling constants in the various approximate methods are entered in Tables IV and V, respectively. The geometry and INDO–FPT results in column A are identical with those reported previously.[6] However, the calculations were performed at 15° intervals of the dihedral angle ϕ, except in the region between 75 and 90°, as the minima are sometimes shifted from the 90° value.

The extended Hückel results are given in column B of the two tables. The π-electron mechanism is not implicit in these results, because the one-center exchange integrals are not included in this approximation. As a consequence, these results are indicative of electron-transfer mechanisms in the σ-electron framework and are not extremely different from the values for propane obtained in this approximation. In particular, note that the maximum, positive value occurs for

Table V. Calculated Values of the Cisoid Allylic Coupling Constants[a] in Propene at 15° Intervals of the Dihedral Angle ϕ

Dihedral angle ϕ, deg	INDO-FPT A	EHMO B	VB-SOT C	B + C D
0	-1.15	0.00	-0.43	-0.43
15	-1.29	0.00	-0.57	-0.57
30	-1.67	0.01	-0.95	-0.94
45	-2.20	0.01	-1.48	-1.47
60	-2.72	0.01	-2.00	-1.99
75	-3.08	0.01	-2.39	-2.38
80	-3.14	0.01	-2.46	-2.45
85	-3.18	0.02	-2.52	-2.50
90	-3.17	0.02	-2.54	-2.52
105	-2.96	0.04	-2.40	-2.36
120	-2.50	0.05	-2.03	-1.98
135	-1.90	0.06	-1.51	-1.45
150	-1.33	0.07	-1.00	-0.93
165	-0.91	0.07	-0.62	-0.55
180	-0.76	0.07	-0.48	-0.41

[a] In hertz.

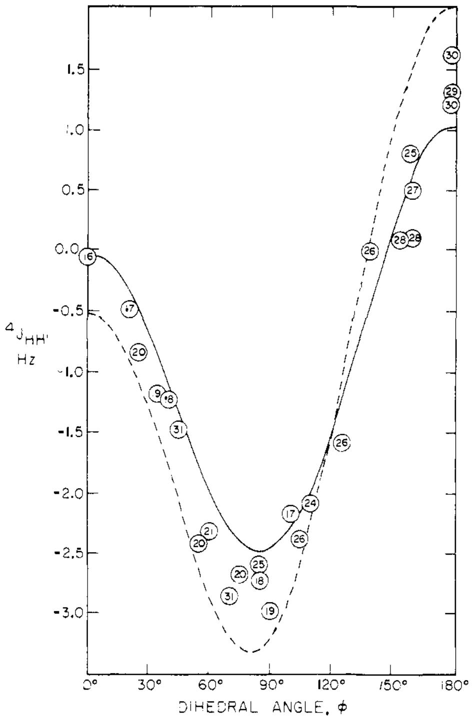


Figure 6. Comparison of calculated and experimental transoid allylic coupling constants as a function of the dihedral angle ϕ. The solid curve is based on the sum of the EHMO and VB-SOT treatments (column 5, Table IV), and the dashed curve corresponds to the INDO-FPT treatment (column 2, Table IV). The circles represent experimental data, the numbers referring to the formulas in Table VI.

the transoid arrangement with ϕ = 180°, corresponding to the "W" orientation of propane.

The VB-SOT results in column C of Tables IV and V were based on a ten-electron fragment of the propene molecule, consisting of a ten-electron moiety. In addition to the bonds containing the coupled nuclei, the fragment included the $2p$ orbitals on carbons C_1 and C_2, and the C_2-H and C_2-C_3 bonds. Exchange integrals were taken from independent investigations.[14,73,74] The VB results are indicative of the importance of indirect mechanisms in both the σ- and π-electron systems.

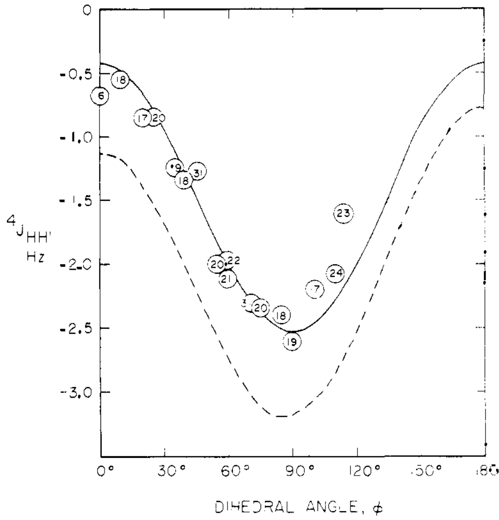
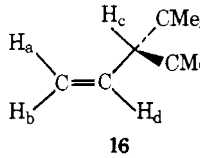


Figure 7. Comparison of calculated and experimental cisoid allylic coupling constants as a function of the dihedral angle ϕ. The solid curve is based on the sum of the EHMO and VB-SOT treatments (column 5, Table V), and the dashed curve corresponds to the INDO-FPT treatment (column 2, Table V). The circles represent experimental data, the numbers referring to the formulas in Table VI.

The sum of the EHMO and VB-SOT results is entered in the last column of Tables IV and V. Transoid and cisoid results are plotted in Figures 6 and 7 as a function of the dihedral angle ϕ. It can be seen from Tables IV and V, columns D, that the two curves exhibit crossover points similar to those predicted by the INDO-FPT calculations[6,69,70] but absent in the corresponding curves from the original VB calculations.[4] This feature is in qualitative agreement with experiment[6,69,70] where differences between $^4J_{\text{transoid}}$ and $^4J_{\text{cisoid}}$ are in the range of 0.3–0.5 Hz for ϕ values near 90°.

In order to compare the relative agreement of the INDO-FPT[6] and EHMO + VB-SOT treatments with experimental results, the data from the appropriate columns in Tables IV and V were plotted together against selected experimental values (Table VI) of transoid and cisoid allylic coupling constants in Figures 6 and 7, respectively. The experimental data presented in Table VI were chosen from a much larger collection and can be considered typical.[2,3,6,69,70] The criteria for inclusion were: (i) accuracy of NMR data; (ii) well-defined stereochemistry; (iii) minimization of angle strain; and (iv) absence of strongly electronegative substituents along the coupling path. Clearly, not all of these criteria can be completely fulfilled in all cases.

Coupling constants obtained in these laboratories are believed to be accurate to ±0.03 Hz, unless otherwise stated. Data quoted from the literature lacked confidence limits but are probably meaningful to better than ±0.1 Hz. Dihedral angles were measured from Dreiding models and are at best accurate to ±5°.



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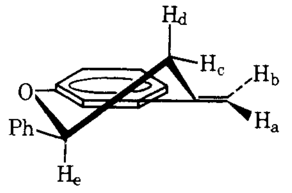

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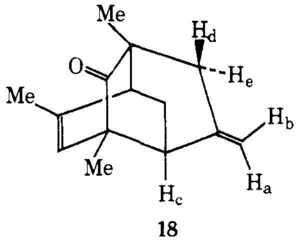

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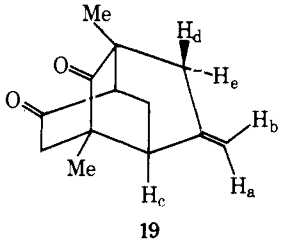

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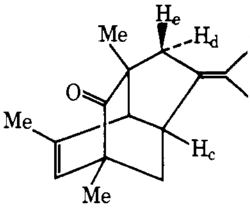

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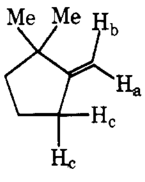

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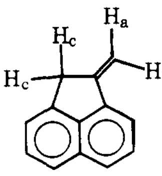

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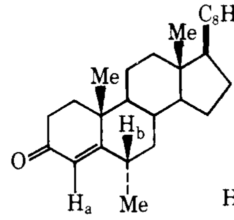

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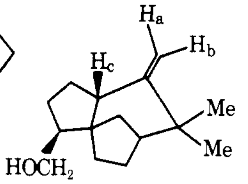

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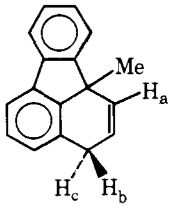

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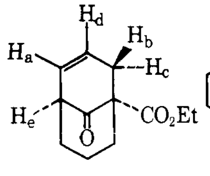

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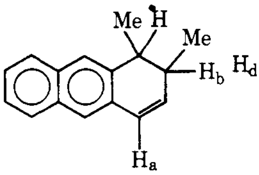

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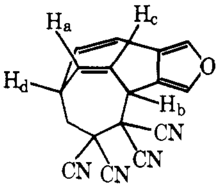

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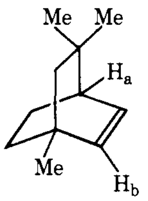

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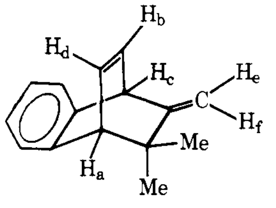

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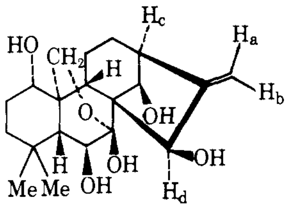

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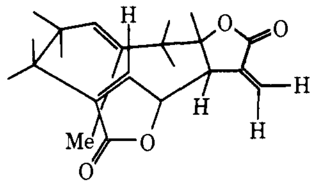

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Table VI. Experimental Values of Allylic Coupling Constants

Compd	Interacting protons	ϕ, deg	Allylic coupling constants, Hz	Ref
16	a,c	0	−0.66	70[a]
	b,c	0	−0.04	
17	a,c	20	−0.85	70
	b,c	20	−0.48	
	a,d	100	−2.19	
	b,d	100	−2.17	
18	a,c	10	−0.55	*b,c*
	b,c	10	(−)≤0.2	
	a,d	40	−1.24	
	b,d	40	−1.34	
	a,e	85	−2.73	
	b,e	85	−2.39	
19	a,c	10	−0.55	*b,c*
	b,c	10	(−)≤0.2	
	a,d	35	−1.18	
	b,d	35	−1.24	
	a,e	90	−2.97	
	b,e	90	−2.60	
20	a,c	25	−0.85	*b,c*
	b,c	25	−0.85	
	a,d	55	−2.42	
	b,d	55	−2.00	
	a,e	75	−2.69	
	b,e	75	−2.35	
21	a,c	60	−2.12	*d,c*
	b,c	60	−2.32	
22	a,c	60	−1.97	69[c]
	b,c	60	−2.32	
23	a,b	110	−1.6 ± 0.1	2[c]
24	a,c	110	−2.07	69[c]
	b,c	110	−2.10	
25	a,b	160	+0.8	*e*
	a,c	85	−2.6	
26	a,b	105	−2.4 ± 0.05	*f,c*
	a,c	125	−1.6 ± 0.05	
	d,e	140	(±)≤0.1	
27	a,b	160	+0.5	*g,c*
28	a,b	160	+0.1	*h*
	c,d	155	+0.1	
29	a,b	180	+1.30	*i*
30	a,b	180	+1.62	*d*
	c,d	180	+1.21	
31	a,c	45	−1.27	69
	b,c	45	−1.49	
	b,d	70	−2.31	
	a,d	70	−2.85	

[a] Very similar results have been previously reported by A. A. Bothner-By, C. Naar-Colin, and H. Günther, *J. Am. Chem. Soc.*, 84, 2748 (1962). [b] H. Greuter and H. Schmid, *Helv. Chim. Acta*, 55, 2382 (1972). The details of the NMR spectra of these compounds were reexamined in these laboratories using samples kindly provided by Professor H. Schmid. [c] Signs of allylic coupling constants were not determined and are assumed to be as stated by analogy. [d] This work. [e] R. G. Harvey, D. F. Lindow, and P. W. Rabideau, *Tetrahedron*, 28, 2909 (1972). [f] E. W. Colvin and W. Parker, *J. Chem. Soc.*, 5764 (1965). The details of the NMR spectrum of this compound were reexamined in these laboratories using a sample kindly supplied by Dr. Parker. [g] R. Gerdil and E. A. C. Lucken, *Helv. Chim. Acta*, 44, 1966 (1961). [h] E. Le Goff and R. B. LaCount, *Tetrahedron Lett.*, 2787 (1965). [i] C. M. Cimarusti and J. Wolinsky, *J. Org. Chem.*, 36, 1871 (1971).

Even bearing these limitations in mind, it can be seen from Figures 6 and 7 that experimental transoid allylic coupling constants fit reasonably well to either of the theoretical curves, while the experimental cisoid allylic coupling constants fit significantly better to the curve corresponding to the sum of the EHMO and VB-SOT treatments.

From the point of view of structural correlations, it must be realized that certain structural fragments are associated with allylic coupling constants which differ significantly from the typical values listed in Table VI and Figures 6 and 7, although they still obey the general angular dependence on the magnitude of ϕ.

Thus in sesquiterpenoid γ-lactones, values for ${}^4J_{\text{transoid}}$ are commonly found in the range of −3.0 to −3.5 Hz with the corresponding ${}^4J_{\text{cisoid}}$ ca. 0.3–0.5 Hz more positive,[69] and in the case of the major conformer of isabelin (**32**),[75] ${}^4J_{\text{transoid}} = -3.9$ and ${}^4J_{\text{cisoid}} = -3.4$ Hz. It is possible that these disparities from the VB-SOT + EHMO curve are not genuine substituent effects but are due to the reparameterization of the σ–π exchange integral.[14]

In the case of propene, the experimental coupling constants for the transoid and cisoid arrangements are −1.33 and −1.75 Hz, respectively.[76] Since the protons on the C_3 carbon atom can assume all of the positions available to a methyl group, the coupling constants are calculated from the formula

$$\langle {}^4J_{\text{HH}'}\rangle_{\text{av}} = (1/3)[{}^4J_{\text{HH}'}(0°) + {}^4J_{\text{HH}'}(120°) + {}^4J_{\text{HH}'}(240°)] \qquad (8)$$

Substitution of the values for the transoid coupling constants from Table IV yields calculated values of −1.20, 0.49, −1.47, and −0.98 Hz for approximations A–D, respectively. Clearly the underestimation in the last value is directly related to the shallowness of the minimum in Figure 6. Substitution of the coupling constant values for cisoid coupling from Table V yields the values −2.05, 0.03, −1.50, and −1.47 Hz for approximations A-D, respectively. Here we have the situation in which the experimental value lies between the first and last results.

V. Conclusions

The problem of long-range H-H coupling over four bonds is much more complicated than the problem of vicinal or directly bonded coupling because of the competition of several different mechanisms, some of which have opposite sign. In this study, we have shown by means of a combination of experimental and theoretical work that previous theoretical treatments did not include all of the relevant factors. It now seems clear that the substantial positive value for propanic coupling in the "W" conformation arises from a direct mechanism which overcomes a negative indirect mechanism. The large negative value predicted in the INDO-FPT treatment for the case in which the protons are in the proximate orientation is probably an overestimation.

A major difficulty in comparing the experimental and theoretical results is the scarcity of data for propanic coupling for a wide range of dihedral angles. However, data for coupling over four bonds involving a methyl group and for transoid and cisoid allylic coupling provide key data for testing the theoretical formulations.

The suggestion that certain types of valence-bond and molecular-orbital descriptions represent mutually exclusive contributions to the nuclear spin-spin coupling constant can be best understood by noting the relationship of these parameters to ESR hyperfine coupling constants. Electron-transfer mechanisms are implicit in MO schemes, but no spin polarization is included if the one- and two-center exchange integrals are ignored. On the other hand, the VB methods without ionic terms include only spin-polarization mechanisms. The sum of the coupling constant results from the MO and VB schemes is in better agreement with the experimental data than the INDO-FPT results[6] and the VB results,[4] which incorrectly assumed that direct mechanisms were not important for cases in which the nuclei were not close together.

Experimental Section and Analysis of NMR Spectra

Light petroleum refers to fraction with bp 55-65°. Melting points were determined on a Koffler block and are uncorrected. Infrared and ultraviolet spectra were recorded on Perkin-Elmer 221 and Perkin-Elmer 4000A spectrophotometers and mass spectra on an AEI-MS-9 spectrometer. ^{1}H NMR spectra were recorded on Varian HA-100D or Varian XL-100 spectrometers. Unless otherwise stated, NMR data refer to dilute (less than 10% w/v) solutions in deuteriochloroform and were obtained by first-order analysis in cases where all $\Delta\nu/J$ ratios were larger than 6 or by iterative computer analysis using the LAOCN3[77] or LAME[78] programs executed on an IBM 7040 computer. The parameters listed are believed to be significant to better than ±3 in the last place quoted. Chemical shifts (δ) are given in parts per million from internal TMS and coupling constants in hertz.

cis-**1,2-Dimethylacenaphthene** (**4**) was prepared by hydrogenolysis of *cis*-1,2-dimethyl-1,2-acenaphthenediol[79] as colorless crystals, mp 52-54° (lit.[80] 53-54°). Analysis of the $A_3BB'A'_3$ portion of the NMR spectrum using LAME[78] gave: δ_A 1.28, δ_B 3.70, J_{AB} 7.42, $J_{AB'}$ −0.26, $J_{BB'}$ 7.71, $J_{AA'}$ 0.00 (rms error: 0.097).

trans-**1,2-Dimethylacenaphthene** (**5**) was prepared by hydrogenolysis of *trans*-1,2-dimethyl-1,2-acenaphthenediol[79] as colorless crystals, mp 182-183° (lit.[80] 182-183°). Analysis of the $A_3BB'A'_3$ portion of the NMR spectrum using LAME[78] gave: δ_A 1.42, δ_B 3.15, J_{AB} 7.15, $J_{AB'}$ −0.08, $J_{BB'}$ 3.98, $J_{AA'}$ 0.00 (rms error: 0.112).

1-Methylacenaphthene (**6**). The preparation of this compound and of its *3,5,6,8-d*$_4$ derivative have been described elsewhere.[81] The data listed under structure **6** were obtained as part of the same computer output which yielded the remaining NMR parameters listed previously.[81]

cis,endo-**1,4,5,6,7,7-Hexachloro-2,3-dimethylbicyclo[2.2.1]-5-heptene** (**7**) was prepared in 94% yield (by NMR) by heating *cis*-2-butene (6 g) and hexachlorocyclopentadiene (20 g) in a steel pressure vessel for 6.5 hr at 170°. The material was purified by sublimation and crystallization from methanol to yield white crystals, mp 200-201° (sealed tube) (lit.[82] 200-202°). Analysis of the $A_3BB'A'_3$ NMR spectrum (10% w/v in CCl_4) using LAME[78] gave: δ_A 1.00, δ_B 2.91, J_{AB} 7.38, $J_{AB'}$ −0.32, $J_{BB'}$ 9.35, $J_{AA'}$ 0.00 (rms error: 0.049).

trans-**1,4,5,6,7,7-Hexachloro-2,3-dimethylbicyclo[2.2.1]-5-heptene** (**8**). *trans*-2-Butene (3 g) and hexachlorocyclopentadiene (50 ml) were heated in a steel pressure vessel for 22.5 hr at 173° to give a brown liquid which was shown (by NMR) to contain *trans*-1,4,5,6,7,7-hexachloro-2,3-dimethylbicyclo[2.2.1]-5-heptene in 31% yield. Similar treatment of *trans*-2-butene (6 g) and hexachlorocyclopentadiene (17 ml) for 6.5 hr at 170° yielded only 8% of the desired product. The material was purified by preparative GLC to give colorless crystals: mp 69-71°; ir (Nujol mull) 1608, 1450, 1385, 1175, 730 cm^{-1}. *Anal.* Calcd for $C_9H_8Cl_6$: C, 32.8; H, 2.4; Cl, 64.8. Found: C, 32.3; H, 2.3; Cl, 66.0. The NMR spectrum (9% w/v in CCl_4) of the A_3BCD_3 system was analyzed using LAME,[78] and the assignments were made on the basis of closely analogous compounds:[81] δ_A (endo methyl) 1.13, δ_B (exo methine) 2.60, δ_C (endo methine) 1.81, δ_D (exo methyl) 1.41, J_{AB} 6.89, J_{AC} 0.15, J_{BC} 5.66, J_{BD} −0.10, J_{CD} 7.35, J_{AD} 0.00 (rms error: 0.051).

endo-**1,4,5,6,7,7-Hexachloro-2-methylbicyclo[2.2.1]-5-heptene** (**9**). Propene (3.6 g) and hexachlorocyclopentadiene (55 ml) were heated in a steel pressure vessel for 3.5 hr at 173° to give a brown oil which was shown (by NMR) to contain *endo*-1,4,5,6,7,7-hexachloro-2-methylbicyclo[2.2.1]-5-heptene in 66% yield. The material was purified by fractional distillation, sublimation at 140° (0.1 mm), and crystallization from aqueous methanol to give colorless crystals: mp 123-124° (sealed tube); ir (Nujol mull) 1610, 1450, 1385, 1175, 830, 730 cm^{-1}. *Anal.* Calcd for $C_8H_6Cl_6$: C, 30.5; H, 1.9; Cl, 67.6. Found: C, 30.4; H, 1.5; Cl, 68.1. The NMR spectrum (10% w/v in CCl_4) of the $ABCD_3$ system was analyzed using LAOCN3,[77] and the assignments were made on the basis of closely analogous compounds:[81] δ_A (exo proton at C-3) 2.65, δ_B (endo proton at C-3) 1.62, δ_C (exo proton at C-2) 2.90, δ_D (endo methyl at C-2) 1.07, J_{AB} −12.28, J_{AC} 8.83, J_{BC} 4.02, J_{AD} −0.13, J_{BD} −0.17, J_{CD} 6.92 (rms error: 0.069).

9,10-Dihydro-9,10-(*cis***-11,12-dimethylethano)anthracene** (**10**) was prepared by the method of Walborski[83] as colorless crystals, mp 173-174° (lit.[83] 173-174°). The NMR spectrum (10% w/v in CCl_4) showed an AA'BB' multiplet centered on δ 7.06 (aromatic protons) and a broad doublet at 3.83 (benzylic protons). On irradiation of the latter signal, the upfield portion of the spectrum became reduced to an $A_3BB'A'_3$ system, which was analyzed using LAME[78] to give: δ_A 0.79, δ_B 1.31, J_{AB} 6.89, $J_{AB'}$ −0.02, $J_{BB'}$ 4.87, $J_{AA'}$ 0.00 (rms error: 0.0578).

9,10-Dihydro-9,10-(*trans***-11,12-dimethylethano)anthracene** (**11**) was prepared by the method of Nozaki et al.[84] as colorless crystals, mp 89-89.5° (lit.[84] 89.0-89.5°). The NMR spectrum (10% w/v in CCl_4) showed an AA'BB' multiplet centered on δ 7.05 (aromatic protons) and a broad doublet at 3.79 (benzylic protons). On irradiation of the latter signal, the upfield portion of the spectrum became reduced to an $A_3BB'A'_3$ system, which was analyzed using LAME[78] to give: δ_A 0.79, δ_B 1.31, J_{AB} 6.89, $J_{AB'}$ −0.02, $J_{BB'}$ 4.87, $J_{AA'}$ 0.00 (rms error: 0.0578).

2,5-Bornadione (**15**) was prepared via the sequence outlined by Heinänen[85] as colorless crystals mp 212-213° (lit.[85] 213.5-215.5°). The NMR spectrum (20% w/v in benzene-d_6) showed singlets at δ 0.44 and 0.58 (geminal dimethyl group, assigned on the basis of small mutual coupling),[62-65] singlet at 0.75 (methyl (C-1), and a complex multiplet due to the remaining five protons which was analyzed using LAOCN3 to give δ_A 2.02 (H-3 exo), δ_B 1.71 (H-3 endo), δ_C 2.06 (H-4), δ_D 1.81 (H-6 exo), δ_E 1.59 (H-6 endo), J_{AB} −18.70, J_{AC} 5.29, J_{AD} 0.26, J_{AE} −0.04, J_{BC} 0.44, J_{BD} 0.04, J_{BE} −0.01, J_{CD} 1.33, J_{CE} −0.15, J_{DE} −18.67 (rms error: 0.049). The narrowing of appropriate resonances in double irradiation experiments showed that $J_{C\text{-}1Me,H\text{-}6endo}$ is in the range of 0.1-0.2 Hz.

3-*tert***-Butyl-4,4-dimethyl-1-pentene** (**16**) was prepared by a previously described method[86] as a colorless oil, bp 148-150°. The

NMR spectrum (15% w/v in CCl_4) consisted of a singlet δ 0.98 due to the *tert*-butyl groups and a very weakly coupled four-spin system due to the olefinic protons, which was analyzed using LAOCN3.[77] Following previous workers[86] and on general grounds,[87] it was assumed that all vicinal coupling constants as well as the geminal coupling constant J_{ab} are positive in sign, and the iterative part of the analysis[77] was then performed with several combinations of signs for allylic coupling constants J_{ac} and J_{bc}. The iterative analysis converged for two solutions with rms errors of 0.024 and 0.029, respectively:

$$\text{solution I: } J_{ac}\ -0.66,\ J_{bc}\ -0.04$$

$$\text{solution II: } J_{ac}\ +0.49,\ J_{bc}\ -0.05$$

There were no significant differences between solutions I and II in the magnitudes of the remaining parameters, which were indeed almost identical with those obtained previously.[86] The parameters for solution I are as follows: δ_a 4.78, δ_b 4.98, δ_c 1.57, δ_d 5.73, J_{ab} 2.52, J_{ad} 17.04, J_{bd} 10.20, J_{cd} 10.59. Solutions I and II were clearly differentiated by means of tickling experiments.[88] Use was made of the method developed by Castellano and Bothner-By,[89] which relates the progressively connected, regressively connected, and unconnected pairs of transitions with the transition numbers in the LAOCN3 program.[77] Only solution I was found to be acceptable, but the negative sign of the very small J_{bc} could not be directly verified.

4-Methylene-2-phenylchroman (17). Flavanone (2.1 g) in ether (20 ml) was added dropwise with stirring to a solution of methylenetriphenylphosphorane [prepared from methyltriphenylphosphonium bromide (3.8 g) and *n*-butyllithium (Fluka, 5.0 ml)] in ether (30 ml). The reaction was stirred overnight, worked up in the usual manner, and purified by chromatography on alumina. 4-Methylene-2-phenylchroman was eluted as a colorless oil (500 mg) with a mixture of pentane (99%) and ether (1%): ir ($CHCl_3$) 1635, 1605, 1570, 1492, 1475, 1450, 1435, 1125, 1065, 690 cm^{-1}; uv (hexane) 250.5 nm (ϵ 7690), 301.5 (3320), 312 (2710). *Anal.* Calcd for $C_{16}H_{14}O$: C, 86.5; H, 6.4. Found: C, 86.3; H, 6.6. The NMR spectrum (benzene-d_6, 12.5% w/v) showed aromatic resonances between 6.7 and 7.9 ppm and a five-spin system which was analyzed using LAOCN3.[77] The relative assignments of H_a and H_b were based on the well-documented deshielding effect of the aromatic ring[69] and the assignments of H_c, H_d, and H_e follow from their internal coupling constants.[87] The signs of all the coupling constants were assumed to be as shown by analogy[87] except for J_{ab}, J_{ac}, and J_{bc}. It was then found that the iterative part of the LAOCN3 analysis would not converge on solutions with either or both J_{ac} and J_{bc} positive. Tickling experiments[88,89] eliminated the solutions with J_{ab} negative to give: δ_a 4.69, δ_b 5.43, δ_c 2.46, δ_d 2.63, δ_e 4.87, J_{ab} 0.89, J_{ac} −0.85, J_{ad} −2.19, J_{ae} 0.00, J_{bc} −0.48, J_{bd} −2.17, J_{be} 0.00, J_{cd} −14.81, J_{ce} 2.57, J_{de} 11.48 (rms error: 0.022).

2,2-Dimethylmethylenecyclopentane (21). 2,2-Dimethylcyclopentanone[90] (8.75 g) was added dropwise with stirring to a solution of methylenetriphenylphosphorane [prepared from sodium hydride (3.8 g) and methyltriphenylphosphonium bromide (27.9 g)] in dimethyl sulfoxide (80 ml). The mixture was stirred at room temperature for 30 min and distilled under reduced pressure to yield a fraction, bp 45° (85 mm), which on redistillation gave 2,2-dimethylmethylenecyclopentane as a colorless liquid: (4.8 g) bp 106°; ir (CCl_4) 1635, 1455, 1428, 1360, 1202, 1125, 883 cm^{-1}; nmr (CCl_4, 10% w/v) s, 1.04, 6 H (geminal dimethyl), m, 1.4–1.8, 4 H (methylene groups at C-3 and C-4), 2.36, m, 2 H (methylene group at C-5, i.e., H_c). *Anal.* Calcd for C_8H_{14}: C, 87.2; H, 12.8. Found: C, 87.5; H, 13.0. The multiplet assigned to the protons of the exocyclic methylene group was analyzed by a procedure used to analyze the similar spectrum of 4-methylenespiro[2.5]octane[69] to give: δ_a 4.71, δ_b 4.67, $|J_{ab}|$ 0.85, J_{ac} −2.12, J_{bc} −2.32. The relative assignment of the signals due to H_a and H_b is based on the observation of a 14% enhancement of intensity of the signal at 4.67 ppm on irradiation at 1.04 ppm.

3,3-Dimethyl-2-methylene-5,6-benzobicyclo[2.2.2]octa-5,7-diene (30). 4-Bromo-6,6-dimethylcyclohex-2-enone[91] (15 g) and quinaldine (20 g) were heated in a distillation flask at 135° (40 mm) under a slow flow of nitrogen. The distillate (ca. 3 g, bp 70–75°) was immediately dissolved in dichloromethane (25 ml), washed briefly with cold dilute hydrochloric acid and water, and was treated with isoamyl nitrite (10 g). This solution was refluxed, while treated dropwise with a solution of anthranilic acid (8 g) in acetone (100 ml); reflux was continued for an additional hour, and the solvent was removed *in vacuo*. Work-up gave a neutral fraction which was purified by chromatography on silica gel. A mixture of benzene and light petroleum (75:25), eluted **3,3-dimethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one** as a yellow oil (1.6 g): bp 80–82° (0.2 mm); ir ($CHCl_3$) 1722, 1470, 1460, 1060 cm^{-1}; uv (ethanol) 254 nm (ϵ 765), 261 (730), 267 (715), 273.5 (610), 296 (350), 301 (350); NMR s, 0.68, 3 H and s, 1.20, 3 H (geminal dimethyl), dd (1.8 and 6.0 Hz), 3.80, 1 H (H-4), dd (1.4 and 6.0 Hz), 4.39, 1 H (H-1), m, 6.4–6.8, 2 H (H-7 and H-8), m, 7.0–7.3, 4 H (H aromatic). *Anal.* Calcd for $C_{14}H_{14}O$: C, 84.8; H, 7.1. Found: C, 84.5; H, 7.1. 3,3-Dimethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one (0.8 g) in ether (30 ml) was added dropwise with stirring to a solution of methylenetriphenylphosphorane [prepared from methyltriphenylphosphonium bromide (1.8 g) and *n*-butyllithium (Fluka, 2 ml)] in ether (30 ml). The mixture was stirred for 1 hr and then refluxed for 17 hr to give on work-up a neutral red oil which was purified by chromatography on alumina. Elution with light petroleum gave 3,3-dimethyl-2-methylene-5,6-benzobicyclo[2.2.2]octa-5,7-diene (30) (0.55 g) which crystallized slowly at 0° to give colorless crystals: mp ca. 10°; ir (CCl_4) 1645, 1465, 1455, 1380, 1365, 1155, 880 cm^{-1}; uv (hexane) 260 nm (ϵ 570), 265.5 (755), 272 (625), 283 (515). *Anal.* Calcd for $C_{15}H_{16}$: C, 91.8; H, 8.3. Found: C, 91.8; H, 8.3. NMR (CCl_4, 12% w/v) showed that simultaneous irradiation of the two singlets assigned to the geminal methyl groups at δ 0.71 and 1.16 produced an enhancement of 8% in the intensity of the narrow multiplet at 4.56, which was therefore assigned to H_f, and a small (ca. 1%) reduction in intensity of the narrow multiplet at 4.89 assigned to H_e. Appropriate decoupling experiments gave the following values for the coupling constants involving the exocyclic methylene group: J_{ef} 0.85, J_{ce} 0.6 ± 0.1, J_{cf} <0.2, J_{ae} 0.5 ± 0.1, J_{af} <0.2. No sign determinations could be obtained because of insufficient resolution, and no signs are implied. On irradiation of the signals at δ 4.56 and 4.89, the resonances assigned to H_a, H_b, H_c, and H_d were analyzed using LAOCN3[77] and were found to form an AA′MX system because of accidental equivalence of H_b and H_d. Slight alterations in the relative chemical shifts of these two protons during the noniterative portion of the analysis always resulted in the convergence of the iterative process on the solution with $\delta H_b = \delta H_d$, presumably because of the fact that even at the highest resolution achievable ($W_{1/2}$ of single transitions ca. 0.15 Hz), a number of transitions had to be assigned as degenerate. All coupling constants, except the negligible J_{ac}, were considered to be positive by close analogy.[87,92] The final parameters were: δ_a 3.45, $\delta_b = \delta_d$ = 6.46, δ_c 4.21, J_{ab} 1.62, J_{ac} 0.00, J_{ad} 5.89, J_{bc} 6.20, J_{bd} 7.51, J_{cd} 1.21 (rms error: 0.022).

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Operational Scale of Hydronium Ion Activities for Strongly Acidic Media

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Abstract: The new acidity function, H_{GF}, established previously for aqueous solutions of H_2SO_4 and $HClO_4$ by a combined polarographic–glass electrode approach with the ferrocene–ferricenium couple as reference, has been extended to solutions of H_3PO_4, H_3PO_3, and methanesulfonic and *p*-toluenesulfonic acids. The variation of the activity coefficients of ferrocene and ferricenium ion with acid concentration has been determined for all six acids by distribution and solubility methods. These data, combined with H_{GF} values, have made it possible to calculate, for these media proton activities, log a_{H^+}, relative to the standard ion (TEA^+). The resulting acidity scale is considered to be a better operational measure of acidity in concentrated acids than spectrophotometrically determined acidity functions. Its potential utility in mechanistic studies of acid-catalyzed reactions is discussed.

As an operational measure of the acidity of nondilute acid solutions, the acidity function approach has serious shortcomings, particularly for the interpretation of rate-acidity dependence in concentrated acids. These difficulties arise mainly from the presence of the indicator activity coefficient ratios which are inherent in the definition of any