Allylic Interproton Spin-Spin Coupling

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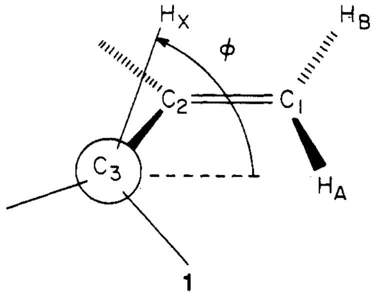
Contents

I. Introduction

Interproton spin–spin coupling across three single bonds and one double bond, ^4J(H—C1═C2—C3—H), where C-3 has tetrahedral hybridization, is designated as allylic coupling. Clearly, besides major steric factors defined in fragment **1**, there are a number of other variables such as substitution at C-1, C-2, or C-3, the bond order of the C1–C2 double bond, and angular distortion at either C-1, C-2, or C-3 resulting, for example, from incorporation into cyclic structures. Despite the complexity of the physical situation which gives rise to allylic coupling, theoretical[1-3] and empirical[4-9a] results established some general correlations between the magnitudes of allylic coupling constants and structural parameters, which are sufficiently well defined to be useful for structural studies. This is particularly true for the relationship of allylic coupling constants to the dihedral angle ϕ. The dihedral angle is measured from the C3–C2–C1 plane in the sense indicated in **1**.



1

$J(\text{allylic, cisoid}) = J_{AX} = {}^4J_{csd}(\phi)$

$J(\text{allylic, transoid}) = J_{BX} = {}^4J_{trd}(\phi)$

The subject of allylic H-H coupling has been reviewed in the context of long-range H-H coupling constants in general,[5-7,9a] but a large proportion of significant experimental data remains scattered in the recent literature, and recent advances in theoretical treatments[2,3] have not been reviewed. Furthermore, many calculated results and experimental data are available in these laboratories in an unpublished form.

The emphasis in this review will be placed on a critical comparison of experimental results, especially with respect to the use of allylic coupling constants in structural investigations. A major goal of this review is to provide a conceptual basis in terms of the most recent theory for understanding the dependence of the allylic coupling constants on the variables mentioned above. A full coverage of important collections of results is intended, but, for reasons detailed below, it is selective with respect to experimental data. To avoid unnecessary repetition, the experimental results are presented with the minimum of comment in section II, and any extensive discussions of data are deferred to sections IV and V, where they are correlated with the theoretical studies. The literature is covered systematically to about the middle of 1974.

II. Experimental Results

A. Instrumental Considerations and Selection of Data

Experimental results relevant to this review, i.e., the magnitudes and signs of allylic coupling constants, are widely scattered in the literature, and a large proportion of them had been obtained in the course of investigations where details of NMR spectra were of only incidental interest. Consequently in many cases no special effort appears to have been made to obtain highly accurate results, in particular with respect to accurate measurements of small line separations (see below), which is usually critical in the accurate assessment of the magnitudes of allylic coupling constants. For this reason certain general problems connected with measurement of small splittings are discussed below.

While the results presented below may appear to be numerous, they are but a small fraction of the data scattered in the literature. The principal criterion used for the selection of data, besides their experimental reliability, was their relevance, i.e., the presence of important and well-defined structural and stereochemical features. A compromise had also to be struck between the desire to present confirmatory evidence, i.e., the wish to base conclusions on more than a single result and the need to avoid endless repetition. Clearly a great deal of critical and

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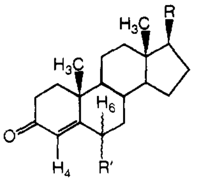
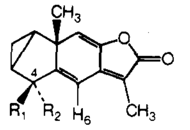
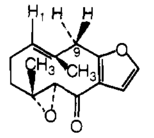
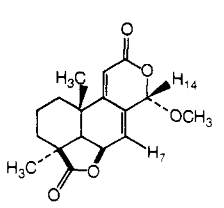
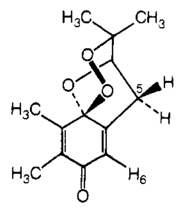
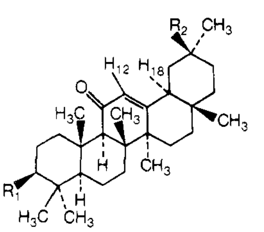
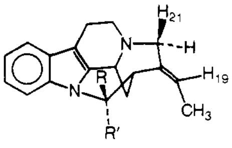
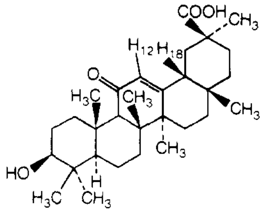
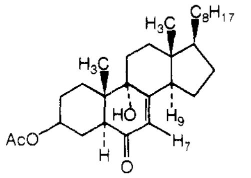
TABLE I. Cisoid Allylic Coupling Constants in Substances of Defined Configuration

Structure	J_{allyl}	Structure	J_{allyl}
 **2**		 **6**	
$R = C_8H_{17};\ R' = \alpha\text{-}CH_3;\ \phi_{4,6\beta} = 110^\circ$	−1.6[a]	$R_1 = CH_3;\ R_2 = H;\ \phi_{4\alpha,6} = 30^\circ$	−1.02[f]
$R = C_8H_{17};\ R' = \alpha\text{-}OH, OAc;\ \phi_{4,6\beta} = 110^\circ$	−1.7[a]	$R_1 = H;\ R_2 = CH_3;\ \phi_{4\beta,6} = 90^\circ$	−2.2[f]
$R = C_8H_{17};\ R' = \alpha\text{-}Br;\ \phi_{4,6\beta} = 110^\circ$	−1.8[a]	 **7**	
$R = C_8H_{17};\ R' = \alpha\text{-}Ac;\ \phi_{4,6\beta} = 110^\circ$	−2[b]	$\phi_{1,9\alpha} = 20^\circ$	−0.6[g]
$R = OH, Ac;\ R' = \alpha\text{-}CH_3;\ \phi_{4,6\beta} = 110^\circ$	−2.0[c]	$\phi_{1,9\beta} = 110^\circ$	−1.5[g]
$R = COCH_2OH;\ R' = \alpha\text{-}CH_3;\ \phi_{4,6\beta} = 110^\circ$	−1.5[c]	 **8**	
$R = C_8H_{17};\ R' = \beta\text{-}CH_3, OH, OAc, Br;\ \phi_{4,6\alpha} = 10^\circ$	≤0.5[a]	$\phi_{7,14} = 100^\circ$	−2.0[h]
$R = C_8H_{17};\ R' = \beta\text{-}D;\ \phi_{4,6\alpha} = 10^\circ$	≤0.5[c]	 **9**	
 **3**		$\phi_{6,5\beta} = 60^\circ$	−2[i]
$R_1 = OH;\ R_2 = COOH;\ \phi_{12,18} = 115^\circ$	−1.3[a]	$\phi_{6,5\alpha} = 60^\circ$	−2[i]
$R_1 = H;\ R_2 = CH_3;\ \phi_{12,18} = 115^\circ$	−1.7[d]	 **10**	
 **4**		$R = COOCH_3;\ R' = H;\ \phi_{19,21\beta} = 80^\circ$	−2[j]
$\phi_{12,18} = 10^\circ$	≤0.5[a]	$R = H;\ R' = COOCH_3;\ \phi_{19,21\beta} = 80^\circ$	−2[j]
 **5**			
$\phi_{7,9} = 115^\circ$	−1.5[e]		

[a] D. J. Collins, J. J. Hobbs, and S. Sternhell, *Tetrahedron Lett.*, 197 (1963). [b] M. Gorodetsky and Y. Mazur, *J. Am. Chem. Soc.*, **86**, 5213 (1964). [c] T. A. Wittstruck, S. K. Malhotra, and H. J. Ringold, *ibid.*, **85**, 1699 (1963). [d] D. H. R. Barton, E. F. Lier, and J. F. McGhie, *J. Chem. Soc. C*, 1031 (1968). [e] C. Djerassi, J. C. Knight, and H. Brockman, Jr., *Chem. Ber.*, **97**, 3118 (1964). [f] K. Takeda, M. Ikuta, M. Miyawaki, and K. Tori, *Tetrahedron*, **22**, 1159 (1966). [g] H. Hikino, K. Tori, I. Horibe, and K. Kuriyama, *J. Chem. Soc. C*, 688 (1971). [h] G. A. Ellestad, R. H. Evans, M. P. Kunstmann, J. E. Lancaster, and G. O. Morton, *J. Am. Chem. Soc.*, **92**, 5483 (1970). [i] D. Creed, H. Werbin, and E. T. Strom, *ibid.*, **93**, 502 (1971). [j] M. Hesse, W. v. Philipsborn, D. Schumann, G. Spiteller, M. Spiteller-Friedmann, W. I. Taylor, H. Schmid, and P. Karrer, *Helv. Chim. Acta*, **47**, 878 (1964).

possibly subjective judgement was involved on our part, and we wish to apologize to authors whose work has been overlooked.

The NMR spectrometers now in routine use normally yield an experimentally available resolution[9b] of 0.2–0.6 Hz and thus many small allylic coupling constants which were not observed in the earlier literature are now experimentally accessible. In order that the optimum resolution be obtained, signals should be recorded at optimum field homogeneity employing the smallest spectral width available with the instrument, e.g., 0.5–1.0 Hz per 1 cm of chart length and slow sweep rates in continuous wave (CW) experiments. If the observed coupling is sufficiently large, in relation to the resolution of the spectrometer, to cause a degree of splitting in the resonance concerned without affording *complete* resolution of lines, a correction factor[9a,10] must be applied. Where splittings are resolved to better than 60%, the correction is negligible.

As a major contribution to line broadening is due to the difficulty of reaching slow-passage conditions in the CW mode, the rapidly expanding instrumentation for Fourier transform (FT) NMR spectroscopy should ensure a greater availability of high-quality spectra for accurate estimation of small coupling constants. In fact, it has been demonstrated[11] that splittings as small as 0.05 Hz can be measured by such methods.

Clearly, splittings must not be equated with coupling constants, although, fortunately, this is often permissible with many allylic coupling constants due to the common occurrence of large $\Delta\nu/J$ ratios. Data from the literature had to be selected *both* for relevance and reliability. Small (<1 Hz) allylic coupling constants, when quoted, have not usually been corrected for imperfect splittings (see above), and thus the reported values represent the minimum magnitudes of these coupling constants, whereas larger values are sometimes found "rounded off", e.g., 2 Hz, 2.5 Hz, etc., and no errors are given. Many data were rejected because of these uncertainties, but in some cases data, which were believed to be particularly relevant, are quoted even though their accuracy was undesirably low. This will be indicated where applicable. In most instances only the absolute magnitudes of allylic coupling constants are found in the literature. In the overwhelming majority of such compounds, the signs of allylic coupling constants can be safely attributed by analogy with well-established examples.[1-9a]

An attempt has been made to group the experimental data, both published and originating here, into tables according to the *principal influence* being considered but, because of the inevitable overlap (the data from one compound may be relevant to more than one aspect of the problem), sharp differentiation between groups of data could not be achieved. Furthermore, in some cases the problem of defining the principal influence is inherently difficult. Therefore, a number of compounds could have been interchanged within the various tables.

B. Experimental Data

1. *Conformational Dependencies of Cisoid and Transoid Allylic Coupling Constants*

Data for compounds of defined configuration exemplifying cisoid and transoid coupling constants are collected in Tables I and II, respectively. The dihedral angles (ϕ) were estimated from Dreiding models and the signs of the allylic coupling constants were assumed by analogy.[1-9a] Care was taken to exclude (as far as possible) structures in which serious deviations from standard hybridization occur in the allylic fragment, but many compounds have an electronegative substituent (generally oxygen) attached at C-1, C-2, or C-3. The data are not generally precise enough to allow the drawing of far-reaching conclusions about the substituent dependencies of allylic coupling constants, but it is quite apparent that both substantial negative and negligible allylic coupling constants are not sufficiently influenced by the presence of oxygen at C-1 (compare structures **13, 20, 25, 42,** and **55**), C-2 (**38, 57**), or C-3 (**2, 8, 16, 21, 28, 33, 45, 48–51, 55,** and **56**) to deviate significantly from the general relationship between allylic coupling constants and stereochemistry (see sections IV and V). Further examples of the same phenomenon are given in Table III, and it appears that the presence of oxygen (and by implication, other electronegative substituents) does not limit the use of the relationships between dihedral angles and allylic coupling constants for structural studies. It will be shown below, however, that in more carefully defined series it is possible to establish distinct trends between the magnitudes of the coupling constants and the nature of the substituents at C-2 and C-3, but to a lesser extent at C-1.

2. *Relative Magnitudes of Cisoid and Transoid Allylic Coupling Constants*

Critical studies of this relationship must be restricted to compounds with exocyclic or terminal methylene groups rather than pairs of *E* and *Z* isomers. This limitation has been noted in previous studies,[3,8] in particular with relevance to the "crossover effect", i.e., the observation of $^4J_{\text{trd}}$ either larger *or* smaller in absolute magnitude than $^4J_{\text{csd}}$. Data collected in Table III bear out and amplify previous observations.[3,8] It should be noted that, unlike for data in Tables I and II, signs of coupling constants are not assumed in Table III (see footnote *a*) to permit a more complete presentation of unpublished results from these laboratories. However, on the basis of analogy with the very large number of sign determinations in the literature[1-9a] and all the new data (note compounds **61, 62, 88,** and **94** in Table III), it can be safely assumed that all allylic coupling constants listed in Table III are negative in sign.

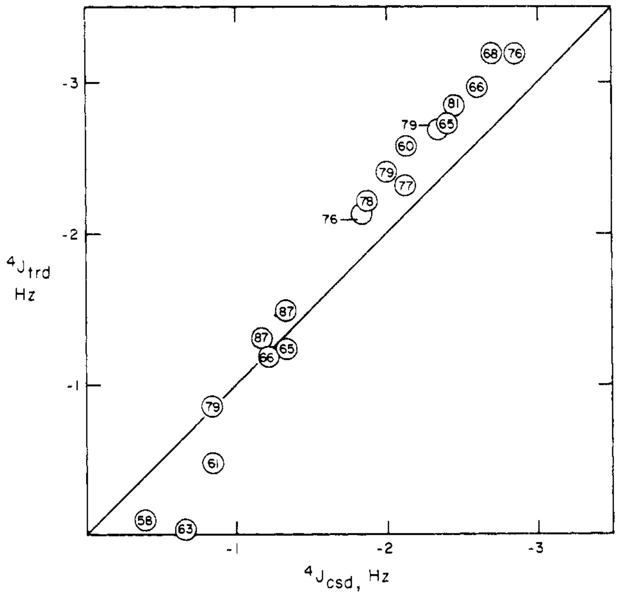


Figure 1. Plot of cisoid allylic coupling constants against transoid allylic coupling constants in selected compounds with terminal or exocyclic methylene groups. The numbers in circles refer to structural formulas and the straight line represents the condition $^4J_{\text{csd}} = {}^4J_{\text{trd}}$.

To determine the position of the "crossover point" it would be most desirable to plot the differences between the values of $^4J_{\text{trd}}$ and $^4J_{\text{csd}}$ for the methylene derivatives against the dihedral angle ϕ. The latter quantity is, however, only approximately known in most cases (Dreiding models), and an alternative procedure was therefore adopted. A number of data were selected from those given in Table III, on the following basis: (i) only those compounds were selected where ϕ was in the range of 0 to 90°, since those for larger dihedral angles are relevant to the second crossover point required by symmetry; (ii) data for methylene derivatives of norbornane were specifically excluded because a comparison of allylic coupling constants for $\phi = 0°$ in such compounds and in analogous unstrained derivatives (compare the examples **58, 60, 63, 73, 82** and **84**) shows them to be atypical (on the other hand, it is interesting that the same systems, cf. **74** and **85,** show no special effects for allylic coupling constants for ϕ = ca. 60°); (iii) data for methylenecyclopropanes (**94–97**) and methylenecyclobutanes (**88–93**) were also excluded because they clearly do not meet the criteria of "standard" hybridization, although it can be readily seen that they exhibit no greatly exceptional values. The largest deviations (smaller coupling constants) appear to be associated with cyclobutene derivatives (**89** and **93**).

The selected results were plotted in Figure 1. The solid line represents the condition for which $^4J_{\text{trd}} = {}^4J_{\text{csd}}$, and it can be seen clearly that a crossover point occurs. Turning to the data clustered nearest to the point of crossover (compounds **65, 66,** and **87**), it can be inferred that this point corresponds approximately to $\phi = 42°$ and $^4J_{\text{HH}'} = -1.2$ Hz. The point for compound **79,** which is experimentally reliable, must be considered as a deviation due to a second-order effect so that it is more correct to refer to a "crossover range" rather than a "crossover point". The symmetry properties of the relationship proposed[2,3,8] for the relative values of $^4J_{\text{trd}}$ and $^4J_{\text{csd}}$ (also see the discussion in section IV) require a second crossover point at $\phi > 90°$. While insufficient data are available for the construction of a diagram analogous to Figure 1 for this region, the results for compounds

TABLE II. Transoid Allylic Coupling Constants in Substances of Defined Configuration

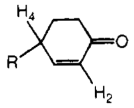
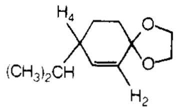
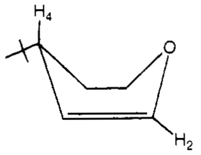
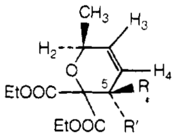
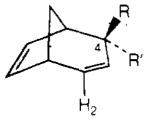
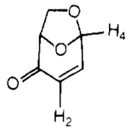
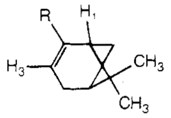
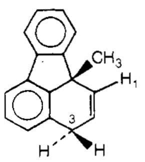
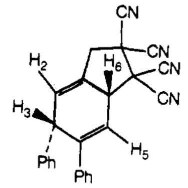
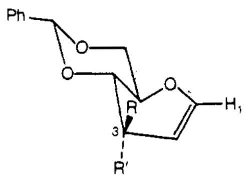
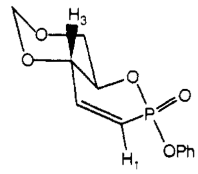
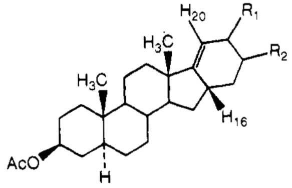
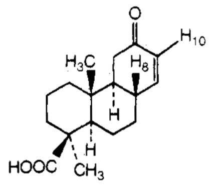
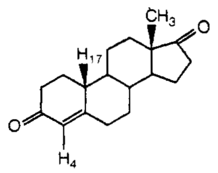
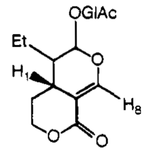
Structure	J_{allyl}
 11	
R = t-Bu; $\phi_{2,4} = 100^\circ$	-2.3[4]
R = i-Pr; $\phi_{2,4} = 100^\circ$	-2.1[4]
 12	
$\phi_{2,4} = 100^\circ$	-2.1[4]
 13	
$\phi_{2,4} = 110^\circ$	-2.0[a]
 14	
R = H; R′ = CH_3; $\phi_{3,5} = 115^\circ$	-1.67[b]
$\phi_{2,4} = 110^\circ$	-1.55[b]
R = CH_3; R′ = H; $\phi_{3,5} = 140^\circ$	-0.74[b]
$\phi_{2,4} = 110^\circ$	-1.80[b]
 15	
R = $COOCH_3$; R′ = H; $\phi_{2,4\alpha} = 125^\circ$	-2.3[c]
R = H; R′ = $COOCH_3$; $\phi_{2,4\beta} = 115^\circ$	-2.6[c]
 16	
$\phi_{2,4} = 155^\circ$	0.5[d]
 17	
R = CH_3; $\phi_{1,3} = 180^\circ$	1.4[e]
R = CHO; $\phi_{1,3} = 180^\circ$	1.49[f]
 18	
$\phi_{1,3\alpha} = 155^\circ$	0.8[g]
$\phi_{1,3\beta} = 85^\circ$	-2.6[g]
 19	
$\phi_{3,5} = 80^\circ$	-1.9[h]
$\phi_{2,6} = 85^\circ$	-2.5[h]
 20	
R = CH_2I, CH_3; R′ = H; $\phi_{2,4\alpha} = 95^\circ$	-2.7[i]
R = CH_2OH, CH_2OTs; R′ = H; $\phi_{2,4\alpha} = 95^\circ$	-2.5[i]
R = H; R′ = CH_2I, CH_3; $\phi_{2,4\beta} = 130^\circ$	-1.3[i]
 21	
$\phi_{1,3} = 100^\circ$	-2.5[j]
 22	
$\phi_{16,20} = 80^\circ$	
R_1 = α-OH; R_2 = α-CN	-2.2[k]
R_1 = α-OH; R_2 = β-CN	-2.3[k]
R_1 = β-OH; R_2 = α-CN	-2.6[k]
R_1 = β-OH; R_2 = β-CN	-2.3[k]
 23	
$\phi_{8,10} = 95^\circ$	-2.6[l]
 24	
$\phi_{4,17} = 105^\circ$	-2.0[m]
 25	
$\phi_{1,8} = 110^\circ$	-2[n]

TABLE II (Continued)

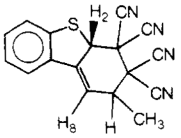
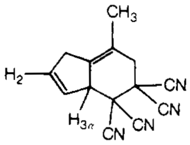
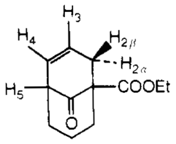
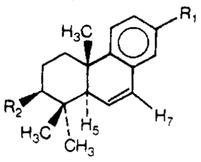
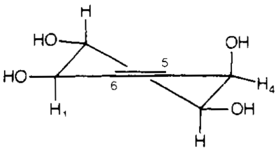
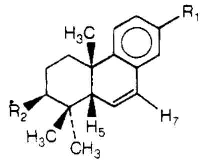
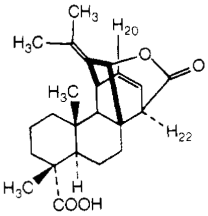
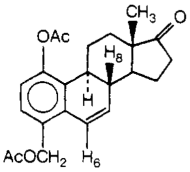
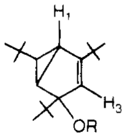
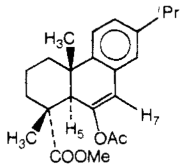
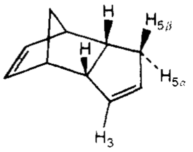
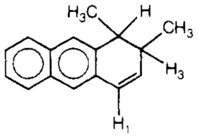
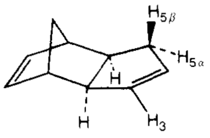
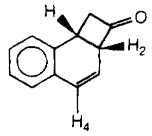
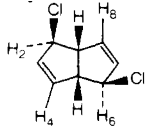
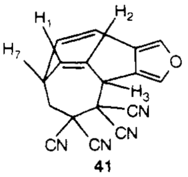
Structure	J_{allyl}	Structure	J_{allyl}
 26 $\phi_{2,8} = 90^\circ$	-3.28^{o}	 34 $\phi_{2,3a} = 100^\circ$	-2.03^{w}
 27 $\phi_{4,2\beta} = 110^\circ$ $\phi_{4,2\alpha} = 130^\circ$ $\phi_{3,5} = 145^\circ$	$-2.4^{p,q}$ $-1.6^{p,q}$ $\leqslant 0.2^{p,q}$	 35 $R_1 = R_2 = H; \phi_{5,7} = 85^\circ$ $R_1 = H; R_2 = OH; \phi_{5,7} = 85^\circ$ $R_1 = OCH_3; R_2 = H; \phi_{5,7} = 85^\circ$	-2.8^{x} -3^{y} -3.0^{z}
 28 $\phi_{1,5} = 105^\circ$ $\phi_{4,6} = 140^\circ$	-2.1^{r} -0.5^{r}	 36 $R_1 = H; R_2 = OH; \phi_{5,7} = 155^\circ$ $R_1 = OCH_3; R_2 = H; \phi_{5,7} = 155^\circ$	0^{y} 0^{z}
 29 $\phi_{20,22} = 130^\circ$	-1.7^{s}	 37 $\phi_{6,8} = 80^\circ$	-2.3^{aa}
 30 $R = CH_3; \phi_{1,3} = 120^\circ$ $R = CH_2CF_3; \phi_{1,3} = 120^\circ$	-1.5^{t} -1.4^{t}	 38 $\phi_{5,7} = 85^\circ$	-3^{bb}
 31 $\phi_{3,5\beta} = 120^\circ$ $\phi_{3,5\alpha} = 120^\circ$	-2.2^{u} -2.0^{u}	 39 $\phi_{1,3} = 160^\circ$	0.5^{cc}
 32 $\phi_{3,5\beta} = 120^\circ$ $\phi_{3,5\alpha} = 120^\circ$	-2.0^{u} -2.2^{u}	 40 $\phi_{2,4} = 115^\circ$	-2.0^{dd}
 33 $\phi_{2,4} = \phi_{6,8} = 105^\circ$	-2.5^{v}	 41 $\phi_{1,3} = 160^\circ$ $\phi_{2,7} = 155^\circ$	0.1^{ee} 0.1^{ee}

TABLE II (Continued)

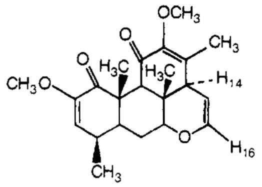
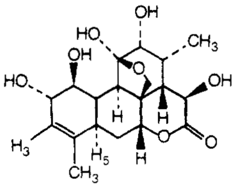
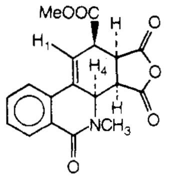
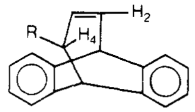
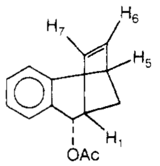
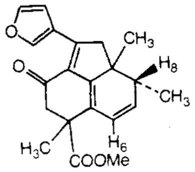
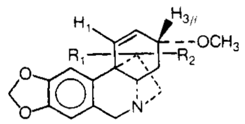
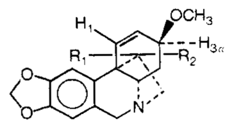
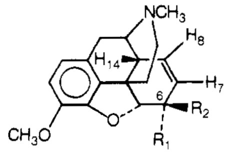
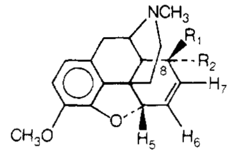
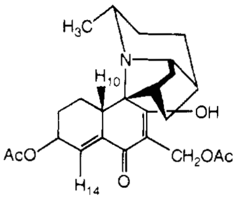
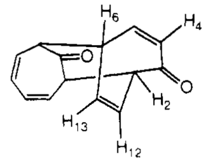
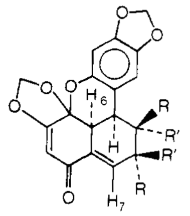
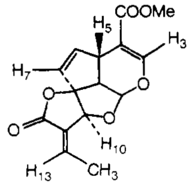
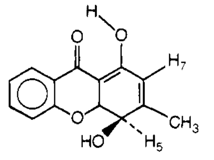
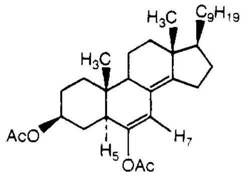
Structure	J_{allyl}
 42	
$\phi_{14,16}$ = 85°	−3.1[ff]
 43	
$\phi_{3,5}$ = 85°	−2.6[gg]
 44	
$\phi_{1,4}$ = 75°	−3[hh]
 45	
R = Cl; $\phi_{2,4}$ = 125°	−0.7[ii]
R = OAc; $\phi_{2,4}$ = 125°	−0.6[ii]
 46	
$\phi_{1,6}$ = 150°	0[jj]
$\phi_{5,7}$ = 150°	0[jj]
 47	
$\phi_{6,8}$ = 90°	−3.0[kk]
 48	
R_1 = OH, OAc, H; R_2 = OH, OAc, H, *or* R_1,R_2 = O; $\phi_{1,3\beta}$ = 140°	0[ll]
 49	
R_1 = H; R_2 = OAc; $\phi_{1,3\alpha}$ = 100°	−2.0[ll]
R_1,R_2 = O; $\phi_{1,3\alpha}$ = 100°	−2.0[ll]
 50	
R_1 = OH; R_2 = H; $\phi_{6\beta,8}$ = 75°	−2.9[mm]
$\phi_{7,14}$ = 80°	−3.0[mm]
R_1 = H; R_2 = OH; $\phi_{6\alpha,8}$ = 170°	0[mm]
$\phi_{7,14}$ = 80°	−2.8[mm]
R_1 = OH; R_2 = CH_3; $\phi_{7,14}$ = 80°	−3.0[nn]
R_1 = CH_3; R_2 = OH; $\phi_{7,14}$ = 80°	−2.75[nn]
 51	
R_1 = OH; R_2 = H; $\phi_{6,8\alpha}$ = 70°	−1.8[mm]
$\phi_{5,7}$ = 140°	0[mm]
R_1 = H; R_2 = OH; $\phi_{6,8\beta}$ = 170°	0[mm]
$\phi_{5,7}$ = 140°	0[mm]
 52	
$\phi_{10,14}$ = 95°	−3.10[oo]
 53	
$\phi_{4,6}$ = 160°	±0.2[oo]
$\phi_{6,12}$ = 175°	1.2[oo]
$\phi_{2,13}$ = 175°	1.0[oo]
 54	
R = H; R′ = CH_3; $\phi_{6,7}$ = 105°	−2.3[pp]
R = CH_3; R′ = H; $\phi_{6,7}$ = 70°	−2.6[pp]
 55	
$\phi_{5,7}$ = 110°	−2.5[qq]
$\phi_{10,13}$ = 60°	−1.5[qq]
$\phi_{3,5}$ = 155°	±0.5[qq]

TABLE II (Continued)

Structure	J_{allyl}	Structure	J_{allyl}
 **56** $\phi_{5,7} = 90°$	-2.3[rr]	 **57** $\phi_{5,7} = 95°$	-2.7[ss]

[a] A. De Boer, *Org. Magn. Reson.*, **5**, 7 (1973). [b] K. Jankowski and J. Couturier, *J. Org. Chem.*, **37**, 3997 (1972). [c] B. C. C. Cantello, J. M. Mellor, and G. Scholes, *J. Chem. Soc. C*, 2915 (1971). [d] O. Achmatowicz, Jr., P. Bukowski, B. Szechner, Z. Zwierzchowska, and A. Zamojski, *Tetrahedron*, **27**, 1973 (1971). [e] R. B. Bates and V. P. Thalacker, *J. Org. Chem.*, **33** 1730 (1968). [f] F. Kaplan, C. O. Schulz, D. Weisleder, and C. Klopfenstein, *ibid.*, **33**, 1728 (1968). [g] R. G. Harvey, D. F. Lindow, and P. W. Rabideau, *Tetrahedron*, **28**, 2909 (1972). [h] N. K. Hamer and M. E. Stubbs, *J. Chem. Soc., Perkin Trans. 1*, 2971 (1972). [i] B. Fraser-Reid, B. J. Carthy, and B. Radatus, *Tetrahedron*, **28**, 2741 (1972). [j] H. Paulsen, W. Bartsch, and J. Thiem, *Chem. Ber.*, **104**, 2545 (1971). [k] C. R. Engel and J. Lessard, *Can. J. Chem.*, **48**, 2819 (1970). [l] L. Mander, private communication, 1967. [m] T. A. Wittstruck, S. K. Malhotra, and H. J. Ringold, *J. Am. Chem. Soc.*, **85**, 1699 (1963). [n] L. Canonica, F. Pellizzoni, P. Manitto, and G. Jommi, *Tetrahedron*, **16**, 192 (1961). [o] G. P. Newsoroff and S. Sternhell, *Tetrahedron Lett.*, 6117 (1968). [p] E. W. Colvin and W. Parker, *J. Chem. Soc.*, 5764 (1965). [q] The NMR spectra were rerun in these laboratories on a 100-MHz instrument. [r] R. J. Abraham, H. Gottschalck, H. Paulsen, and W. A. Thomas, *J. Chem. Soc.*, 6268 (1965). [s] W. A. Ayer and C. E. McDonald, *Can. J. Chem.*, **43**, 1429 (1965). [t] I. E. Den Besten, L. Kaplan, and K. E. Wilzbach, *J. Am. Chem. Soc.*, **90**, 5868 (1968). [u] K. C. Ramey and D. C. Lini, *J. Magn. Reson.*, **3**, 94 (1970). [v] D. Bryce-Smith, B. E. Foulger, and A. Gilbert, *Chem. Commun.*, 769 (1972). [w] D. B. Knight, R. L. Hartless, and D. A. Jarvis, *J. Org. Chem.*, **37**, 688 (1972). [x] M. Fétizon and G. Moreau, *Bull. Soc. Chim. Fr.*, 3479 (1965). [y] D. Mansuy and M. Julia, *ibid.*, 2689 (1972). [z] M. Fétizon, G. Moreau and B. Waegell, *ibid.*, 1229, (1967); R. C. Cambie, W. A. Denny, and J. A. Lloyd, *Aust. J. Chem.*, **25**, 375 (1972). [aa] P. Villotti, A. Cervantes, and A. D. Cross, *J. Chem. Soc.*, 3621, (1964). [bb] R. C. Cambie and R. A. Franich, *Aust. J. Chem.*, **24**, 571 (1971). [cc] R. Gerdil and E. A. C. Lucken, *Helv. Chim. Acta*, **44**, 1966 (1961). [dd] R. S. Givens, W. F. Oettle, R. C. Coffin, and R. G. Carlson, *J. Am. Chem. Soc.*, **93**, 3957 (1971). [ee] F. Le Goff and R. B. LaCount, *Tetrahedron Lett.*, 2787 (1965). [ff] R. M. Carman and A. D. Ward, *Aust. J. Chem.*, **15**, 807 (1962). [gg] A. Guademer, *Bull. Soc. Chim. Fr.*, 406 (1967). [hh] S. F. Dyke, M. Sainsbury, D. W. Brown, and R. D. J. Clipperton, *Tetrahedron*, **26**, 5969 (1970); see also K. Bailey and A. A. Grey, *Can. J. Chem.*, **50**, 3876 (1972). [ii] S. J. Cristol, R. M. Sequeira, and G. O. Mayo, *J. Am. Chem. Soc.*, **90**, 5564 (1968). [jj] H. Tanida, K. Tori, and K. Kitahonoki, *ibid.*, **89**, 3212 (1967). [kk] A. Sato, M. Kurabayashi, A. Ogiso, and H. Mishima, *Tetrahedron Lett.*, 839 (1971). [ll] R. D. Haugwitz, P. W. Jeffs, and E. Wenkert, *J. Chem. Soc.*, 2001 (1965). [mm] T. J. Batterham, K. H. Bell, and U. Weiss, *Aust. J. Chem.*, **18**, 1799 (1965); U. Weiss, J. V. Tillack, and C. H. L. Kennard, *Proc. R. Aust. Chem. Inst.*, **41**, 106 (1974). [nn] A. E. Jacobson, H. J. C. Yeh, and L. J. Sargant, *Org. Magn. Reson.*, **4**, 875 (1972). [oo] T. Tezuka, Y. Akasaki, and T. Mukai, *Tetrahedron Lett.*, 1397 (1967). [pp] G. C. Brophy, J. Mohandas, M. Slaytor, S. Sternhell, T. R. Watson, and L. A. Wilson, *ibid.*, 5159 (1969), and unpublished data from these laboratories. [qq] G. Albers-Schönberg and H. Schmid, *Helv. Chim. Acta*, **44**, 1447 (1961). [rr] B. Franck, J. Stöckigt, U. Zeidler, and G. Franckowiak, *Chem. Ber.*, **106**, 1198 (1973). [ss] W. B. Smith and G. P. Newsoroff, *Steroids*, **23**, 579 (1974).

61, 62, and **67,** together with the data for $\phi = 90°$ (**66, 68,** $^4J_{trd}$ always more negative than $^4J_{csd}$), are in good agreement with this hypothesis.

Exocyclic methylene groups are very commonly found[8] in sesquiterpenoid γ-lactones, e.g., **98** and **99.** It can be seen from these two examples that the magnitudes of allylic coupling constants in this fragment span a large range of values,[8] but no crossover point has been observed so far. Because of the occurrence of this fragment in an important class of natural products, they are at present the subject of a separate investigation in these laboratories.

A number of compounds shown in Table III are not rigid; i.e., they exist as two (or more) conformers. It has previously been observed[8] that for nonrigid methylenecyclohexanes, $|^4J_{csd}| > |^4J_{trd}|$, and this is illustrated in entries **69** to **72** of Table III. These compounds must, by symmetry, exist as two equally populated, rapidly interconverting conformers, and $J_{1,2}$ will be given by the expression $(1/2)[J_{1,2}(\phi = 100°) + J_{1,2}(\phi = 20°)]$. Therefore, it should be possible to interrelate the values of allylic coupling constants in closely related rigid and flexible systems. Thus, one may compare the results for 2-phenyl-4-methylenechroman (**61**) and 4-methylenechroman (**69**, X = O), making the reasonable assumption that the two conformers of the latter compound are approximately the same as the single conformer of the former. It follows that $J_{3,4}$ in **69,** X = O, should be given by $(1/2)[J_{3\alpha,4} + J_{3\beta,4}]$ from **61.** This gives the following prediction for values in. **69,** X = O:

$$\langle {}^4J_{3,4}(\text{transoid})\rangle = (1/2)[-2.17 - 0.48] = -1.32 \text{ Hz}$$

$$\langle {}^4J_{3,4}(\text{cisoid})\rangle = (1/2)[-2.19 - 0.85] = -1.52 \text{ Hz}$$

which are in fair agreement with the experimental values for **69,** X = O. It is thus easy to rationalize the fact that $|^4J_{trd}| < |^4J_{csd}|$ in the flexible methylenecyclohexanes (**69–72**).

Besides throwing light on the question of the relative magnitudes of cisoid and transoid allylic coupling constants, the data in Table III are also clearly relevant to the question of the dependence of both $^4J_{trd}$ and $^4J_{csd}$ on ϕ, and data for compounds **76–81** further confirm the suggestions made above regarding the relative insensitivity of allylic coupling constants to electronegative substituents.

3. *Effects of Ring Size*

The presence of ring strain and the resulting nonstandard hybridization within the coupling path could be expected to be associated with abnormal values of allylic coupling constants. Such effects are difficult to investigate theoretically (section IV) because the relevant calculations would only be entirely satisfactory with integral reparameterization. Thus, while data in Tables I–III do not suggest that any special effects are associated with five- or six-membered rings, we have already alluded to abnormal values of allylic coupling constants at ϕ approaching 0° in methylenenorbornanes and to abnormally small allylic coupling constants in methylenecyclobutenes (consider, for example, the data for compounds **76** and **89** in Table III).

Two further types of data could yield information on effects of ring strain: endocyclic allylic coupling constants in such systems (Table IV) and exocyclic coupling constants for fragments with very similar conformation (for example, the methyl group, Table V).

It can be seen by comparing the data for norbornene (**100**) and norbornadiene (**101**) with related bicyclo[2.2.2]octane systems (see section 4 below) that a decrease in the (positive) allylic coupling constants appears to be associated with ring strain. However, the effect is most likely due to a deviation from ideal planarity (ϕ = ca. 165°). A much more pronounced effect can be observed in cyclobutenes **102–105** where very small allylic coupling constants may be observed. This is most likely due to a second path (across four single bonds), which is associated with a positive contribution[3] to the spin–spin interaction, thus diminishing the negative allylic coupling contribution. This hypothesis is consistent with the very large range of values assumed by endocyclic allylic coupling constants in cyclobutene derivatives (especially compare those values for compounds **106** and **108**) because the steric dependence of the long-range interactions across the two coupling paths is different.[3] Data

TABLE III. Allylic Coupling Constants Involving Exocyclic Methylene Groups

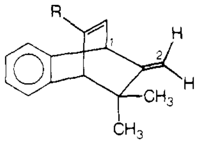
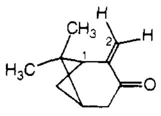
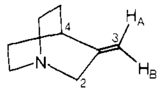
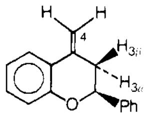
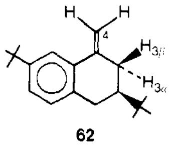
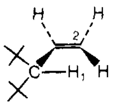
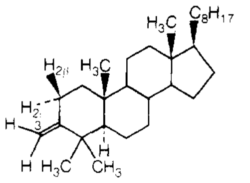
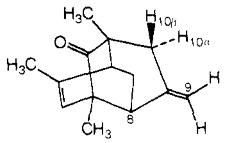
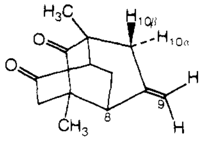
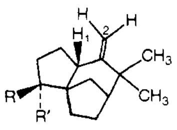
		J_{allylic}, Hz[a]		
Structure	J (ϕ)	Transoid	Cisoid	Ref
 58 R = H	J_{12} (0°)	⩽0.3	0.6 ± 0.1	3
R = Br	J_{12} (0°)	⩽0.1	0.4 ± 0.1	
 59	J_{12} (0°)	⩽0.1	0.4 ± 0.1	3
 60	J_{23} (60°)	2.58	2.12	3
	J_{34} (0°)	⩽0.15	0.47	
 61	$J_{3\beta,4}$ (100°)	−2.17	−2.19	3
	$J_{3\alpha,4}$ (20°)	−0.48	−0.85	
 62	$J_{3\beta,4}$ (100°)	−1.95	−2.03	b
 63	J_{12} (0°)	−0.04	−0.66	3
 64	$J_{2\beta,3}$ (120°)	1.0 ± 0.2	1.4 ± 0.1	b
	$J_{2\alpha,3}$ (10°)	⩽0.3	⩽0.3	
 65	$J_{8,9}$ (10°)	⩽0.2	0.55	3
	$J_{9,10\alpha}$ (85°)	2.73	2.39	
	$J_{9,10\beta}$ (40°)	1.24	1.34	
 66	$J_{8,9}$ (10°)	⩽0.2	0.55	3
	$J_{9,10\alpha}$ (90°)	2.97	2.60	
	$J_{9,10\beta}$ (35°)	1.18	1.24	
 67				
R = CH$_2$OH; R′ = H	$J_{1,2}$ (110°)	2.10	2.07	8
R = COOMe; R′ = H	$J_{1,2}$ (110°)	2.04	2.21	c
R = H; R′ = COOMe	$J_{1,2}$ (110°)	2.00	2.04	c

TABLE III (Continued)

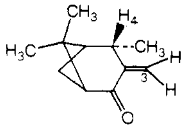
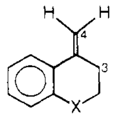
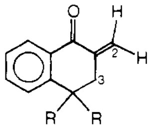
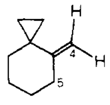
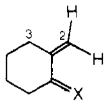
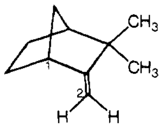
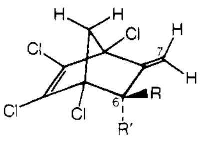
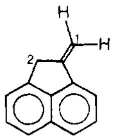
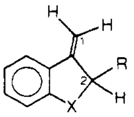
Structure	J (ϕ)	J_{allylic}, Hz[a]		Ref
		Transoid	Cisoid	
 68	$J_{3,4}$ (90°)	−3.2	−2.7	*d*
 69				
X = CMe$_2$	$J_{3,4}$	1.01	1.48	8
X = O	$J_{3,4}$	1.1 ± 0.1	1.4	*b*
 70				
R = H	$J_{2,3}$	1.10	1.50	8
R = CH$_3$	$J_{2,3}$	1.30	1.72	
 71	$J_{4,5}$	−0.73	−1.25	8
 72				
X = O	$J_{2,3}$	1.62	1.84	*b*
X = CH$_2$	$J_{2,3}$	1.0	1.3	*e*
 73	$J_{1,2}$ (10°)	0.55 ± 0.1	0.55 ± 0.1	*f*
 74				
R = H; R′ = Br	$J_{6\text{exo},7}{}^{i}$	2.2	1.9	
R = Br; R′ = H	$J_{6\text{endo},7}{}^{i}$	1.8	1.7	*g*
 75	$J_{1,2}{}^{i}$	2.32	1.97	8
 76				
X = CH$_2$; R = H	$J_{1,2}{}^{i}$	2.38	2.10	8
X = O; R = H	$J_{1,2}{}^{i}$	3.20	2.85	*h*
X = O; R = OCH$_3$	$J_{1,2}{}^{i}$	2.15	1.83	8

TABLE III (Continued)

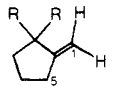
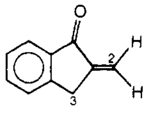
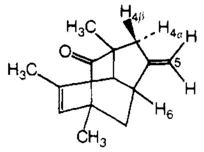
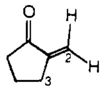
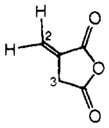
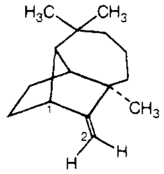
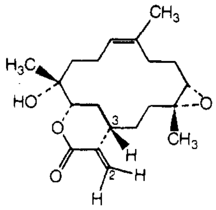
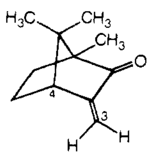
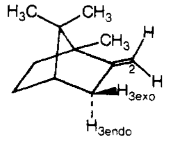
Structure	J (ϕ)	J_{allylic}, Hz^{a}		Ref
		Transoid	Cisoid	
 77				
R = CH_3	$J_{1,5}{}^{i}$	2.32	2.12	3
R–R = CH_2–CH_2	$J_{1,5}{}^{i}$	2.32	1.98	8
 78	$J_{2,3}{}^{i}$	2.21	1.86	8
 79	$J_{4\alpha,5}$ (55°) $J_{4\beta,5}$ (75°) $J_{5,6}$ (25°)	2.42 2.69 0.85	2.00 2.35 0.85	8
 80	$J_{2,3}{}^{i}$	2.65	2.39	*b*
 81	$J_{2,3}{}^{i}$	2.85	2.45	*b*
 82	$J_{1,2}$ (10°)	≤0.1	0.55 ± 0.1	3
 83	$J_{2,3}$	2.4	2.2	*b*
 84	$J_{3,4}$ (10°)	0.8 ± 0.1	≤0.4	3
 85	$J_{2,3\text{exo}}$ $J_{2,3\text{endo}}$	2.53 2.15	2.32 1.94	*b*

TABLE III (Continued)

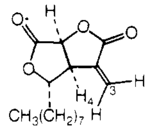
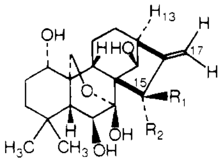
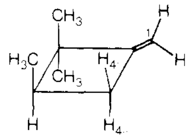
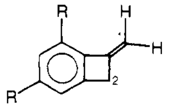
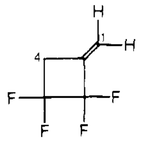
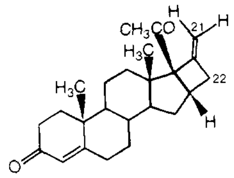
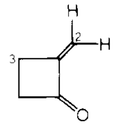
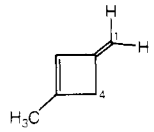
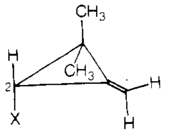
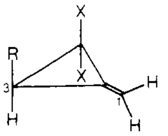
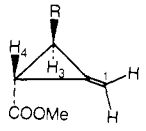
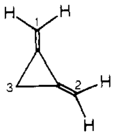
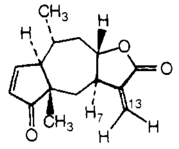
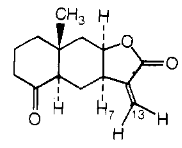
		J_{allylic}, Hz[a]		
Structure	J (φ)	Transoid	Cisoid	Ref
 86	$J_{3,4}$[i]	2.56	2.17	8
 87 $R_1 = R_2 = O$ $R_1 = OH$; $R_2 = H$	$J_{13,17}$ (45°) $J_{13,17}$ (45°) $J_{17,15\alpha}$ (70°)	1.31 1.49 2.85	1.17 1.27 2.31	3
 88	$J_{1,4\alpha}$ $J_{1,4\beta}$	−2.45 −2.65	−1.97 −2.16	*b*
 89				
R = H	$J_{1,2}$	1.74	1.24	8
R = CH_3	$J_{1,2}$	1.65	1.15	
 90	$J_{1,4}$	3.2	3.0	*j*
 91	$J_{21,22\alpha}$ $J_{21,22\beta}$	2.7 ± 0.1 3.15	2.2 ± 0.1 2.65	8
 92	$J_{2,3}$	3.11	2.57	*k*
 93	$J_{1,4}$	1.28	0.83	*l*
 94				
X = H	J_{12}	−2.55	−1.79	*m, n*
X = Br	J_{12}	−1.98	−1.22	

TABLE III (Continued)

Structure	$J(\phi)$	J_{allylic}, Hz[a] Transoid	Cisoid	Ref
 **95**				
R = H; X = Cl	$J_{1,3}$	3.3	2.6	*o*
R = H; X = CN	$J_{1,3}$	3.2	2.7	*p*
R = *n*-Pr or *n*-Bu; X = Cl	$J_{1,3}$	2.8	2.4	*q*
R = *n*-Pr or *n*-Bu; X = Br	$J_{1,3}$	2.8	2.3	*q*
 **96**				
R = *t*-Bu	$J_{1,3}$	2.6	2.3	*r*
	$J_{1,4}$	2.4	1.9	
R = Et	$J_{1,3}$	2.6 ± 0.1	2.1 ± 0.1	*r*
	$J_{1,4}$	2.4 ± 0.1	2.4 ± 0.1	
 **97**	$J_{1,3} = J_{2,3}$	2.6	1.7	*s*
 **98**	$J_{7,13}$	3.47	3.17	*n*, *t*
 **99**	$J_{7,13}$	1.25	1.16	8

[a] Where error limits are not shown, the results are accurate to ±0.05 Hz or better, or they could not be estimated from the literature. The signs of the coupling constants are only indicated where they have been determined. [b] Unpublished data from these laboratories. [c] Linda Drake, private communication. [d] M. Muhlstädt, M. Herrmann, and A. Zschunke, *Tetrahedron*, **24**, 1611 (1968). [e] D. Koster, private communication, 1967. [f] S. H. Grover and J. B. Stothers, *J. Am. Chem. Soc.*, **91**, 4331 (1969). [g] R. Alexander and D. I. Davies, *J. Chem. Soc. C*, **5** (1971). [h] W. J. M. Van Tilborg, J. R. Van der Vecht, H. Steinberg, and Th. J. De Boer, *Tetrahedron Lett.*, 1681 (1972). [i] $\phi = 60°$. [j] D. R. Taylor, M. R. Warburton, and D. B. Wright, *J. Chem. Soc., Perkin Trans. 1*, 1365 (1972). [k] G. P. Newsoroff, R. J. Spear, and S. Sternhell, *Aust. J. Chem.*, **25**, 1325 (1972). [l] P. E. Butler and K. Griesbaum, *J. Org. Chem.*, **33**, 1956 (1968). Note reversal of original assignments. [m] W. Rahman and H. G. Kuivila, *ibid.*, **31**, 772 (1966). [n] The NMR spectra were rerun in these laboratories on a 100-MHz instrument. [o] H. G. Peer and A. Schors, *Recl. Trav. Chim. Pays-Bas*, **86**, 161 (1967). [p] E. Ciganek, *J. Am. Chem. Soc.*, **88**, 1979 (1966). [q] P. Battioni, L. Vo-Quang, and Y. Vo-Quang, *Bull. Soc. Chim. Fr.*, 3938 (1970). [r] J.-L. Pierre, M. Vidal, P. Arnaud, and C. Grey, *ibid.*, 1544 (1970). [s] R. Bloch, P. Le Perchec, and J.-M. Conia, *Angew. Chem., Int. Ed. Engl.*, **9**, 798 (1970). [t] W. Herz, K. Aota, and A. L. Hall, *J. Org. Chem.*, **35**, 4117 (1970).

collected in Table III also suggest that significant substituent effects may operate, but in view of the possibility of conformational changes, this cannot be rigorously demonstrated.

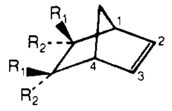
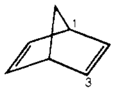
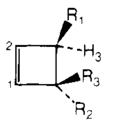
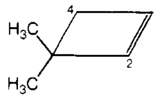
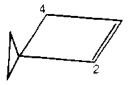
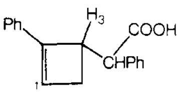
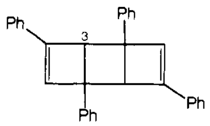
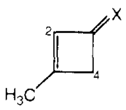
By contrast with the above, the (necessarily cisoid) allylic interactions of exocyclic methyl groups appear to be less sensitive to the size of the ring, the total range of values shown in Table V lying between (−)1.1 and (−)1.7 Hz. The typical values for the four-, five-, and six-membered rings appear to be very close to (−)1.5 Hz, and it is possible to discern clear examples of substituent effects in compounds such as **126**, **127**, and **128**. Although the data for methylcyclopropenes **137** are scarce, it appears that a ring-size effect is indeed operating in this extreme case.

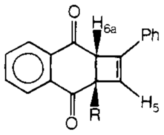
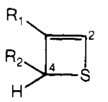
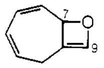
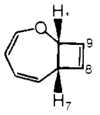
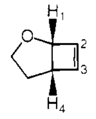
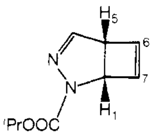
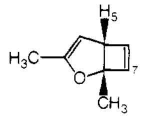
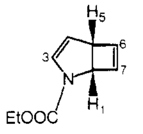
4. *Substituent Effects outside the Coupling Path*

Very little systematic work has been published on electronic effects on allylic coupling constants, presumably because of the complex nature of this problem. A complete study would, of necessity, consider direct electronic effects, not only the effects of substitution at C-1, C-2, and C-3, but also those due to indirect or remote electronic effects. In certain cases substituent effects will vary with steric factors such as dihedral angle and/or *E–Z* stereochemistry.

Because of the large effects on the magnitudes of allylic coupling associated with changes in the dihedral angle ϕ, the most extensive sets of available data, i.e., those for derivatives of propene and 2-butene (Table VI), are not ideal for the study of substituent effects since the populations of different rotamers may change with substitution. Despite this limitation, some systematic work of this type has been carried out.[12,13] It can be seen that quite large substituent effects can be observed in such cases as the 2-substituted propenes **138**, 2-substituted iso-

TABLE IV. Allylic Coupling Constants Involving Endocyclic Bonds in Strained Rings

Structure		J_{allyl}[a]
 **100**		
R$_1$ = R$_2$ = H; $J_{1,3}$ = $J_{2,4}$		+0.77[b]
R$_1$ = H; R$_2$ = Cl		+0.65[c]
R$_1$ = Cl; R$_2$ = H		+0.7[c]
 **101**	$J_{1,3}$	+0.99[b]
 **102**		
R$_1$ = R$_2$ = R$_3$ = H; $J_{1,3}$ = $J_{2,4}$		−0.35[d]
R$_1$ = R$_3$ = Cl; R$_2$ = H; $J_{1,3}$ = $J_{2,4}$		1.6[e]
R$_1$ = R$_2$ = Cl; R$_3$ = H; J_{13} = $J_{2,4}$		1.9[e]
R$_1$ = COOH; R$_2$ = Cl; R$_3$ = H; $J_{1,3}$		0.4[f]
$J_{2,4}$		0[f]
R$_1$ = COOH; R$_2$ = H; R$_3$ = Cl; $J_{1,3}$		0[f]
$J_{2,4}$		0.85[f]
 **103**	$J_{2,4}$	0.0[g]
 **104**	$J_{2,4}$	0.0[g]
 **105**	$J_{1,3}$	<0.5[h]
 **106**	$J_{1,3}$	2.5[i]
 **107**		
X = CH$_2$; $J_{2,4}$		0.50[j]
X = O; $J_{2,4}$		0.63[k]

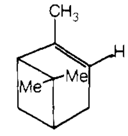
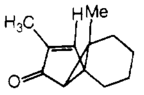
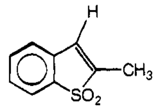
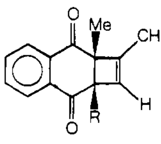
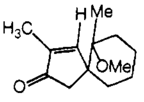
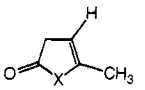
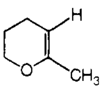
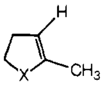
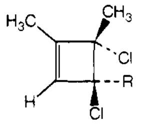
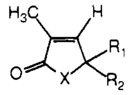
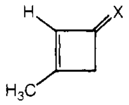
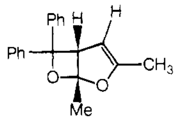
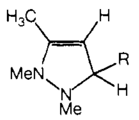
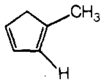
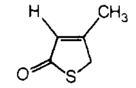
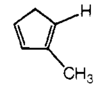
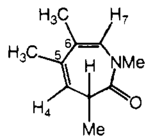
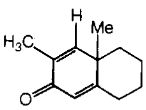
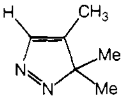
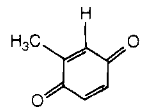
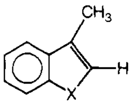
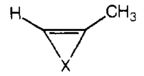
Structure		J_{allyl}[a]
 **108**		
R = H; $J_{5,6a}$		0.7[l]
R = CH$_3$; $J_{5,6a}$		0.85[l]
 **109**		
R$_1$ = R$_2$ = H; $J_{2,4}$		0[m]
R$_1$ = Et; R$_2$ = Me; $J_{2,4}$		0[m]
 **110**	$J_{7,9}$	2.9[n]
 **111**	$J_{1,8}$ $J_{7,9}$	0.8[n] 1.1[n]
 **112**	$J_{1,3}$ $J_{2,4}$	2.8[o] 1.5[o]
 **113**	$J_{1,6}$ $J_{5,7}$	2.0[p] 1.0[p]
 **114**	$J_{5,7}$	1.5[q]
 **115**	$J_{1,6}$ $J_{5,7}$ $J_{3,5}$	2.6[q] 0.4[q] 0.5[q]

[a] Unless otherwise indicated, the signs of the coupling constants are not known. [b] E. W. Garbisch, *Chem. Commun.*, 332 (1968). [c] P. Laszlo and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964). [d] E. A. Hill and J. D. Roberts, *ibid.*, **89**, 2047 (1967). [e] H. Hüther and H. A. Brune, *Org. Magn. Reson.*, **3**, 737 (1971). [f] W. H. Pirkle and L. H. McKendry, *J. Am. Chem. Soc.*, **91**, 1179 (1969). [g] W. Hartmann, L. Schrader, and D. Wendisch, *Chem. Ber.*, **106**, 1076 (1973). [h] S. Masamune and K. Fukumoto, *Tetrahedron Lett.*, 4647 (1965). [i] F. H. White and H. C. Dunathan, *J. Am. Chem. Soc.*, **86**, 453 (1964). [j] P. E. Butler and K. Griesbaum, *J. Org. Chem.*, **33**, 1956 (1968). [k] P. Dowd and K. Sachdev, *J. Am. Chem. Soc.*, **89**, 715 (1967). The NMR spectrum was rerun in these laboratories. [l] S. Farid, W. Kothe, and G. Pfundt, *Tetrahedron Lett.*, 4151 (1968). [m] D. C. Dittmer, P. L. F. Chang, F. A. Davis, M. Iwanami, I. K. Stamos, and K. Takahashi, *J. Org. Chem.*, **37**, 1111 (1972). [n] J. M. Holovka, P. D. Gardner, C. B. Strow, M. L. Hill, and T. V. Van Auken, *J. Am. Chem. Soc.*, **90**, 5041 (1968). [o] L. A. Paquette, J. H. Barrett, R. P. Spitz, and R. Pitcher, *ibid.*, **87**, 3417 (1965). [p] J. Streith, J. P. Luttringer, and M. Nastasi, *J. Org. Chem.*, **36**, 2962 (1971). [q] L. A. Paquette and J. H. Barrett, *J. Am. Chem. Soc.*, **88**, 1718 (1966).

butylenes **139**, and 2-butenes **143** and **144**, where owing to the unique symmetry of the methyl group, the conformational changes should be small, although not necessarily absent.

Data summarized in Table VI also underline the previously noted[5,8,9a,14] danger of any simple correlation between the relative magnitudes of allylic coupling constants and *E*–*Z* stereochemistry in acyclic compounds. In fact, Table VI contains examples of $^4J_{\text{trd}}$ being smaller, larger, or equal to $^4J_{\text{csd}}$, and this is not surprising in view of the fact that the allylic coupling constants in acyclic compounds are averages for several rotamers and that rotamer populations may vary while substituent effects may be different for each rotamer. Because of this, the

TABLE V. Allylic Coupling Constants Involving Methyl Groups Attached to Cyclic Systems

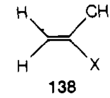
Structure	J_{allyl}[a]	Structure	J_{allyl}[a]	Structure	J_{allyl}[a]
 116	1.6[b]	 124	1.5[h]	 132	1.7[n]
 117		 125	1.6[h]	 133	
R = H	1.6[c]	 126	1.1[b]	X = O	−1.6[o]
R = Me	1.65[c]	 127		X = S	1.5[p]
 118		X = C=O	1.6[s]	 134	
R = Me	1.6[d]	X = O	1.1[b] −1.17[j]	X = O; R_1 = Me; R_2 = H	1.8[q]
R = H	1.7[d]	X = S	−1.49[j]	X = S; R_1 = R_2 = H	1.5[r]
 119		 128	1.4[g]	X = O; R_1 = Me; R_2 = OH	1.7[s]
X = CH_2	1.55[e]	 129		X = NH; R_1 = Me; R_2 = OH	1.5[s]
X = O	1.48[f]	R = H	1.8[k]	X = NH; R_1 = Me; R_2 = H	1.7[s]
 120	−1.6[g]	R = Me	1.6[k]	 135	1.5[r]
 121	−1.5[g]	R = Ph	1.5[k]	 136	
 122	1.5[h]	 130	1.7[l]	$J_{\text{Me}_6,\text{H}_7}$	1.0[t]
 123	1.6[i]	 131		$J_{\text{Me}_5,\text{H}_4}$	1.5[t]
		X = CH_2	1.66[m]	 137	
		X = SO_2	1.5[n]	X = CMe_2	1.1[u]
				X = SO_2	1.1[v]

[a] Here $J_{\text{Me—C=C—H}}$. Signs are given only when actually determined, but can be assumed to be negative in all cases. [b] R. J. Abraham, M. A. Cooper, J. R. Salmon, and D. Whittaker, *Org. Magn. Reson.*, **4**, 489 (1972). [c] S. Farid, W. Kothe, and G. Pfundt, *Tetrahedron Lett.*, 4151 (1968). [d] H. Hüther and H. A. Brune, *Org. Magn. Reson.*, **3**, 737 (1971). [e] P. E. Butler and K. Griesbaum, *J. Org. Chem.*, **33**, 1956 (1968). [f] P. Dowd and K. Sachdev, *J. Am. Chem. Soc.*, **89**, 715 (1967). The NMR spectra were rerun in these laboratories. [g] V. A. Korenevsky and N. M. Sergeyev, *ibid.*, **94**, 8586 (1972). [h] P. J. Kropp, *ibid.*, **86**, 4053 (1964). [i] R. K. Norris and S. Sternhell, *Aust. J. Chem.*, **19**, 841 (1966). [j] R. J. Abraham, K. Parry, and W. A. Thomas, *J. Chem. Soc. B*, 446 (1971). [k] J.-L. Aubagnac, J. Elguero, and R. Jacquier, *Bull. Soc. Chim. Fr.*, 3316 (1969). [l] G. L. Closs, L. E. Closs, and W. A. Böll, *J. Am. Chem. Soc.*, **85**, 3796 (1963). [m] G. Bergson and A.-M. Weidler, *Acta Chem. Scand.*, **17**, 862 (1963). [n] F. G. Bordwell, R. W. Hemwall, and D. A. Schexnayder, *J. Org. Chem.*, **33**, 3226 (1968). [o] D. Gagnaire, A. Rousseau, and P. Servez-Gavin, *J. Chim. Phys.*, **61**, 1207 (1964). [p] S. Gronowitz and R. A. Hoffman, *Ark. Kemi*, **15**, 499 (1960). [q] H. C. Volger, W. Brackman, and J. W. F. M. Lemmers, *Recl. Trav. Chim. Pays-Bas*, **84**, 1203 (1965). [r] A.-B. Hörnfeldt and S. Gronowitz, *Ark. Kemi*, **21**, 239 (1963). [s] R. Scheffold and P. Dubs, *Helv. Chim. Acta*, **50**, 798 (1967); H. R. Kricheldorf and W. Regel, *Chem. Ber.*, **106**, 3753 (1973). [t] L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4096 (1964). [u] P. Arnaud, J.-L. Pierre, and M. Vidal, *Bull. Soc. Chim. Fr.*, 3810 (1967). [v] L. A. Carpino and R. H. Rynbrandt, *J. Am. Chem. Soc.*, **88**, 5682 (1966).

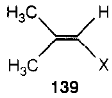
existence of still further effects[14] cannot be fully demonstrated. It may still be possible to use the relative magnitudes of allylic coupling constants for assignments of NMR resonances in such compounds as 2-substituted propenes **138** and for cases where very close analogies exist.

More easily interpreted[7,8,15–19] are data for compounds of somewhat better defined stereochemistry collected in Table VII. In particular, the series of compounds incorporating a transoid coupling path with ϕ = 180° (**147–156**) exhibit regular and appreciable variations in $^4J_{\text{trd}}$ with substitution at C-2.[15–18] The plot of one of the sets of such data[17] against the meta coupling constant across a carbon atom bearing the same substituent in the monosubstituted benzene series is given in Figure 2, and shows that the substituent effect is of a very similar type. The data for most of the monosubstituted benzenes are available,[20] but those for trimethylsilylbenzene were obtained from the

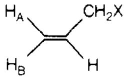
TABLE VI. Allylic Coupling Constants in Derivatives of Propene and 2-Butene[a]


138

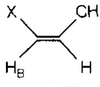
X	$^4J_{trd}$	$^4J_{csd}$	Ref
H	−1.33	−1.75	*b*
F	−0.4	−1.0	*c*
Cl	−0.77	−1.35	12
Br	−0.85	−1.42	12
I	−1.01	−1.6	*d*
Ph	−0.82	−1.52	12
CHO	−1.02	−1.53	12
COOH	−1.01	−1.61	12
$COOCH_3$	−1.02	−1.61	12
CN	−1.20	−1.71	12
$CONH_2$	−0.95	−1.50	*e*
COCl	−0.9	−1.5	*e*
$COCH_3$	−0.7	−1.3	*e*

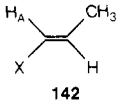

139

X	$^4J_{trd}$	$^4J_{csd}$	Ref
Ph	−1.41	−1.53	13
p-CH_3Ph	−1.39	−1.48	13
p-CH_3OPh	−1.39	−1.50	13
p-ClPh	−1.44	−1.56	13
$COOCH_3$	−1.27	−1.32	*f*
$COCH_3$	−1.1	−1.1	*g*
COEt	−1.0	−1.0	*g*
Br	−1.5	−1.5	*h*
CN	−0.45	−0.75	*i*
$^tC_4H_9$	−1.38	−1.47	*j*
$\mathrm{CH_3\overline{NBN(CH_3)CH_2CH_2}}$	−0.9	−1.3	*k*
$B(OH)_2$	−1.2	−1.0	*k*
BCl_2	−1.2	−1.1	*k*
$\overline{\mathrm{OBOCH_2CH_2}}$	−1.3	−1.0	*k*

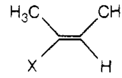

140

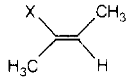
X	$^4J_{trd}$	$^4J_{csd}$	Ref
CH_3	−1.2	−1.7	*l*
F	−1.27	−1.63	*m*
Cl	−0.93	−1.41	*n*
Br	−0.59	−1.21	*n*
I	−0.43	−1.04	*n*
OH	−1.25	−1.55	*o*
OCH_3	−1.42	−1.67	*p*
Ph	−1.47	−1.47	*n*
$-CH{=}CH_2$	−1.50	−1.30	*q*
CN	−1.68	−1.90	2
NO_2	−0.99	−1.50	*r*


141

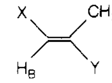

142

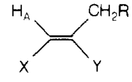
X	$^4J_{trd}$	$^4J_{csd}$	Ref
	141	142	
F	−1.6	−1.8	*c*
Cl	−1.7	−1.7	*c*
Br	−1.6	−1.8	*c*
I	−1.5	−1.8	*o*
COOH	−1.65	−1.73	*s*
$COOCH_3$	−1.57	−1.58	*t*
$N(CH_3)_2$	−1.6	−1.3	*u*
NEt_2	−1.6	−1.3	*u*
$\overline{\mathrm{NCH_2CH_2}}_2$	−1.7	−1.4	*u*
Ph	−1.81	−1.51	*s*
CN	−1.3	−1.8	*v*
CN	−1.4	−1.5	*w*
NO_2	−0.99	−1.32	*r*
^tBu	−1.82	−1.66	*s*
CON_3	−1.8	−1.6	*x*
NCO	−1.7	−1.2	*x*
$\mathrm{CH_3\overline{NBN(CH_3)CH_2CH_2}}$	−1.25	−1.7	*k*
$\overline{\mathrm{OBOCH_2CH_2}}$	−1.5	−1.69	*k*
BCl_2	−1.5	−1.46	*k*


143


144

X	$^4J_{trd}$	$^4J_{csd}$	Ref
	143	144	
H	−1.85	−1.72	*y*
COOMe	−1.37	−1.22	*z*
COOH	−1.43	−1.28	*z*
Br	−1.40	−1.30	*aa*
$Sn(CH_3)_3$	−1.80	−1.40	*aa*
Ph	−1.3	−1.5	*bb*
p-OCH_3Ph	−1.3	−1.5	*bb*
OCH_3	−1.1	−0.9	*cc*
OAc	−1.1	−1.1	*dd*
OTs	−1.0	−1.0	*ee*
N_3	−1.0	−1.5	*ff*
COPh	−1.25	−1.5	*gg*


145


146

R	X	Y	$^4J_{trd}$ (J_{H_B,CH_2R})	$^4J_{csd}$ (J_{H_A,CH_2R})	Ref
^{n}Pr	Br	H	−1.5	−1.35	*hh*
^{n}Pr	SCOMe	H	−1.3	−1.1	*ii*
H	CO_2Et	Cl	−1.20	−1.16	*jj*
H	SMe	SMe	−1.0	−1.4	*kk*
Ph	CN	H	−1.6	−1.2	*v*
⊖Ph	CN	H	−2.2	−1.5	*v*
H	CN	Ph	−1.1	−1.2	*v*
H	^{i}Pr	CN	−1.6	−1.8	*v*
OEt	COOH	H	−2.5	−2.0	*ll*
CH_3	^{t}Bu	H	−1.56	−1.28	*x*

[a] Although only a proportion of the data quoted included sign determination, it can be safely assumed that all allylic coupling constants quoted here are, in fact, negative. [b] A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961). [c] M. Y. DeWolf and J. D. Baldeschwieler, *J. Mol. Spectrosc.*, **13**, 344 (1964). [d] F. Hruska, D. W. McBride, and T. Schaefer, *Can. J. Chem.*, **45**, 1081 (1967). [e] L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881 (1960); H. Rottendorf, S. Sternhell, and J. R. Wilmshurst, *Aust. J. Chem.*, **18**, 1759 (1965). [f] P. J. Collin and S. Sternhell, *ibid.*, **19**, 317 (1966). [g] M. Vidal, C. Dumont, and P. Arnaud, *Tetrahedron Lett.*, 5081 (1966). [h] G. J. Martin and M. L. Martin, *J. Chim. Phys.*, **61**, 1222 (1964). [i] G. Boularand and R. Vessiere, *Bull. Soc. Chim. Fr.*, 1706 (1967). [j] D. H. Hunter and R. W. Mair, *Can. J. Chem.*, **47**, 2361 (1969). [k] M. P. Simonnin and J. Braun, *Bull. Soc. Chim. Fr.*, 4918 (1968). [l] C. N. Banwell and N. Sheppard, quoted by R. A. Hoffman and S. Gronowitz, *Ark. Kemi*, **16**, 471 (1960). [m] A. A. Bothner-By, S. Castellano, and H. Günther, *J. Am. Chem. Soc.*, **87**, 2439 (1965). [n] A. A. Bothner-By and H. Günther, *Discuss. Faraday Soc.*, **No. 34**, 167 (1962); J. Feeney and P. J. S. Pauwels, *Mol. Phys.*, **14**, 209 (1968). [o] W. Brügel, "Nuclear Magnetic Resonance Spectra and Chemical Structure", Vol. 1, Academic Press, New York, N.Y., 1967. [p] A. A. Bothner-By, S. Castellano, S. J. Ebersole, and H. Günther, *J. Am. Chem. Soc.*, **88**, 2466 (1966). [q] D. F. Koster and A. Danti, *J. Phys. Chem.*, **69**, 486 (1965). [r] H. J. Fröhlin, K. R. Loos and Hs. H. Günthard, *Helv. Chim. Acta*, **51**, 1593 (1968). [s] F. H. A. Rummens and J. W. De Haan, *Org. Magn. Reson.*, **2**, 351 (1970). [t] R. R. Fraser and D. E. McGreer, *Can. J. Chem.*, **39**, 505 (1961). [u] J. Sauer and H. Prahl, *Tetrahedron Lett.*, 2863 (1966); *Chem. Ber.*, **102**, 1917 (1969). [v] G. Descotes and P. Laconche, *Bull. Soc. Chim. Fr.*, 2149 (1968). [w] G. S. Reddy, J. H. Goldstein and L. Mandell, *J. Am. Chem. Soc.*, **83**, 1300 (1961). [x] M. B. Hocking, *Can. J. Chem.*, **46**, 2275 (1968). [y] F. H. A. Rummens and L. Kaslander, *Can. J. Spectrosc.*, **17**, 99 (1972). [z] R. R. Fraser, *Can. J. Chem.*, **38**, 549 (1960). [aa] P. Baekelmans, M. Gielen, P. Malfroid, and J. Nasielski, *Bull. Soc. Chim. Belg.*, **77**, 85 (1968). [bb] M. Barbieux, N. Defay, J. Pechèr, and R. H. Martin, *ibid.*, **73**, 716 (1964). [cc] G. Benndorf, H. G. Hauthal, R. Holm, and W. Höbold, *J. Prakt. Chem.*, **311**, 586 (1969). [dd] W. E. Parham and J. F. Dooley, *J. Org. Chem.*, **33**, 1476 (1968). [ee] P. E. Peterson and J. M. Indelicato, *J. Am. Chem. Soc.*, **91**, 6194 (1969). [ff] A. Hassner and F. W. Fowler, *J. Org. Chem.*, **33**, 2686 (1968). [gg] G. Combaut and L. Giral, *Bull. Soc. Chim. Fr.*, 3715 (1970). [hh] G. J. Martin and M. L. Martin, *ibid.*, 1636 (1966). [ii] J. A. Kampmeier and G. Chen, *J. Am. Chem. Soc.*, **87**, 2608 (1965). [jj] J. S. Pizey and W. E. Truce, *J. Chem. Soc.*, 865 (1964). [kk] E. I. Heiba and R. M. Dessau, *J. Org. Chem.*, **32**, 3837 (1967). [ll] M. L. Martin, G. J. Martin, and P. Caubere, *Bull. Soc. Chim. Fr.*, 3066 (1964).

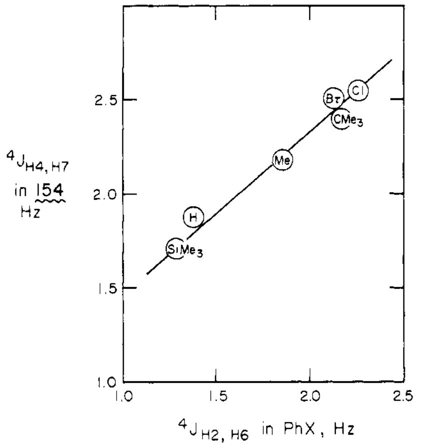


Figure 2. Plot of allylic coupling constants in structure **154** (Table VII) against meta coupling constants across the same group X in the corresponding monosubstituted benzene PhX. The groups X are identified in the circles and the straight line represents a visually drawn line of best fit.

analysis of a 300-MHz NMR spectrum in CCl_4 by Mr. R. K. Duffin in these laboratories.

It must be noted that secondary effects must also operate. Thus, there are significant differences between $J_{4,7}$ and $J_{1,8}$ in **154** (X = H) and in **155** (X = H), but the analogous effect is absent in **153**. On the other hand, the introduction of successive double bonds into the [2.2.2] bicyclooctane system **148–152** is not associated with very pronounced effects.

Another reasonably extensive set of data exists for endocyclic allylic coupling in five-membered rings (ϕ = ca. 120°) with substituents at C-1 or C-3 (**157–164**). While undoubtedly some substituent effects can be deduced, they are smaller than those noted above (see particularly the reliable data for **158** and **159**)[19] and the larger deviations (see, for example, compounds **157**, **160**, and **161**) cannot be considered absolutely free from conformational distortion. A similar situation is encountered for exocyclic allylic coupling[8] in **165** and **166**, while data for six-membered rings (**167–172**, **176**) must reflect significant conformational factors and are listed only to permit empirical correlations with very similar structures.

It is interesting to note that even multiple substitution by oxygen or sulfur (**173**, **174**, **175**, and **177**) does not produce *very* wide divergence from data for less substituted compounds (Table III), for values of ϕ close to 60°.

5. Substituent Effects with Heteroatoms in the Coupling Path

It was noted early[5,9a] that the replacement of an sp^2-hybridized carbon atom in the allylic coupling path by a heteroatom does not, in general, destroy the transmission of spin information along the path. Data summarized in Table VIII show that this indeed appears to be the case at least for substitution of an sp^2-hybridized nitrogen atom for an sp^2-hybridized carbon atom. Thus, whenever the signs have been determined they were found to be negative, the absolute magnitudes are comparable for analogous steric situations, and the results for compounds **180**, **181**, and, particularly **182**, strongly suggest that the familiar dependence on ϕ (see section IV) operates. Less can be deduced about the influence of the nature of the heteroatom on the magnitude of the allylic coupling constants, but a systematic investigation by Tori et al.[21] and data for compounds **180**, **181**, **185–187** show that a significant effect exists.

The results for *N,N*-dimethylformamide and *N,N*-dimethylthioformamide **184** are typical of a large number of results available for peptide derivatives.[9a] The allylic coupling path in these cases contains a partial double bond (see the next section), and it can be seen that no significant change is associated with substitution of a sulfur atom for the oxygen atom.

6. Influence of Bond Order

The decrease of the absolute magnitudes of allylic coupling constants with the lowering of the π-bond order of the double bond in the coupling path was recognized in early studies,[5,7,9a] and, in particular, a number of detailed investigations[22–25] established the close relationship between allylic and ortho benzylic[5,7,9a,22,26] coupling constants. Correlations between magnitudes of the (necessarily cisoid) allylic coupling constants involving methyl groups and bond order have been used extensively, but principally by Clar and co-workers[27] in the study of polynuclear aromatic compounds, and more rarely[28,29] for investigations of the degree of ground-state delocalization in heteronuclear systems.

Some examples of the latter type (especially compounds **201** and **202**) are also listed in Table IX, but the remaining examples are not necessarily compounds of potentially aromatic character, but simply molecules which contain an electron source and an electron sink attacked to C-1 and C-2 atoms of the allylic coupling path.

The delocalization of the π electrons, which can be used to rationalize the small magnitudes of the allylic coupling constants, is indicated by curly arrows in structures **191–202**, and the values of the allylic coupling constants should be compared with appropriate examples listed in Table V (particularly **127** and **133**). Clearly, it can be seen that the effect is very pronounced and could provide valuable evidence in structural studies. Particularly convincing are the data for the β-amino carbonyl derivatives **199** where allylic coupling across a "delocalized" and "undisturbed" allylic coupling paths can be observed in the same molecule, although the precision of this particular set of data is probably not very high.

Besides delocalization of π electrons in conjugated systems, the bond order of the double bond in the allylic coupling path can also be lowered by the formation of π bonds with transition metals and the consequent appearance of abnormally small, or even unobservable, allylic coupling constants in appropriate fragments.[5,9a,30] This phenomenon is of obvious utility in the study of transition metal complexes, but caution should be exercised because it is possible that sigma bonds to transition metals may have a profound effect on the magnitudes of allylic coupling constants.[31]

III. Theoretical Formulations

Most theoretical formulations of nuclear spin–spin coupling constants have been based on the second-order perturbation formulation of Ramsey,[32] and for coupling involving protons the assumption of the adequacy of inclusion of only the Fermi contact term seems to be justified. The mathematical details of spin coupling theory are given in several reviews[33–35] and in many of the references cited here. In all of the computational schemes, which are based on the Fermi contact term, the coupling constant $J_{HH'}$ between protons H and H′ can be put into the form

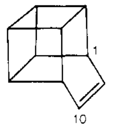
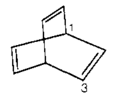
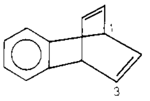
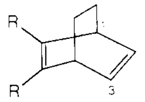
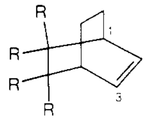
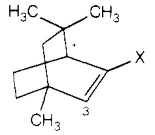
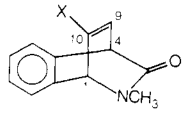
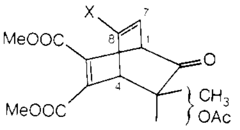
$$J_{HH'} = -(2h)^{-1}A_HA_{H'}\mathcal{F}_{hh'} \qquad (1)$$

where

$$A_H = (16\pi\beta\hbar/3)\gamma_H\phi_h{}^2(H) \qquad (2)$$

in which β is the Bohr magneton, γ_H is the magnetogyric ratio of the proton, and $\phi_h{}^2(H)$ is the 1s electron density at the proton H. The analogous expression for the constant $A_{H'}$ would assume the identical numerical value. The quantity $\mathcal{F}_{hh'}$ in eq 1 is called a *spin coupling function*. Because this term depends on the molecular electronic environments, its mathematical form de-

TABLE VII. Miscellaneous Examples of Substituent Effects on Allylic Coupling Constants

Structure	J_{allyl}[a]
 **147** $J_{1,10}$	+1.0[b]
 **148** $J_{1,3}$	+1.60[c]
 **149** $J_{1,3}$	+1.27[d]
 **150** R = H or COOMe; $J_{1,3}$	+1.3[4]
 **151** R = H or CN; $J_{1,3}$	+1.3[4]
 **152** $J_{1,3}$	
X = NMe_2	+1.90[15]
OAc	+1.85[15]
Cl	+1.75[15]
I	+1.63[15]
Ph	+1.4[15]
COMe	+1.40[15]
COOH	+1.30[15]
COOMe	+1.30[15]
H	+1.30[15]
 **153**	
X = Cl; $J_{1,9}$	+2.43[16]
X = Me; $J_{1,9}$	+1.95[16]
X = H; $J_{1,9}$	+1.72[16]
$J_{4,10}$	+1.73[16]
 **154**	
X = Cl; $J_{4,7}$	+2.55[17]
X = Br; $J_{4,7}$	+2.50[17]
X = CMe_3; $J_{4,7}$	+2.40[17]
X = $SiMe_3$; $J_{4,7}$	+1.70[17]
X = Me; $J_{4,7}$	+2.19[17]
X = H; $J_{4,7}$	+1.89[17]
$J_{1,8}$	+1.55[17]

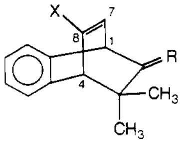
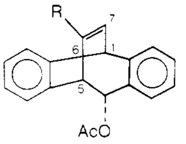
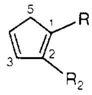
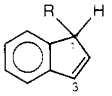
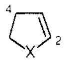
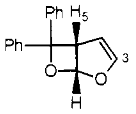
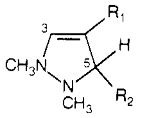
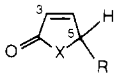
Structure	J_{allyl}[a]
 **155**	
X = Br; R = O; $J_{4,7}$	+2.48[18]
X = H; R = O; $J_{4,7}$	+1.79[18]
$J_{1,8}$	+1.38[18]
X = Br; R = CH_2; $J_{4,7}$	+2.30[18]
X = H; R = CH_2; $J_{4,7}$	+1.62[18]
$J_{1,8}$	+1.21[18]
 **156**	
R = OAc; $J_{5,7}$	+1.9[e]
R = Cl; $J_{5,7}$	+2.2[e]
R = H; $J_{5,7}$	+1.2[e]
$J_{1,6}$	+1.4[e]
 **157**	
$R_1 = R_2$ = H; $J_{2,5}$	−1.51[f]
R_1 = Me; R_2 = H; $J_{2,5}$	−1.3[g]
$J_{3,5}$	−1.5[g]
R_1 = H; R_2 = Me; $J_{3,5}$	−1.4[g]
 **158** $J_{1,3}$	
R = H	−1.98[f]
R = Me	−1.94[h]
R = $CHPh_2$	−1.65[i]
R = CPh_3	−1.8[i]
 **159** $J_{2,4}$	
X = O	−2.36[19]
X = S	−2.23[19]
X = SO_2	−2.29[19]
X = CO	−2.14[19]
 **160** $J_{3,5}$	−1.3[j]
 **161** $J_{3,5}$	
R_1 = H; R_2 = Ph	−2.1[k]
R_1 = Ph; R_2 = H	−1.6[k]
 **162**	
X = O; R = NHOAc; $J_{3,5}$	−2.0[l]
X = NH; R = H; $J_{3,5}$	−1.91[m]

TABLE VII (Continued)

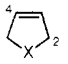
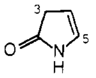
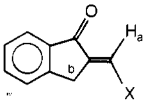
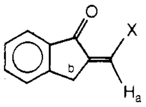
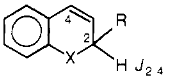
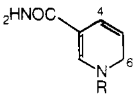
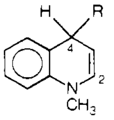
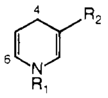
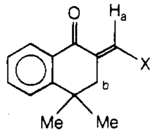
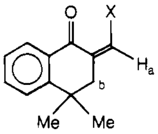
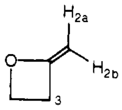
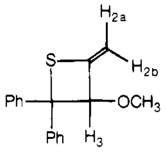
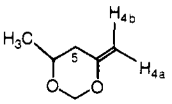
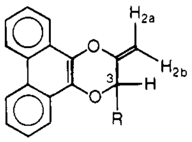
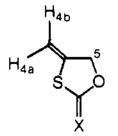
Structure	J_{allyl}[a]
	
163 $J_{2,4}$	
X = O	-2.51[n]
X = S	-2.36[n]
X = SO_2	-2.34[n]
	
164 $J_{3,5}$	-2.33[m]
	
165 $J_{a,b}$	
X = H	-2.21[8]
X = Me	-2.20[8]
X = Ph	-1.88[8]
X = Cl	-2.34[8]
X = Br	-2.34[8]
	
166 $J_{a,b}$	
X = H	-1.86[8]
X = Me	-1.67[8]
X = Ph	-1.40[8]
X = Cl	-1.68[8]
X = Br	-1.63[8]
	
167 $J_{2,4}$	
X = CH_2; R = H	-1.86[f]
	-1.8[o]
X = O; R = H	-1.8[p]
X = S; R = H	-1.5[p]
X = NMe; R = H	-1.8[q]
X = NCOOEt; R = H	$\leqslant 0.4$[r]
X = NH; R = Ph	-1.2[r]
X = NMe; R = Ph	-0.5[s]
X = NCN; R = CN	-0.5[s]
X = NCN; R = OEt	-0.6[s]
X = NCN; R = OMe	-0.5[s]
	
168 $J_{4,6}$	
R = CH_2Ph	-1.5[t]
R = CH_2(2,5-di-ClPh)	-0.9[t]
R = CN or COMe	-0.9[t]
	
169 $J_{2,4}$	
R = H	-1.6[q]
R = CN	-0.9[q]
	
170 $J_{2,6}$	
R_1 = CH_2Ph; R_2 = COMe	-1.6[t]
R_1 = CH_2Ph; R_2 = $CONH_2$	-1.6[t]
R_1 = Ph; R_2 = H	-1.6[t]
	
171 $J_{a,b}$	
X = H	-1.30[8]
X = Me	-1.71[8]
X = Ph	-1.78[8]
X = Cl	-1.81[8]
X = Br	-1.73[8]
	
172 $J_{a,b}$	
X = H	-1.72[8]
X = Me	-1.44[8]
X = Ph	-1.35[8]
X = Cl	-1.50[8]
X = Br	-1.38[8]
	
173 $J_{2a,3}$	-2.4[u]
$J_{2b,3}$	-1.8[u]
	
174 $J_{2a,3}$	-2.2[v]
$J_{2b,3}$	-2.2[v]
	
175 $J_{4a,5ax}$	-1.95[w]
$J_{4b,5ax}$	-1.95[w]
$J_{4a,5eq}$	-0.4[w]
$J_{4b,5eq}$	-0.4[w]
	
176	
R = H; $J_{2a,3}$	$\leqslant 0.3$[x]
$J_{2b,3}$	-0.60[x]
R = Me; $J_{2a,3}$	$\leqslant 0.3$[x]
$J_{2b,3}$	-0.80[x]
R = OMe or SMe; $J_{2a,3}$	$\leqslant 0.3$[x]
$J_{2b,3}$	$\leqslant 0.3$[x]
R = Ph; $J_{2a,3}$	$\leqslant 0.3$[x]
$J_{2b,3}$	-0.8[x]
	
177	
X = NCOOEt; $J_{4a,5}$	-2.5[y]
$J_{4b,5}$	-2.5[y]
X = O; $J_{4a,5}$	-2.1[y]
$J_{4b,5}$	-2.1[y]

TABLE VII (footnotes)

[a] Although only some of the signs of allylic coupling constants listed in this table were determined, others can be firmly deduced by analogy and are thus listed. [b] S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Lett.*, 1017 (1966). [c] H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, and M. A. Sherwin, *J. Am. Chem. Soc.*, **91**, 2330 (1969). [d] R. G. Miller and M. Stiles, *ibid.*, **85**, 1798 (1963). [e] S. J. Cristol, R. M. Sequeira and G. O. Mayo, *ibid.*, **90**, 5564 (1968). [f] M. A. Cooper, D. D. Elleman, C. D. Pearce, and S. L. Manatt, *J. Chem. Phys.*, **53**, 2343 (1970). [g] V. A. Korenevsky and N. M. Sergeyev, *J. Am. Chem. Soc.*, **94**, 8586 (1972). [h] G. Bergson and A.-M. Weidler, *Acta Chem. Scand.*, **17**, 862 (1963). [i] L. Meurling, *ibid.*, *Ser. B*, **28**, 295 (1974). [j] D. Gagnaire and E. Payo-Subiza, *Bull. Soc. Chim. Fr.*, 2627 (1963). [k] J.-L. Aubagnac, J. Elguero, and J.-L. Gilles, *ibid.*, 288 (1973). [l] S. G. Yates, H. L. Tookey, J. J. Ellis, and H. J. Burkhardt, *Tetrahedron Lett.*, 621 (1967). [m] R. Mondelli, V. Bocchi, G. P. Gardini, and L. Chierici, *Org. Magn. Reson.*, **3**, 7 (1971). [n] R. Lozac'h and B. Braillon, *J. Magn. Reson.*, **12**, 244 (1973). [o] M. J. Cook, A. R. Katritzky, F. C. Pennington, and B. M. Semple, *J. Chem. Soc. B*, 523 (1969). [p] L. Lunazzi and F. Taddei, *J. Mol. Spectrosc.*, **25**, 113 (1968). [q] J. W. Bunting and W. G. Meathrel, *Tetrahedron Lett.*, 133 (1971). [r] C. E. Crawforth, O. Meth-Cohn, and C. A. Russell, *J. Chem. Soc., Perkin Trans. 1*, 2807 (1972). [s] R. Bramley and M. D. Johnson, *J. Chem. Soc.*, 1372 (1965). [t] H. Diekmann, G. Englert, and H. Wallenfels, *Tetrahedron*, **20**, 281 (1964). [u] P. F. Hudrlik and A. M. Hudrlik, *Tetrahedron Lett.*, 1361 (1971). [v] H. J. T. Bos, H. Schinkel, and T. C. M. Wijsman, *ibid.*, 3905 (1971). [w] M. Anteunis and R. Camerlynek, *J. Chem. Soc., Perkin Trans. 2*, 1434 (1975). [x] H. J. T. Bos, C. Slagt, and J. S. M. Boleij, *Recl. Trav. Chim. Pays-Bas*, **89**, 1170 (1970); J. S. M. Boleij and H. J. T. Bos, *ibid.*, **91**, 1212 (1972); H. J. T. Bos, private communication, 1973. [y] M. Nagano, T. Matsui, J. Tobitsuka, and K. Oyamada, *Chem. Pharm. Bull.*, **21**, 62 (1973).

pends on the approximations which are implicit in the various theories. In subsequent sections a variety of different forms of the spin coupling function will be introduced provided that they are relevant to some aspect of allylic coupling.

A. The "Average Energy" Procedure. Relationship of Coupling Constants to Bond Orders

For a number of years theoretical descriptions of nuclear spin-spin coupling constants were based on the so-called "average energy approximation", which was carried out by making the closure approximation in the numerator of the second-order perturbation expression for the coupling constant, and replacing the denominators by some average value ΔE. For some time it has been clear[36] that this is not an approximation in the usual sense of the word but, rather, an expedient procedure which gives incorrect results even for "reasonable" choices of ΔE. This procedure is introduced here within the molecular orbital (MO) and valence-bond (VB) formulations because the equations are qualitatively and conceptually useful for interpreting electronic features associated with spin-spin coupling, and for interrelating NMR coupling constants and hyperfine coupling constants from electron spin resonance (ESR) spectra. Unfortunately, the simplicity of these equations often leads to their use in unsuitable situations.

In MO theory the "average energy" procedure leads to the rather simple form of the spin coupling function,[37]

$$\mathcal{J}_{hh'} = -(2\Delta E)^{-1}\eta_{hh'}{}^2 \tag{3}$$

where $\eta_{hh'}$ is the bond order of Coulson and Longuet-Higgins,[38]

$$\eta_{hh'} = \sum_i n_i c_{ih} c_{ih'} \tag{4}$$

in which c_{ih} and $c_{ih'}$ are the coefficients of the atomic orbitals h and h' in the ith MO with occupation number n_i. Since $\eta_{hh'}$ in eq 4 is not an imaginary number, coupling constants based on eq 1–3 are necessarily positive. Furthermore, in the absence of certain σ–π exchange integrals in the MO formulation leading to the coefficients in eq 4, there would be no interproton (allylic, for example) coupling transmitted via the π-electronic system of the molecule. To overcome these two difficulties in theoretical descriptions of spin-spin coupling in unsaturated and aromatic systems, McConnell showed[39] that the π-electron contribution, $J^{\pi}{}_{HH'}$ could be related to ESR hyperfine coupling constants (the notation used here is slightly different than in the original reference[39] to conform to that used in the remainder of this section),

$$J^{\pi}{}_{HH'} = h(\Delta E)^{-1} a_H a_{H'} \eta_{pp'}{}^2 \tag{5}$$

where a_H and $a_{H'}$ are the ESR hyperfine coupling constants (in hertz) in related free radical fragments and $\eta_{pp'}$ is the π-electron bond order associated with the 2p atomic orbitals p and p' on the carbons attached to the coupled protons. In the single configuration MO description for even alternant hydrocarbons $\eta_{pp'}$ (hence $J^{\pi}{}_{HH'}$) vanish identically if p and p' are in the same subset[38] (for example, the ${}^4J^{\pi}{}_{HH'} = 0$ in this approximation if H and H′ denote the meta protons in an aromatic system).

Within the VB approximation applied to spin-spin coupling and the assumption of the "average energy" procedure, it has been shown[40,41] that the spin coupling function in eq 1 is proportional to the Penney-Dirac bond order,[42] $p(h,h')$,

$$\mathcal{J}_{hh'} = -(\Delta E)^{-1} p(h,h') \tag{6}$$

where for a system of 2n electrons

$$p(h,h') = (1/3) \sum_{jl} c_j c_l (1/2)^{n-i_{jl}} [1 + 2f_{jl}{}^{hh'}] \tag{7}$$

in which c_j and c_l are the coefficients of the singlet, nonpolar canonical VB structures, and in the superposition diagram of structure j and l, i_{jl} denotes the number of islands and $f_{jl}{}^{hh'}$ is the usual exchange factor for orbitals h and h'.[43] Since both one- and two-center exchange integrals are included in the matrix elements of the Hamiltonian operator, which is used to calculate the coefficients in eq 6, the calculated coupling constants will include contributions from both σ and π electrons. It is interesting to note that for unit bond order and the same value of ΔE, the VB spin coupling function in eq 6 has twice the magnitude of the MO spin coupling function in eq 3.

It has been noted that in molecular systems in which a localized bond description is a reasonable approximation, i.e., nonaromatic hydrocarbons, the Penney-Dirac bond orders can be related to nonlocal bond orders for four electron fragments comprising two bond pairs.[41] Since this provides a useful procedure for separating the various contributions to the coupling constants, it will be of interest to restate the formulas here. Consider two bonds c–h and c'–h', which contain the coupled nuclei and j other bonds t_j–t_j'. Up to second order the Penney-Dirac bond order is given by the approximate expression[41]

$$p(h,h') = p^0(h,h') + (3/2) \sum_j p^0(h,t_j) p^0(t_j',h') \tag{8}$$

where $p^0(h,h')$, $p^0(h,t_j)$, and $p^0(t_j',h')$ denote the nonlocal bond orders for the four electron fragments $[h\text{–}c, c'\text{–}h']$, $[h\text{–}c, t_j\text{–}t_j']$, and $[t_j\text{–}t_j', c'\text{–}h']$, and are related to the exchange integrals by the expressions,

$$p^0(h,h') = (1/2)\left[\frac{K(h,h') + K(c,c') - K(c,h') - K(c',h)}{K(h,c) + K(c',h')}\right] \tag{9}$$

$$p^0(h,t_j) = (1/2)\left[\frac{K(h,t_j) + K(c,t_j') - K(h,t_j') - K(c,t_j)}{K(h,c) + K(t_j,t_j')}\right] \tag{10}$$

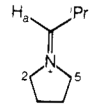
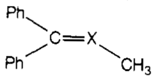
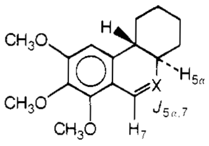
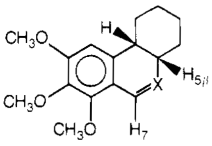
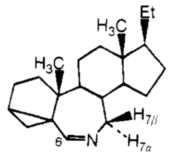
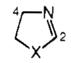
The exchange integrals in eq 9 and 10 are of the form

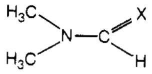
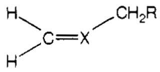
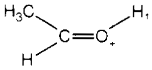
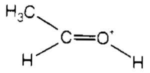
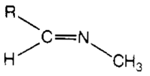
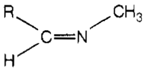
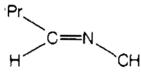
$$K(h,h') = \int\int h(1)h'(2)\mathcal{H}h(2)h'(1)\,d\tau_1 d\tau_2 \tag{11}$$

where $\mathcal{H}$ is the two-electron Hamiltonian operator.[43]

Contributions to the coupling constant from eq 9 (via eq 1 and 6) have been termed *direct*[41] (electron mediated, and will not in this review be confused with the simple nuclear dipole-nuclear dipole interactions), whereas those arising from the second term in eq 8 are called *indirect* since the bond t_j–t_j' "relays" the spin coupling from the first bond containing the coupled nucleus to

TABLE VIII. Allylic Coupling Constants with Heteroatoms in the Coupling Path

Structure	J_{allyl}[a]
 **178**	
½($J_{a,2}$ + $J_{a,5}$)	2.0[b]
 **179**	
X = $^+$N-O$^-$	−0.5[21]
X = $^+$NH	−1.1[21]
 **180**	
X = N	3[c]
X = $^+$NH	2[c]
 **181**	
X = N	2[c]
X = $^+$NH	1.8[c]
 **182** $J_{6,7\alpha}$	1.5[d]
$J_{6,7\beta}$	<1[d]
 **183** $J_{2,4}$	
X = O	−2.20[19]
X = S	−2.24[19]

Structure	J_{allyl} Transoid	J_{allyl} Cisoid	Ref
 **184**			
X = O $J_{CH_3,H}$	0.8	0.4	*e*
X = S $J_{CH_3,H}$	0.84	0.6	*f*
 **185**			
X = N; R = H	−1.61	−1.61	*g*
X = O$^+$; R = H	−0.97	−0.88	*h*
X = O$^+$; R = Cl	−1.54	−1.09	*h*
 **186** J_{CH_3,H_1}		1.2	*i*
 **187** J_{CH_3,H_1}	<0.3		*i*
 **188**			
R = 9-anthryl		1.6	*j*
R = 1-naphthyl		1.6	*j*
R = Ph		1.7	*j*
		−1.6	21
		1.6	*k*
R = Me		1.60	*l*
		1.40	*m*
R = Et		1.57	*l*
R = ^{i}Pr		1.57	*l*
		1.6	*n*
 **189**			
R = 9-anthryl	2.2		*j*
R = 1-naphthyl	2.3		*j*
R = Ph	2.2		*j*
	1.9		*k*
 **190**			
R = Me, ^{n}Pr		1.3	*n*
R = Et, CH$_2$Ph		1.4	*n*
R = CH$_2$NMe$_2$, CH$_2$CF$_3$		1.3	*n*
R = C≡CH, CH$_2$CN		1.8	*n*
R = CH (OMe)$_2$, CH$_2$CH$_2$OMe		1.3	*n*

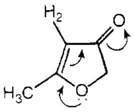
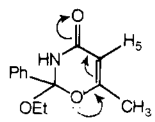
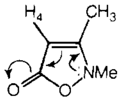
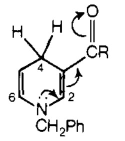
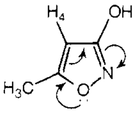
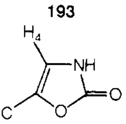
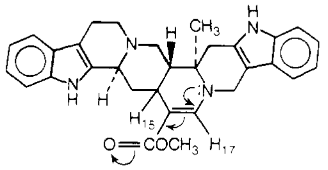
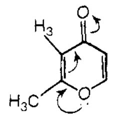
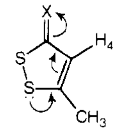
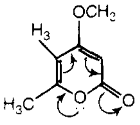
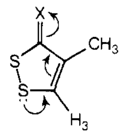
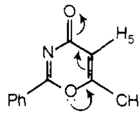
[a] The signs of the coupling constants are only shown when they have been determined, but they are most probably all negative. [b] N. J. Leonard and J. V. Paukstelis, *J. Org. Chem.*, **28**, 3021 (1963). [c] B. R. Lowry and A. C. Huitric, *ibid.*, **37**, 2697 (1972); [d] A. C. Huitric et al., *ibid.*, **40**, 965 (1975); Q. Khuong-Huu and A. Pancrazi, *Tetrahedron Lett.*, 37 (1971). [e] E. W. Randall and J. D. Baldeschwieter, *J. Mol. Spectrosc.*, **8**, 365 (1962). [f] L. Maier, *Helv. Chim. Acta*, **53**, 1216 (1970). [g] C. F. Chang, B. J. Fairless, M. R. Willcott, R. F. Curl Jr., J. Hinze, D. F. Koster, and A. Danti, *J. Mol. Spectrosc.*, **22**, 112 (1967). [h] A. M. White and G. A. Olah, *J. Am. Chem. Soc.*, **91**, 2943 (1969). [i] G. A. Olah, D. H. O'Brien, and M. Calin, *ibid.*, **89**, 3582 (1967). [j] H. J. C. Yeh, H. Ziffer, D. M. Jerina, and D. R. Boyd, *ibid.*, **95**, 2741 (1973). [k] G. A. Olah, and P. Kreienbühl, *ibid.*, **89**, 4756 (1967). [l] G. J. Karabatsos and S. S. Lande, *Tetrahedron*, **24**, 3907 (1968). [m] J. Meier, F. Akermann, and Hs. H. Günthard, *Helv. Chim. Acta*, **51**, 1686 (1968). [n] J. Hine and C. Y. Yeh, *J. Am. Chem. Soc.*, **89**, 2669 (1967); J. Hine, C. Y. Yeh, and F. C. Schmalstieg, *J. Org. Chem.*, **35**, 340 (1970).

the second. The "through the bond" contributions were presumed[41] to arise from a coupling path involving each and every bond linking the coupled nuclei. This corresponds to Hund coupling between each of the bonds,[44] and very small contributions from the higher order terms which were neglected in eq 8.

B. Sum over States Methods

A theoretical treatment of π-electron coupling in unsaturated molecules by Karplus,[45] which considered contributions to the second-order perturbation sum[32] from triplets formed by exciting individual σ and π bonds in the molecule, gave the result

TABLE IX. Allylic Coupling Constants across Partial Double Bonds

Structure	J_{allyl}[a]	Structure	J_{allyl}[a]
 191 $J_{\text{Me,H2}}$	0.8[b]	 198 $J_{\text{Me,H5}}$	0.9[f]
 192 $J_{\text{Me,H4}}$	0.8[c]	 199 R = NH_2; $J_{4,6}$ $J_{2,4}$ R = Me; $J_{4,6}$ $J_{2,4}$	1.6[g] 0[g] 1.6[g] 0[g]
 193 $J_{\text{Me,H4}}$	0.9[d]		
 194 $J_{\text{Me,H4}}$	1.5[d]	 200 $J_{15,17}$	0.6[h]
 195 $J_{\text{Me,H3}}$	0.8[e]	 201 X = O; $J_{\text{Me,H4}}$ X = S; $J_{\text{Me,H4}}$	1.08[i] 0.97[i]
 196 $J_{\text{Me,H3}}$	0.9[e]	 202 X = O; $J_{\text{Me,H3}}$ X = S; $J_{\text{Me,H3}}$	1.13[i] 0.92[i]
 197 $J_{\text{Me,H5}}$	0.8[f]		

[a] No sign determinations for these data are available, but it can be safely assumed that they are all negative. [b] A. Hofmann, W. v. Philipsborn, and G. H. Eugster, *Helv. Chim. Acta*, **48**, 1322 (1965). [c] A. R. Katritzky, S. Oksne, and A. J. Boulton, *Tetrahedron*, **18**, 777, (1962). [d] H. Göth, A. R. Gagneux, C. H. Eugster, and H. Schmid, *Helv. Chim. Acta*, **50**, 137 (1967). [e] P. Beak and H. Abelson, *J. Org. Chem.*, **27**, 3715 (1962). [f] T. Kato and Y. Yamamoto, *Chem. Pharm. Bull.*, **15**, 1334 (1967). [g] H. Diekmann, G. Englert, and H. Wallenfels, *Tetrahedron*, **20**, 281 (1964). [h] L. Merlini, R. Mondelli, G. Nasini, and M. Hesse, *ibid.*, **26**, 2259 (1970). [i] R. F. C. Brown, I. D. Rae, and S. Sternhell, *Aust. J. Chem.*, **18**, 1211 (1965).

$$J^{\pi}_{HH'} = h \sum_{\kappa} (2\Delta E_{\kappa}^{\pi})^{-1} a_H(\kappa) a_{H'}(\kappa) \qquad (12)$$

where the summation is over the π-electron triplets with excitation energies ΔE_{κ}^{π} and hyperfine coupling constants for the related radicals given by $a_H(\kappa)$ and $a_{H'}(\kappa)$. Although the original formulation of Karplus has undergone considerable revision and discussion,[46] the calculated results are in reasonable correspondence with the more sophisticated theoretical methods to be discussed below, so that eq 12 provides a reasonable starting point for the discussion of allylic coupling constants in section IV.

In the sum over virtual orbital scheme of Pople and Santry,[47] the spin-spin coupling function is proportional to the mutual atom-atom polarizability, $\pi_{hh'}$,

$$\mathcal{J}_{hh'} = -(1/2)\pi_{hh'} = -2 \sum_{i,j} [\epsilon_i - \epsilon_j]^{-1} c_{ih}c_{ih'}c_{jh}c_{jh'} \qquad (13)$$

where the summation is over the *i*th occupied and *j*th unoccupied MO's with energies ϵ_i and ϵ_j, respectively. Again, it should be noted that the neglect of the one-center exchange integrals in the MO scheme which leads to the coefficients and energies in eq 13 will preclude the possibility for certain types of π-electron contributions. In contrast to eq 3 the spin coupling function will not vanish for orbitals in the same subset of an even alternant. However, in this case the mutual atom-atom polarizabilities of simple Hückel theory are quite small.[48]

The original VB formulations were extended[49] to include an explicit sum over the VB triplet states in the second-order perturbation expression,

$$\mathcal{J}_{hh'} = \sum_{\kappa} [{}^3E_{\kappa} - {}^1E_0]^{-1} \sum_{jklm} (1/2)^{2n-i_{jl}-i_{km}} \times c_j c_{\kappa l} c_k c_{\kappa m} f^{h}_{jl} f^{h'}_{km} \qquad (14)$$

where the first summation is over the VB triplets with coefficients $c_{\kappa l}$ and energies ${}^3E_{\kappa}$. The coefficients c_j arise in the ground-state singlet wave function with energy ${}^1E_0$. The other terms in eq 14 are determined by the superposition diagrams of the singlet and triplet canonical structures as described in ref 49.

C. Finite Perturbation Methods

A very large number of calculations of nuclear spin-spin coupling constants have been performed by the finite perturbation theory (FPT) formulation,[50] especially within the semiempirical, intermediate neglect of differential overlap (INDO) approximation of unrestricted, self-consistent-field molecular orbital (SCF–MO) theory. The INDO method is an improvement over the complete neglect of differential overlap (CNDO) applied to coupling constants because of the inclusion of the one-center exchange integrals, which are important for inclusion of π-electron effects.

The spin coupling function in the FPT scheme[50] is given simply by[50]

$$\mathcal{J}_{hh'} = -(1/2)\rho_{h'}(B_H)/B_H \qquad (15)$$

where B_H is the magnitude of the perturbation of the electronic system at nucleus H due to the Fermi contact term

$$B_H = A_H/2$$

where A_H is given in eq 2. This term is added to the diagonal element corresponding to the orbital h in the Fock matrix for electrons of α spin, and subtracted from the corresponding diagonal element in the Fock matrix for electrons of β spin. This has the effect of producing unpaired spin density, $\rho = \rho^{\alpha} - \rho^{\beta}$ throughout the molecular electronic system. The spin coupling function in eq 15 is proportional to the spin density $\rho_{h'}$ in the orbital associated with proton H′.

In the FPT schemes it is usually difficult to sort out the various factors which give rise to the calculated coupling constants. One new method has been used to ascertain the relative importance of various coupling paths for interproton coupling over four bonds,[3] long-range H–F coupling constants,[51] and certain vicinal coupling constants.[52] In the INDO procedure[53] off-diagonal elements of the Fock matrices are given by

$$F^{\alpha}_{\mu\nu} = (1/2)(\beta_A{}^0 + \beta_B{}^0)S_{\mu\nu} - P^{\alpha}_{\mu\nu}\gamma_{AB} \qquad (16)$$

where $F^{\alpha}_{\mu\nu}$ is the off-diagonal element of the Fock matrix for electrons of α spin, $\beta_A{}^0$ and $\beta_B{}^0$ are empirical parameters for atoms A and B, $S_{\mu\nu}$ is the overlap integral between atomic orbitals μ and ν, $P^{\alpha}_{\mu\nu}$ is an element of the charge density-bond-order matrix for electrons of α spin, and γ_{AB} is approximated as a Coulomb integral involving valence shell s-type orbitals for atoms A and B. The expression for $F^{\beta}_{\mu\nu}$ is similar.[53] These elements will vanish if $S_{\mu\nu}$ and γ_{AB} are set equal to zero. Since $P^{\alpha}_{\mu\nu}$ is small unless μ and ν are centered on adjacent atoms, it was sufficient for most calculations simply to set the overlap integrals equal to zero. This has the effect of removing the interaction between certain pairs of orbitals as a possible coupling path. The results[3] of such a procedure are discussed in section IV to examine the problems of the mechanisms and conformational dependencies of σ-electron coupling over four bonds.

Although the INDO–FPT method will be used extensively in sections IV and V as a method of interpreting a variety of aspects of allylic coupling, it should not be inferred that there are not inherent inadequacies in the method. Indeed, as a consequence of some of the very careful experimental work on allylic coupling constants, some of the difficulties with this computational scheme have become apparent and will be briefly discussed in section IV.

D. Other Theoretical Methods

Ab initio methods applied to molecules with more than a few electrons have been generally unsuccessful for quantitative studies of spin–spin coupling constants.[54,55] The obvious extension to multiconfiguration calculations with extended basis sets will certainly be performed, but will be limited in applicability because of the computational expense associated with the chemically interesting problems of conformational and substituent dependencies in moderately complicated molecules.

Because of the disparities between existing theoretical formulations and recent experimental data for coupling over four bonds involving a methyl group, and for certain conformations associated with allylic coupling, the theoretical basis for discussing these various types of long-range H–H coupling have been reexamined.[3] The theoretical development follows in part from the suggestion of Hiroike,[56] who used double perturbation theory in suggesting that the results from eq 6 and 13 represent mutually exclusive contributions, and correspond to successive terms in a more general expansion of the coupling constant expression. The summing of the results of independent MO and VB formulations may seem, at first, to be heretical. However, a plausible justification can be given on the basis of the relationship of nuclear spin–spin coupling constants to ESR hyperfine coupling constants (e.g., eq 5, 12, or the unpaired spin density in eq 15).

From a large number of studies it has been found to be convenient to discuss unpaired spin densities and the related ESR hyperfine coupling constants in terms of *spin polarization* and *electron transfer* mechanisms.[57] Valence-bond theories without ionic structures only give spin polarization effects associated with the one- and two-center, two-electron exchange integrals, and electron-transfer mechanisms are entirely absent. At the other extreme, simple Hückel MO theory, which does not include exchange integrals, gives rise to electron transfer mechanisms to the total exclusion of spin polarization mechanisms![57] As a consequence, the method which was developed in ref 3 and applied to the problem of H–H coupling over four bonds, used the sum of the results from eq 13 and 14. The calculated results for coupling over four bonds in propanic and allylic systems were in substantially better agreement with the experimental data than either of the separate results.

A generalization[58] of many of the theories of nuclear spin–spin coupling, based on the second-order perturbation theory, used a density matrix notation and the group function formulation of McWeeny.[58] A similar treatment by van der Hart led to a simple expression for the π-electron contribution to H–H coupling,[58]

$$J^{\pi}{}_{HH'} = (1/4)a_H a_{H'}\pi_{pp'}\beta'^{-1} \qquad (17)$$

where $\pi_{pp'}$ is the mutual atom–atom polarizability (in units of β'^{-1}) associated with the 2p atomic orbitals p and p', and β' is the usual resonance integral of simple Hückel MO theory.

IV. Conformational and Structural Changes

A. Mechanisms of Allylic Coupling

A separation of the contributions to cisoid and transoid allylic coupling constants into σ- and π-electron parts provides a useful basis for understanding the conformational dependencies. For example, the frequent observation of $J_{trd} > J_{csd}$ in propenes can easily be seen to arise from a nonnegligible positive σ-electron contribution, $J^{\sigma}{}_{trd} > J^{\sigma}{}_{csd}$, superimposed on a negative π-electron contribution, $J^{\pi}{}_{csd} = J^{\pi}{}_{trd}$.

1. π-Electron Contributions

Allylic interproton coupling was described theoretically by means of eq 12, which related the π-electron contribution ${}^4J^{\pi}{}_{HH'}$ to ESR hyperfine coupling constants for the $\dot{C}$–H and $\dot{C}$–C–H radicals ($a_H = -65 \times 10^6$ Hz and $a_{H'} = 150 \times 10^6 \sin^2 \phi$ Hz, respectively). Assuming that $\Delta E^{\pi} = 6.0$ eV, it follows from eq 12 that the π-electron contribution to the allylic coupling is given by[45]

$${}^4J^{\pi}{}_{HH'}(\phi) = -3.36 \sin^2 \phi \text{ Hz} \qquad (18)$$

where the dihedral angle ϕ is measured from the C_1–C_2–C_3 plane as depicted in Figure 3. For the case of allylic coupling in propene it is necessary to average over the barrier hindering internal rotation, $V(\phi)$,

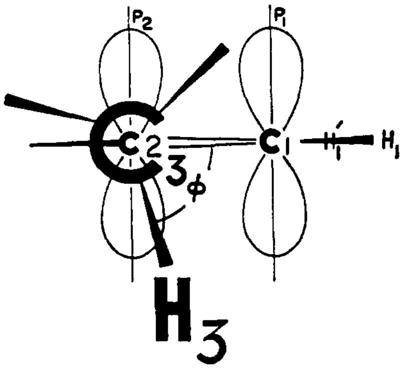


Figure 3. Specification of the dihedral angle ϕ in propene. The C-3 carbon atom eclipses the C-2 carbon atom, and the cisoid proton H_1 eclipses the transoid proton H_1'. The figure was taken from ref 3.

$$\langle {}^4J_{HH'}\rangle = \frac{\int_0^{2\pi} {}^4J_{HH'}(\phi)e^{-V(\phi)/kT}\,d\phi}{\int_0^{2\pi} e^{-V(\phi)/kT}\,d\phi} \qquad (19)$$

In the case of free rotation of the methyl, V would be a constant independent of ϕ, so that the exponentials can be taken outside the integrals and cancelled in numerator and denominator. Thus,

$$\langle {}^4J^{\pi}{}_{HH'}\rangle = -3.36\ \langle \sin^2\phi\rangle = -1.68\ \text{Hz}$$

is seen to fall between the experimental values of −1.33 and −1.75 Hz for the transoid and cisoid allylic coupling constants, respectively, in propene **138**. An alternative assumption is that the methyl group will rapidly interconvert between those rotamer conformations in which one of the hydrogens eclipses the double bond in Figure 3.[59] This would correspond to $V(\phi) = 0$ for $\phi = 0°, 120°$, and $240°$, and $V(\phi) \rightarrow \infty$ for all other ϕ; hence eq 19 gives the result

$$\langle {}^4J_{HH'}\rangle = (1/3)[{}^4J_{HH'}(0°) + {}^4J_{HH'}(120°) + {}^4J_{HH'}(240°)] \qquad (20)$$

Substitution of the numerical results from eq 18 into eq 20 gives the same result as the free rotation model, i.e., $\langle {}^4J^{\pi}{}_{HH'}\rangle = -1.68$ Hz. It is interesting to note (see below) that numerical integration of eq 19 with theoretical values for $V(\phi)$ gives results that differ from those obtained from eq 20 by no more than 0.02 Hz.

By 1964 it was clear[1,4,5] that the general features of allylic coupling in cyclic and acyclic molecules could be described by means of the $\sin^2\phi$ dependence of the π-electron contribution, but that σ-electron contributions would also be important, especially near the planar conformations ($\phi = 0$ and $180°$).

The assumptions which led to eq 12 are closely related to VB methods in which one considers that the various triplets can be formed by exciting localized bonds in the molecule to triplets. This approach leads directly to eq 6, which in conjunction with eq 8–11, provides an excellent qualitative model for discussing allylic coupling. Consider the six electron fragment of the propene molecule depicted in Figure 4. The indirect, π-electron contributions will arise from the second term in eq 8, so if we set $t_j = p$ and $t_j' = p'$, the π-electron contribution to the spin coupling function follows from eq 6:

$$\mathcal{J}^{\pi}{}_{hh'} = -3(2\Delta E)^{-1} \times \left[\frac{K(h,p) + K(c,p') - K(h,p') - K(c,p)}{2K(h,c) + 2K(p,p')}\right] \times \left[\frac{K(h',p') + K(c',p) - K(h',p) - K(c',p')}{2K(h',c') + 2K(p,p')}\right] \qquad (21)$$

The exchange integrals in eq 21, which are assumed to be nonvanishing are given in Table X. The first term in brackets in eq 21, which is dominated by the exchange integral, $K(c,p)$, is proportional to the hyperfine coupling constant for the $\dot{C}$–C–H radical and has a $\sin^2\phi$ dependence on dihedral angle. The second term in brackets in eq 21, which is proportional to the hyperfine coupling constant in the $\dot{C}$–H radical, corresponds to the difference in the exchange integrals $K(h',p')$ and $K(c',p')$. The two terms in brackets correspond to two types of spin polarization, and do not imply any type of electron-transfer mechanisms.

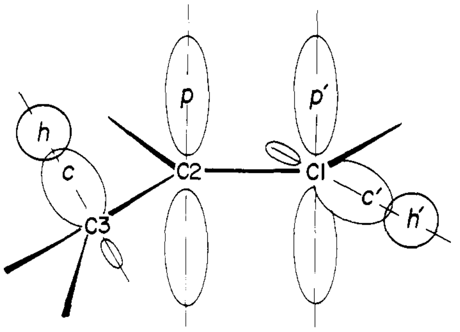


Figure 4. Labeling of the atomic and hybrid orbitals in an eight-electron fragment of the propene molecule. The three bonds are c–h, p–p', and c'–h'.

TABLE X. One- and Two-Center Exchange Integrals Used in the VB Calculations of the π-Electron Contribution to Allylic Coupling[a]

$K(c,h) = -3.80$ eV	$K(c',p') = 1.26$ eV
$K(c',h') = -3.916$	$K(p,p') = -2.256$
$K(h',p') = 0.792$	$K(c,p) = -0.52 \sin^2\phi$

[a] These integrals were compiled from sources quoted in ref 49 and were used to calculate long-range coupling constants in a variety of compounds. See Figure 4 for the specification of orbitals.

TABLE XI. Calculated VB Results for the π-Electron Contributions to the Allylic Coupling in the Six Orbital Fragment Depicted in Figure 4[a]

${}^3E_{\kappa} - {}^1E_0$, eV	${}^4J_{HH'}(\kappa)$,[b] Hz
4.48	−7.63
7.49	50.06
7.61	−45.76
11.91	0.03
13.72	−0.05
15.19–22.16	0.00
	${}^4J_{HH'}{}^{\pi} = -3.35$ Hz

[a] Reference 49. Calculated results obtained from eq 1 and 14 with wave functions based on the exchange integrals given in Table X.
[b] Individual contributions from the nine terms corresponding to the nine triplets for a six-electron fragment.

Assuming a value of 9.0 eV for ΔE and the exchange integrals from Table X, eq 21 leads to a calculated value of the π-electron contribution to the allylic coupling constant which is just about one-third of that given in eq 18. This inadequacy is due to the localized triplet assumption, which is implicit in the derivation of eq 6. The effects of triplet delocalization can be introduced by explicitly calculating the VB triplet-state wave functions and energies and using eq 14 to obtain the coupling constant.[49] This was done for the six-electron allylic fragment in Figure 4 with the same exchange integrals [$K(c,p) = -0.52$ eV from Table X, corresponding to $\phi = 90°$]. Entered in Table XI are the calculated ground to triplet-state energies, ${}^3E_{\kappa} - {}^1E_0$, and the contribution, ${}^4J_{HH'}(\kappa)$, of each of the nine VB triplets to the total coupling constant. The total of −3.35 Hz in Table XI is almost identical with the value from eq 18. Although some rather severe approximations were used in obtaining the latter equation, the more sophisticated VB technique vindicates the results for π-electron coupling.

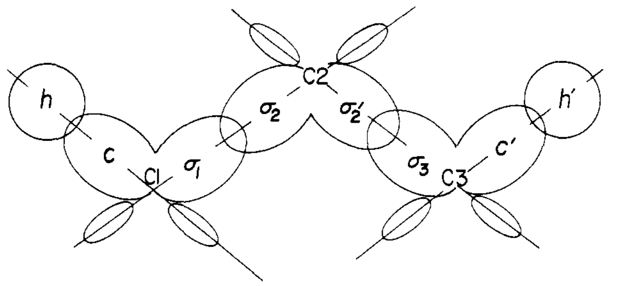


Figure 5. Labeling of the orbitals in a propanic fragment or the σ-electron framework of a propenic fragment.

2. *σ-Electron Contributions*

Previous theoretical discussions[1-3,7] of σ-electron contributions to allylic coupling have been preceded by a discussion of $^4J_{HH'}$ in saturated systems (propanic coupling) because it has been assumed that the same kind of mechanisms (with some minor effects due to differing numbers of hydrogens at the C-1 and C-2 carbon atoms) would be present in both systems. Since the major difficulties with theoretical discussions of the conformational dependence of allylic coupling are due to problems associated with σ-electron coupling in saturated systems, it is conceptually useful to review some of the important features of this type of coupling.

Before any calculations were attempted, it was proposed[60] on empirical grounds that the long-range H-H coupling constants observed for the "W" arrangement of the bonds in certain bicyclic molecules were due to the overlap of the "rear lobes" of the carbon hybrid orbitals directed toward the coupled protons. This arrangement is depicted in Figure 5 for an eight orbital fragment. In terms of the more recent formulation[41] in terms of fragment bond orders, this suggestion implies a direct coupling mechanism associated with the first term on the right in eq 8. If the overlap integral between the rear lobes of the hybrid orbitals c and c' in Figure 5 is not negligible in this conformation, then the exchange integral $K(c,c')$ in the numerator of eq 9 would be nonnegligible, and probably negative in sign. It would, therefore, follow from eq 1, 6, and 8 that the coupling in this conformation would be positive in sign (the denominator of eq 9 is also negative).

In one of the first studies of σ-electron coupling between protons separated by four bonds, it was assumed that the stereoselectivity could be due to a variety of indirect mechanisms associated with the terms under the summation sign in eq 8. For example, one such coupling path would be associated with the product of the vicinal bond order, $p^0(h,\sigma_2')$, and the geminal bond order, $p(\sigma_2',h')$, where the orbitals are labeled as in Figure 5. The first of these bond orders has a dependence on dihedral angle given by[41]

$$p^0(h,\sigma_2') = A\cos^2\phi + B\cos\phi + C, \qquad |A| \gg |B|, |C|$$

by analogy to the vicinal H-H coupling,[41,61] where ϕ is the dihedral angle measured about the C1-C2 bond, and the second (geminal) bond order will be independent of dihedral angle. The vicinal bond order, $p^0(h,\sigma_2')$, and, therefore, the indirect contribution to $^4J_{HH'}$ will have their maximum magnitudes for the conformation in which $\phi = 180°$ in Figure 5, and it will decrease to nearly zero as $\phi \rightarrow 90°$. There would be another completely analogous indirect term in eq 8 associated with the vicinal bond order $p^0(\sigma_2,h')$, which would depend on the dihedral angle ϕ' measured about the C2-C3 bond in Figure 5. This would also lead to maximum magnitude of coupling in the "W" arrangement. It now appears (see below) that contributions from these two coupling paths are probably small and negative in sign. There would be several other terms in the summation of eq 8 due to coupling paths associated with other bonds in the molecule, but these should make even smaller contributions to $^4J_{HH'}$. Thus, in 1964 the hypothesis that the σ-electron coupling proceeded by a variety of indirect mechanisms seemed reasonable, and in conformity with the available experimental data.[41]

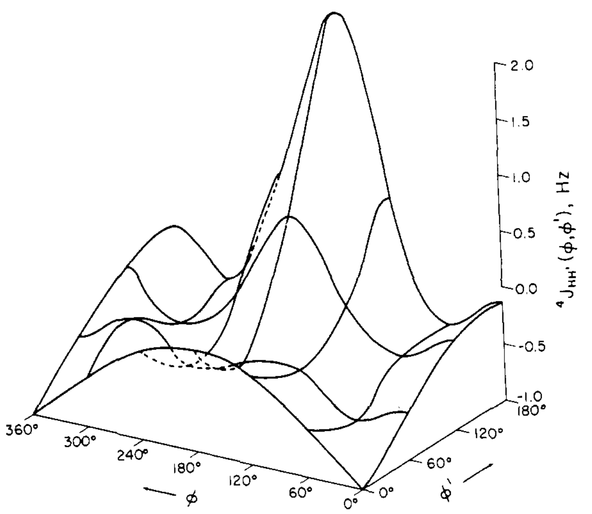


Figure 6. Calculated INDO-FPT results for coupling over four single bonds in propane as a function of the dihedral angles ϕ and ϕ', which are measured about the C1-C2 and C2-C3 bonds, respectively. At a very crude level, it is suggested that the σ-electron contributions to the $^4J_{csd}$ and $^4J_{trd}$ correspond to the front "face" and back "face" of the surface, i.e., $\phi' = 0$ and 180°, respectively. This figure was taken from ref 3.

In an attempt to approach the problem of long-range σ-electron coupling from a different viewpoint, all-valence electron calculations for propane and propene were performed[2] by means of the INDO-FPT molecular orbital formulation.[50] The calculated results for $^4J_{HH'}$ in propane are plotted in Figure 6 as a function of the dihedral angles ϕ and ϕ'. To the extent that any of the previously discussed σ-electron mechanisms are the important ones, then the σ-electron coupling in propene should be of the same type as that in propane. If this is the case, then the σ-electron contributions to the cisoid and transoid allylic coupling constants correspond to the curves on the front and rear "faces", respectively of the surface, i.e., the plots obtained on passing planes through the surface at $\phi' = 0$ and 180°, respectively. The maximum positive coupling occurs for $\phi = 180°$, which would correspond to $^4J^{\sigma}_{trd}(180°)$, which is consistent with the experimental results. On the other hand, one would infer from Figure 6 that $^4J^{\sigma}_{csd}$ would become more negative as ϕ ranges from 180 to 0°. Recent experimental and theoretical results[3] suggest that the minimum of -1 Hz is too steep and indicative of inadequacies in the INDO-FPT method applied to this type of coupling.

In an attempt to sort out the factors responsible for $^4J^{\sigma}_{HH'}$ (see section III.C), overlap integrals in eq 16 between valence atomic orbitals on the C-1 and C-3 carbon atoms of propane were set equal to zero.[3] The calculated values of $^4J_{HH'}$ in propane decreased from $+2.09$ to -0.60 Hz for $\phi = \phi' = 180°$, and increased from -1.06 to $+1.09$ Hz for $\phi = \phi' = 0°$. Since the changes in the values of $^4J_{HH'}$ were smaller than these for the out-of-plane conformations,[3] it must be concluded that direct interactions, associated with the carbon hybrid orbitals, make substantial contributions to $^4J_{HH'}$, not only for the "W" conformation, in accordance with the original suggestion,[60] but for the other possible planar conformations. It is particularly interesting that the direct interaction is predicted to be negative for proximate orientations of the coupled protons as this was suggested in the initial investigation.[1]

B. Conformational Dependencies of Cisoid and Transoid Allylic Coupling Constants

Previously reported[2,3] INDO-FPT results for transoid and cisoid allylic coupling constants are given at 15° intervals of the

TABLE XII. Calculated Values of the Transoid Allylic Coupling Constants (Hz) in Propene at 15° Intervals of the Dihedral Angle ϕ^a

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

^{a}This table was taken from ref 3.

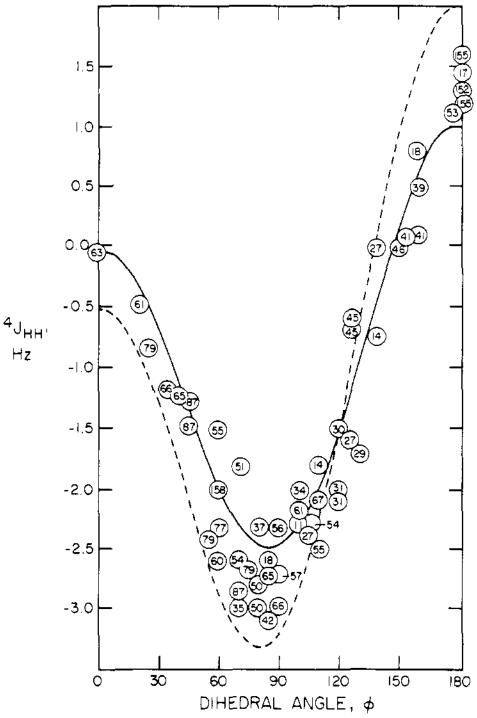


Figure 7. Comparison of calculated and experimental transoid allylic coupling constants as a function of the dihedral angle ϕ. The solid curve is based on the sum of the EHMO and VB–SOT treatments and the dashed curve corresponds to the INDO–FPT treatment (see text). The circles represent experimental data, the numbers referring to formula numbers.

dihedral angle ϕ in column A of Tables XII and XIII, respectively. These results are also plotted (dashed lines) as functions of ϕ in Figures 7 and 8. Considering the spread in the experimental data, which were taken from the appropriate tables and represented by circles (taken to be somewhat indicative of the experimental error in the measured coupling constant and an excessively optimistic estimate of the error in the dihedral angle), the agreement is reasonable for $^4J_{trd}$ in Figure 7. If one were to hope that the calculated values were to constitute some sort of "best-fit", then it would be necessary to suggest that the calculated values for $^4J_{trd}$ are about 0.5 Hz too low in the region 0–90° and about 1 Hz too high near ϕ = 180°. The calculated INDO–FPT results for $^4J_{csd}$ in Figure 8 are uniformly too low in comparison with the experimental results.

TABLE XIII. Calculated Values of the Cisoid Allylic Coupling Constants (Hz) in Propane at 15° Intervals of the Dihedral Angle ϕ^a

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

^{a}This table was taken from ref 3.

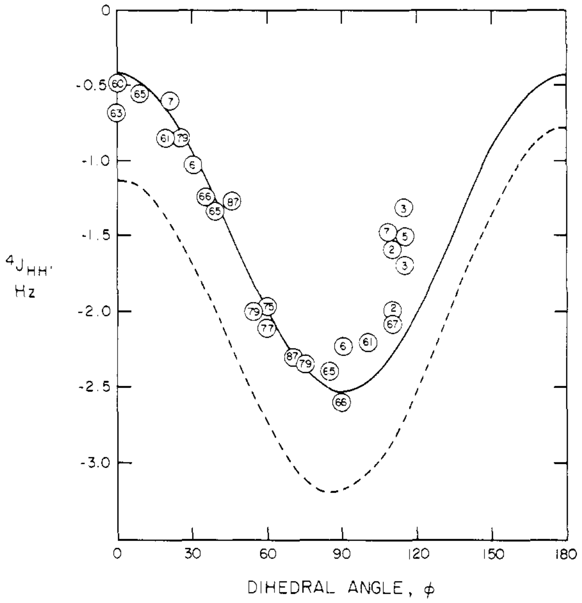


Figure 8. Comparison of calculated and experimental cisoid allylic coupling constants as a function of the dihedral angle ϕ. The solid curve is based on the sum of the EHMO and VB–SOT treatments and the dashed curve corresponds to the INDO–FPT treatment (see text). The circles represent experimental data, the numbers referring to formula numbers.

There are a variety of reasons that could be proposed for inadequacies of the INDO–FPT results in Figures 7 and 8. For example, it could be argued with considerable justification that the calculated results are based on the unsubstituted propene molecule, whereas the experimental data in the two figures must conform to at least one carbon substituent at C-1 and/or a carbon bonded to C-2 or C-3 to form some type of cyclic structure for which an estimate of the dihedral angle may be inferred. For the case of the propene molecule itself, the methyl group will undergo hindered rotation. From the results of Tables XII and XIII and the assumption of a simple average over the 0, 120, and 240° values in eq 20, calculated $\langle ^4J_{trd} \rangle$ and $\langle ^4J_{csd} \rangle$ are −1.20 and −2.05 Hz, respectively. These may be compared with the experimental values of −1.33 and −1.75 Hz for the respective coupling constants from Table VI. Numerical integration of eq

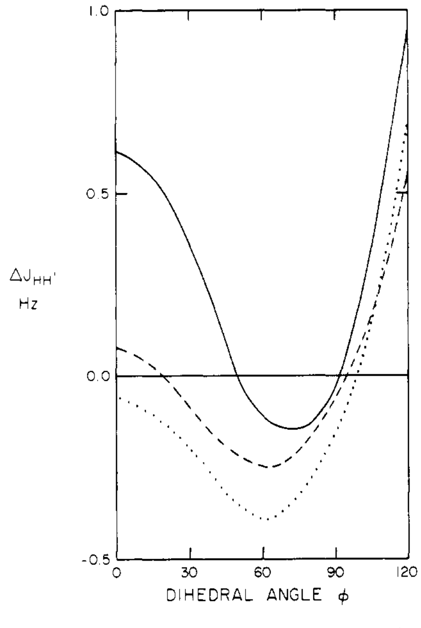


Figure 9. A plot of the differences in the INDO-FPT results for $^4J_{trd}$ and $^4J_{csd}$, $\Delta J_{HH'} = {}^4J_{trd} - {}^4J_{csd}$ as a function of the dihedral angle ϕ in the range 0 to 120° for propene (solid line), isobutylene (dotted line), and *cis*- and *trans*-2-butenes (dashed line). The "crossover" range occurs on the line for $\Delta J_{HH'} = 0$.

19 with the calculated coupling constant data in Tables XII and XIII and the corresponding energies from the INDO calculations yields −1.18 Hz and −2.04 Hz for the transoid and cisoid coupling constants in propene. The underestimation of the cisoid coupling is to be expected since the total INDO-FPT curve in Figure 8 is about 0.5 Hz too low in comparison with the experimental values.

Another very obvious source of disparity between calculated and experimental results in Figures 7 and 8 is that the geometry assumed for propene[2] was based on representative bond angles and bond lengths from representative unstrained and unsubstituted molecules. The implications of the effects of changes in geometry and substituents on the calculated INDO-FPT results will be discussed in detail in subsequent sections.

Other factors which could account for nonconformities of calculated and experimental results are inherent inadequacies of the INDO-FPT scheme, although the method gives remarkably good results for a large variety of long-range interproton coupling constants.[62] An alternative approach, which was developed in ref 3, makes use of the fact that simple MO and VB descriptions give rise to mutually exclusive contributions (section III.D). Not only does this procedure give improved agreement with the experimental results in Figures 7 and 8, it provides a more intuitive basis for interpreting the factors controlling allylic coupling constants.

Calculated values of $^4J_{trd}$ and $^4J_{csd}$ were based on all-valence-electron Hückel-type (HMO) calculations. These results are entered in Tables XII and XIII (column B) at 15° intervals of the dihedral angle ϕ. Spin polarization mechanisms, which would be associated with one- and two-center exchange integrals, are not implicit in simple MO calculations of this type. As a consequence, the substantial, negative π-electron contributions, which dominate the allylic coupling constants, do not occur, so that the MO results in column B are indicative of the stereoselectivity of the σ-electron contributions to the allylic coupling constants. It is interesting to note that nonnegligible values for these contributions seem to be confined to transoid coupling constants with maxima near 0 and 180°.

The VB results for $^4J_{trd}$ and $^4J_{csd}$ were based on eq 14 and a group-function formulation[58] for a ten-electron fragment of the propene molecule. These results are entered in column C of Tables XII and XIII at 15° intervals of the dihedral angle ϕ, and the effects of including the σ-π exchange integrals are now apparent. However, these results are based on the usual VB assumption of the neglect of non-next-nearest neighbor exchange integrals, so that any type of direct spin polarization mechanism, i.e., that which would correspond to the first term on the right in eq 8, are, therefore, entirely absent from the summed results in column D of the two tables. This is certainly the major inadequacy with this technique.

The sum of the HMO results from column B and the VB-SOT results from column C are given for the various values of the dihedral angles in column D of the two tables. These are also plotted (solid lines) in Figures 7 and 8. The agreement with the experimental data is substantially better, especially for the cisoid allylic coupling constants for which most of the experimental circles for dihedral angles less than about 90° fall on the calculated curve. For angles greater than 90°, the experimental circles are further away from the calculated curve in Figure 8. However, for a number of examples (**2**, **3**, **5**, and **6**), the allylic coupling constants would be expected to be more positive as the π-bond order of the double bond will decrease to some extent because of delocalization effects associated with the adjacent carbonyl. The maximum effect may be inferred from a consideration of the bond order dependence of the allylic coupling constants.[22-25] On increasing the π-bond order from about 0.9 (as in butadiene, for example) to unity (as in propene), the cisoid allylic coupling constant (averaged over the three orientations as in eq 20) becomes more negative by 0.2 to 0.3 Hz. This would have the effect of bringing the experimental circles in Figure 8 somewhat closer to the calculated curve, although there are too many variables to estimate this with any degree of precision. Experimental cisoid allylic coupling constant data for dihedral angles near 180° would be of interest for completing the conformational dependence, but there appear to be no compounds with $^4J_{csd}$ having dihedral angle greater than about 120°. These would pose challenging synthetic problems.

Transoid and cisoid allylic coupling constants for propene based on the sum of the HMO and VB-SOT results in column D of Tables XII and XIII and eq 20 are −0.98 and −1.47 Hz,[3] to be compared with the experimental values of −1.33 and −1.75 Hz, respectively. The further shift of $\langle {}^4J_{trd} \rangle$ to more positive values is associated with the upward shift of the curve for angles near 0° in Figure 7, whereas the increase in the cisoid value is due to the very reasonable shift of the entire curve in Figure 8 to higher values. It is interesting to note that the disparity between the calculated and experimental results for propene follows not only from the calculated results, but also if the values in eq 20 are experimental ones for the appropriate dihedral angles. However, there is roughly an 0.5-Hz range in the experimental values for ϕ = 120° in Figures 7 and 8, which would correspond to a ca. 0.3-Hz range in the calculated allylic coupling constants for propene from eq 20.

C. Relative Magnitudes of Cisoid and Transoid Allylic Coupling Constants

From a consideration of the experimental data in section II.B, Table III, and Figure 1, it was concluded that there must be a "crossover point" for which $^4J_{csd}$ is greater than $^4J_{trd}$. One such point was shown to be near ϕ = 42° with an allylic coupling constant of about −1.2 Hz. Since both curves follow a trigonometric dependence on dihedral angle in this region, and because $^4J_{trd}$ approaches a value of 2 Hz as ϕ approaches 180°, a second "crossover point" is expected at an angle greater than 90°. This feature is exhibited in the calculated INDO-FPT data, but not by the earlier VB results.[1] The difference in the INDO-FPT results for $^4J_{trd}$ and $^4J_{csd}$, $\Delta J_{HH'} = {}^4J_{trd} - {}^4J_{csd}$, is plotted (solid line) in Figure 9 as a function of the dihedral angle in the range 0 to 120°. It is interesting to note that $\Delta J_{HH'}$ does, indeed, become negative in the range from about 50 to 90°, but the

TABLE XIV. Calculated INDO–FPT Results for Transoid and Cisoid Allylic Coupling Constants in Isobutylene[a]

Dihedral angle, ϕ, deg	$^4J_{\mathrm{trd}}$, Hz	$^4J_{\mathrm{csd}}$, Hz
0	−0.64	−0.59
30	−1.31	−1.13
60	−2.64	−2.25
90	−2.96	−2.80
120	−1.48	−2.23
150	0.66	−1.14
180	1.67	−0.60

[a] The position of the second methyl was fixed at dihedral angles of 60, 180, and 300°, while the first methyl was rotated. Trigonal and tetrahedral bond angles were used and r(C═C) = 1.337 Å, r(═C–H) = 1.08 Å, r(–C–H) = 1.09 Å. In contrast to the propene geometry [r(═C–C) = 1.51 Å], the normal C–C single bond length of 1.54 Å was assumed in conformity with the authors' previous calculations for 2-butenes.[62]

TABLE XV. Calculated INDO-FPT Results for Transoid and Cisoid Allylic Coupling Constants in *cis*- and *trans*-2-Butene[a]

Dihedral angle, ϕ, deg	$^4J_{\mathrm{trd}}$, Hz		$^4J_{\mathrm{csd}}$, Hz
	b	*c*	*b*
0	−0.94	−1.14	−1.02
30	−1.51	−1.64	−1.47
60	−2.55	−2.55	−2.25
90	−2.75	−2.74	−2.70
120	−1.50	−1.68	−2.06
150	0.22	−0.23	−1.14
180	1.07	0.49	−0.65

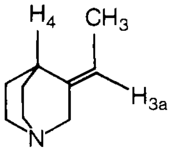
[a] The second methyl group was fixed in the position ϕ' = 0, 120, and 240°. [b] Tetrahedral and trigonal bond angles were assumed, r (C═C) = 1.337, r(C—C) = 1.54, r (═C—H) = 1.08, r(—C—H) = 1.09 Å. [c] The C═C—C bond angle was increased from 120 to 126.7°, and the C═C—H bond angle was decreased from 120 to 117.3°.[67]

greatest magnitude of the effect is only 0.15 Hz. The "crossover" in the summed results from Tables XII and XIII falls in about the same range of dihedral angles, but is of even smaller magnitude.

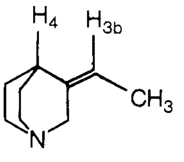
Since all of the compounds, for which experimental data are plotted in Figure 1, correspond to exocyclic methylene groups, it is possible that isobutylene would constitute a better theoretical model for investigating "crossover" effects. Accordingly, the calculated cisoid and transoid allylic coupling constants in isobutylene are given at 30° intervals of the dihedral angle in Table XIV.[63] The corresponding values of $\Delta J_{\mathrm{HH'}}$ are plotted (dotted line) in Figure 9 as a function of the dihedral angle ϕ. Because of the reversal in the relative magnitudes of the transoid and cisoid coupling constants for isobutylene at $\phi = 0°$, the first crossover point does not appear at all in Figure 9. Therefore, on the basis of these calculated results (and others to be discussed below), it appears that $^4J_{\mathrm{trd}}$ can be less than $^4J_{\mathrm{csd}}$ for all angles below the "second" crossover point; i.e., depending on structural, substituent, or other factors, the first crossover point does not occur.

The situation with regard to pairs of *E* and *Z* isomers presents additional difficulties because of different geometrical factors that are apt to occur in the two isomers. In these cases reversals in the relative magnitudes of the $^4J_{\mathrm{trd}}$ and $^4J_{\mathrm{csd}}$ are not uncommon. For example, in the series of *E* and *Z* isomer pairs **171** and **172**, $^4J_{\mathrm{trd}} = -1.71$ to -1.81 Hz, and $^4J_{\mathrm{csd}} = -1.35$ to -1.50 Hz.[8] However, in the unsubstituted compound **70** the respective values are −1.30 and −1.72 Hz. In the interconverting conformers with dihedral angles near −20 and 100°, values from the solid lines in Figures 7 and 8 suggest that the respective averages would be about −1.3 and −1.6 Hz, which are in reasonable agreement with the experimental values in the six-membered rings. These results may be contrasted with those for the *E*- and *Z*-isomer pairs **165** and **166** in which a five-membered ring is involved. In these cases no reversal is noted in the relative magnitudes of $^4J_{\mathrm{trd}}$ and $^4J_{\mathrm{csd}}$ compared with the parent compound **78** with $^4J_{\mathrm{trd}} = -2.21$ Hz and $^4J_{\mathrm{csd}} = -1.86$ Hz.

In the original study[64] of the *E* and *Z* isomers **203** and **204** it



203



204

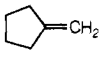
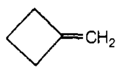
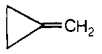
was reported that $J_{3,4}$ (*E* isomer) = 0.4 Hz, and that the corresponding cisoid coupling in the *Z* isomer was zero. More recent experimental study[18] has shown that the respective values are 0.76 and 0.47 Hz. The $^4J_{\mathrm{csd}}$ value for the *Z* isomer is close to the "normal" value for a cisoid coupling with a dihedral angle near 0° in Figure 8. However, for the same dihedral angle, the $^4J_{\mathrm{trd}}$ for the *E* isomer has a larger (presumably, more negative) value than would be inferred from Figure 7. However, it is known[64] that the *E* isomer is strained and readily converts to the more stable *Z* isomer under various conditions.

A number of examples are known[14,65] (see Table VI) of di- and trisubstituted ethylenes in which the relative magnitudes are reversed from the usual trend in the propene series. For example, the experimental values of $^4J_{\mathrm{trd}}$ and $^4J_{\mathrm{csd}}$ in *cis*- and *trans*-2-butenes are −1.85 and −1.72 Hz, respectively.[65] The calculated INDO–FPT results[66] for these two types of coupling are given at 30° intervals of the dihedral angle in Table XV. Note that the calculated value of $^4J_{\mathrm{trd}}$ for $\phi = 20°$ is about 0.5 Hz less than the INDO–FPT result for propene in Table XII. In addition, the differences in the calculated values of $^4J_{\mathrm{trd}}$ and $^4J_{\mathrm{csd}}$ from Table XV are plotted (dashed line) as a function of ϕ in Figure 9. A crossover point is indicated for a dihedral angle near 20°. The calculated values of the coupling constants from the data in Table XV and eq 20 are $\langle ^4J_{\mathrm{trd}} \rangle = -1.33$ Hz and $\langle ^4J_{\mathrm{csd}} \rangle = -1.71$ Hz for *cis*- and *trans*-2-butene, respectively. Although the first of these is rather far off, the second is not only in good agreement with the experimental value for *trans*-2-butene, but for propene (−1.75 Hz), as well.

It has been argued[14,65] that the steric interaction between the methyl groups of *cis*-2-butene would produce increases in the C═C—C angles and decreases in the C═C—H angles, which would (by analogy to vicinal H-H coupling constants) produce more negative contributions to $^4J_{\mathrm{trd}}$. Calculated INDO-FPT results[63] for *cis*-2-butene, which were based on bond angles from the microwave data,[67] are entered in Table XV at 30° intervals of the dihedral angle ϕ. As predicted,[65] the $^4J_{\mathrm{trd}}$ decrease, but only by about 0.2 Hz at 0 and 120° in these calculations. Therefore, the inclusion of the effects of the opening out of the C═C—C bond angles in the calculations decreases the calculated $^4J_{\mathrm{trd}}$ in *cis*-2-butene by only −0.17 Hz (to −1.50 Hz), and still does not reproduce the reversal in the relative magnitudes of $^4J_{\mathrm{trd}}$ and $^4J_{\mathrm{csd}}$. A number of factors could be involved here, such as the bending of the cone of the methyl hydrogens away from the C-C axis, an increase in the C═C bond length, and contributions from the methyl group rotamers other than those for 0, 120, and 240° in eq 20.

It is interesting to note in Table XV that the effect of increasing the C═C—C angles and decreasing the C═C—H angles has the major effect of decreasing the positive, transoid coupling at $\phi = 180°$ by more than a factor of 2. This is consistent with previous observations[3,51] of the extreme sensitivity of long-range coupling to bond orientation and proximity effects.

TABLE XVI. Calculated INDO–FPT Results for $^4J_{\mathrm{trd}}$ and $^4J_{\mathrm{csd}}$ in Methylene Cycloalkanes Compared with Representative Experimental Data from Table III

	$^4J_{\mathrm{trd}}$, Hz		$^4J_{\mathrm{csd}}$, Hz	
Compound	Calcd	Exptl	Calcd	Exptl
	−2.82	−2.32 (77)	−2.43	−2.12 (77)
	−2.17	−2.45 (88) −2.65	−1.61	−1.97 (88) −2.16
	−1.77	−2.55 (94)	−1.20	−1.79 (94)

D. Effects of Ring Size

In the case of allylic coupling involving endocyclic double bonds, there are almost certainly substantial ring size effects. For example, the discussion of the previous section showed that increasing the C═C—C angles has the effect of decreasing the transoid allylic coupling constants. It is reasonable to assume that decreasing these angles would have just the opposite effect. Unfortunately, in actual systems it is exceedingly difficult to find examples in which some other effect is not simultaneously involved; rings with more than six atoms will pucker, and with less than six atoms additional coupling paths become available. For example, there is a large amount of coupling constant data for cyclobutenes in Table IV, but in these cases there are two possible paths so that the situation is much more complex. The experimental data in Table IV suggest that endocyclic allylic coupling constants are small in those cases in which they are observed. A consideration of the factors involved in the σ-electron coupling path would suggest that this is probably small and positive (see Figure 6), and that closing down the C═C—C angle would make the allylic coupling less negative. Thus, the contributions from the two coupling paths must very nearly cancel one another.

The calculated INDO–FPT result[68] for $^4J_{\mathrm{trd}}$ in cyclobutene is +2.25 Hz. Although this is in the right direction, it is indicative of the inadequacy of the INDO parameterization in giving reliable results in strained systems.

Numerous examples of allylic coupling constants involving methyl groups attached to endocyclic double bonds are given in Table V. Although there appear to be some variations with substituents and bond order (see section V.B), there does not appear to be any correlation with ring size.

Inspection of the experimental data in Table III for allylic coupling involving exocyclic methylenes does not reveal any general trend with ring size (although it is also true that dihedral angles will also change as the size of the ring varies). In Table XVI the calculated INDO–FPT results[69] for methylenecyclopentane, methylenecyclobutane, and methylenecyclopropane are compared with experimental allylic coupling data from Table III. Calculated results, which were based on the assumption of planarity of the rings, suggest a definite trend toward more positive allylic coupling constants as the ring size decreases. However, the disparity between calculated and experimental results increases by about the same amount as one proceeds along the series, which again reflects the inadequacy of the INDO parameterization for these highly strained systems. The one feature of the experimental results, which is retained in the calculated ones, is that in all cases $|^4J_{\mathrm{trd}}| > |^4J_{\mathrm{csd}}|$.

V. Substituent and Bond-Order Dependencies

The effects of substituents on allylic coupling constants were discussed from the point of view of simple molecular orbital theory in a previous review.[7] Since that time additional experimental and theoretical studies have appeared or exist in the form of unpublished data from these laboratories. The theoretical basis for the bond-order dependence of allylic coupling constants is not fundamentally different from other type of substituent effects (except possibly that it is most important when the substituent is in the most favorable position for interacting with the π-bond), and so it is appropriately included in this section.

A. Substituent Effects Outside the Coupling Path

Substituent effects outside of the coupling path are exceedingly complicated because of the very large number of variables. Not only do these depend on the nature of the substituent, and the carbon atom (C-1, C-2, or C-3) to which the substituent is attached, but also on the dihedral angle ϕ. Despite the complexity of the physical situation, some systematic and useful correlations do emerge from the experimental and theoretical results.

Effects of substituents outside the allylic coupling path appear to be consistent with the crude predictions of molecular orbital theory for σ-electron coupling over four bonds.[7,70] Such arguments make use of molecular symmetry and the relative magnitudes of terms of different sign, which occur under the summation sign in eq 13. For example, the eight orbital propanic fragment, which is depicted in Figure 5, will have eight MO's. Because of the symmetry of this and other possible conformations, these MO's will be either symmetric or antisymmetric to reflection in a plane (σ_v) passing through C-2 and perpendicular to the C1–C2–C3 plane. There will be 16 terms in eq 13 corresponding to virtual excitations from the four occupied MO's to the four unoccupied MO's. These will give negative and positive contributions to $^4J_{\mathrm{HH'}}$ if the virtual excitations connect MO's of the same or different parity, respectively. It is then possible to consider the effects on $^4J_{\mathrm{HH'}}$ of introducing various types of substituents at C-1 (C-3) and C-2. Since this is done in detail in ref 7, only the results will be summarized here. An inductive, σ-electron substituent (fluorine is the example used in subsequent discussions) will have the major effect of removing electron density from the occupied, symmetric MO's, and there are more positive contributions than negative ones in the sum. A positive shift is clearly predicted.[7,70] Furthermore, a hyperconjugative substituent at C-2 (CN is used in subsequent discussions) having a node in the σ_v plane will have the effect of removing electrons from the antisymmetric MO's. The suggestion[7] that this would also produce a positive shift in $^4J_{\mathrm{HH'}}$ was not as clear-cut, but has been subsequently given experimental verification in the propane series.[71]

A similar analysis of the problems of inductive and hyperconjugative substituents at the C-1 (or C-3) carbon atoms in Figure 5 leads to ambiguous results.[7] However, the situation appears[7] to be analogous to that for vicinal H-H coupling constants, which are relatively insensitive to substituent effects (in comparison with geminal H-H coupling constants, for example), but which tend to become less positive for both inductive and hyperconjugative substituents.[72]

The arguments given above for the substituent dependence of the σ-electron coupling contributions also should be applicable to an allylic fragment, obtained by introducing a π-bond at C1–C2 perpendicular to the plane in Figure 5. However, the presence of the π bond makes possible additional substituent effects at all three of the allylic carbon atoms. For example, it is possible for substituents, having nodes in the C1–C2–C3 plane, to give rise to the effects of π-electron delocalization when substituted at either C-1 or C-2. The magnitude of the allylic coupling will be expected to decrease along with the π-bond order, and will become of greatest importance in those cases in which the C1–C2 bond is part of an aromatic system, thereby making the

TABLE XVII. Comparison of Calculated and Experimental Long-Range H–H Coupling Constants (Hz) in Representative Monosubstituted Propenes[a]

	$^4J_{HH'}$, transoid				$^4J_{HH'}$, cisoid			
Molecule	0°	120°	Av	Exptl	0°	120°	Av	Exptl
Propene	–0.54	–1.52	–1.19[b]	–1.33	–1.15	–250	–2.05[b]	–1.75
1-Fluoropropene	–0.23	–1.73	–1.23[b]	–1.6	–0.68	–2.58	–1.94[b]	–1.8
2-Fluoropropene	–0.28	–1.09	–0.63[b]	–0.4	–0.79	–2.21	–1.73[b]	–1.0
3-Fluoropropene	–0.69[c]	–0.29[c] 1.73[e]	–1.16[d]	–1.27	–0.99[c]	–1.85[c] –2.42[e]	–2.05[d]	–1.63
1-Cyanopropene	–0.71	–1.80	–1.43[b]	–1.3 –1.4	–1.26	–2.76	–2.26[b]	–1.8 –1.5
2-Cyanopropene	–0.59	–1.75	–1.36[b]	–1.20	–0.49	–2.58	–1.88[b]	–1.71
3-Cyanopropene	–0.58[c]	–1.84[c] –1.79[e]	–1.53[d]	–1.68	–1.16[c]	–2.63[c] –2.63[e]	–2.31[d]	–1.90

[a] This table was taken, in part, from ref 2. Experimental data are also given in Table VI. [b] The coupling constant was calculated from the values in the table and eq 20. [c] These values were obtained for the case in which the substituent at the C-3 carbon had a dihedral angle of 120°. [d] These coupling constants were calculated from eq 24 and the three values in the table. [e] These values were obtained for the case in which the substituent at the C-3 carbon atom has a dihedral angle of 0°.

connection between $^4J_{csd}$ and ortho benzylic coupling constants.

In the case of a substituent at the C-3 carbon atom in Figure 3 direct interaction with the 2p atomic orbital on C-2 is possible. In addition, the substituent will have the very important effect of changing the rotamer populations about the C2–C3 bond in Figure 3. Because the substituent factors are different at each of the three carbons of an allylic fragment, these will be treated separately in the following sections.

1. Substituents at C-1

Experimental data for substitution in the terminal methylene of the *E* and *Z* isomer pairs **171** and **172** in Table VII suggest that $^4J_{trd}$ and $^4J_{csd}$ decrease and increase, respectively, with increasing electronegativity of the substituent. The same trend, but with smaller changes in the relative magnitudes in the analogous pair **165** and **166** with a five-membered ring, suggests that at least part of the effect is conformation rather than substituent dependent owing to ring interconversions in the six-membered rings in **171** and **172.** In addition, the data for the 1-substituted propenes in comparison with the unsubstituted compound in Table VI also suggest opposite trends for $^4J_{trd}$ and $^4J_{csd}$. A reinvestigation of some of the data for the 1-substituted propenes would be quite useful in firmly establishing the trends with substitution at C-1.

Calculated INDO-FPT results for the fluoro- and cyano-substituted propenes are given in Table XVI along with the experimental data from Table VI. For substituents at the C-1 position the calculations were performed for a single conformation and the average values of $\langle ^4J_{trd} \rangle$ and $\langle ^4J_{csd} \rangle$ in the table were obtained from eq 20. The agreement between calculated and experimental values in Table XVII is best for the transoid values, and seems to reproduce the trend toward more negative values of $^4J_{trd}$. The situation with regard to $^4J_{csd}$ is confused because of the ambiguities in the experimental results.

2. Substituents at C-2

In contrast to the difficulties with regard to substitution at the C-1 position of the allylic fragment, the results for C-2 substitution follow both the qualitative and quantitative MO predictions. For example, the series of rigid molecules **152–156** in Table VII have a variety of substituents at the C-2 carbon atom (the actual numbering differs in all but the first of these). In all of these compounds the transoid allylic coupling constants have dihedral angles near 180° for which the coupling is positive. Not only is the predicted trend toward more positive coupling constants with inductive substituents followed in this series, but $^4J_{trd}$ increases regularly with substituent electronegativity. The maximum for this type of coupling (+2.55 Hz) occurs in **154** for the case of a chlorine substituent at the C-8 carbon (following the numbering given for this compound in the table). The calculated INDO-FPT result for $^4J_{trd}$ (ϕ = 180°) is 3.2 Hz (see below) for 2-fluoropropene, which should be the upper limit for allylic coupling.

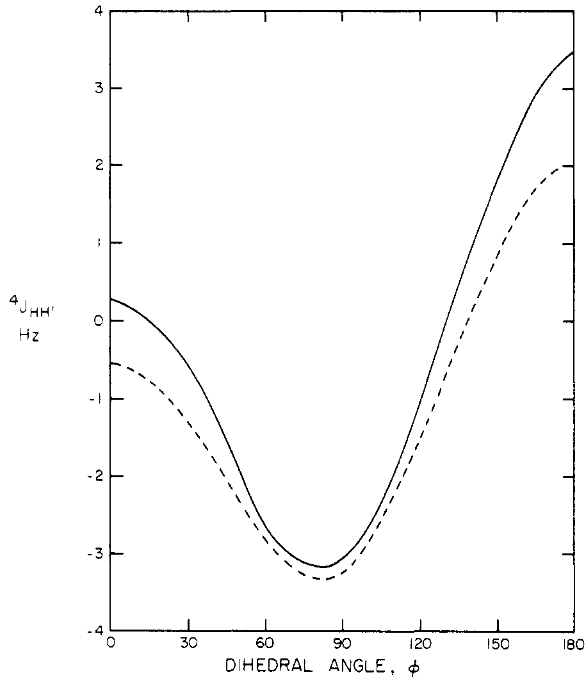


Figure 10. A comparison of the calculated INDO-FPT results for $^4J_{trd}$ in 2-fluoropropene (solid line) with that for propene (dashed line) as a function of the dihedral angle ϕ.

To investigate the conformational dependence of C-2 substitution on allylic coupling, INDO-FPT results for $^4J_{trd}$ and $^4J_{csd}$ in 2-fluoropropene were obtained[63] at 15° intervals, and the results are plotted in Figures 10 and 11 along with the respective INDO-FPT results for propene. It is interesting to note that the effect of fluorine substitution is to give more positive values of both transoid and cisoid allylic coupling constants over the entire range of ϕ, that the largest effects occur for the planar arrangements (ϕ = 0 and 180°), and that the substituent effect drops off to as little as 0.1 Hz in the region near ϕ = 90°. Since other substituents at the C-2 position will have even less effect on the allylic coupling than fluorine, it is not surprising that

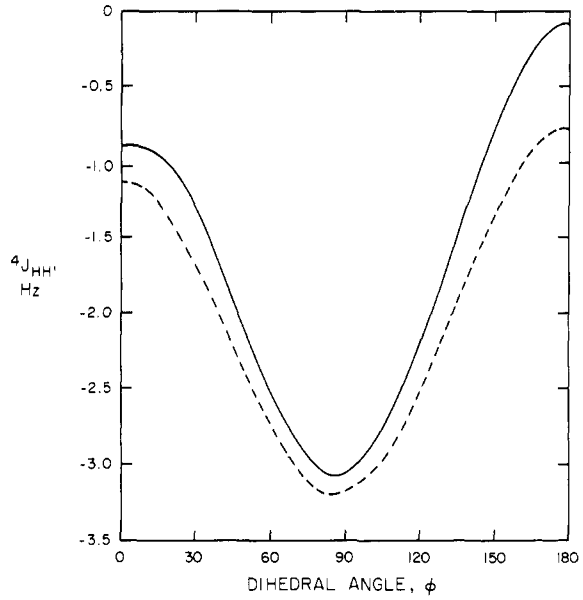


Figure 11. A comparison of the calculated INDO–FPT results for $^4J_{csd}$ in 2-fluoropropene (solid line) with that for propene (dashed line) as a function of the dihedral angle ϕ.

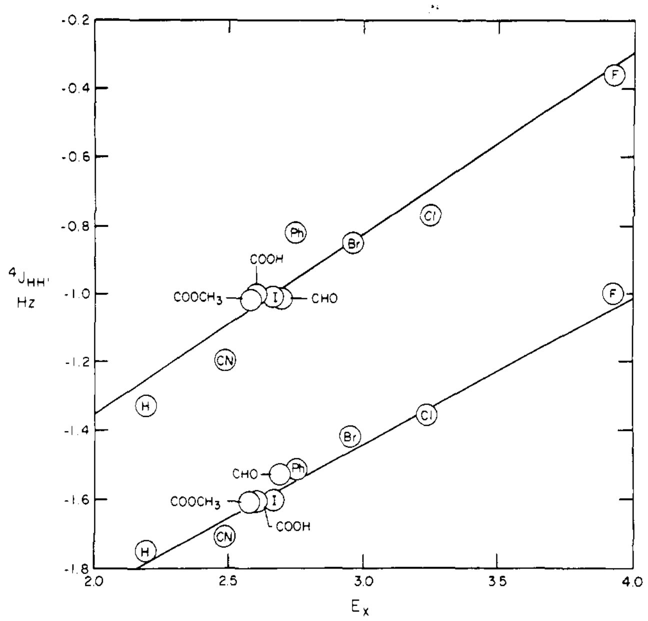


Figure 12. A plot of the experimental data for $^4J_{trd}$ and $^4J_{csd}$ in 2-substituted propenes **138** as a function of substituent electronegativity E_x [J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34,** 1099 (1961)]. The upper and lower lines were obtained from the linear least-squares analyses of the data for $^4J_{trd}$ and $^4J_{csd}$, respectively.

substituent effects at other values of the dihedral angle are not readily apparent from the experimental data in Table VII.

Calculated INDO–FPT results[2] for $^4J_{trd}$ and $^4J_{csd}$ in 2-fluoro- and 2-cyanopropenes at $\phi = 0$ and 120° are entered in Table XVII along with average values from eq 20. The agreement between calculated and experimental results is satisfactory, especially with regard to the quite small value of $^4J_{trd}$ in 2-fluoropropene.

The correlation of the 2-substituted propenes with the substituent electronegativity has been previously noted.[12] The experimental data from ref 12 and others from Table VI are plotted in Figure 12 as a function of the substituent electronegativity, E_x. The circles are indicative of the errors in the experimental values of the coupling constants and the electronegativities. The straight lines correspond to linear least-squares analyses of the two sets of experimental data and follow the equations

$$^4J_{trd} = 0.51E_x - 2.37\text{ Hz} \tag{22}$$

$$^4J_{csd} = 0.44E_x - 2.76\text{ Hz} \tag{23}$$

with correlation coefficients of 0.96 and 0.99, respectively. In view of the possibility that the unsaturated substituents could alter the allylic π-bond order, it is interesting to note that these seem to follow the overall trend in Figure 12 quite well.

3. Substituents at C-3

The series of cyclic molecules **161–164** and **167–169** in Table VII clearly show effects of substituents at the C-3 carbon atoms, but it is difficult to separate electronic effects from those of ring conformations, multiple substituent effects, and coupling over several paths. The first set involves coupling over dual pathways, which has been the subject of several recent studies.[73,74]

To compare the calculated INDO–FPT results with the experimental data for the 3-substituted propenes in Table XVII, it was necessary to perform the calculations for the conformations in which the substituent is at 0 and 120°.[2] Clearly, the result for $^4J_{HH'}(240°)$ will differ, depending on whether the substituent is at $\phi = 0$ or 120°. Furthermore, the substituent will destroy the equality of the rotamer populations, so that it is necessary to modify eq 20,

$$\langle ^4J_{HH'}\rangle = p_a\,^4J_{HH'}(120°) + [(1 - p_a)/2][^4J_{HH'}(0°) + {}^4J_{HH'}(240°)] \tag{24}$$

where p_a is the population of the rotamer in which the substituent eclipses the double bond. The other two coupling constants in eq 24 are those obtained for the substituent at $\phi = 120°$. Rotamer populations, which were used[2] in conjunction with eq 24 to calculate the results for $^4J_{trd}$ and $^4J_{csd}$ in Table XVII, were based on vicinal coupling constant data. Again, the agreement between calculated and experimental results is mixed. The experimental results for $^4J_{trd}$ and $^4J_{csd}$ in 3-fluoro- and 3-cyanopropenes are slightly more positive and negative, respectively, than the propene values in Table XVII. However, this may not represent a definite electronic effect, but simply differences in the values of p_a.

The experimental data in Table VI for 3-substituted propenes appear at first sight to be unusual because the trend with C-3 substitution appears to be just opposite to that for C-2 substitution. As a consequence, the $^4J_{trd}$ and $^4J_{csd}$ for 3-fluoropropene are close to the corresponding values for propene. A space-filling model for 3-iodopropene suggests the following reason for the trends in this series: the iodo group is so large that the conformation in which it eclipses the double bond would be most unfavorable. Thus, p_a in eq 24 must be essentially zero and the major contributions arise from the second term in the equation. With the assumption that p_a is zero, and the even cruder assumption that electronic substituent effects are absent, then the substitution of the propenic coupling constant data from the last columns of Tables XII and XIII into eq 24 leads to "calculated" values of −0.7 and −1.2 Hz for $^4J_{trd}$ and $^4J_{csd}$, respectively. Qualitatively, this is just what is observed in the series of 3-substituted propenes.

The experimental data for the 3-substituted propenes from Table VI are plotted in Figure 13 as a function of the van der Waals radii, *r*(*vdW*).[75] The lines drawn through the circles correspond to linear least-squares fits of the experimental data. Data for the methyl substituent, which was not included in the least-squares determinations, are about 0.5 Hz below the lines and clearly show that factors other than the size of the substituent are involved.

B. Influence of Bond Order

In section III it was noted that the various theoretical formulations, which related coupling constants to bond orders, were

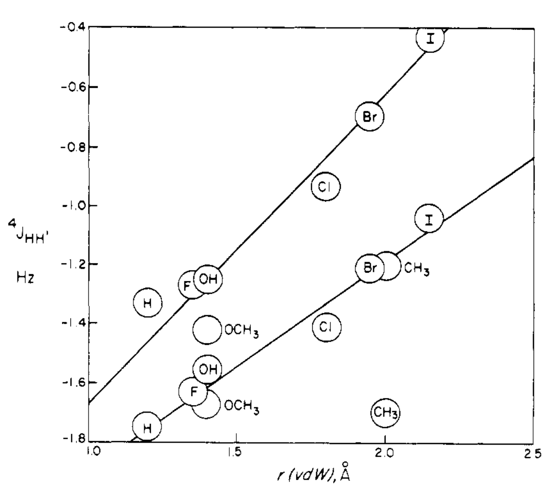
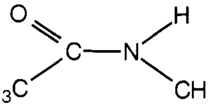


Figure 13. A plot of the experimental data for $^4J_{trd}$ and $^4J_{csd}$ in 3-substituted propenes **140** as a function of the van der Waals radii, *r*(*vdW*),[75] of the substituent. The upper and lower lines, which are drawn through the data points, are based on linear least-squares analyses of the data for $^4J_{trd}$ and $^4J_{csd}$, respectively.

all based on the "average energy" procedure, and were without quantitative justification. Nevertheless, the relationship of coupling constants to bond orders is pervasive, providing a simple way of relating a large amount of experimental NMR data to bond orders. These, in turn, are conceptually related to delocalization in unsaturated and aromatic systems, and to ground-state properties such as bond lengths. The decreased magnitudes of the experimental ortho benzylic coupling constants relative to $^4J_{csd}$ in propene is attributed to the decrease in the aromatic π-bond orders below unity. Detailed discussions and empirical relationships have been proposed.[22-25] However, it was noted in section III that the relationship of π-electron contributions to mutual atom-atom polarizabilities has a firmer basis in theories of nuclear spin-spin coupling. Additional complexities arise on including the effects of conformation or substituents outside[76] the coupling path. Experimental and theoretical studies of such effects are in progress in these laboratories.

C. Miscellaneous Effects

The problems associated with $^4J_{HH'}$ across a heteroatom in systems of the type CH_3-X-CH_3 have been investigated and found to be substantial,[62] but no systematic investigation of the effects of heteroatoms in the allylic coupling path have appeared. This may be due to the fact that no unusual trends are exhibited by the data in Table VIII. However, calculated INDO-FPT results for *cis*- and *trans*-*N*-methylacetamide (**205** and **206**) which were



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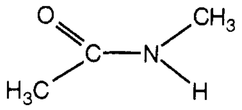

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obtained in connection with studies of other types of H-H coupling,[77] are given in Table XVIII at 60° intervals of the dihedral angle ϕ. The occurrence of a positive sign for the $^4J_{trd}$ is an interesting feature of these results, as well as the fact that the most negative and most positive values occur for the $^4J_{trd}$. Apparently, the σ-electron mechanisms are obscuring the π-electron mechanism, which would be expected to be small because of the small π-bond order of 0.49 for the C-N bond in **205** and **206**. If one of the hydrogen atoms of the carbonyl methyl eclipses the C-O bond in the lowest energy rotamer, then the calculated average values are $\langle ^4J_{trd} \rangle = +0.27$ Hz, and $\langle ^4J_{csd} \rangle = -0.11$ Hz. Clearly, some careful experimental work will be required to extract both the signs and magnitudes of such small coupling constants.

TABLE XVIII. Calculated INDO-FPT Results for $^4J_{trd}$ and $^4J_{csd}$ in *cis*- and *trans*-*N*-Methylacetamides, 205 and 206, Respectively[a]

Dihedral angle, deg	$^4J_{trd}$, Hz	$^4J_{csd}$, Hz
0	−0.98	−0.12
60	−0.43	0.18
120	0.80	−0.05
180	1.66	−0.68

[a] The *N*-methyl group was fixed with the hydrogen atoms at 60, 180, and 300° from the C—C—N plane.

A variety of other experimental and theoretical results are relevant to the allylic coupling problem, but which include additional factors. These can be as important in magnitude as those discussed in connection with allylic coupling constants. For example, recent studies of dihydrofurans and phthalans[73] show the effects of ring puckering as well as coupling over dual paths to be important for both allylic and homoallylic coupling constants. The effects of ring puckering have also been suggested to be of importance for metal substitution effects on the allylic coupling constants in cyclopentadiene compounds.[31,74] Clearly, there are countless other examples of coupling situations which involve an allylic path in one way or another, and it is hoped that this review will prove useful in sorting out some of the major factors involved in that aspect of the problem.

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