

NUCLEAR SPIN-SPIN COUPLING OVER DUAL VICINAL AND
HOMOALLYLIC PATHS IN FOUR MEMBERED RINGS

by

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October 17, 1979
Date

Dedicated To

Ignatius Agbor Bojor and his Family

and

Scholastica Ofoma Nsor Ekere and her Family

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The work described in this paper was carried out under the supervision of Dr. Michael Barfield to whom I would like to express my gratitude for his guidance and encouragement.

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ABSTRACT

A study is presented of the vicinal H-H coupling constants $J_{HH'}$, in the series of molecules cyclobutane, benzocyclobutene, and cyclobutene. It is noted that the experimental coupling constants decrease in magnitude in these molecules and parallel the increase in the π -bond orders. Because this is an unexpected result, a theoretical molecular orbital study is presented of coupling over dual paths in four-membered rings to try to ascertain the relevant electronic factors. The calculated results are in agreement with the experimental data thereby exhibiting the same overall trends.

The factors affecting vicinal and homoallylic coupling constants are discussed as they are relevant to this problem. The role of substituents and conformational effects on these types of coupling is also discussed, and extensive literature data are presented.

INTRODUCTION

Dual-Path Coupling in Cyclobutenes

In their study of the dihydrocyclobutenaphthylenes (Figure 1) Kolc and Michl (1973) suggested that there seemed to be an inverse relationship between the bond order of the unsaturated bond in the cyclobutene ring and the magnitude of the coupling constant, J_{HH} , between the two nonaromatic protons. This kind of relationship is of interest since it is just the opposite of what is expected in the H-C=C-H moiety in which the vicinal coupling constant increases as the bond order of the unsaturated C-C bond increases (Cremer and Günther 1972; Karplus 1963). The major intention of this work, therefore, is to present a study of this apparently anomalous dependence.

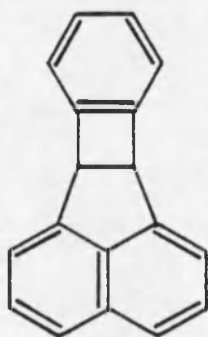
The π -electron system is known to be the major factor determining long-range coupling in unsaturated molecules, and also to be effective in transmitting non-negligible coupling over at least seven bonds (Barfield 1968). Therefore, in undertaking this study it is first necessary to note that the coupling constants in cyclobutenes are transmitted via dual-path (vicinal/homoallylic) mechanisms. As a consequence, the H-H coupling constants of primary concern here are those across three formal single bonds (vicinal coupling), and across four single bonds and one double bond (homoallylic coupling). The experimental and theoretical factors (Sternhell 1964; Barfield and Chakrabarti 1969; Barfield and Sternhell 1972; Barfield and Grant 1965; Karplus and Anderson 1959;

$$J_{HH'}^{cis} = 3.6$$

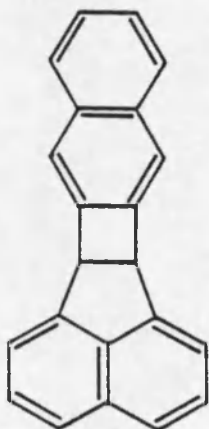
$$J_{HH'}^{cis} = 4.0$$

$$J_{HH'}^{cis} = 3.2$$

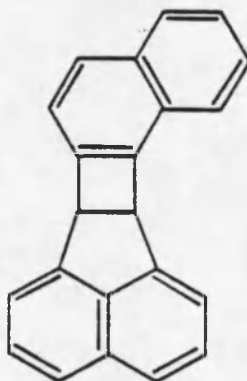
$$J_{HH'}^{cis} = 2.5$$



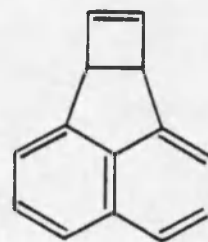
I



II



III



IV

Figure 1. The Dihydrocyclobutenaphthylene Compounds.

Barfield 1976) which give rise to each of these couplings are complex and will be discussed briefly here.

Because of the possibility of using vicinal and long-range coupling constants to aid in conformational analyses and studies of chemical bonding (Jackman and Sternhell 1968; Sternhell 1964, 1969; Bovey 1969), there is interest in the theoretical interpretations of the mechanisms which give rise to the observed couplings.

There are few reports of coupling constants between protons separated by five bonds in saturated organic molecules. In these cases, coupling is believed to occur by "indirect" mechanisms (Barfield and Karplus 1969; Boros et al. 1966), and coupling through sigma electrons has been shown both by experiment (Banwell et al. 1959; Gutowsky, McCall, and Slichter (1951); Leone and Richards 1959; Richards and Schaefer 1958a, 1958b) and by theory (McConnell 1956) to be rapidly attenuated by a factor of about five for each carbon-carbon bond separating the protons. Thus, the observed vicinal couplings in cyclobutanes should be dominated by the three-bond path which involves interaction of the vicinal C-H bonds (Barfield and Karplus 1969).

In view of the above facts, it will be assumed that the observed vicinal coupling constants in cyclobutanes occur via a single-path whereas those in cyclobutenes occur via a dual-path. Assuming equal sigma-electron contribution in both compounds, one would expect that the sum of the coupling constants via the two-path (i.e., ${}^3J_{HH'}$ plus ${}^5J_{HH'}$) in cyclobutenes would be substantially larger in magnitude than the coupling constants in cyclobutanes.

Basic Interactions in Nuclear Spin-Spin Coupling

The nuclear spin-spin coupling phenomenon arises from small splittings of the electron-nuclear energy levels that arise from the presence of other magnetic nuclei (Ramsey 1953; Ramsey and Purcell 1952). The nuclear spin-spin coupling phenomenon is treated in more detail in a number of general texts (Jackman and Sternhell 1968; Pople, Schneider, and Bernstein 1959; Conroy 1960; Roberts 1959, 1961; Bovey 1969; Crooks 1978). Only the pertinent details will be reviewed here.

According to Ramsey's (1953) general theory, nuclear spin-spin interactions occur by four distinct mechanisms: direct dipole-dipole, nuclear spin-electron spin (spin dipolar), nuclear spin-electron orbital (orbital), and Fermi contact interactions. The direct dipole-dipole interactions, which lead to a line broadening in solids, average to zero under rapid rotation in liquids (Hahn and Maxwell 1951, 1952; Ramsey and Purcell 1952; Bloembergen, Purcell, and Pound 1948). The spin-dipolar and orbital interactions are negligible if either of the nuclei involved in the coupling is a proton (Pople and Santry 1964). The interaction between the nuclear and electron spin at the site of the nucleus is called Fermi contact interaction. This work is restricted to couplings involving protons in liquids and, therefore, only the contact contributions to the spin-coupling constant will be discussed in this section.

Nuclear spins in molecules interact via the intervening electrons according to the proposal of Ramsey and Purcell (1952). As an example, consider the case of the directly bonded coupling between a ^{13}C and a ^1H . Because of the Fermi contact interaction, electrons in the vicinity

of the ^{13}C will tend to have their spins antiparallel to the ^{13}C nuclear spin in the electron-nuclear spin state of lowest energy. Since the $^{13}\text{C}-^1\text{H}$ bond is essentially covalent, the $1s$ electron of the ^1H -atom will tend to have its electronic spin antiparallel to that in a hybrid orbital on the ^{13}C -atom. Again, because of the Fermi contact interaction the proton will tend to have its spin antiparallel to that of the associated electronic spin. The net effect is that the electron-nuclear state of lowest energy is the one in which the nuclear spins are antiparallel. The difference in energy between this state and that in which the nuclear spins are parallel is called the coupling constant, J , and is usually expressed in frequency units, Hertz (Hz).

According to independent studies of NMR fine structure by Gutowsky and McCall (1951), Gutowsky et al. (1951), and Hahn and Maxwell (1951, 1952), the nuclear spin-spin interaction energy is of the form

$$\Delta E_{\text{NN}'} = h J_{\text{NN}'} \vec{I}_N \cdot \vec{I}_{N'} \quad (1)$$

where $J_{\text{NN}'}$ is the indirect nuclear spin-spin coupling constant between nuclei N and N' having nuclear spin vectors \vec{I}_N and $\vec{I}_{N'}$, respectively, and h is Planck's constant. Adding the nuclear spin-spin coupling to the nuclear Zeeman term gives the NMR Hamiltonian. Thus, the Hamiltonian operator for a collection of nuclei in a molecule can be written (Pople et al. 1959)

$$H_{\text{op}} = \sum_i V_{0i} I_{zi} + \sum_{i,j} J_{ij} \vec{I}_i \cdot \vec{I}_j \quad (2)$$

The first term in Equation 2 is the nuclear Zeeman term, which may be expressed as

$$V_{oi} = \frac{\gamma_i H_0}{2\pi} \quad (3)$$

where γ_i denotes the magnetogyric ratio of nucleus i , and H_0 is the external magnetic field;

$$\gamma_i = \gamma_N (1 - \sigma_i) \quad (4)$$

in which σ_i is the magnetic shielding constant of the i^{th} nucleus having magnetogyric ratio γ_N .

Vicinal Proton-Proton Coupling

Nuclear H-H coupling over three single bonds in the H-C₁-C₂-H' moiety is called vicinal coupling. It is designated ${}^3J_{\text{HH}'}$, where the left superscript indicates the number of contiguous bonds.

The vicinal H-H coupling construct ${}^3J_{\text{HH}'}$ is a function of the dihedral angle, ϕ , defined in Figure 2.

Using the valence-bond (VB) theory for a six-electron fragment of the ethane molecule, it was shown (Karplus 1959) that the dependence on dihedral angle, ϕ , is given by an equation of the form

$${}^3J_{\text{HH}'} = A + B\cos\phi + C\cos2\phi. \quad (5)$$

For a C-C bond length of 1.543Å and Sp³ hybridized carbons, Karplus (1963) gave the following values for the constants: A = 4.22 Hz, B = -0.5 Hz, and C = 4.5 Hz. Equation 5 and other forms of the Karplus equation have been used in a great number of studies of molecular

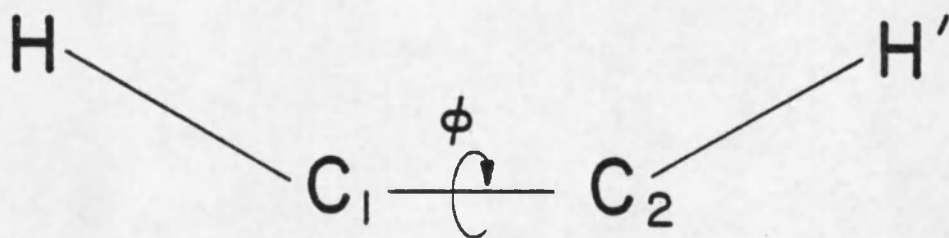


Figure 2. The Dihedral Angle ϕ Measured about the C_1-C_2 Bond.

conformations in solution. A typical plot (Bovey 1969) of vicinal H-H coupling as a function of dihedral angle is depicted in Figure 3. In cyclobutane and cyclobutene for which the dihedral angle is 0° , the cis- and trans-coupling constants from Figure 3 are equal--about 8.2 Hz.

For constant bond angles and hybridization, the vicinal H-H coupling constant is expected to be a function of the C-C bond length. A decrease of $^3J_{HH'}$ is expected on increasing the bond length (Karplus 1963; Cremer and Günther 1972).

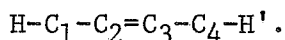
The vicinal H-H coupling constants are also expected to depend on the bond angles, θ and θ' , defined as in Figure 4 (Karplus 1963). Fragment-model calculations show that the vicinal coupling constant should decrease for most dihedral angles as θ and θ' increase (Karplus 1963; Gutowsky and Porte 1961).

Other factors that can influence vicinal constants include substituent electronegativities and orientation (Karplus 1963; Williams and Bhacca 1964; Booth 1965; Fishman 1965), and molecular properties such as molecular vibrations (Lentz and Heeschen 1961; Gutowsky, Mochel, and Somers 1962), and changes in π -bonding (Karplus 1960).

Homoallylic Proton-Proton Coupling

Definition and Dihedral Angle Dependence

Nuclear spin-spin coupling constants, $^5J_{HH'}$, over four single bonds and one double bond are said to be of the homoallylic type (Pinhey and Sternhell 1963) between protons H and H' in the system



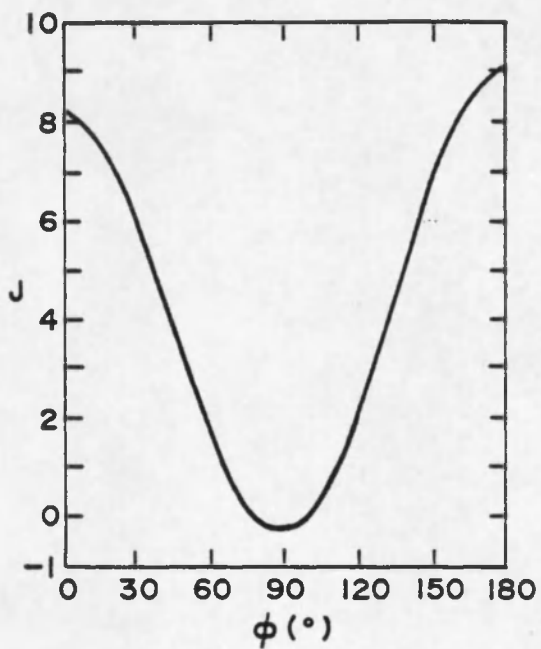


Figure 3. The Karplus Function Describing the Magnitude of Vicinal Proton-Proton J Coupling as a Function of Dihedral Angle ϕ in the H-C₁-C₂-H' Bond System.

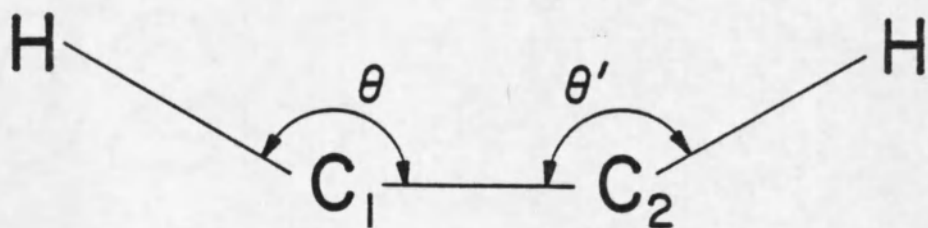


Figure 4. Definition of Bond Angles in the Vicinal Fragment.

Homoallylic coupling constants have been studied experimentally and theoretically (Karplus 1960; Sternhell 1964, 1969; Barfield and Chakrabarti 1969; Barfield and Sternhell 1972). Using the cis- and trans-2-butene molecules as models, Barfield and Sternhell (1972) applied both the FPT-INDO and VB-Sum-over-Triplet-States methods to investigate the conformational dependence of homoallylic coupling constants. The variables of major importance are the dihedral angles ϕ and ϕ' measured from the plane of the carbon atoms as shown in Figure 5.

Homoallylic coupling has been shown to have an approximate $\sin^2\phi \sin^2\phi'$ dependence on the dihedral angles ϕ and ϕ' (Barfield and Sternhell 1972).

The respective plots (Barfield and Sternhell 1972) of ${}^5J_{HH'}$ in cis-2-butene for the VB and INDO calculations are shown in Figures 6 and 7.

The VB calculations give only the π -electron contributions, which are equal for cis- and trans-2-butenes. These are given by

$${}^5J_{HH'}^{\pi}(\phi, \phi') = 4.99 \sin^2\phi \sin^2\phi'. \quad (6)$$

Assuming dihedral angles of 120° for the orientation corresponding to both the cis and trans coupled protons in cyclobutene, the coupling constants from Figures 6 and 7 are about 2.8 Hz.

Homoallylic coupling is expected to be substantial (about 2.8 Hz) in cyclobutenes because of the more favorable angular disposition of the C-H bonds in Figure 5. In acyclic butenes the methyl groups are free to rotate (Sternhell 1964). Coupling is greatest when the dihedral angles equal 90° (Barfield and Sternhell 1972; Pinhey and Sternhell 1963).

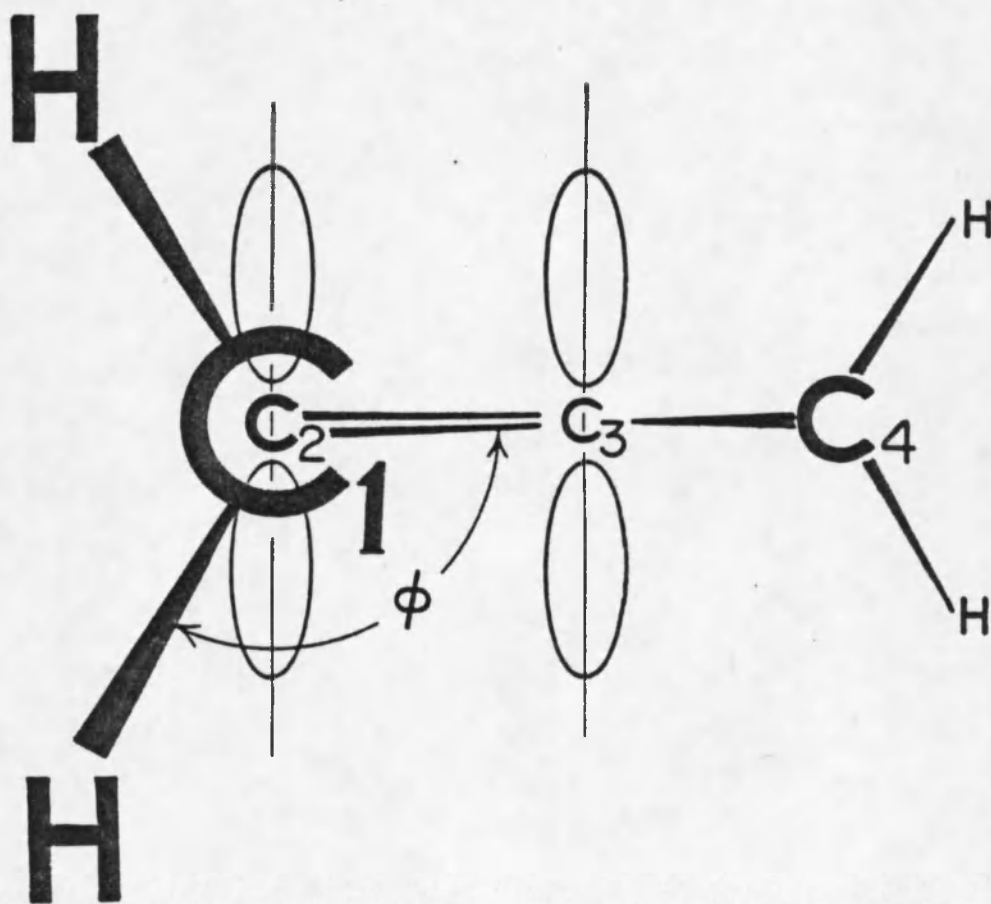


Figure 5. A Fragment of the *cis*-2-butene Molecule.

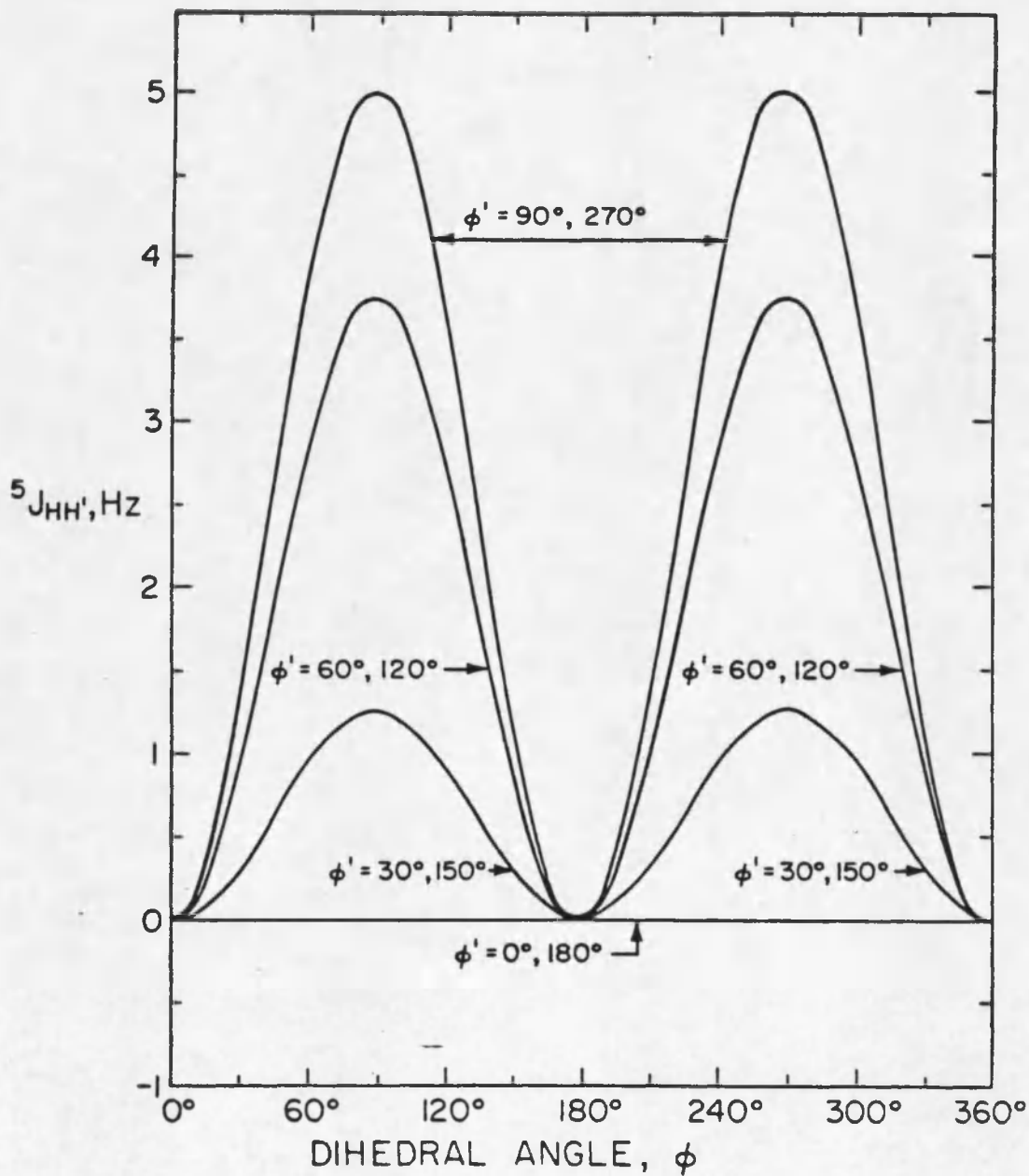


Figure 6. Calculated Valence-Bond Results for ${}^5J_{HH'}^\pi$ in the cis- and trans-2-butene Molecules Plotted as a Function of the Dihedral Angles ϕ and ϕ' .

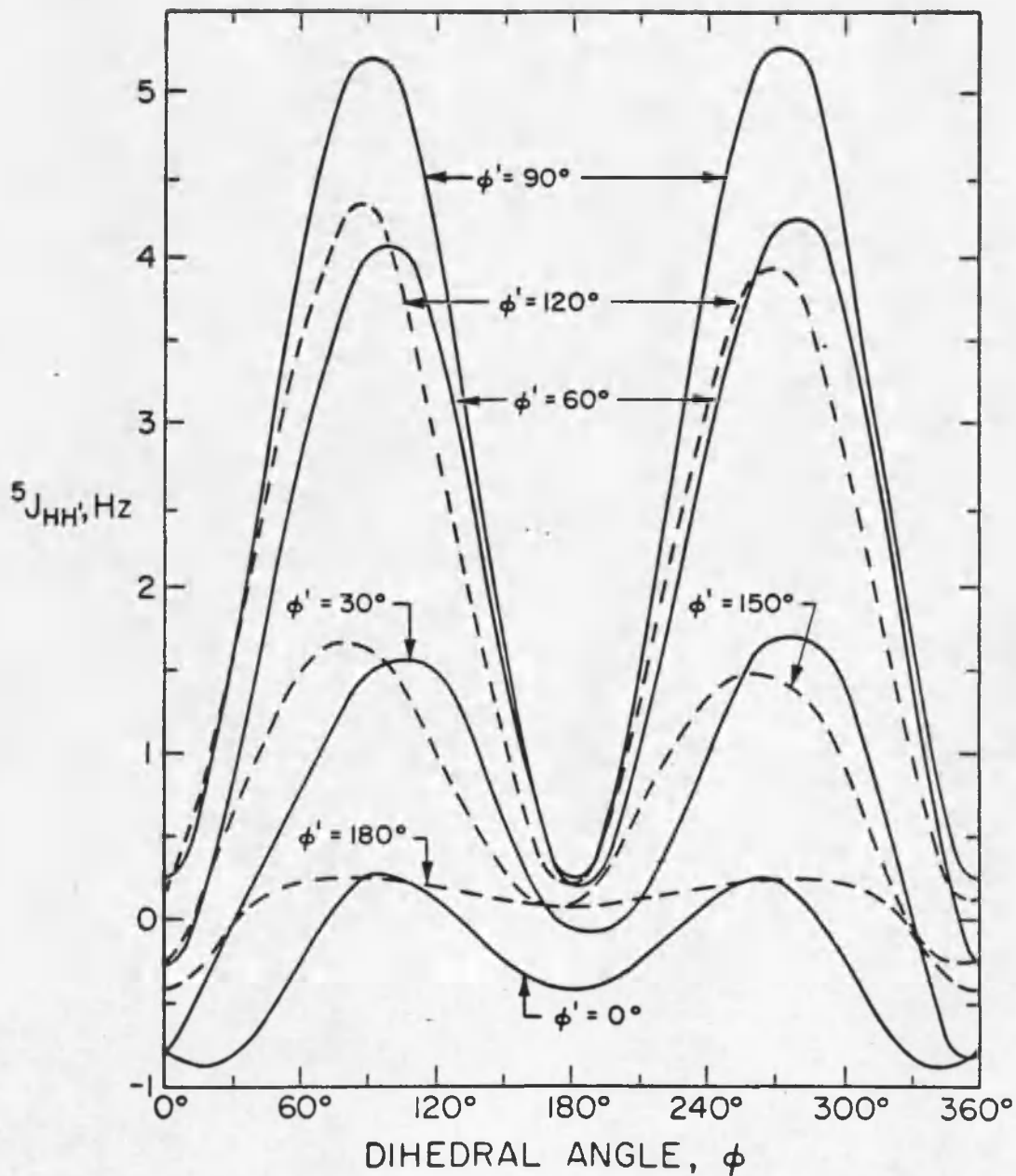


Figure 7. Calculated Results for Homoallylic Coupling in the cis-2-butene Molecule Plotted as a Function of the Dihedral Angles ϕ and ϕ' .

According to Baeyer's (1885) strain theory, one pair of bonds to each carbon atom in cyclobutane cannot assume the tetrahedral angle but must be compressed to 90° to conform to the geometry of the ring. As noted previously, the change from cyclobutane to cyclobutene should open up the H-C-H angles due to increased ring strain. From Figures 6 and 7, it is seen that this change should produce significant homoallylic coupling and hence larger values of $^5J_{\text{cis}}$.

Relation to π -electron Bond Order

McConnell (1957) pointed out that π electrons could participate in transmitting the spin density induced by the Fermi contact interaction, though their density vanishes at the coupled nuclei. He used MO theory to derive the following formula for the π -electron contribution to coupling constants between protons:

$$J_{\text{HH}'}^{\pi} = (h\Delta E)^{-1} \beta^2 Q Q' P_{\mu\nu}^2 \quad (7)$$

where Q and Q' are the proton hyperfine constants, β is the Bohr magneton, $P_{\mu\nu}$ is the π -electron bond order between π -orbitals μ and ν on the carbon atoms to which protons H and H' are attached, h is Planck's constant, and ΔE is the "average excitation energy." From Equation 7 it is seen that a plot of $^5J_{\text{HH}'}$ as a function of the square of the calculated π -bond orders should be linear.

Taking the π -bond orders in cyclobutane and cyclobutene to be zero and one, respectively, Equation 7 clearly predicts that cyclobutene would have larger H-H coupling constant than cyclobutane.

Relation to the Mutual Atom-Atom Polarizability

In second order perturbation theory the MO expression (Pople and Santry 1964; Coulson and Longuet-Higgins 1947) for the contact contribution to coupling is given by

$$J_{HH'} = -h^{-1}(16\pi\beta\hbar/3)^2 \gamma_H\gamma_{H'} \phi_h^2(H) \phi_{h'}^2(H') \pi_{hh'} \quad (8)$$

where the mutual atom-atom polarizability, $\pi_{hh'}$, of orbitals h and h' at nuclei H and H' is given by

$$\pi_{hh'} = -4 \sum_{\substack{i, \text{occ} \\ j, \text{unocc}}} (\epsilon_j - \epsilon_i)^{-1} c_{ih} c_{jh} c_{ih'} c_{jh'} \quad (9)$$

Equations 8 and 9 have been quite useful in qualitative descriptions of substituent (Pople and Bothner-By 1965; Gil and Teixeira-Diaz 1968; Barfield and Chakrabarti 1969) and solvent effects (Bell and Danyluk 1966, 1970; Johnston and Barfield 1971) on nuclear spin-spin coupling constants. The terms $\phi_h^2(H)$ and $\phi_{h'}^2(H')$ in Equation 8 denote the atomic orbital densities at the two nuclear sites, and β is the Bohr magneton. In Equation 9, c_{ih} and c_{jh} denote the coefficients of atomic orbital h in the i^{th} occupied and in the j^{th} unoccupied molecular orbitals with energies ϵ_i and ϵ_j , respectively. The summation is over both occupied and unoccupied molecular orbitals.

From Equation 9 it is evident that ${}^5J_{HH'}$ should be a linear function of $\pi_{hh'}$. Therefore, both cis and trans couplings should be greater in cyclobutenes than in cyclobutanes.

In independent studies Van der Hart (1971) and Schastnev, Chuvylkin, and Zhidomirov (1971) formulated identical expressions for the π -electron contributions to coupling constants

$$J_{HH'} = \frac{1}{4} QQ' \beta^{-1} \pi_{\mu\nu} \quad (10)$$

where Q is the proton hyperfine constant, $\pi_{\mu\nu}$ is the atom-atom polarizability in units of β^{-1} , where β is the MO resonance integral. Representative values are: $Q = -150 \sin^2\phi \times 10^6$ Hz, $Q' = -150 \sin^2\phi' \times 10^6$ Hz (Karplus 1960), and $\beta = -2.5$ eV = -0.6×10^{15} Hz, so that $J_{HH'}^\pi$ can be estimated as

$$J_{HH'}^\pi = -9.4 \pi_{\mu\nu} \sin^2\phi \sin^2\phi'. \quad (11)$$

The $\pi_{\mu\nu}$ for a double bond according to Equation 9 is -0.5 in units of β^{-1} . With this value of $\pi_{\mu\nu}$ it follows from Equation 11 that

$$J_{HH'}^\pi = 4.7 \sin^2\phi \sin^2\phi' \text{ Hz}. \quad (12)$$

Taking ϕ and ϕ' to be both 120° , Equation 12 predicts that the coupling constant in cyclobutene should be larger than in cyclobutane by a value of about 2.6 Hz.

The INDO-FPT Method

All calculations performed in this study are based on the coupling constant formulation of finite perturbation theory (FPT) (Pople, McIver, and Ostlund 1968) in the intermediate neglect of differential overlap (INDO) (Pople et al. 1968) approximation of unrestricted self-consistent-field (SCF) MO theory. This method has been quite useful for calculating molecular properties such as geometries,

dipole moments, and hyperfine as well as nuclear spin-spin coupling constants (Pople et al. 1968; Pople, Beveridge, and Dobosh 1967).

In the SCF-MO-FPT method for contact coupling, a Fermi contact perturbation of magnitude

$$\eta_N = (8\pi/3) \gamma_N \phi_S^2(N) \quad (13)$$

is added to the diagonal element for the s-orbital, which is centered on nucleus N in the Fock matrix corresponding to electrons of α spin, and it is subtracted from the corresponding element of the Fock matrix for electrons of β spin. In the iterative SCF-MO-FPT scheme this has the effect of inducing a small spin density $\rho_t(\eta_N)$ throughout the molecular electronic system. The coupling constant at N' is proportional to this spin density,

$$J_{NN'} = h(4\beta)^2 \gamma_N \gamma_{N'} \phi_S^2(N) \phi_{S'}^2(N') [\rho_t(\eta_N)/\eta_N] \quad (14)$$

where $\phi_{S'}^2(N')$ denotes the s' orbital density at nucleus N', $\rho_t(\eta_N)$ is the diagonal element of spin-density matrix corresponding to the s-orbital which is centered on nucleus N, β is the Bohr magneton, and γ_N is the magnetogyric ratio of the proton. In another common terminology (Dalgarno 1962; Langhoff, Karplus, and Hurst 1966), this type of calculation corresponds to the coupled Hartree-Fock approximation, and the use of SCF orbitals in Equation 8 corresponds to one type of uncoupled Hartree-Fock method (Langhoff et al. 1966).

The major advantage of the INDO approximation in the SCF-MO theory over the widely used CNDO (complete neglect of differential overlap) method is the inclusion of the one center exchange integrals.

The one center exchange integrals are essential in providing an adequate description of π -electron effects in nuclear spin-spin coupling (Pople et al. 1968).

The calculations reported in this study were based on the INDO computer program of Dobosh (1969) as modified by M. Barfield to include the calculation of coupling constants. Bond lengths were taken as (Sutton 1965) $r(C = C) = 1.337\text{\AA}$; $r(C = C)(\text{aromatic}) = 1.40\text{\AA}$; $r(C - C) = 1.54\text{\AA}$; $r(C - H) = 1.08\text{\AA}$; and $r(=C-C) = 1.483\text{\AA}$. Bond angles were taken to be either trigonal or tetrahedral. In each case the cyclobutene rings in benzocyclobutene and naphthocyclobutenes were assumed coplanar with the benzene and the naphthalene rings, respectively.

RESULTS AND DISCUSSION

Experimental Data

Literature Results

Available literature data for vicinal coupling constants on the key compounds of this study are given in Table 1. Relevant coupling constants observed for molecules having four-membered rings are summarized in Tables 2, 3, and 4, i.e., for the substituted compounds of cyclobutanes, cyclobutenes, and benzocyclobutene, respectively. All the literature data are quoted in the manner in which they were presented.

Although a large number of experimental results for vicinal coupling constants have been published, suitable experimental data for vicinal coupling over three formal single bonds in cyclobutenes are sparse and appear rather erratic. For example, the experimental values for $^3J_{HH'}$ quoted here for the naphthocyclobutenes are those reported for their dihydrocyclobutacenaphthylene (refer to Figure 1) derivatives (Kolc and Michl 1973) since those of the parent compounds are not available.

For cyclobutanes, however, experimental data are extensive. The vicinal cis and trans coupling constants vary widely (4.6 - 11.5 Hz and 2.0 - 10.7 Hz respectively) with cis couplings generally larger than trans couplings. A similar pattern exists for the case of cyclobutenes although the couplings are consistently lower than in cyclobutanes. There is, however, a fairly uniform increase in J_{trans} from cyclobutene to benzocyclobutene and then to cyclobutane.

Table 1. Vicinal Proton-Proton Coupling Constants, π -Bond Orders, and Atom-Atom Polarizabilities of Representative Compounds.



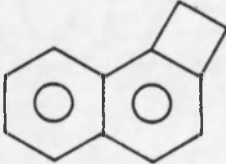
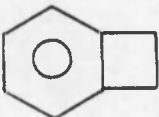

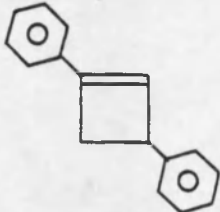
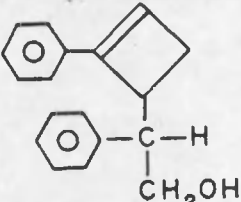
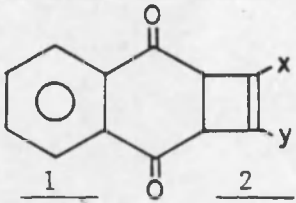
Compound	calculated ^a		calculated ^b		$^3J_{\text{exp}}$ (Hz)	
	$^3J_{\text{HH}'}$ (Hz)		P_{uv}	π_{uv}	cis	trans
	cis	trans				
	7.44	5.59	0.00	0.00	10.4 ^c	4.9 ^c
	4.03	2.70	1.00 (0.959) ^a	-0.500	4.65 ^d 2.5 ^e	1.75 ^d
	5.52	4.16	0.725 (0.699) ^a	-0.213	3.2 ^e	
	5.17	3.82	0.667 (0.624) ^a	-0.157	5.0 ^f 3.6 ^e	3.5 ^f
	6.26	4.88	0.603 (0.536) ^a	-0.110	4.0 ^e	

Table 1, Continued

Compound	calculated ^a		calculated ^b		³ J _{exp} (Hz)	
	³ J _{HH'} (Hz)		P _{μν}	π _{μν}	cis	trans
	cis	trans				
	-	-	0.911 ^j	-0.419 ^j	4.9 ^g	1.9 ^g
	-	-	0.911 ^j	-0.419 ^j	4.3 ^h	1.6 ^h
 1 2 x=Ph x=Ph y=H y=Me	-	-	0.911 ^j	-0.419 ^j	1) 3.9 ⁱ 2) 4.0 ⁱ	

a. Calculation using LCAO-SCF-MO method based on the INDO-FPT approximation.

b. C. A. Coulson and A. Streitwieser, Dictionary of π -Electron Calculations, New York: Pergamon Press, 1965.

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e. For dihydrocyclobutacenaphthylene derivatives, J. Kolc and J. Michl, J. Amer. Chem. Soc., 95, 7391 (1973).

Table 1, Continued

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- f. I. Fleming and D. H. Williams, *Tetrahedron*, 23, 2747 (1967).
 - g. S. Masamune, *Tetrahedron Lett.*, 945 (1965).
 - h. S. Masamune and K. Fukumoto, *Tetrahedron Lett.*, 4647 (1965).
 - i. S. Farid, W. Kothe, and G. Pfundt, *Tetrahedron Lett.*, 4151 (1968).
 - j. Values for styrene.

Table 2. Vicinal Proton-Proton Coupling Constants of Substituted Cyclobutanes.

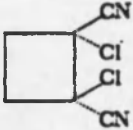
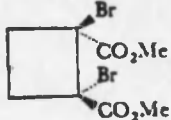
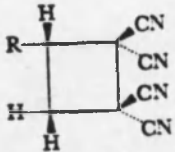
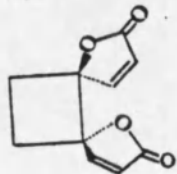
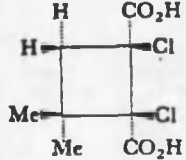
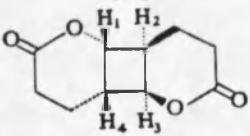
Entry	Compound	$^3J_{HH'}$ (Hz)		Reference*
		cis	trans	
1		9.4	9.3 4.5	a
2		6.2	10.0 8.4	a
3	 R=OMe 9.2 R=OEt 8.6 R=-C ₆ H ₄ OMe 11.5	9.2 8.6 11.5	7.8 7.4 9.5	a
4		10.19	10.72 2.24	a
5		$J_{24}=9.64$	$J_{14}=9.64$ $J_{34}=9.38$	a
6		$J_{14}=J_{23}=8.3$ $J_{12}=J_{34}=4.1$		a

Table 2, Continued. Vicinal Proton-Proton Coupling Constants of Substituted Cyclobutanes.

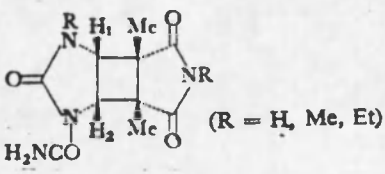
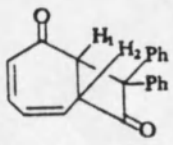
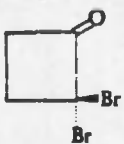
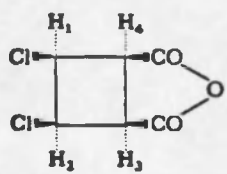
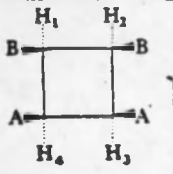
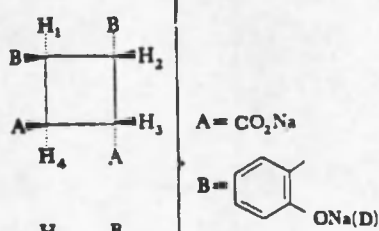
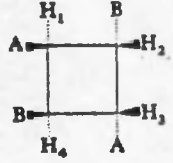
Entry	Compound	$^3J_{HH'}$ (Hz)		Reference *
		cis	trans	
7	 (R = H, Me, Et)	$J_{12} = 9.0 \pm 0.6$		a
8		$J_{12} = 4.6$		a
9		11.2 ± 0.2	7.7 ± 0.2	a
10		$J_{12} = 6.7$ $J_{34} = 8.1$ $J_{14} = 8.8$		a
11		$J_{12} = 9.4 \pm 1.4$ $J_{34} = 10.1 \pm 1.4$ $J_{14} = 10.1 \pm 0.3$		a
12		$J_{14} = 10.2 \pm 0.2$	$J_{12} = 4.0 \pm 0.2$ $J_{34} = 10.7 \pm 0.2$	a
13		$J_{14} = 10.6 \pm 0.3$	$J_{12} = 7.5 \pm 0.3$	a

Table 2, Continued. Vicinal Proton-Proton Coupling Constants of Substituted Cyclobutanes.

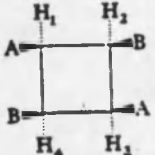
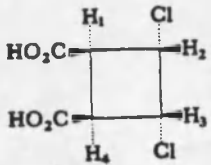
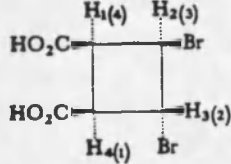
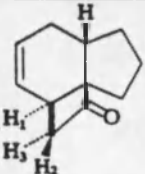
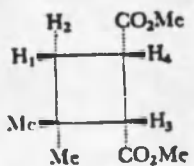
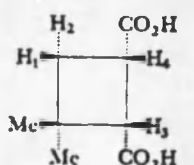
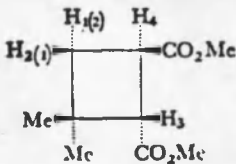
Entry	Compound	$^3J_{HH'}$ (Hz)		Reference*
		cis	trans	
14		$J_{12} = J_{23} = 9.6 \pm 0.3$		a
15		$J_{14} (J_{23}) = 6.3$ $J_{23} \text{ (or } J_{14}) = 10.6$	$J_{12} = 5.9$	a
16		$J_{12} = 8.7$ $J_{14} = 9.2$	$J_{23} = 8.7$ $J_{34} = 8.7$	a
17		$J_{13} = 10.3$	$J_{12} = 6.8$	a
18		$J_{14} = 9.23 \pm 0.25$ $J_{34} = 8.82 \pm 0.35$	$J_{24} = 9.18 \pm 0.32$	a
19		$J_{14} = 8.90 \pm 0.23$ $J_{34} = 8.58 \pm 9.37$	$J_{24} = 9.77 \pm 0.30$	a
20		$J_{14} = 9.32$	$J_{24} = 9.32$ $J_{34} = 9.02$	a

Table 2, Continued. Vicinal Proton-Proton Coupling Constants of Substituted Cyclobutanes.

Entry	Compound	$^3J_{HH'}$ (Hz)		Reference*
		cis	trans	
21		$J_{14} = 9.64 \pm 0.10$	$J_{24} = 9.64 \pm 0.10$ $J_{34} = 9.38 \pm 0.14$	a
22		$J_{13} = 10.81$ ± 0.07	$J_{23} = 7.93 \pm 0.09$	a
23		$J_{23} = 11.38$ ± 0.21	$J_{13} = 9.52 \pm 0.18$	a
24		$J_{13} = 10.75$	$J_{23} = 7.78$	a
25		8.0		a
26			6.9	a

Table 2, Continued. Vicinal Proton-Proton Coupling Constants of Substituted Cyclobutanes.

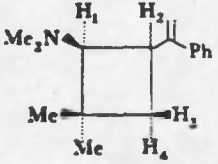
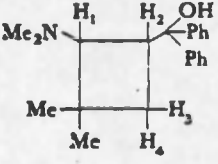
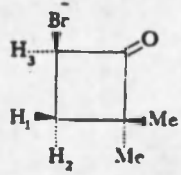
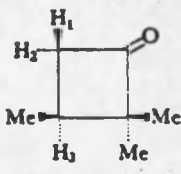
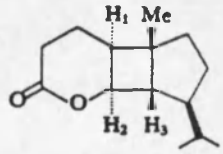
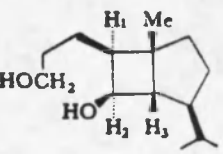
Entry	Compound	$^3J_{HH'}$ (Hz)		Reference*
		cis	trans	
27		$J_{24} = 9.0 \pm 1$ $J_{12} = 9.0 \pm 1$	$J_{23} = 9.0 \pm 1$	a
28		$J_{24} = 9.0 \pm 0.5$ $J_{12} = 9.0 \pm 0.5$	$J_{23} = 9.0 \pm 0.5$	a
29	For six alkyl, bromo, and alkylbromo cyclobutanones For eight alkyl, bromo and alkylbromo cyclobutanones	8.7 - 9.7	6.4 - 9.0	a
30		$J_{13} = 7.2 \pm 0.1$	$J_{23} = 8.9 \pm 0.3$	a
31		$J_{13} = 6.4 \pm 0.5$	$J_{23} = 8.9 \pm 0.3$	a
32		$J_{12} = 7.5$ $J_{23} = 4.0$		a
33		$J_{12} = 6.5$ $J_{23} = 2.0$		a

Table 2, Continued. Vicinal Proton-Proton Coupling Constants of Substituted Cyclobutanes.

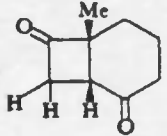
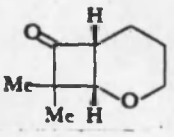
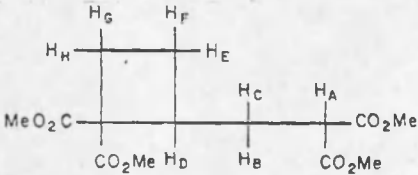
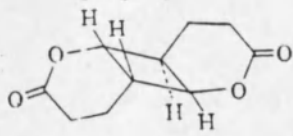
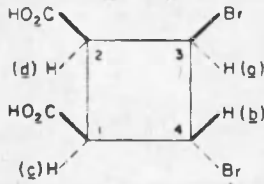
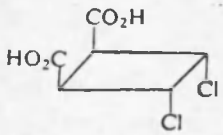
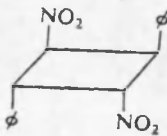
Entry	Compound	$^3J_{HH}$, (Hz)		Reference*
		cis	trans	
34		8.8	9.0	a
35		6		a
36		$J_{DF}=8.80$ $J_{EH}=9.36$ $J_{FG}=9.12$	$J_{DE}=10.11$ $J_{EG}=9.94$ $J_{FH}=2.72$	b
37		4.1	8.3	c
38		$J_{ad}=8.7$ $J_{cd}=9.2$	$J_{ab}=8.7$ $J_{bc}=8.7$	d
39		± 6.3 ± 10.6	± 5.9	e
40		± 10.0	± 6.2	e

Table 2, Continued. Vicinal Proton-Proton Coupling Constants of Substituted Cyclobutanes.

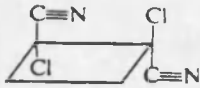

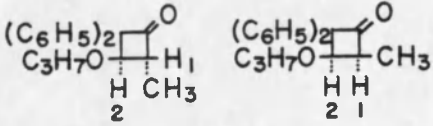
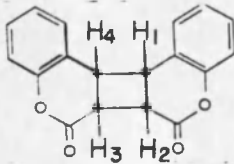
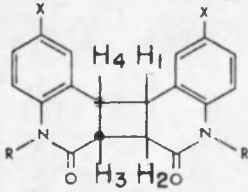
Entry	Compound	$^3J_{HH'}$ (Hz)		Reference*
		cis	trans	
41		± 9.4	± 9.3 ± 4.5	e
42		± 11.16	± 7.67	e
43		$J_{12} = 8.1$	$J_{12} = 7.0$	f
44		$J_{14} = 8.28$ $J_{34} = 8.56$ $J_{23} = 9.97$		g
45	 <ul style="list-style-type: none"> a. R = H, X = H b. R = CH₃, X = H c. R = CH₃, X = CH₃ d. R = CH₃, X = Cl 	b) $J_{34} = 8.77$ c) $J_{34} = 8.99$ d) $J_{34} = 8.77$	$J_{14} = 2.97$ $J_{23} = 7.87$ $J_{14} = 2.76$ $J_{23} = 7.53$ $J_{14} = 2.65$ $J_{23} = 7.53$	g

Table 2, Continued. Vicinal Proton-Proton Coupling Constants of Substituted Cyclobutanes.

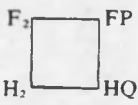
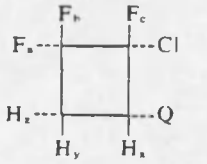
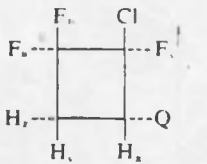
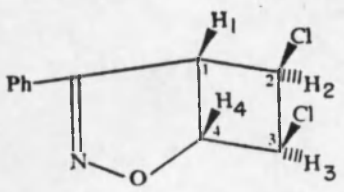
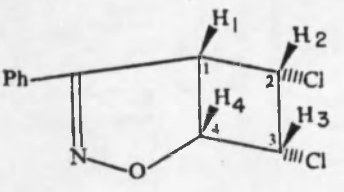
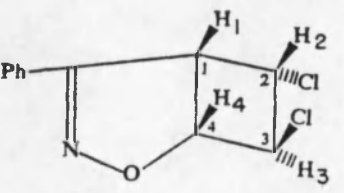
Entry	Compound	$^3J_{HH'}$ (Hz)		Reference*	
		cis	trans		
46	 <p>1: P = H, Q = Cl 2: P = I, Q = Cl 3: P = Br, Q = Br 4: P = Cl, Q = Cl 5: P = Cl, Q = Br</p>	2)	8.39	6.09	h
		3)	8.98	6.73	
		4a)	9.42	9.53	
		4b)	8.91	7.19	
		5a)	9.52	10.03	
		5b)	9.17	7.61	
	 <p>a: cis</p>  <p>b: trans</p> <p>4: Q = Cl 5: Q = Br</p>				
47		$J_{14} = 8.59$ $J_{23} = 6.89$	$J_{12} = 2.87$ $J_{34} = 4.06$	i	
48		$J_{14} = 7.63$ $J_{23} = 6.79$ $J_{12} = 7.05$ $J_{34} = 5.12$		i	
49		$J_{14} = 7.75$ $J_{12} = 8.30$	$J_{23} = 6.71$ $J_{34} = 3.68$	i	

Table 2, Continued. Vicinal Proton-Proton Coupling Constants of Substituted Cyclobutanes.

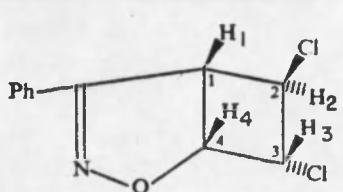
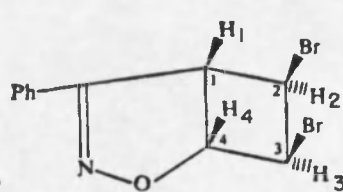
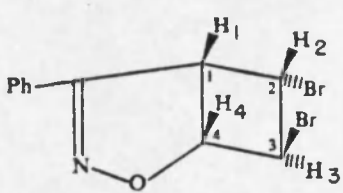
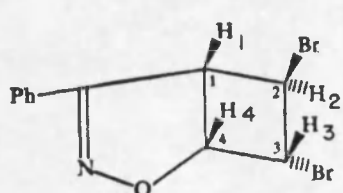
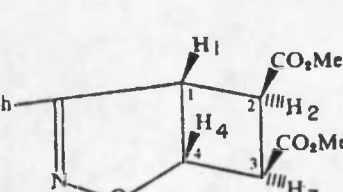
Entry	Compound	$^3J_{HH'}$ (Hz)		Reference*
		cis	trans	
50		$J_{14}=7.67$ $J_{34}=6.00$	$J_{23}=5.05$ $J_{12}=3.93$	i
51		$J_{14}=8.49$ $J_{23}=7.28$	$J_{12}=3.26$ $J_{34}=4.29$	i
52		$J_{14}=7.65$ $J_{12}=8.25$	$J_{23}=6.98$ $J_{34}=3.57$	i
53		$J_{14}=7.51$ $J_{34}=6.10$	$J_{23}=5.47$ $J_{12}=4.01$	i
54		$J_{14}=7.88$ $J_{23}=9.85$	$J_{12}=3.25$ $J_{34}=4.54$	i

Table 2, Continued. Vicinal Proton-Proton Coupling Constants of Substituted Cyclobutanes.

Entry	Compound	$^3J_{HH'}$ (Hz)		Reference*
		cis	trans	
55		$J_{14} = 7.66$	$J_{23} = 6.18$	i
		$J_{12} = 8.11$	$J_{34} = 3.35$	
56			$J_{12} = 9.3$	i
			$J_{14} = 9.2$	
			$J_{23} = 9.2$	
			$J_{34} = 9.3$	
57			$J_{12} = 8.9$	j
			$J_{14} = 10.3$	
			$J_{23} = 9.2$	
			$J_{34} = 9.6$	
58			$J_{12} = 10.2$	j
			$J_{14} = 9.2$	
			$J_{23} = 9.9$	
			$J_{34} = 9.0$	
59			$J_{12} = 9.5$	j
			$J_{14} = 9.2$	
			$J_{23} = 9.2$	
			$J_{24} = 9.5$	

Table 2, Continued. Vicinal Proton-Proton Coupling Constants of Substituted Cyclobutanes.

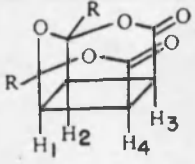
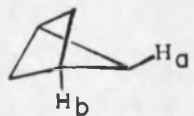
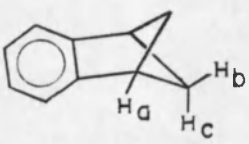
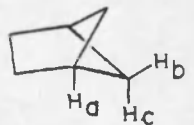
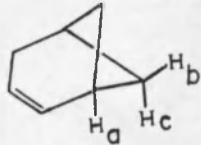
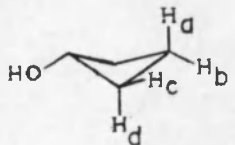
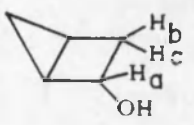
Entry	Compound	$^3J_{HH'}$ (Hz)		Reference*
		cis	trans	
60		$J_{12}=7.6$ $J_{14}=6.6$ $J_{23}=6.6$ $J_{34}=7.6$		j
61			$J_{ab}=0$	k
62		$J_{ac}=0$	$J_{ab}=2.4$	k
63		$J_{ac}=0$	$J_{ab}=2$ to 3	k
64		$J_{ac}=0$	$J_{ab}=5.1$ to 5.9	k
65		$J_{bc}=2.3$	$J_{ac}=7.9$ to 9.7 $J_{ad}=10.4$	k
66		$J_{ab}=9$	$J_{ac}=3.5$	k

Table 2, Continued. Vicinal Proton-Proton Coupling Constants of Substituted Cyclobutanes.

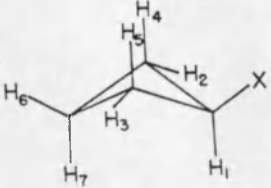
Entry	Compound	$^3J_{HH'}$ (Hz)		Reference*
		cis	trans	
67			X=F, $J_{12}=J_{13} = 6.77$	1
			$J_{14}=J_{15} = 7.28$	
			$J_{26}=J_{36} = 2.59$	
			$J_{27}=J_{37} = 7.91$	
		$J_{46}=J_{56} = 10.32$		
		$J_{57} = 10.20$		
		X=Cl, $J_{12}=J_{13} = 7.31$	1	
		$J_{14}=J_{15} = 8.24$		
		$J_{26}=J_{36} = 2.98$		
		$J_{27}=J_{37} = 8.04$		
		$J_{46}=J_{56} = 9.85$		
		$J_{57} = 9.87$		
		X=Br, $J_{12}=J_{13} = 7.36$	1	
		$J_{14}=J_{15} = 8.32$		
		$J_{26}=J_{36} = 3.18$		
		$J_{27}=J_{37} = 8.05$		
		$J_{46}=J_{56} = 9.83$		
		$J_{57} = 9.67$		
		X=I, $J_{12}=J_{13} = 7.50$	1	
		$J_{14}=J_{15} = 8.58$		
		$J_{26}=J_{36} = 3.35$		
		$J_{27}=J_{37} = 8.01$		
		$J_{46}=J_{56} = 9.64$		
		$J_{57} = 9.41$		

Table 2, Continued. Vicinal Proton-Proton Coupling Constants of Substituted Cyclobutanes.

Entry	Compound	$^3J_{HH'}$ (Hz)		Reference*
		cis	trans	
67 continued			X=OH, $J_{12} = J_{13} = 6.96$ $J_{14} = J_{15} = 8.09$ $J_{26} = J_{36} = 2.25$ $J_{27} = J_{37} = 7.90$ $J_{46} = J_{56} = 9.65$ $J_{57} = 10.37$	1

- * a. I. Fleming and D. H. Williams, *Tetrahedron*, 23, 2747 (1967).
 b. S. Castellano, *J. Magn. Resonance*, 21, 143 (1976).
 c. P. E. Eaton, *J. Amer. Chem. Soc.*, 84, 2344 (1962).
 d. V. Georgian, L. Georgian, and A. V. Robertson, *Tetrahedron*, 19, 1219 (1963).
 e. A. A. Bothner-By, *Advan. Magn. Resonance*, 1, 195 (1965).
 f. R. Huisgen, L. Feiler, and G. Binsch, *Angew. Chem.*, 76, 892 (1964).
 g. L. Paolillo, H. Ziffer, and O. Buchardt, *J. Org. Chem.*, 35, 38 (1970).
 h. R. A. Newmark, R. E. Watson, and T. S. Croft, *Tetrahedron*, 30, 3253 (1974).
 i. R. Mondelli, and A. Gamba, *Org. Magn. Resonance*, 5, 101 (1973).
 j. J. Laing, A. W. McCulloch, D. G. Smith, and A. G. McInnes, *Can. J. Chem.*, 49, 574 (1971).
 k. R. J. Abraham, M. A. Cooper, J. R. Salmon, and D. Whittaker, *Org. Magn. Resonance*, 4, 489 (1972).
 l. K. B. Wiberg, D. E. Barth, and W. E. Pratt, *J. Amer. Chem. Soc.*, 99, 4286 (1977).

Table 3. Vicinal (and Homoallylic) Proton-Proton Coupling Constants of Substituted Cyclobutenes and Compounds Containing the Cyclobutene Ring.

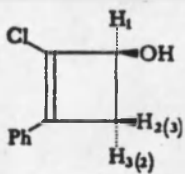
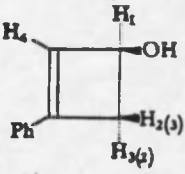
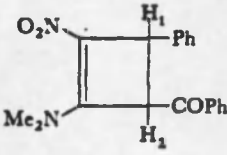
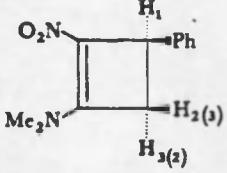
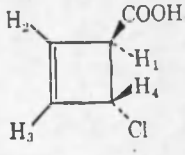
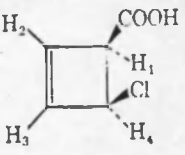
Entry	Compound	$^3J_{HH'}$ (Hz)		Reference*
		cis	trans	
1		4.1	1.6	a
2		3.81	1.2	a
3		1.8		a
4		6	2	a
5			$J_{14} = 2.1$	b
6			$J_{14} = 4.3$	b

Table 3, Continued

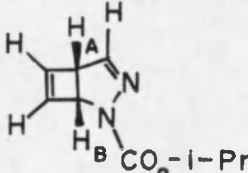
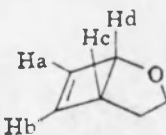
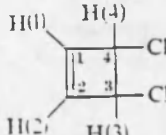
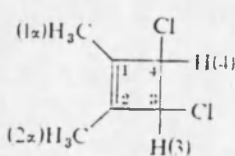
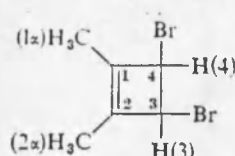
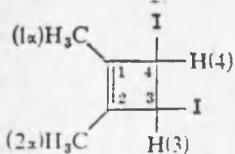
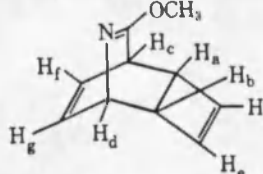
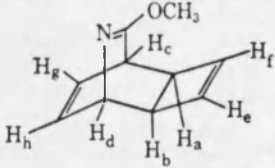
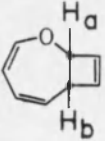
Entry	Compound	$^3J_{HH'}$ (Hz)		Reference*
		cis	trans	
7		$J_{ab} = 2.0$		c
8		$J_{cd} = 2.2$		d
9		$J_{34} = 3.2$		e
10		$J_{34} = 0.7$		e
11		$J_{34} = 1.0$		e
12		$J_{34} = 1.0$		e
13		$J_{ab} = 1.8$		f

Table 3, Continued

Entry	Compound	$^3J_{HH'}$ (Hz)		Reference*
		cis	trans	
14		$J_{ab} = 1.8$		f
15		$J_{ab} = 3.4$		g

*a. I. Fleming and D. H. Williams, *Tetrahedron*, 23, 2747 (1967).

b. W. H. Pirkle and L. H. McKendry, *J. Amer. Chem. Soc.*, 91, 1179 (1969).

c. J. Streith, J. P. Luttringer, and M. Nastasi, *J. Org. Chem.*, 36, 2962 (1971).

d. L. A. Paquette and J. H. Barrett, *J. Amer. Chem. Soc.*, 88, 1718 (1966).

e. H. Hüther and H. A. Brune, *Org. Magn. Resonance* 3, 737 (1971).

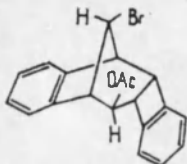
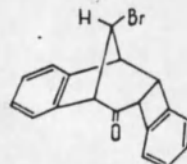
f. L. A. Paquette and G. R. Krow, *J. Amer. Chem. Soc.*, 90, 7149 (1968).

g. J. M. Holovka, P. D. Gardner, C. B. Strow, M. L. Hill, and T. V. Van Arken, *J. Amer. Chem. Soc.*, 90, 5041 (1968).

Table 4. Vicinal Proton-Proton Coupling Constants of Substituted Benzocyclobutenes.

Entry	Compound	${}^3J_{HH'}$ (Hz)		Reference*
		cis	trans	
1		4.76	1.95	a
2		4.06	4.00	a
3		X=OH, 4	≤ 1	a
		X=Br, 4	≤ 1	
4		6.1	3.2	a
5		± 6.1	± 3.2	a
6		$J_{25}=5.0$		b

Table 4, Continued

Entry	Compound	$^3J_{HH'}$ (Hz)		Reference*
		cis	trans	
7		$J_{25}=5.5$		b
8		$J_{25}=5.0$		b

*a. I. Fleming and D. H. Williams, *Tetrahedron*, 23, 2747 (1967).

b. I. G. Dinulescu, F. Chiraleu, M. S. Pop, and M. Avram, *Rev. Roum. Chim.*, 20, 85 (1975).

An NMR study of cyclobutane in a liquid crystal, a microwave study, and dipole moment measurements of substituted cyclobutanes have shown that the cyclobutane ring is normally puckered by 20° to 30° (Meiboom and Synder 1970; Rothschild and Dailey 1962; Lambert and Roberts 1965a). This leads to pseudoaxial (a) and pseudoequatorial (e) positions for each substituent. Whipple and Evanega (1970) have given the dependence of the aa, ae, and ee vicinal proton-proton coupling constants in cyclobutanes on puckering angle using the Karplus equation (Equation 5). They show that J_{ee} is always small (under 3 Hz). For puckering angles under 30° , the J_{ae} coupling should be greater than J_{aa} , but for angles above 30° , J_{aa} becomes larger than J_{ae} . Using the dihedral angle dependence of hydrogen-fluorine coupling constants, Lambert and Roberts (1965b) have shown that alkyl or monohalo substituted cyclobutanes prefer conformations in which the large substituent is locked in the equatorial position. Similar results have been found by Hopkins (1968) in other substituted cyclobutanes. Thus, a trans dialkyl cyclobutane should have both substituents equatorial and be found exclusively as one conformer, whereas a cis dialkyl cyclobutane should have equal populations of the two possible conformations in which one substituent is axial and the other equatorial.

Plots of experimental coupling constant data from Table 1 versus $P_{\mu\nu}$, $P_{\mu\nu}^2$, and $\pi_{\mu\nu}$ are given in Figures 8, 9, and 10; $P_{\mu\nu}$ is the bond order of Coulson and Longuet-Higgins (1947) and the $\pi_{\mu\nu}$ is the mutual atom-atom polarizability of orbitals μ and ν . Figure 11 shows the correlation between the calculated and observed cis vicinal coupling constants.

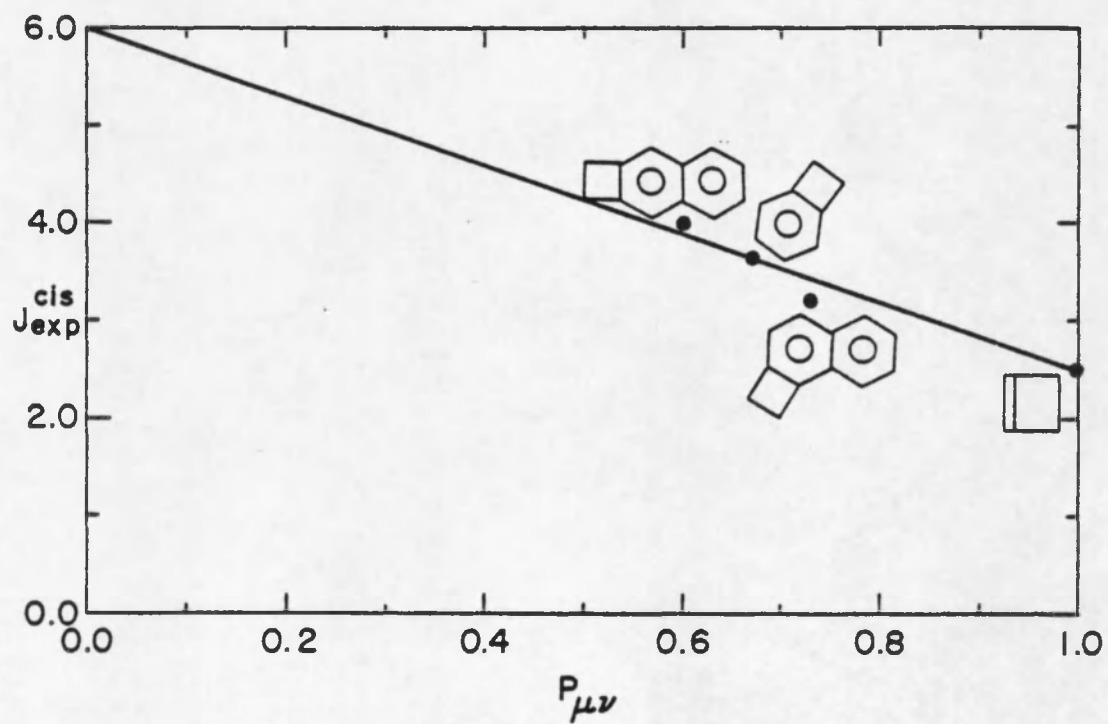


Figure 8. Plot of Vicinal Coupling Constant with π Bond Order.

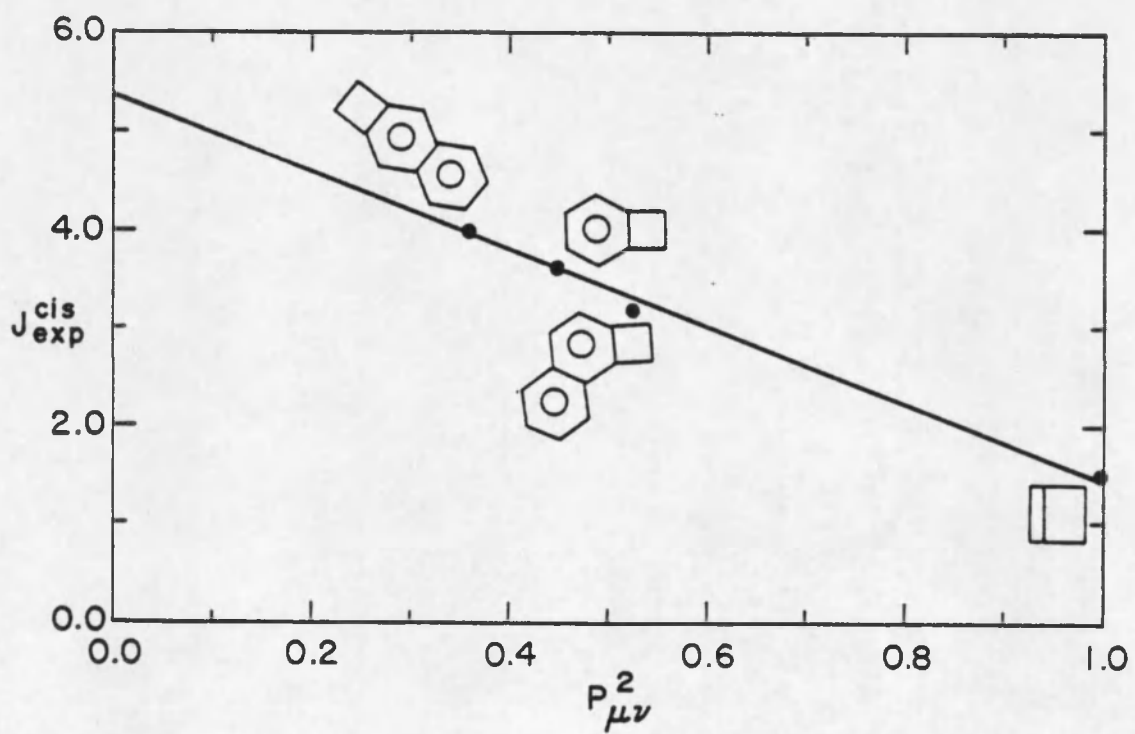


Figure 9. Plot of Vicinal Coupling Constant with Square of π Bond Order.

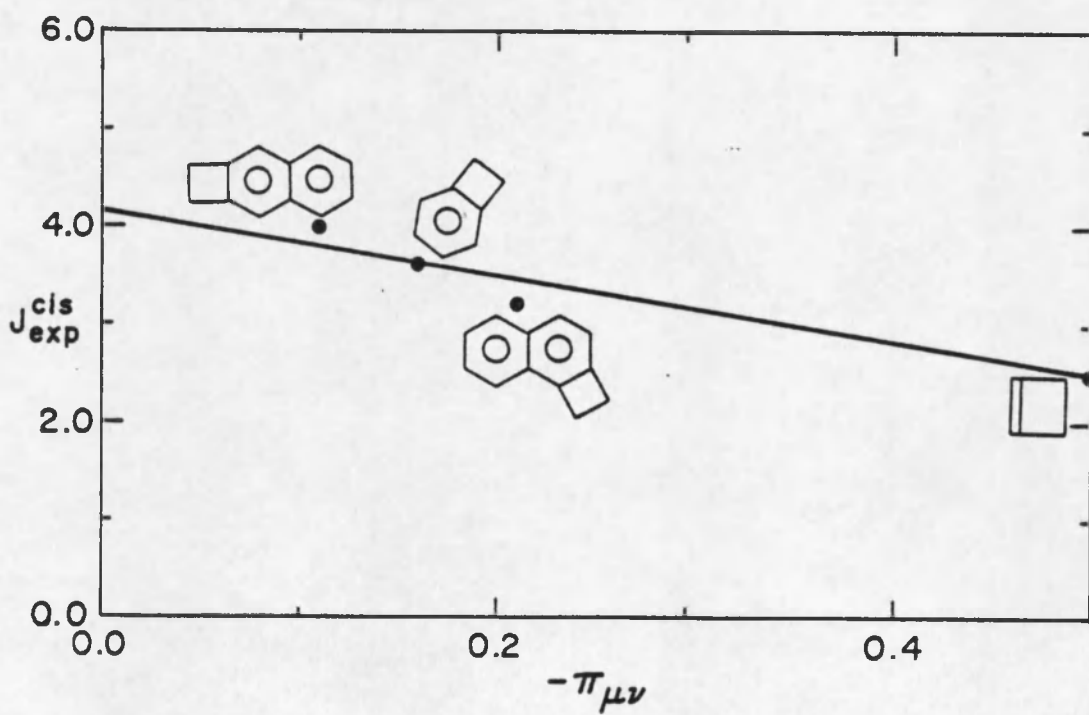


Figure 10. Plot of Vicinal Coupling Constant with Atom-Atom Polarizability.

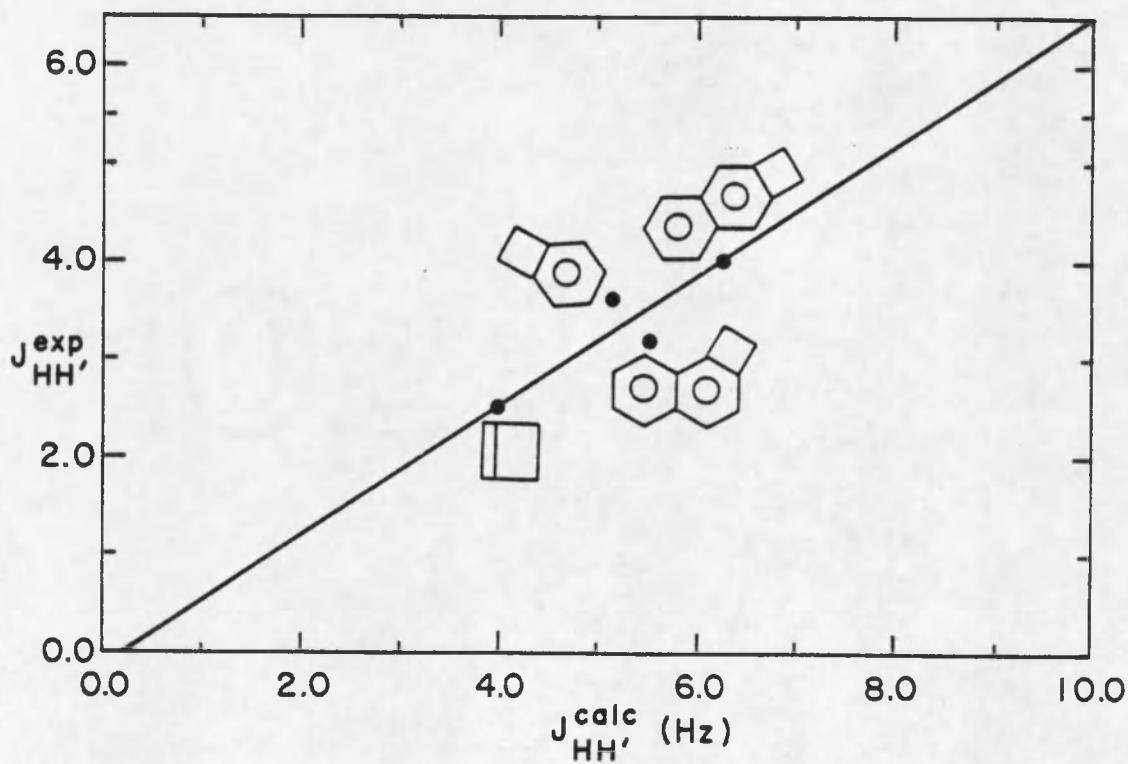


Figure 11. Plot of Experimental $J_{HH'}^{cis}$, with Calculated (LCAO-SCF-MO, INDO) $J_{HH'}^{calc}$.

Substituent Effects

Both cis and trans H-H coupling constants in cyclobutane rings appear to show strong dependence on the nature of substituents in those cases where experimental evidence is available (Williams and Bhacca 1964; Booth 1965; Fishman 1965). It is well-known that $^3J_{HH'}$ decreases on increasing the electronegativity of a substituent R in the system -HCH-CH'(R)- (Williamson 1963). The data in Table 2 seem to indicate a similar dependence. Complete rationalization is complicated by the fact that the rings are not planar (Meiboom and Synder 1970; Lambert and Roberts 1965a) but are conformationally mobile with low barriers to inversion (Lambert and Roberts 1963; Meiboom and Synder 1967; Stone and Mills 1970; Miller and Capwell 1971).

The cyclobutyl halides exist predominantly in one conformation (Wiberg, Barth, and Pratt 1977), and because of the similarity of the coupling constants between the 2,4 and 6,7 protons (entry 67, Table 2) from one halide to the next, the conformations are believed to be essentially the same. If the ring were to approach planarity (or if the conformer with an axial halogen dropped in energy so that the observed spectrum became an average of the equatorial and axial species) J_{26} would increase while J_{47} would decrease. The smallest conformational preference would be expected with fluorine, but here the equatorial-equatorial coupling has the smallest value and the axial-axial coupling has the largest value (Wiberg et al. 1977).

In the case of cyclobutenes no clear pattern emerges as regards the electronegativity of substituents. But the FPT-INDO calculations performed by Barfield, Spear, and Sternhell (1971) for compounds of the

type depicted in Figure 12 (with X = CH₂, NH, O) predicted J_{25'} to be larger than J₂₅ in agreement with experimental evidence. The authors (Barfield et al. 1971) carefully analyzed the origin of the differences both within the molecules and in the series, using INDO calculations on smaller acyclic systems and qualitative MO analysis of the type used by Pople and Bothner-By (1965) for geminal proton couplings. The conclusion they reached was that the differences they obtained were mainly due to the substituent effects on the homoallylic contributions to the couplings.

Because of the sensitivity of the homoallylic coupling constants to stereochemistry, the examination of the influence of substituents must be made with caution to ensure that the observed effect is not due to the influence of the substituent on the geometry of the molecule (Barfield and Sternhell 1972).

Calculated Results

Molecular Orbital Calculations

The INDO-FPT results of primary interest are entered in Table 1 while the Appendix contains a summary of the coupling constants of the various protons and ring carbon atoms with the proton of interest.

The calculated results parallel the experimental data and show the same changes in the coupling constants in the series of molecules from cyclobutane to cyclobutene, a decrease instead of the apparently anomalous increase. Although the calculated results are somewhat larger than the corresponding experimental data, the ratio of calculated to experimental data exhibits uniformity as shown in Figure 11.

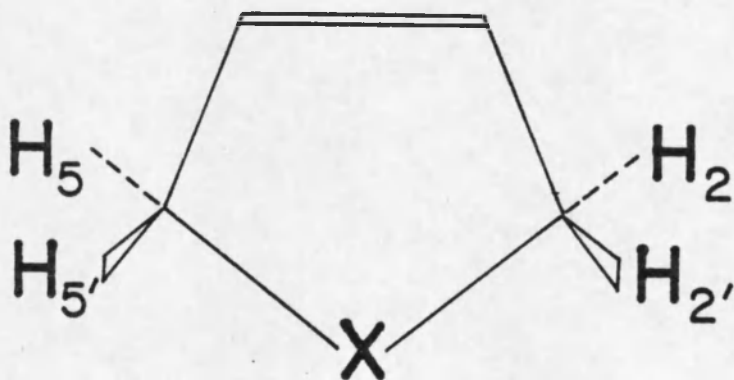


Figure 12. Five-Membered Ring Fragment ($X = CH_2, NH, O$).

Correlation of Coupling Constants with Bond Orders and Mutual Atom-Atom Polarizabilities

Figures 8 and 9 confirm the trend in which the coupling constant increases as the bond order goes down.

The dependence of the coupling constant on mutual atom-atom polarizability is shown in Figure 10. The same trend is indicated, implying that both cis and trans couplings should decrease from cyclobutane to cyclobutene, which is unexpected.

CONCLUSIONS

In general, the magnitudes of the calculated INDO-FPT coupling constants reproduce the trends of the experimental values but in a few cases the values are overestimated by as much as 50%. However, there is a considerable spread in the experimental values. The INDO-FPT method, notwithstanding the dangers (Armour and Stone 1967) inherent in the calculation of coupling constants, is quite a successful criterion against which molecular wavefunctions and therefore theoretical treatments might be tested.

Considering the change from cyclobutane to cyclobutene, one would expect the bond angles to increase and the coupling to decrease since it is predicted theoretically (Muller and Pritchard 1959) that the H-C-H angle will open as the ring size of cycloalkanes decreases. But any decrease in the coupling might be more than offset by the increase arising from the dropping off of the dihedral angle from 90° as seen in Figure 3.

A satisfactory qualitative and quantitative explanation for the expected increase in the vicinal coupling in going from cyclobutane to cyclobutene may be given on the basis of theoretical arguments which take into account the π -electron system which is undoubtedly important for homoallylic coupling. In view of the expected large homoallylic coupling contribution to the observed vicinal coupling constants in cyclobutene, the decrease in the coupling constant in going from

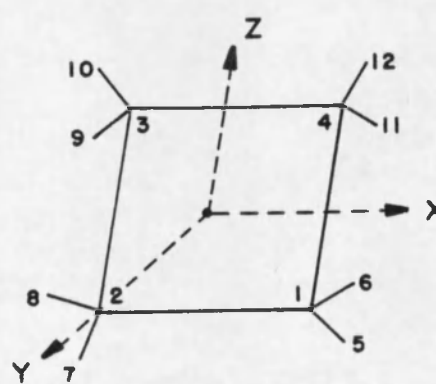
cyclobutane to cyclobutene has not yet been rationalized in terms of the electronic factors involved. It may be speculated that the additional resonance structures which could be drawn in the case of the benzo-cyclobutenes could partly explain the observed trends.

Finally, it seems likely that when variations occur in the differences between two or more coupling constants across the same carbon-carbon bond in four-membered rings, they can be attributed to ring puckering. However, more evidence is needed to test this proposal.

APPENDIX

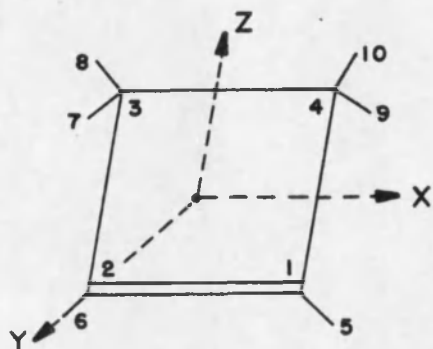
SUMMARY OF THE MISCELLANEOUS COUPLING CONSTANTS OF THE SYSTEMS STUDIED

Calculation is based on the LCAO-SCF-MO method in the INDO approximation.

<u>SYSTEM*</u>	$J_{p,q}$ (Hz) (where q is nucleus of interest)
	$J_{1,12} = - 5.85$ $J_{2,12} = 4.44$ $J_{3,12} = - 5.85$ $J_{4,12} = 131.39$ $J_{5,12} = 5.59$ $J_{6,12} = 7.44$ $J_{7,12} = - 0.04$ $J_{8,12} = 1.00$ $J_{9,12} = 5.59$ $J_{10,12} = 7.44$ $J_{11,12} = - 3.05$

*cyclobutane: angles were taken to be tetrahedral: $r(\text{C-C}) = 1.54\text{\AA}$;
 $r(\text{-C-H}) = 1.08\text{\AA}$.

SYSTEM*


 $J_{p,q}$ (Hz)
 (where q is nucleus of interest)

$$J_{1,10} = - 8.37$$

$$J_{2,10} = 10.88$$

$$J_{3,10} = - 5.14$$

$$J_{4,10} = 135.06$$

$$J_{5,10} = 0.30$$

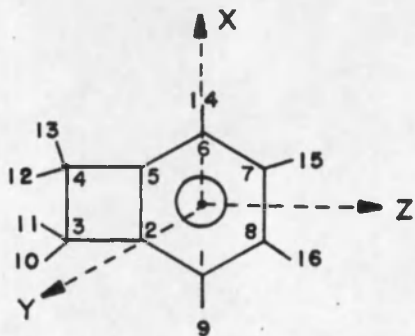
$$J_{6,10} = 2.25$$

$$J_{7,10} = 2.70$$

$$J_{8,10} = 4.03$$

$$J_{9,10} = - 2.52$$

*cyclobutene: angles were taken to be either trigonal or tetrahedral: $r(\text{C}=\text{C}) = 1.330\text{\AA}$; $r(\text{C}-\text{C}) = 1.483\text{\AA}$; $r(\text{C}-\text{C}) = 1.54\text{\AA}$; $r(\text{C}-\text{H}) = 1.08\text{\AA}$



$$J_{1,10} = 3.34$$

$$J_{2,10} = - 7.83$$

$$J_{3,10} = 128.56$$

$$J_{4,10} = - 5.01$$

$$J_{5,10} = 9.42$$

$$J_{6,10} = - 1.04$$

$$J_{7,10} = 3.25$$

$$J_{8,10} = - 2.83$$

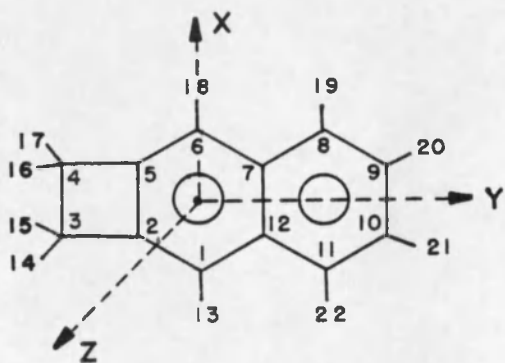
$$J_{9,10} = - 0.65$$

$$J_{11,10} = - 4.68$$

SYSTEM* $J_{p,q}$ (Hz)
 (where q is nucleus of interest)

$J_{12,10}$	=	5.17
$J_{13,10}$	=	3.82
$J_{14,10}$	=	1.12
$J_{15,10}$	=	- 0.82
$J_{16,10}$	=	0.62

*benzocyclobutene: angles were taken to be either trigonal or tetrahedral; $r(C=C) = 1.40\text{\AA}$; $r(C-C) = 1.54\text{\AA}$; $r(C-H) = 1.08\text{\AA}$; $r(=C-C) = 1.483\text{\AA}$.



$J_{1,14}$	=	5.42
$J_{2,14}$	=	- 8.81
$J_{3,14}$	=	128.49
$J_{4,14}$	=	- 5.44
$J_{5,14}$	=	9.42
$J_{6,14}$	=	- 2.08
$J_{7,14}$	=	2.78
$J_{8,14}$	=	- 2.59
$J_{9,14}$	=	2.49
$J_{10,14}$	=	- 2.29
$J_{11,14}$	=	2.69
$J_{12,14}$	=	- 2.87
$J_{13,14}$	=	- 1.25
$J_{15,14}$	=	- 5.54
$J_{16,14}$	=	6.26

SYSTEM*

$$J_{p,q} \text{ (Hz)}$$

(where q is nucleus of interest)

$$J_{17,14} = 4.88$$

$$J_{18,14} = 1.47$$

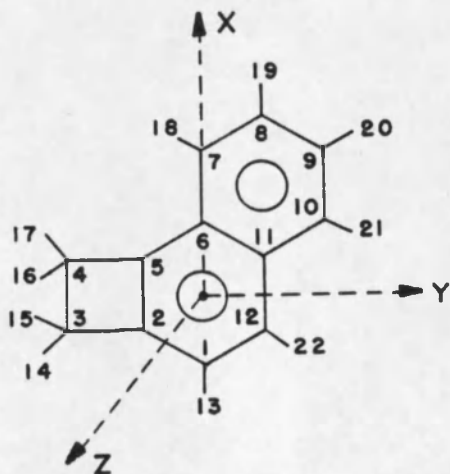
$$J_{19,14} = 0.71$$

$$J_{20,14} = -0.68$$

$$J_{21,14} = 0.59$$

$$J_{22,14} = -0.79$$

*naphthocyclobutene: angles were taken to be either trigonal or tetrahedral: $r(\text{C}=\text{C}) = 1.40\text{\AA}$; $r(\text{C}-\text{C}) = 1.54\text{\AA}$; $r(\text{C}-\text{H}) = 1.08\text{\AA}$; $r(\text{C}=\text{C}-\text{C}) = 1.483\text{\AA}$.



$$J_{1,14} = 3.68$$

$$J_{2,14} = -9.12$$

$$J_{3,14} = 128.56$$

$$J_{4,14} = -5.39$$

$$J_{5,14} = 11.61$$

$$J_{6,14} = -1.48$$

$$J_{7,14} = 3.11$$

$$J_{8,14} = -2.41$$

$$J_{9,14} = 2.69$$

$$J_{10,14} = -2.79$$

$$J_{11,14} = 2.94$$

$$J_{12,14} = -4.00$$

$$J_{13,14} = -0.65$$

$$J_{15,14} = -4.91$$

$$J_{16,14} = 5.52$$

SYSTEM* $J_{p,q}$ (Hz)
 (where q is nucleus of interest)

$$J_{17,14} = 4.16$$

$$J_{18,14} = - 0.83$$

$$J_{19,14} = 0.70$$

$$J_{20,14} = - 0.75$$

$$J_{21,14} = 0.79$$

$$J_{22,14} = 1.03$$

*naphthocyclobutene: angles were taken to be either trigonal or tetrahedral: $r(C=C) = 1.40\text{\AA}$; $r(C-C) = 1.54\text{\AA}$; $r(C-H) = 1.08\text{\AA}$; $r(=C-C) = 1.483\text{\AA}$.

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