

LONG-RANGE PROTON SPIN-SPIN COUPLING

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I. Introduction

A. SCOPE

Long-range nuclear spin-spin coupling constants in high resolution nuclear magnetic resonance (nmr) spectra are those which occur between nuclei separated by more than three bonds. In this review emphasis will be placed on comparison of experimental and theoretical results, conformational and substituent dependencies, and the detailed mechanisms which lead to the observed long-range coupling constants. To limit the length of this review, only coupling between protons will be considered.

Previous reviews in this field include a brief discussion¹ of

all types of proton coupling constants in hydrocarbons and an extensive compilation² of long-range H-H coupling constants. Three monographs^{3a,b,4} on high resolution nmr spectroscopy include discussions and compilations of coupling constant data. An extensive tabulation of nmr spectral parameters has appeared.⁵

B. NOMENCLATURE

With few exceptions classification of types of long-range coupling will conform to molecular structure, *i.e.*, allylic, homoallylic, etc.¹⁻⁴ The coupling constant between nuclei, N and N', in which there are *n* intervening bonds will be denoted by ⁿJ_{NN'}. However, in certain cyclic molecules in which there can be more than one coupling path the superscript *n* will be omitted.

Coupling constants can have either positive or negative signs. The signs of long-range coupling constants are usually measured relative to a large coupling of "known" sign. The signs of the latter are determined either by absolute sign measurements or they are inferred from theoretical calculations. Important absolute sign measurements include the determination of a positive value for the *ortho* H-H coupling in *p*-nitrotoluene by orientation in a strong electric field.^{6,7} By partial alignment in a nematic liquid crystal, all positive values were obtained for the *ortho*, *meta*, and *para* H-H coupling constants in benzene,^{8,9} the *cis* and *trans* H-H coupling constants,¹⁰ and the directly bonded C¹³-H coupling constants¹⁰ in cyclopropane and cyclobutane. The long-range coupling constant ⁴J_{HH} in methylacetylene is negative.¹¹ All of the H-H and H-F coupling constants in fluorobenzene are positive or zero.⁹ With these and other absolute sign determina-

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tions and a very large number of relative sign measurements, the pattern of coupling constant signs is well established. Some important exceptions to this statement occur for certain long-range coupling constants, and these will be discussed in subsequent sections.

II. Experimental Techniques

In principle, all of the nuclear magnetic moments in a molecule are spin coupled to one another, and, if the interactions do not vanish accidentally or they are not smaller than the natural line width, failure to observe them is due to instrumental difficulties or spectral complexity. Small splittings in high resolution nmr spectra are often obscured by magnetic field inhomogeneities or unfavorable relaxation times.

Major difficulties in detecting weak coupling constants can occur when there is strong coupling in some part of the spectrum. In such cases the simple rules for first-order analysis may not be applicable.^{3a} A case in point is the deceptively simple spectrum of the methyl protons of toluene for which a triplet splitting from only two protons is indicated.¹² However, a detailed spectral analysis¹³ indicates coupling of comparable magnitude to all five of the strongly coupled aromatic protons.

In cases where the magnitudes of coupling constants are near the limit of instrumental resolution, accurate values are not easily obtained. Furthermore, usual methods for determining relative signs (first-order analyses and/or nuclear magnetic double resonance) often are not applicable. As a consequence, it is difficult to set error limits on many of the long-range coupling constants which are reported.

A variety of experimental techniques are available¹⁴ to overcome these difficulties. Several methods of resolution enhancement have been developed¹⁵ for slow-sweep (~ 0.01 Hz/min) nmr spectra. These include trial and error fitting of the multiplet lines from an assumed line shape,¹⁶ and linear transformation (convolution and Fourier transform) techniques¹⁴ in which a digital computer is interfaced to an nmr spectrometer. Another method uses analog transformation performed inside the spectrometer.¹⁶ The advantage claimed¹⁵ for the last methods is that the measured splittings are independent of the choice of the transformation function such that the component line shape need not be known accurately.

Weak splittings obscured by magnetic field inhomogeneity effects can be detected by a variety of double irradiation techniques¹⁷⁻²⁰ which make use of the fact that effects originating from nuclear spin-spin coupling are confined within the molecule and thereby experience almost exactly correlated local fields with nonuniformity of the applied magnetic field.

Relative signs of long-range coupling constants have been determined from temperature²¹ and solvent²² dependencies

of the nmr spectra. INDOR (internuclear double resonance) techniques^{23,24} have also been applied²⁵ to the problems of detecting hidden transitions, resolving multiplet lines, and determining relative signs of long-range coupling constants.

III. Theoretical Formulations

In this section the various theoretical formulations, which have been used to calculate coupling constants, will be examined. Particular emphasis will be placed on the various theoretical treatments which will be useful for discussing mechanisms of long-range coupling. Detailed mathematical descriptions can be found in the original literature references, a 1965 review,²⁶ and a recent monograph²⁷ which discusses all types of nmr parameters.

Most of the theoretical descriptions follow from the interpretation of Ramsey and Purcell²⁸ and the formulation of Ramsey,²⁹ who showed that the electron spins are important in the interaction and that the electron and nuclear spins can interact *via* a magnetic dipole-dipole interaction, an orbital-dipole interaction, and a Fermi contact interaction. The latter term appears to provide the most important contributions for coupling between protons, and essentially all theoretical descriptions are based on this assumption. There have been no theoretical estimates of the importance of the other terms to long-range coupling.

Since the interaction energy is bilinear in the nuclear spins,^{30,31} the second-order perturbation expression for the contact nuclear spin coupling constant is

$$J_{NN'} = -(2/3h)(16\pi\beta\hbar/3)^2\gamma_N\gamma_{N'} \times \sum_{\kappa} [E_{\kappa} - E_0]^{-1} \langle \Psi_0 | \sum_j \delta(\mathbf{r}_{jN}) \mathbf{S}_j | \Psi_{\kappa} \rangle \langle \Psi_{\kappa} | \sum_k \delta(\mathbf{r}_{kN'}) \mathbf{S}_k | \Psi_0 \rangle \quad (1)$$

where β is the Bohr magneton, γ_N is the magnetogyric ratio of nucleus N, Ψ_0 and Ψ_{κ} are the ground-state and triplet-state wave functions with energies E_0 and E_{κ} , respectively, $\delta(\mathbf{r}_{jN})$ is a Dirac delta function for electron j at nucleus N, and the summation is to be taken over all of the triplet levels. Equation 1 is the starting point for most formulations of contact nuclear spin-spin coupling.

A theoretical description,³² which used single determinant molecular orbital (MO) wave functions, also invoked the "average energy approximation" to eliminate the sum over excited states in eq 1. The resulting expression was proportional to the square of the mobile bond order for the coupled atoms. This implies necessarily positive coupling constants between protons and vanishing coupling constants between atoms in the same subset of an alternant system. Subsequently, the same investigator³³ introduced electron spin resonance

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(esr) hyperfine splittings in free radicals as a criterion for the interaction between σ and π electrons and obtained an expression for the π -electron contributions to the coupling constants

$$J_{NN'} = (h\Delta E)^{-1} \beta^2 Q_N Q_{N'} p_{NN'} \quad (2)$$

where ΔE is an "average excitation energy, Q_N and $Q_{N'}$ are the hyperfine splittings for nuclei N and N' , and $p_{NN'}$ is the bond order connecting the carbon atoms to which N and N' are attached. Equation 2 does not remove all of the difficulties of simple MO theory, but the introduction of valence-bond (VB) wave functions for aromatic systems does lead to the possibility of coupling constants of either sign.³⁴

A subsequent theoretical formulation³⁵ for the π -electron contributions to proton coupling in hydrocarbon molecules also used esr hyperfine coupling data for free radicals as an experimental criterion for σ - π configuration interaction, but included a finite sum over π -electron triplets

$$J_{HH'} = 2.1 \times 10^{-16} \sum_T [a_H(T) a_{H'}(T) / \Delta\pi(T)] \quad (3)$$

where $a_H(T)$ and $a_{H'}(T)$ are hyperfine coupling constants in hertz, and the $\Delta\pi(T)$'s are the ${}^1\Pi \rightarrow {}^3\Pi$ excitation energies in electron volts. This method was particularly successful in predicting the correct signs and magnitudes of a number of long-range coupling constants in acyclic hydrocarbons, and provides the basis for many discussions of coupling mechanisms in unsaturated systems. This π -electron formalism was extended³⁶ to include the effects of delocalization in conjugated systems by including a sum over the occupied and unoccupied MO's. Despite the neglect of important terms in the coupling constant expression,³⁷ the calculated long-range results³⁵⁻³⁸ appear to agree satisfactorily with the experimental values.

A theoretical formulation^{39, 40} based on VB wave functions, and the assumption of an "average excitation energy" in eq 1, was most successful in describing vicinal H-H coupling⁴¹ and the π -electron enhancement⁴² of geminal H-H coupling constants. In the VB schemes nonvanishing coupling constants between nondirectly bonded nuclei are attributed to the importance of nonperfect pairing structures to the ground-state wave function, since certain long-bonded structures provide a mechanism for correlating the electron spins at the sites of the coupled nuclei. These methods are closely related to the Dirac vector-model descriptions of contact coupling,^{42, 43} which provide easily visualized models for discussing²⁶ mechanisms of nuclear spin-spin coupling.

The original VB descriptions^{39, 40} have been reformulated⁴⁴ in terms of Penney-Dirac bond orders^{45, 46} for which eq 1 with the "average energy approximation" gives

$$J_{NN'} = (2h\Delta E)^{-1} (16\pi\beta\hbar/3)^2 \gamma_N \gamma_{N'} \times \sum_{t,u} p(t,u) \phi_t^2(N) \phi_u^2(N') \quad (4)$$

where $\phi_t(N)$ and $\phi_u(N')$ denote the values of the atomic orbital wave functions at nuclei N and N' , respectively, and $p(t,u)$ is the Penney-Dirac bond order

$$p(t,u) = (1/3) \sum_{j,l} c_j c_l (1/2)^{n-i_j} [1 + 2f_{j,l}^{tu}] \quad (5)$$

In eq 5 the c_j 's are the coefficients of the nonpolar, singlet VB canonical structures,³⁹ and in the superposition diagram of structures j and l , i_j is the number of islands and $f_{j,l}^{tu}$ is the usual exchange factor for orbitals t and u . Evaluation of the constants in eq 4 gives a very simple form⁴⁷ for coupling between protons

$$J_{HH'} = 4185(\Delta E)^{-1} p(h,h') \quad (6)$$

For molecular systems in which a localized bond description is a reasonable approximation (nonaromatic hydrocarbons), the Penney-Dirac bond orders in eq 4-6 can be related⁴⁴ to nonlocal bond orders, $p^\circ(t,u)$, for the four-electron systems comprising two bond pairs. For example, consider a hydrocarbon with N bonds $\sigma_f\sigma'_j$, in addition to the bonds h - c and c' - h' , where h and h' denote 1s hydrogenic orbitals centered on the coupled protons. In this case a concise but approximate relation follows⁴⁴ from eq 6

$$J_{HH'} = 4185(\Delta E)^{-1} [p^\circ(h,h') + (3/2) \sum_j p^\circ(h,\sigma_j) p^\circ(\sigma'_j, h')] \quad (7)$$

where $p^\circ(h,h')$, $p^\circ(h,\sigma_j)$, and $p^\circ(\sigma'_j, h')$ denote nonlocal bond orders for the four-electron fragments $[h$ - c , c' - h'], $[h$ - c , $\sigma_f\sigma'_j]$, and $[\sigma_f\sigma'_j$, c' - h']. For some discussions it will be convenient to express these bond orders in terms of the individual exchange integral parameters

$$p^\circ(h,h') = (1/2) \left[\frac{K(h,h') + K(c,c') - K(c,h') - K(c',h)}{K(h,c) + K(c',h')} \right] \quad (8)$$

$$p^\circ(h,\sigma_j) = (1/2) \left[\frac{K(h,\sigma_j) + K(c,\sigma'_j) - K(h,\sigma'_j) - K(c,\sigma_j)}{K(h,c) + K(\sigma_j,\sigma'_j)} \right] \quad (9)$$

where the K 's denote the formal, two-electron VB exchange integrals associated with the orbital arguments. Equations 6-9 form a satisfactory theoretical basis for *qualitative* discussions of mechanisms of coupling between protons. Equation 6 can be taken to higher order of perturbation theory,⁴⁸ but for this approximate method, the increased complexity of the resulting expressions does not seem to be justified.

In a recent theoretical description⁴⁹ of nuclear spin coupling, which used a sum over a finite set of triplet-state VB wave functions, it was shown that VB results based on the "average energy approximation" cannot be justified quantitatively. However, a perturbation treatment⁴⁴ indicates that results by the two methods are proportional for localized systems and, therefore, that the same mechanisms must be operative in either case. This provides the justification for the discussions of mechanisms by means of eq 6-9.

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The single-sign difficulties of the earlier MO theory³² can be superseded, also, by means of an LCAO-MO formulation⁵⁰ which includes an explicit sum over the excited-state wave functions. The resulting contact coupling constant expression is

$$J_{NN'} = (4h)^{-1}(16\pi\beta\hbar/3)^2\gamma_N\gamma_{N'}\phi_i^2(N)\phi_u^2(N')\pi_{iu} \quad (10)$$

where

$$\pi_{iu} = 4 \sum_{\substack{i, \text{occ} \\ j, \text{unocc}}} [\epsilon_i - \epsilon_j]^{-1} c_{it} c_{iu} c_{jt} c_{ju} \quad (11)$$

and the other expressions have been defined previously. In eq 11 the c_{it} and c_{jt} are the coefficients of atomic orbital t in the i th occupied and j th unoccupied MO's with energies ϵ_i and ϵ_j , respectively. In general, calculations of long-range H-H coupling constants by means of eq 10 have not been particularly successful.⁵¹ However, a perturbation approach⁵² in conjunction with eq 10 has been used to identify the important delocalization terms which give rise to long-range H-H coupling.⁵³ It should be noted that the MO formulation is quite different in form from the VB description but leads to similar mechanisms for transmission of coupling in the σ -electron framework.^{44,54}

Recent advances in the spin coupling theory include a generalization⁵⁷ of those formulations based on eq 1 by means of density matrix theory and group functions with intergroup configuration interaction. In a treatment⁵⁵ which uses double perturbation theory it has been shown that the $J_{HH'}$ calculated by Pople-Santry MO theory (eq 10) is mutually exclusive of that part calculated *via* the VB theory (eq 41) which used the "average energy approximation." One of the most promising new developments is the calculation of contact coupling constants by means of self-consistent perturbation theory⁵⁶ and INDO (intermediate neglect of differential overlap) wave functions. This method, which does not make use of eq 1, considers the transmission through the molecule of the effective spin density produced by the contact perturbation.

A. MECHANISMS OF LONG-RANGE COUPLING

Coupling between protons is generally believed to be dominated by the Fermi contact interaction. These terms may also give rise to the most significant contributions to coupling between other nuclei such as C¹³, F¹⁹, and P³¹, but very little is known about the importance of the noncontact terms in the electron-nuclear Hamiltonian. Furthermore, theoretical calculations of contact coupling are not of sufficient accuracy to attribute discrepancies between calculated and experimental values to contributions from other terms. Thus, the emphasis is necessarily confined to contact coupling. The details of contact mechanisms are of interest in providing a conceptual basis for the transmission of the spin-coupling "information" from one nucleus to its coupled partner.

At the qualitative level most discussions of the mechanisms of contact coupling can be based simply on the VB perturba-

tion formalism. The relationship of the contact coupling constants to the fragment bond orders provides concise mathematical expressions, but an alternative approach⁵³ which uses MO perturbation theory in the Pople-Santry formalism is expected to lead to similar conclusions.⁵²

Terms in eq 7 which are linear in the fragment bond orders, *i.e.*, $p^\circ(h, h')$, are classified⁴⁴ as *direct* as only those bonds which include the coupled nuclei are involved. Terms in eq 7 which are of second order or higher are called *indirect* because one or more intermediate bonds are included in the coupling path. Since these terms follow from the coupling constant expression they should provide a clearer basis for discussing spin-coupling mechanisms. These expressions have been used, also, in the MO description⁵⁷ of the interaction between radical lobes separated by several intervening σ bonds.

Consider the case of coupling between protons H and H' in two C-H bonds, $h-c$ and $c'-h'$, where orbitals c and c' are centered on the same or on different carbon atoms. The direct contribution to the coupling constant is proportional to the bond order, $p^\circ(h, h')$, which is related to the exchange integrals by means of eq 8. Depending on the distance between the two C-H bonds and their relative orientation, any or all of the exchange integrals in the numerator of eq 8 may be nonnegligible. For example, if only the first term, $K(h, h')$, were nonnegligible, then the direct term could be identified⁴⁴ with the "through-space" mechanism^{58,59} since only the electrons centered on the coupled nuclei are involved. The suggestion⁶⁰ that the large values of $J_{HH'}$, observed in strained bicyclic hydrocarbons, could be explained in terms of interactions between the "rear lobes" of the hybrid orbitals c and c' , corresponds to the importance of $K(c, c')$ in the numerator of eq 8. The *direct* contributions are also related to the importance of the long-bonded VB structures which link the coupled atoms.

Calculated coupling constants in which direct mechanisms provide the dominant contributions include $J_{HH'}$ in methane³⁹ and $J_{HH'}$ in ethane.⁴¹ For coupling over more than three bonds, there are no theoretical results which can be identified with the direct mechanism. This difficulty can be attributed to the inadequacy of semiempirical criteria for estimating the integral parameters.

Existing theoretical results for long-range coupling correspond to contributions from *indirect* mechanisms. For example, indirect contributions will arise in the second-order sum in eq 7 if the coupled C-H bonds both interact with some other bond in the molecule. Higher order terms would correspond to additional links in the coupling chain. It may reasonably be expected that the magnitudes of the indirect coupling contributions will fall off more rapidly in saturated systems than in unsaturated ones because of the smaller delocalization terms associated with individual links. The decrease with number of intervening bonds must be maximal for the "through-bond" contributions^{59,61} since the coupling paths include the bonds containing the coupled nuclei and one bond between every pair of atoms in the chain linking the coupled nuclei.⁴⁴ "Through-bond" couplings in saturated systems cannot depend on the dihedral angles of the system²⁶ and are

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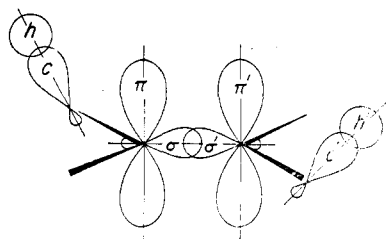


Figure 1. Labeling of orbitals in a fragment of the 2-butene molecule.

probably negligible for coupling over more than two bonds.⁴⁸

Long-range coupling constants over no more than five bonds are to be expected from the second-order terms in eq 7 with the assumption that only nearest neighbor exchanges are important. For example, in the 2-butene fragment depicted in Figure 1 only the bonds σ - σ' and π - π' are centered on atoms which are nearest neighbors to both c - h and c' - h' . For coupling in the σ -electron framework, the second-order terms in eq 7 are probably sufficient, corresponding to negligible coupling over six or more saturated bonds. For coupling in delocalized systems higher order terms would certainly be required in the perturbation expression.

A number of terms have been used, also, to describe the indirect coupling which is transmitted *via* the π -electron system. For example, the term "hyperconjugation," which has been used frequently, is not particularly useful because it has several different definitions.²⁶ In the simple MO scheme hyperconjugation implies charge redistribution for molecules in which the π - and σ -electron systems can overlap.⁶² To account for coupling in those cases in which one or both of the coupled nuclei is on an α -carbon atom and, therefore, is in the nodal plane of the π system, the "spin polarization" mechanism can be invoked. The spin polarization mechanism is attributable to nonvanishing σ - π exchange interactions, *i.e.*, σ - π configuration interaction. In VB terminology in which deviations from perfect pairing arise because of nonzero exchange interactions between different bonds, the hyperconjugative⁶³ and spin polarization mechanisms are not fundamentally different. However, no charge redistribution is implied in the simple VB scheme.

It has been shown⁶⁴ that both spin polarization and electron-transfer mechanisms are important in determining the hyperfine coupling constants in methyl groups of free radicals. Comparable theoretical studies of the importance of the two mechanisms for long-range coupling constants have not appeared. Presumably those theoretical formulations,^{33, 35-38} which use esr hyperfine coupling constant data as a semi-empirical criterion for σ - π configuration interaction or σ - π exchange, implicitly introduce the effects of electron transfer as well as spin polarization.

B. SUBSTITUENT EFFECTS

The dependence of long-range coupling constants on the nature of nearby substituents is quite complex, and no systematic theoretical investigations have appeared. In this section a qualitative MO description of substituent effects on

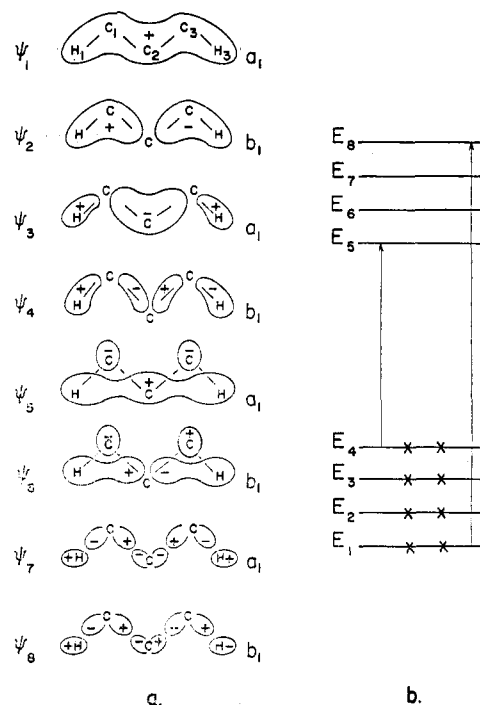


Figure 2. (a) Nodal behavior of the eight molecular orbitals of an eight-electron fragment for the propane molecule. (b) Molecular orbital energies for the wave functions depicted in (a).

${}^4J_{HH'}$ is performed for an eight-electron fragment of the propane molecule. This method is based on eq 10 and 11 and arguments which are completely analogous to those introduced by Pople and Bothner-By⁶⁵ to discuss the effects of substituents on geminal coupling constants. Similar analyses could be performed for other types of long-range coupling, such as ${}^5J_{HH'}$, in a butanic fragment.

The nodal behavior of the eight MO's and the corresponding symmetry designations appropriate to C_{2v} symmetry for the all-*trans* arrangement of a propanic fragment are depicted in Figure 2a. The ordering of the MO energies, which is depicted qualitatively in Figure 2b, follows from the same considerations which were used for a CH_2 fragment.⁶⁵

The signs of the products of the coefficients of the 1s orbitals on H_1 and H_3 , $c_{1h}c_{1h'}$, $c_{3h}c_{3h'}$ in eq 11, are entered in the second column of Table I for each of the possible transitions from occupied (i) to unoccupied (j) MO's. Transition energies in the first column are given in order of increasing separation. The signs of the contributions of each transition to ${}^4J_{HH'}$, which according to eq 10 and 11 are opposite to the product signs, are entered in the third column.

Now consider the effect of the introduction of an electron-withdrawing group at the C_2 carbon atom. Electron density will be withdrawn from the bonding regions of the symmetric MO, ψ_1 , resulting in a decrease of the 1s atomic orbital coefficients, c_{1h} and $c_{1h'}$. The 1s coefficients in the other symmetric MO's will be increased accordingly, but they will be unchanged for the antisymmetric MO's. In the fourth column of Table I are entered the changes in the magnitudes of the coupling constants on substitution of an electron-withdrawing group at the C_2 carbon atom. Since the positive shifts outweigh

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Table I

Changes in the Magnitude of $J_{HH'}$ due to Inductive and Hyperconjugative Substituents at the C_2 and C_1 Carbon Atoms of a Propanic Fragment

Transition	Sign of $c_{iH}c_{iH'}c_{jH}c_{jH'}$	Sign of $J_{HH'}$	Change of $J_{HH'}$ - C_2 substitution		Change of $J_{HH'}$ - C_1 substitution	
			Inductive	Hyperconjugative	Inductive	Hyperconjugative
4 → 5	-	+	>+	>+	>+	...
3 → 5	+	-	>-	∴	>-	...
4 → 6	+	-	∴	>-	>-	...
2 → 5	-	+	>+	<+	∴	>+
3 → 6	-	+	>+	>+	>+	...
4 → 7	-	+	>+	>+	>+	...
1 → 5	+	-	∴	∴	∴	>-
2 → 6	+	-	∴	∴	∴	>-
3 → 7	+	-	>-	∴	>-	∴
4 → 8	+	-	∴	>-	>-	∴
1 → 6	-	+	<+	>+	∴	>+
2 → 7	-	+	>+	<+	∴	>+
3 → 8	-	+	>+	>+	>+	∴
1 → 7	+	-	∴	∴	∴	>-
2 → 8	+	-	∴	∴	∴	>-
1 → 8	-	+	<+	>+	∴	>+

the negative shifts, it appears that the over-all effect should be to produce a positive change in the value of $J_{HH'}$.

The introduction of a hyperconjugative, electron-withdrawing substituent on the C_2 carbon atom would have the effect of reducing the electron density about the two hydrogen atoms in the antisymmetric MO ψ_2 if the nodal plane of the substituent is perpendicular to the plane of the fragment. With the same type of arguments as before, the substituent shifts in $J_{HH'}$ are entered in the fifth column of Table I. The over-all effect of the substituent is not as clear in this case. However, the occupied and unoccupied MO's have well-separated energies and adjacent items should not be very different in energy. Thus, a positive shift is also indicated for a hyperconjugative substituent on the C_2 carbon atom.

The changes in $J_{HH'}$ due to inductive and hyperconjugative substituents at the C_1 carbon atom are given in the last two columns of Table I. An electron-withdrawing group at C_1 will decrease the electron density near H_1 in both ψ_1 and ψ_2 in Figure 2a, whereas a hyperconjugative substituent will have the same effect in ψ_3 and ψ_4 . The qualitative results for these cases in Table I are ambiguous. However, if the propanic fragment is broken at C_2 and the right-hand fragment is twisted clockwise about C_1 and the left-hand fragment is twisted counter-clockwise about C_3 , an ethanic fragment is obtained. The results for substitution at the C_1 carbon atom for this ethanic fragment are identical with those in Table I. A large amount of experimental data in substituted ethanes⁶⁶ indicates a negative shift in the vicinal coupling constants due to both inductive and hyperconjugative substituents. By analogy negative shifts in $J_{HH'}$ would be expected for substitution at the C_1 carbon atom.

These results for substituent effects on long-range coupling are based on very crude qualitative arguments. They are introduced here on a tentative basis to help rationalize the observed trends in subsequent sections.

IV. Long-Range H-H Coupling

With few exceptions the classifications of long-range H-H

coupling constants according to molecular types here conform to the usual nomenclature.³ Relatively more space will be devoted to coupling in saturated systems because these are the least understood and because σ -electron coupling is important in unsaturated systems as well. In certain conformations of an unsaturated fragment the π -electron contributions to the coupling constant may be negligible in comparison with the σ -electron contributions. In a few cases the classification may therefore be artificial.

A. SATURATED MOLECULES

1. Four Intervening Bonds. Propanic Coupling

A large number of experimental values have been reported for coupling over four bonds in saturated systems. The physical situation is complex and there are disagreements about the most important mechanisms. Coupling over four saturated bonds will be discussed in terms of the propanic fragment depicted in Figure 3. The coupled nuclei H and H' interact with

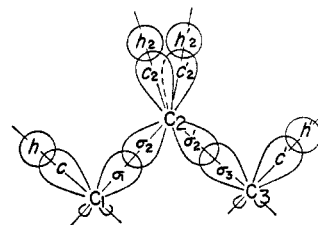


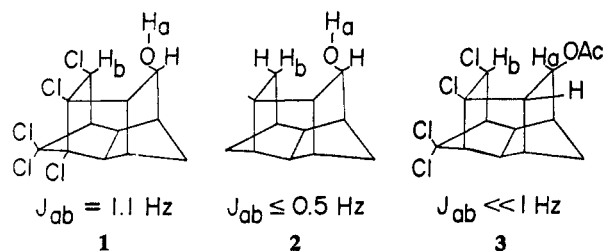
Figure 3. Designation of orbitals in a 12-electron fragment of the propane molecule.

the atomic orbitals h and h' via the Fermi contact term, and from eq 7 the coupling constant is given semiquantitatively by

$$J_{HH'} = 4185(\Delta E)^{-1} \{ p^\circ(h, h') + (3/2)[p^\circ(h, \sigma_1)p^\circ(\sigma_2, h') + p^\circ(h, \sigma'_2)p^\circ(\sigma_3, h')] - (3/2)[p^\circ(h, c_2)p^\circ(c_2, h') + p^\circ(h, c'_2)p^\circ(c'_2, h')] \} \quad (12)$$

The first term in the braces corresponds to the direct interaction between the two C-H bonds, and it is related to the exchange integrals *via* eq 8. The next two terms correspond to the two possible indirect geminal-vicinal interactions, and the last two terms to the indirect vicinal-vicinal interactions. Equation 12 does not include the third-order term corresponding to the indirect "through-bond" coupling mechanism⁶¹ since it is expected to be an order of magnitude smaller than the second-order terms.

As indicated previously the greatest difficulty in applying eq 12 is the absence of any quantitative information about the direct term. In the all-*trans* or "W" conformation depicted in Figure 3 the exchange integral $K(c, c')$ between the hybrid orbitals c and c' could be nonnegligible. Since it is probably negative in sign, it would lead to significant positive contributions to ${}^4J_{\text{HH}'}$. In other conformations of the propane fragment any or all of the exchange integrals in the numerator of eq 8 could be of importance.⁴⁴ Experimental studies⁶⁷ designed to exhibit evidence for direct coupling in compounds 1-3 with the half-cage structure show that long-range coupling



between nonbonded protons is negligible in 3, but interaction with an intermediate oxygen atom in 1 and 2 leads to measurable H-H coupling.

Since evidence for the importance of a direct mechanism to H-H coupling is ambiguous, consider the indirect terms in eq 12. The last two terms describe the mutual interactions between the bonds containing the coupled nuclei and the external C-H bonds for the propane fragment in Figure 3. Since both of these terms involve the products of two vicinal interactions, contributions will be angularly dependent and necessarily negative in sign. The second and third terms in eq 12 describe the two possible geminal-vicinal interactions. Since the geminal bond orders, $p^\circ(h, \sigma_1)$ and $p^\circ(\sigma_3, h')$ in eq 12, are independent of dihedral angle, these indirect mechanisms will depend on the sum of the vicinal bond orders, $p^\circ(h, \sigma_2')$ and $p^\circ(\sigma_2, h')$

$$p^\circ(h, \sigma_2') = A \cos^2 \phi + B \cos \phi + C \quad (13a)$$

$$p^\circ(\sigma_2, h') = A \cos^2 \phi' + B \cos \phi' + C \quad (13b)$$

where ϕ and ϕ' denote the dihedral angles measured from the $C_1-C_2-C_3$ plane as depicted in Figure 4. As the two vicinal bond orders have their maximum value for $\phi = \phi' = 180^\circ$, the indirect contributions to ${}^4J_{\text{HH}'}$ will have their maximum absolute value for the all-*trans* or "W" arrangement.⁶⁸ Since

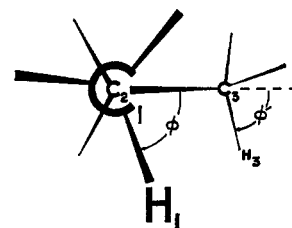


Figure 4. Specification of the dihedral angles, ϕ and ϕ' , in propane.

the vicinal bond orders in eq 13 are positive, the sign of these indirect contributions will be the same as that for the geminal bond orders. The problem here is that geminal bond orders are extremely sensitive to the cancellation between integrals in the numerator of eq 8.^{26,69} In fact, this is the difficulty which was encountered in the VB calculation⁸⁹ of ${}^2J_{\text{HH}'}$ in methane. As a consequence, there can be no justification for transferring the geminal bond order from an HCH grouping in methane to an HCC grouping in propane.^{61,70} Furthermore, this assumption incorrectly leads to maximum *negative* coupling for the all-*trans* conformations.⁷⁰

An alternative procedure⁶⁴ uses the empirical criterion of a positive geminal HCC bond order in eq 12. Entered in Table II are the calculated values for the indirect contributions,

Table II

Calculated VB Results for ${}^4J_{\text{HH}'}$ in a 12-Electron Propane Fragment^a

ϕ , deg	ϕ' , deg	${}^4J_{\text{HH}'}$, Hz	ϕ , deg	ϕ' , deg	${}^4J_{\text{HH}'}$, Hz
0	0	1.05	120	120	-0.11
	60	0.61		180	0.70
	120	0.59		240	0.09
	180	1.14		300	-0.21
	240	0.59			
	300	0.61		180	1.21
60	60	-0.32	240	180	0.70
	120	0.06		240	0.65
	180	0.65		300	-0.11
	240	-0.21		300	0.06
	300	0.04		300	-0.32

^a Dihedral angles are measured from the $C_1-C_2-C_3$ plane as shown in Figure 4.

${}^4J_{\text{HH}'}$, to long-range coupling in a 12-electron propane fragment at 60° intervals of the dihedral angles.⁷¹ Although these values are based on the VB formalism^{87, 49} which does not invoke the "average energy approximation," they are in substantially good agreement with previous results⁶⁴ because of a readjustment in the magnitude of the empirical geminal interaction parameter.

A major difficulty in ascertaining whether the direct or indirect mechanism is dominant for coupling over four saturated bonds is the unavailability of experimental data for unstrained and unsubstituted molecules. A number of values of ${}^4J_{\text{HH}'}$

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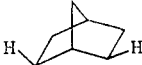
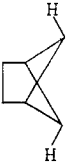
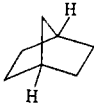

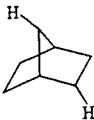
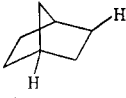



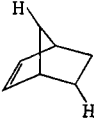
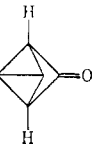
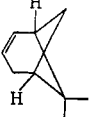

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Table III
Representative Coupling over Four Saturated Bonds in Strained, Bicyclic Molecules

Molecule	$^4J_{HH'}$, Hz	Ref	Molecule	$^4J_{HH'}$, Hz	Ref
1. Bicyclo[2.2.1]heptanes			4. Bicyclo[2.1.1]hexanes		
a. 	1.0-1.2 1.0-1.4 1.35-1.8	68, 73 75 76	a. 	6.7-8.1	60, 81
b. 	1.0-1.6	73	b. 	8	82
c. 	3-4 1.7-2.6	72 73	5. Bicyclo[1.1.1]pentane		
d. 	1.0	74	a. 	10	83
2. Bicyclo[2.2.1]heptenes			b. 	18	83
a. 	0-1.0	77	6. Tricyclo[1.1.1.0 ^{4,5}]pentanone		
b. 	2.0-3.1	77, 78		14	84
3. Bicyclo[3.1.1]heptenes			7. Bicyclo[1.1.0]butane		
	5.8-6.4	79, 80		10	83

have been observed^{60, 68, 72-84} in strained bicyclic molecules, and representative values are entered in Table III. Coupling constants range from 1.0 Hz in the bicyclo[2.2.1]heptanes to 18 Hz in bicyclo[1.1.1]pentane (item 5b). The latter is the largest known value of $^4J_{HH'}$. In almost all of the molecules in Table III the criterion for a straightest zig-zag path¹ applies, and it could be argued⁶⁰ that the separations between the "rear lobes" of the hybrid orbitals, which are bonded to the coupled nuclei, decrease with increasing ring strain, thereby increasing

the importance of a direct mechanism.⁸⁵

Alternatively, it has been noted⁸⁶ that $^4J_{HH'}$ increases with the number of coupling paths which link the coupled protons. On this basis it could be argued that the larger values of $^4J_{HH'}$ in Table III arise as the sum of indirect mechanisms over multiple paths, and that there should be a further enhancement in $^4J_{HH'}$ if the effects of ring strain are associated with an increase in the magnitude of the geminal HCC interactions.

A large number of experimental values for $^4J_{HH'}$ in unstrained, saturated systems have been reported^{68, 87-98} and

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representative values are compiled in Table IV. Signs are unknown unless indicated otherwise. Important relative sign measurements include those for the conduritols (items 6 and 7), pyranose derivatives (items 9–11 and 13), benzopyran derivatives (item 16), and a tetrahydrofuran derivative (item 17). Since inductive or hyperconjugative substituents are near one or both of the coupled protons in all of the molecules in Table IV, the problem of the conformational dependency of ${}^4J_{\text{HH}'}$ is inextricably tied to the problem of substituent effects. General trends in the signs and magnitudes which can be inferred from the coupling constant data in Table IV are as follows.

1. Coupling constants between equatorial protons, which are in the all *trans* or "W" relationship, are positive and in the range 1–2 Hz.

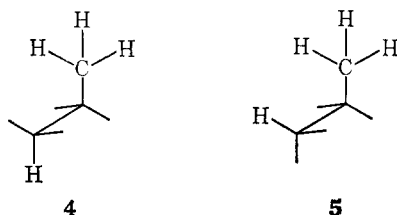
2. Between protons in the axial and equatorial positions, ${}^4J_{\text{HH}'}$'s are in the range 0.4–0.8 Hz and can be of either sign.

3. On the basis of a few values, coupling constants between axial protons are negative and in the range 0.3–0.9 Hz. An exceptionally large value of magnitude 2.25 Hz has been reported for a substituted cyclohexanone derivative (item 3).

Semiempirical VB results in Table II are ${}^4J_{ee'} = +1.20$ Hz, ${}^4J_{ae} = +0.65$ Hz, and ${}^4J_{aa'} = -0.32$ Hz. Clearly, there are some major discrepancies with the experimental results in Table IV, and these may not be attributable to substituent effects. For example, coupling constants of magnitudes 2.28 and 1.90 Hz have been reported between axial protons in 2-chloro-3,3,5,5-tetramethylcyclohexanone (item 3) and a pentaerythritol derivative (item 15), respectively. These may be contrasted with values of -0.3 Hz in a conduritol (item 6) and ± 0.3 – 0.4 in dioxane (item 14). Coupling between axial and equatorial protons has been shown by relative sign determinations to be negative in two pyranose derivatives (items 10 and 11), but both positive and negative signs have been inferred⁹⁹ for the two types of ${}^4J_{ae}$ in a conduritol (item 7).

In the absence of coupling constant data for the unsubstituted molecules in Table IV, it is difficult to find any qualitative trends due to substituents. In a rigid structure (item 4) replacement of hydrogen by bromine on the carbon which is linked to one of the coupled protons has no effect on ${}^4J_{ee'}$. However, replacement of Br by more electronegative Cl or OH in another rigid structure (item 5) leads to a decrease in the magnitude of ${}^4J_{ee'}$. This trend is observed also for coupling between the bridge proton and the 5-*endo* proton of a number of 2,6-bridged bicyclo[2.2.1]heptane derivatives (item 1c in Table III) and is consistent with the qualitative considerations of substituent effects in section III.B. On the basis of these substituent effects it is suggested that ${}^4J_{ee}$ in the unsubstituted cyclohexane should be about $+2$ Hz.

The presence of oxygen atoms in the ring adjacent to the carbon atoms bearing the coupled protons produces an en-



hancement of ${}^4J_{4e,6e}$ in dioxane (item 14) and the pentaerythritol derivatives (item 15). It seems likely that this effect is re-

lated to the very large positive shifts in the values of ${}^2J_{\text{HH}'}$ which have been observed in cyclic ethers.^{99,100} The enhancement in the positive contribution⁶⁵ appears to be due to the lone pairs, since the maximum positive contribution to ${}^2J_{\text{HH}'}$ is observed when the lone pairs "eclipse" the CH_2 group.^{99,100}

There is some experimental data for coupling over four saturated bonds in which one of the protons can assume all of the equilibrium orientations of a methyl group. The upper limit for coupling of this type in the *trans* conformation (4) is about 0.9 Hz^{95,101–104} with a positive sign⁹⁶ in those cases in which it has been measured. In the *gauche* conformations (5), the ${}^4J_{\text{H-CH}_3}$ are negative in sign and in the range 0.15–0.5 Hz.⁹⁶ The *trans* and *gauche* H- CH_3 coupling constants are obtained as an average over the equilibrium conformations of a methyl group

$${}^4J_{\text{H-CH}_3}^{\text{trans}} = (1/3)[{}^4J_{\text{HH}'}(180^\circ, 180^\circ) + 2{}^4J_{\text{HH}'}(180^\circ, 60^\circ)]$$

$${}^4J_{\text{H-CH}_3}^{\text{gauche}} = (1/3)[{}^4J_{\text{HH}'}(60^\circ, 180^\circ) + {}^4J_{\text{HH}'}(60^\circ, 60^\circ) + {}^4J_{\text{HH}'}(60^\circ, 300^\circ)]$$

Substitution of the indirect values from Table II leads to calculated *trans* and *gauche* values of $+0.83$ and $+0.12$ Hz, respectively. It seems likely that this incorrect sign for indirect coupling in the *gauche* conformation is attributable to the wrong sign predicted for ${}^4J_{\text{HH}'}(60^\circ, 180^\circ)$ in Table II. The use of empirical values of $+2$ Hz for ${}^4J_{\text{HH}'}(180^\circ, 180^\circ)$ and -0.4 Hz for ${}^4J_{\text{HH}'}(60^\circ, 180^\circ)$ from Table IV leads to much better results ($+0.64$ and -0.22 Hz for ${}^4J_{\text{H-CH}_3}^{\text{trans}}$ and ${}^4J_{\text{H-CH}_3}^{\text{gauche}}$, respectively).

No unambiguous substituent trends are discernible from the available data^{95,96,101–104} for ${}^4J_{\text{H-CH}_3}$. In compounds in which a carbonyl grouping is adjacent to one of the coupled protons,^{102,104} values as large as 1 Hz have been observed. In view of the difficulty in analyzing the spectra of molecules whose conformation is in doubt, it would be hazardous to ascribe this to a definite substituent effect.¹⁰³ Even with these inherent difficulties long-range coupling of this type has been useful in assigning ring fusion stereochemistry in angularly methylated ring compounds.^{102–104}

In cases in which both of the coupled protons can assume all of the equilibrium conformations of methyl groups, *i.e.*, propane, itself, for which $|{}^4J_{\text{HH}'}| = 0.3$ Hz,¹⁰⁵ and *gem*-dimethyl groupings,^{106–108} couplings constants are in the range 0.2–0.7 Hz. Because the positive contributions to ${}^4J_{\text{HH}'}$ are invariably larger in magnitude, it may be concluded that these are all positive in sign. The average of the nine calculated indirect values for the staggered equilibrium conformation of propane is $+0.36$ Hz.

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Table IV
 Representative Long-Range Coupling Constants, ${}^4J_{\text{HH}'}$, in Unstrained, Cyclic Molecules

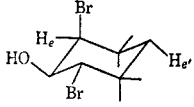
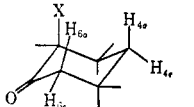
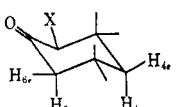
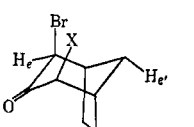
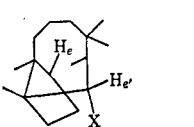
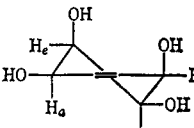
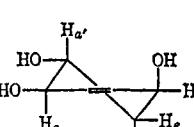
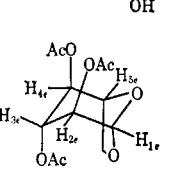
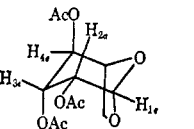
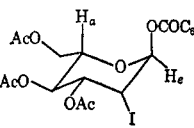
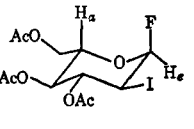

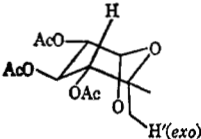
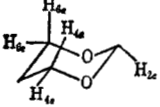
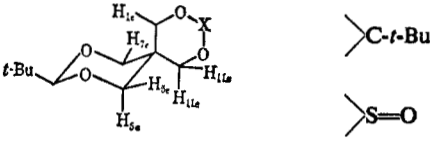
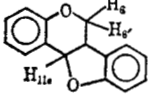
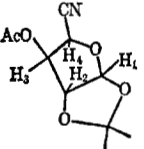
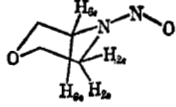
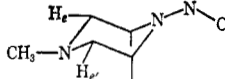
Molecule ^a	X	${}^4J_{\text{HH}'}$, ^b Hz	Ref
1. 	...	$J_{ee'} = 1.7$	68
2. 	Cl Br	$J_{4e,6e} = 1.55$ $J_{4e,6e} = 1.25$ $J_{2e,4e} = 0.70$ $J_{4e,6e} = 0.9$	87
3. 	Cl Br	$J_{4e,6e} = 2.25$ $J_{4e,6e} = 0.6$ $J_{4e,6e} = 1.3$	87
4. 	H Br	$J_{ee'} = 1.8$ $J_{ee'} = 1.8$	68 88
5. 	OH Cl Br	$J_{ee'} = 1.6$ $J_{ee'} = 1.6$ $J_{ee'} = 2.2$	68
6. 	...	$J_{ee'} = 2.1$ $J_{aa'} = -0.3$	89
7. 	...	$J_{ea} = +0.4$ $J_{e'a'} = -0.8$	89
8. 	...	$J_{1e,3e} = 1.2$ $J_{2e,4e} = 1.25$ $J_{3e,5e} = 1.5$	90, 91
9. 	...	$J_{1e,3e} = +1.6$ $J_{2e,4e} = +1.5$ $J_{3e,5e} = 0.45$	90, 91
10. 	...	$J_{a,e} = -0.65$	90
11. 	...	$J_{a,e} = -0.4$	90
12. 	...	$J_{ee'} = 0.5-0.9$	92

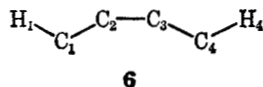
Table IV (Continued)

Molecule ^a	X	⁵ J _{HH'} , ^b Hz	Ref
13. 	...	$J_{HH'(exo)} = +1.2$ ($\phi \approx 180^\circ, \phi' \approx 150^\circ$)	90
14. 	...	$J_{1e,4a} = 1.5, 1.0$ $J_{2e,6a} = 0.4-0.5$ $J_{4e,8e} = 2.50$ $J_{4a,6a} = 0.3-0.4$	93, 94 95 93
15. 	$\text{C-}t\text{-Bu}$ S=O	$J_{1e,5e} = 2.5$ $J_{7e,11e} = 2.5$ $J_{6a,11a} = 1.90$ $J_{1e,6e} = 2.70$ $J_{7e,11e} = 2.25$ $J_{6a,11a} = 1.85$	95
16. 	...	$J_{6,11a} = +0.5-0.7$ ($\phi \approx 120^\circ, \phi' \approx 180^\circ$) $J_{6',11a} = -0.7-0.9$ ($\phi \approx 120^\circ, \phi' \approx 60^\circ$)	96
17. 	...	$J_{1,3} = -0.6$ $J_{1,4} = -0.4$ $J_{2,4} = -0.4$	97
18. 	...	$J_{2e,6e} = 1.4$ $J_{2a,6a} = 1.0$	98
19. 	...	$J_{ee'} = 2.2$	98

^a Subscript e = equatorial; subscript a = axial. ^b Unless specified, signs were not determined.

2. Five Intervening Bonds. Butanic Coupling

In contrast to the large number of experimental values for ⁵J_{HH'} there are only a few reports of coupling constants between protons separated by five saturated bonds. Theoretical treatments include a discussion of ⁵J_{HH',σ} in benzene⁵³ and an investigation¹⁰⁹ of the dependence of ⁵J_{HH'} on the hybridization of the intervening carbon atoms. As noted previously⁴⁴ the interpretation is simple when only second-order terms are retained in eq 7. The proposed indirect mechanism, which leads to coupling over five bonds in a butanic fragment (6), is quadratic in the vicinal bond orders, $p^\circ(h,\sigma)$ and $p^\circ(h',\sigma')$,



with dependence on dihedral angle specified by eq 13a and 13b. Therefore, the dependence of ⁵J_{HH'} on dihedral angle will be of the form

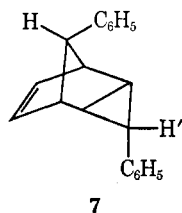
$${}^5J_{HH'} = (A \cos^2 \phi + B \cos \phi + C) \times (A \cos^2 \phi' + B \cos \phi' + C) \quad (14)$$

Maximum coupling will occur for $\phi = \phi' = 180^\circ$, but ⁵J_{HH'} is independent of the dihedral angle measured about the C₂-C₃ bond in 6.

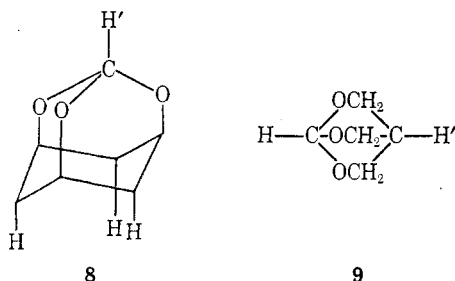
With empirical vicinal bond orders, based on vicinal H-H coupling constants, it is estimated that this type of indirect coupling will lead to maximum values of from +0.5 to +1.0 Hz.⁴⁴ Most of the known examples of coupling between protons separated by five saturated bonds involve multiple coupling paths. Values of $|{}^5J_{14}| \approx 0.1$ Hz and $|{}^5J_{25}| = 0.5$ Hz were reported between equatorial protons in a pyranose derivative (item 8 in Table IV); $|{}^5J_{25}| = 0.9$ Hz was reported^{93,94} for 1,3-dioxane (item 14 in Table IV), and $|{}^5J_{H_1,CH_2}| \leq 0.3$ Hz in a tetrahydrofuran derivative⁹⁶ (item 17 in Table IV). A very large five-bond coupling constant of magnitude 2.3 Hz has been reported¹¹⁰ for a tricyclic molecule (7).

(109) H. Frischleder and G. Bär, *Mol. Phys.*, 11, 359 (1966).

(110) K. Tori and M. Ohtsuru, *Chem. Commun.*, 886 (1966).



A coupling of 1.25 Hz was observed¹¹¹ between the apical and axial protons in **8**, and in **9** a value of 1.7 Hz was obtained.

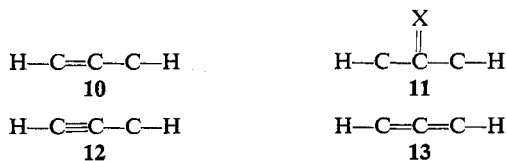


The authors concluded¹¹¹ that the five-bond couplings are in the ratio of the number of paths linking the coupled nuclei and, hence, that the coupling may be attributable to an indirect mechanism. A further significant conclusion, which follows¹¹¹ if the same mechanism is dominant for all of these couplings, is that they are independent of geometry about the central bond. This provides good evidence for the proposed indirect mechanism.⁴⁴

B. UNSATURATED MOLECULES

Long-range H-H coupling constants to be considered in this section include those over four or more bonds having contiguous unsaturation, *i.e.*, one double bond, one triple bond, or cumulated double bonds. Conjugated systems, having alternate single and multiple bonds, will be considered in a subsequent section.

Coupling constants over four bonds are examined for allylic (**10**), isopropylidene (**11**), acetylenic (**12**), and allenic (**13**) fragments.



Coupling over five bonds includes homoallylic (**14**) and cumulenyl (**15**) fragments.



1. Four Intervening Bonds

a. Allylic Coupling

Allylic H-H coupling has been extensively investigated. In substituted propenes allylic coupling constants range from -0.4 to -1.8 Hz,⁵ but in cyclic compounds in which the orientations of both C-H bonds are fixed, experimental values range from $+1.6$ to -3.5 Hz.^{54,112} Since the π -electron con-

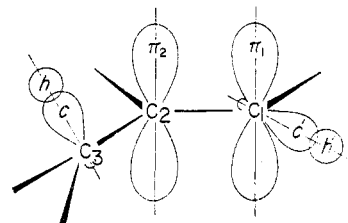


Figure 5. Designation of orbitals in a fragment of the propene molecule.

tributions to ${}^4J_{\text{HH}'}$ are invariably negative in sign, the occurrence of positive allylic coupling constants in certain conformations appears to be only consistent with contributions from the σ -electron framework.^{2,54,112}

The mechanism for π -electron allylic coupling can be discussed in terms of the propenic fragment depicted in Figure 5. The indirect contribution from eq 7 is

$${}^4J_{\text{HH}'\pi} = 4185(\Delta E)^{-1}(3/2)p^\circ(h,\pi_2)p^\circ(\pi_1,h') \quad (15)$$

where the two bond orders provide a measure of the σ - π exchange interaction. Since the σ - π exchange integrals and, therefore, the bond orders are of opposite sign, ${}^4J_{\text{HH}'\pi}$ is necessarily negative. In the semiempirical formulations for π -electron coupling,³³⁻³⁶ esr hyperfine coupling constant data have been used as criteria for the signs, magnitudes, and conformational dependencies of the σ - π interactions. As the Penney-Dirac fragment bond orders are related to the hyperfine coupling constants,^{44,70} $p^\circ(\pi_1,h')$ is independent of dihedral angle, whereas

$$p^\circ(h,\pi_2) = A \sin^2 \phi + B \quad (16)$$

Here ϕ is the dihedral angle measured from the $\text{C}_1-\text{C}_2-\text{C}_3$ plane as shown in Figure 6. Although this choice of dihedral angle conforms to that for the propane molecule in Figure 4, it differs by 90° from the dihedral angle defined in ref 54 and 180° from the dihedral angle of ref 112. For free-radical fragments of the type $\text{C}-\text{C}-\text{H}$, $B \sim 0$ in eq 16 such that ${}^4J_{\text{HH}'\pi}$ will have a $\sin^2 \phi$ dependence on dihedral angle. For the six-electron allylic fragment depicted in Figure 5, the calculated VB result is¹¹³

$${}^4J_{\text{HH}'\pi} = -3.36 \sin^2 \phi \quad (17)$$

which has a maximum negative value for $\phi = 90^\circ$ but vanishes for $\phi = 0$ and 180° .

In acyclic molecules in which the H_3 proton can assume all of the equilibrium conformations accessible to a methyl group, it is necessary to take an average value, weighted with respect to the conformer populations. For propene it is assumed that the populations are equal, and the equilibrium coupling constant is given by

$$\langle {}^4J_{\text{HH}'\pi} \rangle_{\text{equil}} = (1/3)[{}^4J_{\text{HH}'\pi}(60^\circ) + {}^4J_{\text{HH}'\pi}(180^\circ) + {}^4J_{\text{HH}'\pi}(300^\circ)] \quad (18)$$

Substitution of eq 17 into eq 18 leads to a calculated, equilibrium π -electron contribution of -1.68 Hz.¹¹³ This value is in substantially good agreement with the signs and magnitudes of the allylic coupling constants in propene.¹¹⁴ However, the

(111) E. J. Boros, K. J. Coskran, R. W. King, and J. G. Verkade, *J. Amer. Chem. Soc.*, **88**, 1140 (1966).

(112) E. W. Garbisch, *ibid.*, **86**, 5561 (1964), and references cited therein.

(113) M. Barfield, *J. Chem. Phys.*, **48**, 4463 (1968).

(114) A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, **83**, 231 (1961).

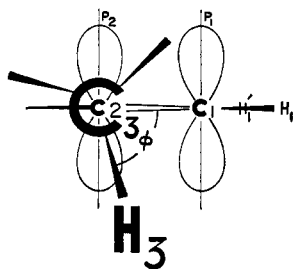


Figure 6. Specification of the dihedral angle, ϕ , in a typical conformation of propene. The C_3 carbon eclipses the C_2 carbon atom, and the cisoid proton, H_1 , eclipses the transoid proton, H_1' .

cisoid coupling constant [$J(H_1-H_3)$ in Figure 6] is larger in magnitude than the transoid coupling constant [$J(H_1'-H_3)$ in Figure 6] in propene and a large number of substituted propenes.⁵ This difference has been rationalized^{2,54,112} in terms of positive σ -electron contributions which have steric requirements similar to $J_{HH'}$ in propane

$$\langle J_{HH'}^{\sigma}(\text{transoid}) \rangle_{\text{equil}} > \langle J_{HH'}^{\sigma}(\text{cisoid}) \rangle_{\text{equil}}$$

Examples are known^{115,116} in which the transoid allylic coupling constants are greater in magnitude than the cisoid, but the responsible factors are not understood.

A large amount of experimental data has been obtained for substituted propenes, and substituent effects can be quite important. Coupling constant data for propene and representative 1,2 and 3-monosubstituted propenes^{114,117-127} are entered in Table V. Cisoid allylic coupling constants in the first column of Table V are essentially unaffected by substitution at the C_1 carbon atom, whereas the transoid values are slightly more negative for all substituents except phenyl. If the major effects of substitution were effective in the σ -electron framework, the qualitative considerations of section III.B would suggest negative shifts for both inductive and hyperconjugative substituents at the C_1 and C_3 carbon atoms. The greater shifts for the transoid values could be compatible with a larger magnitude of $J_{HH'}^{\sigma}$. In the examples of C_2 and C_3 substitution, both hyperconjugative and inductive substituents lead to more positive allylic coupling constants. However, for the C_3 substitution the trend within the series I, Br, Cl, and F is to more negative values. Furthermore, the direction of these shifts is reversed for C_2 substitution. The shifts to more positive values for all examples of inductive and hypercon-

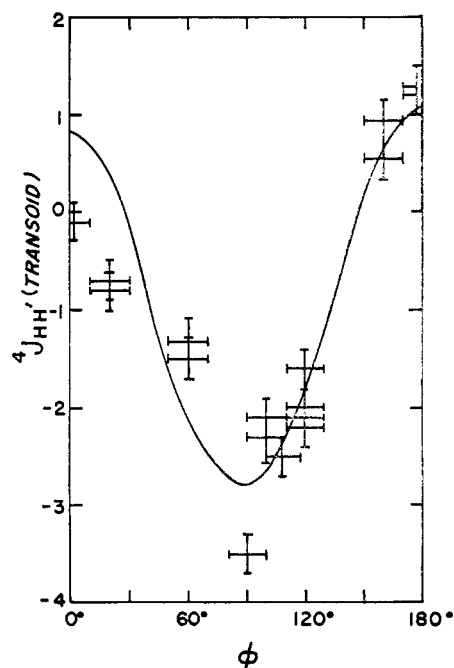


Figure 7. Comparison of calculated and experimental values of transoid allylic coupling constants from Table VI.

jugative C_2 substitution is also compatible with the proposed σ -electron substituent effects.

In cyclic molecules with more or less rigid geometry, a number of transoid and cisoid allylic coupling constants have been reported, and representative values^{2,77,112,128-135} are entered in Table VI. Dihedral angles in Table VI are crude estimates from molecular models.^{54,112} Experimental coupling constants in the third column undoubtedly reflect a variety of uncertainties including substituent effects, coupling through multiple paths, solvent effects, and the usual uncertainties in the accurate measurement of small splittings.

Transoid allylic coupling constants in Table VI are plotted as a function of the estimated dihedral angles in Figure 7. For graphical convenience errors of ± 0.2 Hz were assumed in the values of the coupling constants and $\pm 10^\circ$ in the dihedral angles, but these are undoubtedly optimistic. The solid line included in Figure 7 is that based on semiempirical VB calculations.⁵⁴ A similar plot of the cisoid allylic coupling is not included as there is insufficient experimental data in Table VI to establish the detailed angular dependence.

The agreement of the calculated angular dependence of the transoid allylic coupling constants with the experimental points in Figure 7 is reasonable except for dihedral angles smaller than about 45° . Disagreement here is critical for the

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(134) G. Van Binst, J. C. Nouls, J. Stokoe, C. Danheux, and R. H. Martin, *Bull. Soc. Chim. Belges*, **74**, 506 (1965).

(135) T. A. Wittstruck, S. K. Malhotra, and H. J. Ringold, *J. Amer. Chem. Soc.*, **85**, 1699 (1963).

Table V
Cisoid and Transoid Allylic H-H Coupling Constants ($^4J_{HH'}$, Hz) in Propene and Representative 1,2 and 3-Monosubstituted Propenes^a

X	$\overbrace{HXC=CHCH_2}^{\text{Cisoid}}$		$\overbrace{H_2C=CXCH_2}^{\text{Transoid}}$		$\overbrace{H_2C=CHCH_2X}^{\text{Cisoid}}$		$\overbrace{H_2C=CHCH_2X}^{\text{Transoid}}$	
	Cisoid	Transoid	Cisoid	Transoid	Cisoid	Transoid	Cisoid	Transoid
H	-1.75 ^b	-1.33 ^b	-1.75 ^b	-1.33 ^b	-1.75 ^b	-1.33 ^b	-1.75 ^b	-1.33 ^b
CH ₃	-1.25 ^c	-1.25 ^c	-1.7 ^d	-1.2 ^d	-1.7 ^d	-1.2 ^d
F	-1.8 ^e	-1.6 ^e	-1.0 ^e	-0.4 ^e	-1.63 ^f	-1.27 ^f	-1.63 ^f	-1.27 ^f
Cl	-1.7 ^e	-1.7 ^e	-1.3 ^e	-0.7 ^e	-1.41 ^g	-0.93 ^g	-1.41 ^g	-0.93 ^g
Br	-1.8 ^e	-1.6 ^e	-1.4 ^e	-0.8 ^e	-1.21 ^g	-0.59 ^g	-1.21 ^g	-0.59 ^g
I	-1.7 ^e	-1.5 ^e	-1.6 ^e	-1.0 ^e	-1.04 ^g	-0.43 ^g	-1.04 ^g	-0.43 ^g
OH	-1.55 ^h	-1.25 ^h	-1.55 ^h	-1.25 ^h
OCH ₃	-0.5 ^h	-0.5 ^h	-1.67 ⁱ	-1.42 ⁱ	-1.67 ⁱ	-1.42 ⁱ
C ₆ H ₅	-1.4 ^c	-0.7 ^c	-1.5 ⁱ	-0.8 ⁱ	-1.47 ^g	-1.47 ^g	-1.47 ^g	-1.47 ^g
CH=CH ₂	...	-1.5 ^k	-1.2 ^k	-1.2 ^k	-1.30 ^k	-1.50 ^k	-1.30 ^k	-1.50 ^k
C≡CH	-1.60 ^l	-1.10 ^l
CN	-1.5 ^m	-1.4 ^m	-1.7 ^m	-1.2 ^m	-1.90 ⁿ	-1.68 ⁿ	-1.90 ⁿ	-1.68 ⁿ

^a All allylic coupling constants in this table are assumed to be negative. ^b Reference 114. ^c Reference 5. ^d Reference 117. ^e Reference 118. ^f Reference 119. ^g Reference 120. ^h Reference 121. ⁱ Reference 122. ^j Reference 123. ^k Reference 124. ^l Reference 125. ^m Reference 126. ⁿ Reference 127.

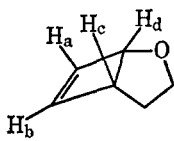
Table VI
Representative Transoid and Cisoid Allylic Coupling Constants in Rigid, Cyclic Molecules

Molecule	Dihedral angle, ϕ , deg	$^4J_{HH'}$, ^a Hz	Ref	Molecule	Dihedral angle, ϕ , deg	$^4J_{HH'}$, ^a Hz	Ref
A. Transoid							
1.	180	+1.3	112	14.	60	-1.94	132
2.	160	+0.5	77	15. Plumericin ($J_{10,12}$)	60	1.5	131
3.	160	+0.95	77	16.	20	0.7-0.8	112
4.	120	2.2	112	17.	0	-0.1	112, 133
5.	120	-1.98	128	18.	0	0.4	134
6.	120	-2.1	129	B. Cisoid			
7.	120	1.3	112	1. Glycyrrhetic acid, 18 α epimer	105-120	1-1.5	131
8.	120	-1.6	130	2. 6-Substituted Δ^4 -3-keto steroids ($J_{4,\beta\alpha}$)	100	1.5-2.0	135
9. Plumericin ($J_{6,7}$)	100-115	2.5	131	3.	60	1.6-2.0	134
10.	100	2.3	112	4.	60	-1.36	132
11.	100	2.1	112	5. 6-Substituted Δ^4 -3-keto steroids ($J_{4,\alpha\delta}$)	15-30	≤ 0.5	135
12.	100	2.1	112	6. Glycyrrhetic acid	5	≤ 0.5	131
13. Himandridine	90	3.5	2	7.	0	-0.63	112, 133

^a Signs are undetermined unless specified.

proposed indirect mechanism for σ -electron coupling,⁵⁴ since the theoretical basis for an indirect σ -electron mechanism requires that the allylic coupling constants in the 0 and 180° conformations be of positive sign and in the ratio of the *cis* and *trans* coupling constants in ethanic or ethylenic systems. The argument¹¹² for a vanishing or small negative value of the transoid allylic coupling for $\phi = 0^\circ$ depends critically on the experimental value of -0.1 Hz reported¹²² for 3,3-di-*t*-butyl-1-propene (item 17 in Table VI). Unfortunately, this is not an entirely rigid system, and the data may reflect significant negative contributions from conformers having the *gauche* orientation.¹¹² Relative sign determinations for small values of the dihedral angle could provide a critical test for a direct *vs.* an indirect mechanism for σ -electron coupling.

With the possible exception of item 7 in Table VI, there are insufficient data to examine substituent effects on allylic coupling constants in cyclic systems. The occurrence of a large substituent effect has been noted¹³⁶ for 2-oxabicyclo[3.2.0]hept-6-ene (16) for which $|^4J_{bd}| = 2.8$ Hz and $|^4J_{ae}| = 1.5$ Hz.



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b. Isopropylidenic Coupling

The term "isopropylidenic" has been proposed¹³⁷ to describe coupling in fragments of the type 11. Since this is a four-bond coupling, nonnegligible contributions from both the π - and σ -electron frameworks are expected. As a consequence of the uncertainties in the steric requirements for the σ -electron mechanism, the precise angular dependence of this type of coupling is not understood.

The π -electron mechanism for isopropylidenic coupling can be discussed in terms of indirect contributions from eq 7 in which each of the bond orders has a $\sin^2 \phi$ dependence on dihedral angle. Valence-bond calculation¹¹³ for the case in which X in 11 corresponds to a carbon atom leads to the approximate result

$$^4J_{HH,\pi} = -4.72 \sin^2 \phi \sin^2 \phi' \quad (19)$$

in which ϕ and ϕ' are the dihedral angles measured from the $C_1-C_2-C_3$ plane. In those cases in which both of the coupled protons can assume all of the equilibrium orientations of a methyl group, the equilibrium coupling constant is obtained as an average [$\langle \sin^2 \phi \rangle_{av} = \langle \sin^2 \phi' \rangle_{av} = (1/2)$]

$$\langle ^4J_{HH,\pi} \rangle_{equil} = -1.18 \text{ Hz}$$

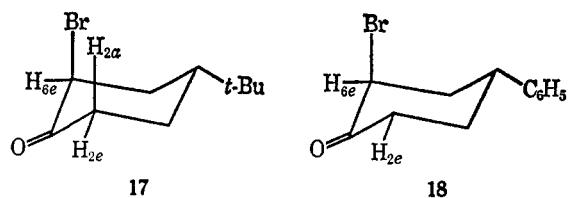
However, it seems likely that this value will be partially offset by positive σ -electron contributions comparable in magnitude to those for saturated systems ($\sim +0.5$ Hz).

Experimental values in this case have magnitudes of 0.4–0.55 Hz.^{138a} A sign determination in 2-methylpropenyl acetate indicates that this type of coupling is negative.^{138b}

Isopropylidenic coupling is most commonly observed in those cases in which X in 11 denotes an oxygen atom. A

theoretical description^{139a} used VB wave functions to rationalize the experimental value of $+0.54$ Hz¹³⁹ for the long-range coupling in acetone. However, neglect of any type of σ -electron contributions by these authors would not seem to be justified, since these could be as large as the observed effect. Although the proposed dependence of $^4J_{HH}$ in acetone on the polarity of the C–O bond appears to have no experimental justification,¹⁴⁰ the change of sign between 2-methylpropenyl acetate (-0.49 Hz)^{138b} and acetone ($+0.54$ Hz) is consistent with a positive shift for an electron-withdrawing substituent at the central carbon atom of a propanic fragment.

Experimental results have been reported for a number of cyclic ketones. In the cyclohexanone derivatives (17 and 18)



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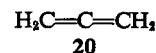
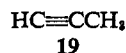
18

$|^4J_{2e,6e}|$'s are 1.7 and 1.4 Hz, respectively, whereas the corresponding $^4J_{2a,6e}$'s were too small to be resolved.¹⁴¹ Since the π -electron contributions should vanish in both cases according to eq 19, the steric requirements for σ -electron coupling appear to be similar to those in cyclic unsaturated molecules. Isopropylidenic coupling constants of magnitude 1.1–0.2 Hz have been reported between the 1 and 3 axial protons in a number of 1-substituted 2-ketotriterpenes,¹⁴² and magnitudes ranging from 1.0 to 1.3 Hz have been found in some 1,3-dibromo-2-decalones.¹⁴³ Negative π -electron contributions should predominate for cases in which both of the protons are out-of-plane. Relative sign measurements will be required to establish the sign reversal expected in going from $^4J_{ee}$ to $^4J_{aa}$ '.

Recent experimental results^{144,145} for cyclobutanone, which are $^4J_{2,c(cis)} = +4.6$ ($+4.2$)¹⁴⁵ Hz and $^4J_{2,c(trans)} = 2.8$ (-2.99)¹⁴⁵ Hz, presumably reflect significant contributions *via* the two possible four-bond coupling paths. However, it is not at all clear how these results fit into the suggested pattern for isopropylidenic coupling.

c. Acetylenic and Allenic Coupling

Long-range H–H couplings over four bonds in methylacetylene (19) and allene (20) are dominated by allylic-type



π -electron mechanisms and are independent of dihedral angles. Free rotation of the methyl C–H bonds in methylacetylene should lead to π -electron contributions which are about one-half of the maximum allylic coupling for each of the two coupling paths. In fact, a VB calculation¹¹³ which does not invoke the "average energy approximation" for an eight-

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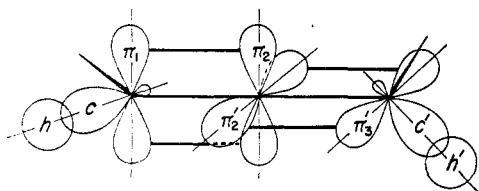


Figure 8. Labeling of orbitals in a fragment of the allene molecule.

electron fragment of **19**, gives a value of -3.10 Hz, which is very close to the maximum for allylic coupling in eq 17. The experimental value for methylacetylene is -2.9 ± 0.2 Hz.^{11,146}

For coupling in the eight-electron fragment of the allene molecule, which is depicted in Figure 8, the conformation is fixed in such a way that ${}^4J_{HH'}$ is a maximum for the two allylic-type coupling paths, $(h-c \dots \pi_1-\pi_2 \dots c'-h')$ and $(h-c \dots \pi_2'-\pi_3' \dots c'-h')$. Therefore, it is reasonable to expect that the coupling in allene should be about twice the maximum for allylic coupling. The calculated VB result¹¹³ in this case is -7.37 Hz which is to be compared with the experimental value of -7.0 ± 0.1 Hz.^{146,147}

For long-range coupling in substituted allenes^{5,148} and methylacetylenes,^{4,5,117} the shifts are generally toward less negative values. Some typical values for monosubstituted compounds are given in the Table VII. All values are assumed

Table VII

Representative Values of ${}^3J_{HH'}$ (Hz) in Substituted Allenes and Methylacetylenes

X	$H_2C=C=CHX$	$HC\equiv CCH_2X$
CH ₃	-6.66	-2.4, -2.6
Cl	-6.1	-2.6
Br	-6.1	-2.7
I	-6.3	-2.8
CN	...	-2.85

to be negative. Note that the changes within the inductive series Cl, Br, I are much smaller than in the corresponding 3-substituted propenes in Table V.

2. Five or More Intervening Bonds

a. Homoallylic Coupling

Homoallylic coupling was extensively discussed in a previous review,² and the angular dependence appears to be well documented. The indirect π -electron contributions for the 2-butene fragment depicted in Figure 1 will have an angular dependence analogous to that for isopropylidene coupling. Valence-bond calculations¹¹³ for a minimal six-electron fragment give

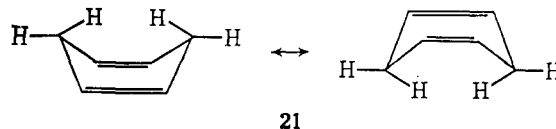
$${}^5J_{HH'}^{\pi} = +4.99 \sin^2 \phi \sin^2 \phi' \quad (20)$$

where ϕ and ϕ' are the dihedral angles measured from the $C_1-C_2-C_3$ and $C_2-C_3-C_4$ planes, respectively. For 2-butene the equilibrium π -electron contribution is obtained by taking the appropriate average

$$\langle {}^5J_{HH'}^{\pi} \rangle_{\text{equil}} = +1.25 \text{ Hz}$$

This calculated value is in good agreement with the experimental value of 1.2 Hz.¹⁴⁹ Since the π -electron contributions are identical for the *cis*- and *trans*-2-butenes, the observation¹⁵⁰ that ${}^5J_{HH'}$ (*trans*) is generally about 0.3 Hz larger than ${}^5J_{HH'}$ (*cis*) is indicative of contributions from the σ -electron framework.

In an interesting application of the angular dependence of the homoallylic coupling specified by eq 20, it has been shown¹⁵¹ that 1,4-dihydronaphthalene (**21**) should be nearly planar in solution. From eq 20 it follows that the ratio of the



cis coupling constant, 5J (*cis*), to the *trans* coupling constant 5J (*trans*), is equal to the ratio of the averages for the two conformations of **21**

$${}^5J(\text{cis})/{}^5J(\text{trans}) = \frac{[\sin^2 \phi]^2 + [\sin^2(120^\circ + \phi)]^2}{2 \sin^2 \phi \sin^2(120^\circ + \phi)} \quad (21)$$

Since experimental values are 9.63 and 8.04 Hz for the *cis* and *trans* coupling constants,¹⁵⁰ respectively, this ratio is 1.19. The angle ϕ in eq 21 which gives this ratio is about 115° , corresponding to a nearly coplanar arrangement of the ring carbon atoms. Numerical results based on the "average energy approximation" were $+8.8$ and $+7.3$ Hz¹⁵¹ for the *cis* and *trans* coupling constant, respectively. However, for equilibration between the two conformations, eq 20 leads to the values $+4.7$ and $+4.1$ Hz, which are much too small.

Coupling over five bonds in dimethylacetylene is of the homoallylic type with an experimental value of 2.7 Hz.¹⁵² Karplus³⁵ obtained a value of $+2.9$ Hz for this case, whereas the VB result is $+2.18$ Hz.¹¹³ The latter value presumably reflects a small contribution of third order through the perpendicular π -electron system.

b. Coupling in the Cumulenes

Calculated^{35,113} and experimental^{124,146,153,154} results for long-range H-H coupling in a series of cumulenes are entered in Table VIII. The very large value for ${}^5J_{HH'}$ in butatriene (item 2) can be attributed to several five-bond, π -electron coupling paths.^{35,113} These are depicted schematically in Figure 9a-c. Approximately 4.3 Hz of the total calculated (7.01 Hz) can be attributed to the homoallylic-type mechanism depicted in Figure 9a. The coupling path depicted in Figure 9b corresponds to a conjugative mechanism and contributes about 1.7 Hz to the total. The remaining 1 Hz can be attributed to two equivalent coupling paths of the type depicted in Figure 9c.

The large value of -5.3 Hz, which was computed for ${}^6J_{HH'}$ in pentatetraene (item 4), is attributable to the very effective conjugation in this system. The theory³⁵ which uses esr hyperfine data as semiempirical criteria did not include the effects of delocalization, and a much smaller value (~ 0.5 Hz) was in-

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Table VIII
Calculated and Experimental Long-Range H-H Coupling
Constants in the Cumulenes

Molecule	${}^4J_{\text{HH}}{}^{\pi}(\text{calcd}),^a$ Hz	${}^4J_{\text{HH}}{}^{\pi}(\text{obsd}),$ Hz
Four Bonds		
1. $\text{CH}_2=\text{C}=\text{CH}_2$	-7.37 (-6.7)	-7.0 ^b
Five Bonds		
2. $\text{CH}_2=\text{C}=\text{C}=\text{CH}_2$	+7.01 (7.8)	8.95 ^c
3. $\text{CH}_3\text{CH}=\text{C}=\text{CH}_2$	+2.50	3.45 ^d
Six Bonds		
4. $\text{CH}_2=\text{C}=\text{C}=\text{C}=\text{CH}_2$	-5.30	...
5. $\text{CH}_3\text{CH}=\text{C}=\text{C}=\text{CH}_2$	-1.60	$\sim 1.2 $ ^e
6. $\text{CH}_3\text{CH}=\text{C}=\text{CHCH}_3$	-0.28	$\leq 0.3 $ ^f
Seven Bonds		
7. $\text{CH}_3\text{CH}=\text{C}=\text{C}=\text{C}=\text{CH}_2$	+1.71	...
8. $\text{CH}_3\text{CH}=\text{C}=\text{C}=\text{CHCH}_3$	+0.93	...
9. $\text{CH}_2=\text{C}=\text{CHCH}=\text{C}=\text{CH}_2$	+1.73	...

^a Reference 113. Values in parentheses are from ref 35.
^b Reference 146. ^c Reference 153. ^d Reference 124. ^e Value obtained for $(\text{CH}_3)_2\text{C}=\text{C}=\text{CHCHO}$ in ref 154. ^f Reference 124. This coupling was not obtained in an analysis of the spectrum of 2,3-pentadiene.

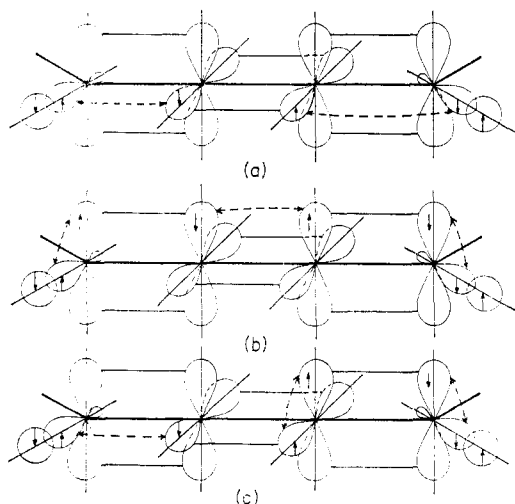


Figure 9. Representation of three possible (a-c) coupling paths for the butatriene molecule.

indicated. Experimental data do not appear to be available for this system.

C. CONJUGATED MOLECULES

1. Acyclic

Measurable long-range coupling has been observed¹⁵⁵ over as many as nine bonds in conjugated systems, *i.e.*, those systems which have two or more multiple bonds each separated by single bonds in the usual structural formula. In these cases the mechanisms which lead to the observed splitting undoubtedly arise from the combined effects of σ - π configuration interaction and delocalization in the π system.

Comparisons of the theoretical¹¹³ and experimental^{124,126,155-161} results for coupling between protons separated by four to nine bonds in conjugated hydrocarbons are given in Table IX. Calculated values in the second column are VB results based on the fragments depicted in the first column.¹¹³ The calculated values for coupling over four bonds (items 1-3) are generally more negative than the observed values. This is consistent with the expectation of nonnegligible positive contributions from the σ -electron framework. Comparison of the calculated with experimental results for *trans*-butadiene and 1,3-cyclohexadiene (item 1) provides a further indication that essentially all of the positive contributions to ${}^4J_{\text{HH}}{}^{\pi}$ arise from the all-*trans* or "W" conformation. The agreement between calculated and experimental results for coupling over more than four bonds in Table IX is quite reasonable and coincides with the expectation of smaller relative contributions from the σ -electron framework with an increasing number of bonds.

The damping of the π -electron contribution to long-range coupling provides a measure of the extent of long-range delocalization.¹⁶² The π -electron contributions to the two-to-nine-bond H-H coupling constants in a 12-electron octatetraene fragment³⁷ are plotted in Figure 10 as a function of the number, n , of intervening C-C and C-H bonds. The damped oscillation and alternation of sign with increasing n is expected. This behavior can be satisfactorily represented (dashed line in Figure 10) by the equation

$${}^nJ_{\text{HH}}{}^{\pi} = -1.71(-1)^r(-0.56)^s \quad (22)$$

where r and s denote the number of C-C double and single bonds, respectively, and $n = r + s + 2$. Equation 22 implies that the spin coupling is transmitted essentially without attenuation over the normal double bonds but is damped by about 44% over each conjugated single bond. Equation 22 also satisfactorily reproduces the calculated results for the polyenes (items 2, 4, 10, 13, 17 and 19) in Table IX.

Long-range H-H coupling in substituted butadienes has been studied extensively with particular emphasis on the relationship of coupling constants to conformation.¹⁶³⁻¹⁶⁷ On the basis of the experimental results it was concluded¹⁶⁴ that the π -electron contributions to ${}^4J_{\text{HH}}{}^{\pi}$ and ${}^5J_{\text{HH}}{}^{\pi}$ in butadiene should be -0.8 and +0.7 Hz, respectively. These values are in substantially good agreement with the calculated ones (items 1 and 4 in Table IX). In Table X are entered the experimental four- and five-bond coupling constants for *trans*-butadiene and a number of 2-substituted butadienes (22). Although the largest variation in the five-bond coupling constants

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Table IX
Comparison of Calculated and Experimental Coupling Constants between Protons Separated by Four to Nine Bonds in Conjugated Hydrocarbons

Fragment ^a	$J_{\text{HH}}^{\text{c}}(\text{calcd})^{\text{b}}$, Hz	Molecule	$J_{\text{HH}}^{\text{c}}(\text{obsd})$, Hz
Four Bonds			
1.	-0.89	<i>trans</i> -C ₂ H=CHCH=CH ₂	-0.86 ^e (<i>trans</i>) -0.83 ^e (<i>cis</i>)
			1.04 ^d
2.	-3.18	HC≡CCH=CH ₂	-2.17 ^e
3.	-0.60	<i>cis</i> -Tagetone	≤ 0.3 ^f
Five Bonds			
4.	0.95	<i>trans</i> -CH ₂ =CHCH=CH ₂	1.30 ^e (<i>trans-trans</i>) 0.60 ^e (<i>trans-cis</i>) 0.69 ^e (<i>cis-cis</i>)
			1.11 ^d
5.	0.78	CH ₂ =CHC≡CH	0.8-0.9 ^{e,g}
6.	1.45	CH≡CC≡CH	2.2 ^h
7.	0.59	CH ₂ =C(CH ₃)C(CH ₃)=CH ₂	~ 1.0 ⁱ
8.	0.54	CH ₂ =C(CH ₃)C≡CH	0.28 ^j
9.	2.68	-C=CHC≡CCH ₃	2.5 ^k
10.	0.36	Halfordin	1.1 ^l
Six Bonds			
11.	-0.71	C ₂ H=CHCH=CHCH ₃	~ 0.6 ⁱ
12.	-1.07	CH≡CC≡CCH ₃	1.27 ^k
Seven Bonds			
13.	0.51
14.	0.77
15.	0.52
16.	0.73	CH ₃ C≡C-C≡CCH ₃	1.3 ^k
Eight Bonds			
17.	-0.30
18.	-0.44
Nine Bonds			
19.	0.24
20.	0.17
21.	0.31	CH ₃ C≡CC≡CC≡CCH ₂ OH	0.4 ^h

^a Assumed single- and double-bond distances for these fragments are given in Tables III-V of ref 113. ^b Reference 113. Some of the values are unpublished VB results (items 2, 8, 10, 13, 14, 17-21) based on the generalized product formulation of ref 37. ^c Reference 156. ^d Reference 157. ^e Reference 158. ^f Reference 159. No detectible splitting was observed for this coupling in the spectrum of *cis*-tagetone. ^g Reference 160. ^h Reference 155. ⁱ Reference 124. ^j Reference 125. ^k Reference 161. ^l F. N. Lahy and C. S. Barnes, unpublished results quoted in ref 2.

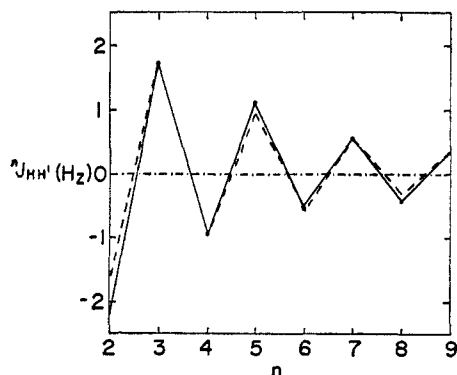


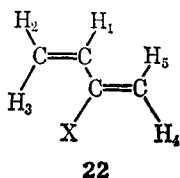
Figure 10. A plot of coupling over two to nine bonds in octatetraene as a function of the number, n , of intervening bonds. The dashed line conforms to eq 22.

Table X
Long-Range H-H Coupling Constants in *trans*-Butadiene and Representative 2-Substituted Butadienes^a

X	${}^4J_{14}$, Hz	${}^4J_{15}$, Hz	${}^5J_{24}$, Hz	${}^5J_{25}$, Hz	${}^5J_{34}$, Hz	${}^5J_{35}$, Hz	Ref
H	-0.86	-0.83	1.30	0.60	0.60	0.60	156
F	0.09	-0.19	1.44	0.73	0.62	0.70	166
Cl	-0.18	-0.60	1.42	0.72	0.61	0.67	166
Br	-0.32	-0.76	1.34	0.69	0.61	0.70	165
I	-0.58	-1.08	1.24	0.65	0.54	0.66	165
OCH ₃	0.00	0.00	1.50	0.57	0.51	0.51	156

^a Proton positions are numbered as in 22.

in Table X is 0.2 Hz, the four-bond coupling constants

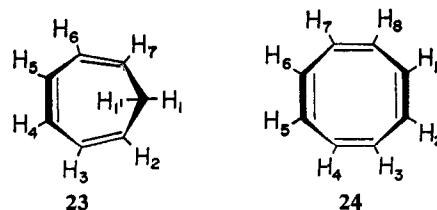


appear to be extremely sensitive to substituent factors. In fact, ${}^4J_{14}$ exhibits a sign change in 2-fluoroprene. The shift to more positive values with increasing electronegativity of the substituent is consistent with that noted for the 2-substituted propenes in Table V. Since ${}^4J_{HH'}$'s for the haloprenes in Table X are approximately proportional to those for the 2-haloprenes in Table V, it seems likely that the same substituent mechanism is responsible.

2. Cyclic

The calculated results for conjugated molecules in Table IX are based on acyclic fragments in which the carbon atoms are coplanar. In highly substituted^{166,167} or cyclic unsaturated molecules this often will not be the case, and it is necessary to consider the changes in the long-range coupling constants due to twisting about the single bonds.

As examples of long-range H-H coupling in cases in which there are significant deviations from planarity and coupling *via* multiple paths, consider the cases of cycloheptatriene (23) and cyclooctatetraene (24). Calculated¹⁶⁸ VB π -electron con-



tributions and experimental results^{169,170} are entered in Table XI. Calculations were performed for two different conformations of the cycloheptatriene fragments. In one set of calculations the angle β between the planes, which is formed by C₃-C₄-C₅-C₆ and C₂-C₃...C₆-C₇, was set equal to 40° since this is close to the microwave result of 40.5 ± 2°. In the other calculation β was set equal to 0° in accordance with X-ray diffraction results¹⁷² for the Mo(CO)₃ complex of 23. The methylene protons were assumed to be tetrahedral with one of the C-H bonds in the nodal plane of the π electrons. In the room-temperature nmr spectrum of 23 the methylene protons are equivalent;¹⁶⁹ hence the couplings to the two methylene protons are computed as an average.

Since the protons H₂, H₃, and H₄ in 23 are separated from the H₁ protons by 3, 4, and 5 bonds, respectively, along one path of the ring and by 8, 7, and 6 bonds along the other path, coupling to the methylene protons includes sums of contributions with opposite signs. The signs of the π -electron contributions are determined by the sign of the larger contributions along the shorter paths.

It is interesting to note that the calculated results for $\beta = 0^\circ$ in Table XI are consistent with both sets of data, but those for $\beta = 40^\circ$ are not. For example, the observed values for $J_{24} + J_{25}$ are 1.48 and 1.38 for cycloheptatriene and the Mo(CO)₃ complex, respectively. For $\beta = 40^\circ$ the calculated sum is negative, but for $\beta = 0^\circ$ the addition of +1.2 Hz due to σ -electron coupling in the all-*trans* arrangement of the bonds linking H₂ and H₄ gives a value of +1.30 Hz, which is in reasonable agreement with data for both compounds. Addition of +1.2 Hz to the ${}^4J_{35} = -0.47$ Hz in the $\beta = 0^\circ$ conformation gives +0.73 Hz which is in very good agreement with the experimental results. For $\beta = 40^\circ$ this coupling should be negative. Since any contributions to the five-bond coupling, ${}^5J_{35}$, are expected to be positive, the calculated value for the $\beta = 0^\circ$ conformation appears to be the only one consistent with both sets of experimental data.

The π -electron contributions to coupling in cyclooctatetraene (24) were based on the "tub" conformation with dihedral angles of 70° between adjacent π -electron systems. The large values for the long-range coupling constants J_{13}^π , J_{16}^π , and J_{23}^π in Table XI can be attributed to the favorable relationship between the C-H bonds containing the coupled protons and the adjacent π -electron bond. The very small values for J_{14}^π and J_{15}^π are due to the near orthogonality of the individual double bonds which has the effect of damping out long-range coupling in the extended π -electron systems. Furthermore, the "tub" conformation for cyclooctatetraene is sufficiently nonplanar that the contributions from the σ -electron framework should be small. Long-range coupling constant data for this molecule are not available.

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Table XI
Calculated π -Electron Contributions to the Spin-Spin Coupling Constants in Fragments of the Cycloheptatriene and Octatetraene Molecules Compared with Available Experimental Data

HH'	Cycloheptatriene			Cyclooctatetraene			
	$J_{HH'}^{\pi}(\text{calcd}),^a$ Hz $\beta = 40^\circ$	$J_{HH'}^{\pi}(\text{calcd}),^a$ Hz $\beta = 0^\circ$	CHT, ^d	$J_{HH'}^{\pi}(\text{exptl}),^b$ Hz Mo(CO) ₃ complex	HH'	$J_{HH'}^{\pi}(\text{calcd}),^a$ Hz	$J_{HH'}^{\pi}(\text{exptl}),^c$ Hz
12	0.93 ^e	0.86 ^e	6.7	{ 2.75 8.70	12	2.42	11.0
13	-0.91 ^e	-0.82 ^e	<0.4	{ -1.32 0.84	13	-2.58	...
14	0.50 ^e	0.04 ^e	<0.1	...	14	0.22	...
23	2.48	2.33	8.9	8.4	15	-0.22	...
24	-1.64	-1.04	1.48 ^f	1.38 ^f	16	2.34	...
25	0.55	1.14			23	4.53	2.0
26	-0.34	-0.42			
27	0.09	0.51	...	<0.3			
34	3.06	0.95	5.51	6.81			
35	-1.99	-0.47	0.72	0.77			
36	1.26	0.36	0.69	0.34			

^a Reference 168. ^b Reference 169. ^c Reference 170. ^d Cycloheptatriene (23). ^e Values taken as averages for the 1 and 1' protons. ^f $J_{24} + J_{25} = 1.48$ Hz for 23 and 1.38 Hz for the complex.

D. AROMATIC MOLECULES

1. meta and para Coupling

Experimental values of the *ortho*, *meta*, and *para* H-H coupling constants have been compiled^{5,66} for several hundred substituted benzenes. Typically, *meta* coupling constants are in the range +1 to +3 Hz, whereas *para* values are also positive with magnitudes less than 1 Hz. Particular values seem to depend as much on the pattern of substitution as the nature of the substituent.⁶⁶ Additivity schemes, based on changes in the *ortho*, *meta*, and *para* coupling constants on substitution, have been proposed.^{173, 174}

meta coupling between the two *ortho* protons in mono-substituted benzenes increases with substituent electronegativity.¹⁷⁵ For example, the *meta* H-H coupling constant in benzene is +1.37 Hz,¹⁷⁶ but on substitution of F, Cl, Br, I, and C≡CH, the shifts in $J_{2,6}$ from this value are 1.37, 0.88, 0.75, 0.51, and 0.40 Hz, respectively. These substituent-induced shifts are slightly larger than the corresponding shifts in the 2-substituted propenes (Table V) and butadienes (Table X), but they are all in the same direction and are roughly proportional to one another. Thus, in every case of 2-substitution which we have encountered, inductive and hyperconjugative substituents product positive shifts. Furthermore, these changes conform to the qualitative predictions of section III.B for substituent induced shifts in the σ -electron framework.

On the basis of existing theoretical results^{34, 53, 56, 168} for coupling in benzene, it appears that the most important contributions to the *ortho* and *meta* coupling constants are due to σ -electron mechanisms, whereas the *para* coupling arises from a π -electron mechanism. Representative theoretical values for the three aromatic coupling constants are compared with experiment in Table XII. In the first column the π -electron re-

Table XII

Comparison of Theoretical and Experimental Values for the *ortho*, *meta*, and *para* Coupling Constants in Benzene

	MO ^a	VB ^b	CNDO ^c	INDO ^c	Exptl ^d
³ $J_{HH'}^{\pi,ortho}$, Hz	0.17	0.76	7.55	8.15	7.54
⁴ $J_{HH'}^{\pi,meta}$, Hz	0	-0.61	1.90	2.13	1.37
⁵ $J_{HH'}^{\pi,para}$, Hz	0.01	0.65	0.44	1.15	0.69

^a Molecular orbital theory without configuration interaction, ref 32. ^b Reference 168. ^c Reference 56. ^d Reference 176.

sults are based on MO wave functions and the "average energy approximation."³² In the next column the calculated π -electron contributions were obtained with a truncated sum over VB triplet states.¹⁶⁸ Results in the third and fourth columns arise from self-consistent perturbation theory⁵⁶ with CNDO¹⁷⁷ (complete neglect of differential overlap) and INDO¹⁷⁸ (intermediate neglect of differential overlap) wave functions, respectively. Since the INDO method differs⁵⁶ from the CNDO method principally in the inclusion of the one-center exchange integrals, differences in the results obtained by the two methods are indicative of the importance of σ - π interactions. Experimental results are given in the last column. Differences between the CNDO and INDO results in Table XII for *ortho* and *para* coupling constants are close to the values for the π -electron contributions in the second column. However, for *meta* coupling the difference is less than the VB result and of a different sign.

2. Benzylic Coupling

The term "benzylic" has been used¹⁷⁹ to describe coupling between an aromatic proton and a proton centered on the α -carbon atom of a side chain. In cases in which the α -carbon atom is sp^3 -hybridized, the *o*- and *p*-benzylic coupling constants are generally larger than the *m*-benzylic coupling con-

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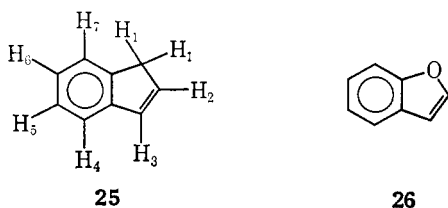
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stants.¹⁸⁰ In toluene, for example, the *o*-, *m*- and *p*-benzylic coupling constants are -0.75 , 0.36 , and -0.62 Hz, respectively.¹³ *o*-Benzylic coupling is analogous to allylic coupling, and the smaller values for the former have been attributed¹⁸¹ to the partial π bonding in the aromatic systems.

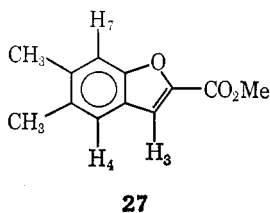
It appears that most aspects of benzylic coupling can be satisfactorily discussed in terms of the σ - π configuration interaction mechanism. Equation 2, which relates π -electron contributions to mobile bond orders, has been used^{179, 182-185} to discuss benzylic coupling but it has the distinct disadvantage of predicting vanishing *m*-benzylic coupling.¹⁸³ This problem does not arise in theoretical descriptions which do not invoke the "average energy approximation."^{186, 168} Calculated values for *o*- and *p*-benzylic coupling constants are -0.87 and -0.37 Hz, respectively,³⁶ whereas the semiempirical VB results¹⁶⁸ for *o*- and *m*-benzylic coupling are -0.73 and 0.59 Hz, respectively.

Because of the $\sin^2 \phi$ dependence of the σ - π interaction between a benzylic proton and an adjacent $2p\pi$ orbital, π -electron contributions should vanish for the in-plane conformations of an sp^3 -hybridized C-H bond. When two bulky substituents are on the α -carbon atom, the in-plane conformation for the C-H bond should be favored. In this case the indications are that the *o*- and *m*-benzylic coupling constants are about the same.¹⁸⁰ It is presumed that indirect σ -electron mechanisms are important in this case, but more quantitative data are needed.

In cases in which the α -carbon atom is sp^2 -hybridized, a π -electron mechanism will also be operative for the in-plane conformations. Experimental results have been obtained in a number of cases of this type. For example, in indene (**25**) and benzofuran (**26**) coupling constants between the 3 and 7 protons are 0.7 ^{128, 186, 187} and 0.8 - 1.0 Hz,^{186, 187} respectively. These



results seem to be typical for protons with comparable relative orientations.² Valence-bond results¹⁶⁸ for indene (**25**) are as follows: $J_{3,4}^{\pi} = -0.34$ Hz, $J_{3,5}^{\pi} = +0.27$ Hz, $J_{3,6}^{\pi} = -0.39$ Hz, and $J_{3,7}^{\pi} = 0.27$ Hz. In the substituted benzofuran **27**, the



experimental results are $J_{34} = \mp 0.12$ Hz, $J_{3,7} = \pm 0.60$ Hz, and $J_{4,7} = \pm 0.99$ Hz.¹⁸⁸ Since the *para* H-H coupling constants are invariably positive, the upper set of signs is selected. The experimental signs are consistent with the theoretical ones but are all slightly more positive possibly because of indirect σ -electron contributions of about $+0.2$ - 0.3 Hz along the four- and five-bond paths.

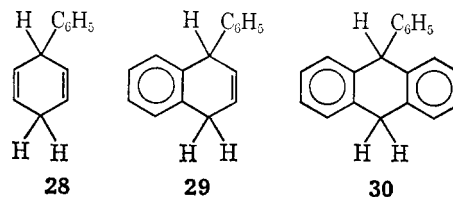
A surprising feature of the benzylic coupling constants is their insensitivity to substituent effects.¹⁸⁸⁻¹⁹¹ For example, in 2-bromo-5-chlorotoluene,¹⁸⁸ the benzylic coupling constants differ at most by 0.1 Hz from the values in toluene.¹³ On this basis it appears¹³ that the mechanisms responsible for aromatic coupling and benzylic coupling may be mutually exclusive. Since it appears that the benzylic coupling constants can be adequately discussed in terms of π -electron mechanisms, this provides a further argument that substituent effects are most important in the σ -electron framework.

3. Interbenzylic Coupling

The term "interbenzylic"¹⁹² is used to describe coupling between protons which are centered on the α -carbon atoms of different side chains. Experimental results for interbenzylic coupling constants are scanty even though the theoretical calculations^{36, 168} indicate that they are of the same order of magnitude as the benzylic coupling constants.

ortho interbenzylic coupling is analogous to homoallylic coupling and should exhibit the same steric requirements, but the partial π -bond orders in aromatic systems should lead to smaller magnitudes. An *ortho*-interbenzylic coupling of magnitude 0.37 Hz has been obtained in a benzofuran derivative (**27**), and this is about one-third of the value for homoallylic coupling in 2-butene. A *meta*-interbenzylic coupling which is ≤ 0.35 Hz has been inferred from the analysis of the nmr spectrum of mesitylene.³⁶

An interesting trend for *ortho*-interbenzylic coupling has been noted¹⁹³ in phenyl-substituted 1,4-dihydrobenzene (**28**), 1,4-dihydronaphthalene (**29**), and 9,10-dihydroanthracene (**30**). The five-bond H-H coupling constants fall from 9 Hz



in **28** to 6 Hz in **29** to 0 Hz in **30**.

4. Inter-Ring Coupling

Failure to detect small coupling constants, such as between protons centered on different rings of a polyacene, seldom implies that they are identically zero. For example, in the case of indene (**25**) the partial analysis¹⁸⁶ suggested extensive inter-ring coupling. Valence-bond calculations¹⁶⁸ of long-range coupling in indene indicate that coupling between the methy-

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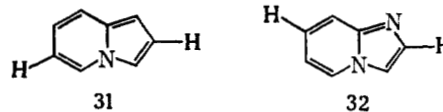
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lene protons and those of the aromatic ring range from 0.56 to 0.83 Hz, and between the 2 proton and the ring protons the range is 0.25–0.32 Hz.

Coupling constants between protons separated by as many as six bonds have been reported¹⁹⁴ for indolizine (31) and azaindolizine (32), both with magnitudes of about 0.5 Hz. A number of additional inter-ring coupling constants are

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reported in ref 2 and 4.



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