Interproton Spin–Spin Coupling across a Dual Path in Five-Membered Rings

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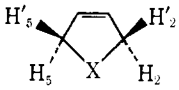
Abstract: A theoretical study of long-range H–H coupling constants across a dual homoallylic (H—C—C=C—C–H) and H—C—X—C—H path in five-membered rings is presented in terms of finite-perturbation theory (FPT) in the semiempirical INDO (intermediate neglect of differential overlap) approximation of self-consistent-field molecular orbital theory (SCF–MO). Calculated results for idealized, planar, five-membered ring systems, **1**, where X denotes CH_2, N–H, or O, indicate that J(trans) ($J_{2,5'}$) should be larger than J(cis) ($J_{2,5}$), in reasonable agreement with experimental data. Since the FPT–SCF–MO method as an example of coupled Hartree–Fock theory does not provide a simple basis for interpreting coupling constant mechanisms, qualitative theoretical arguments are presented in terms of the method which uses a sum over excited states in the second-order perturbation sum. On this basis, it is concluded that the cis and trans H–H coupling constants are inherently different and that the major differences between the two can be attributed to substituent effects on the homoallylic contributions.

Several well-documented examples of long-range coupling ($J_{2,5}$) in system **1** (X = O, NR) can be found in the literature,[2–11] from which the following empirical generalizations may be deduced. (i) The absolute magnitude of $J_{2,5}$(trans) is larger than that of $J_{2,5}$(cis). (ii) It is unlikely that this effect is significantly dependent on ring puckering, because some of the most significant results were obtained with systems which are known to be planar.[4,5] (iii) In cases where signs of coupling constants have been determined,[4,5] they appear to be of the same sign and positive. (iv) It has been suggested[3] that the double bond and the heteroatom are both necessary ("synergistic effect") for the observation of the widely different cis and trans coupling constants. A double bond is clearly important, since no significant coupling has been observed in saturated analogs, but owing to scarcity of data relating to cyclopentene derivatives (see below) and to the virtual impossibility of separating steric and electronic effects, the exact role of the heteroatom cannot be considered experimentally established.



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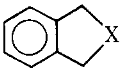

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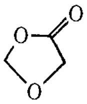

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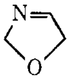

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It has also been found [12–16] that similar, but numerically smaller effects can be found in the benzo analogs of system **1**, *i.e.*, in **2**. Interestingly, systems **3** and **4**, which may be considered as isoelectronic with 2,5-dihydrofuran, also exhibit the above phenomenon.[17,18] The scant amount of data for cyclopentenes[19,20] and their aza analogs[21,22] do not permit far-reaching generalization, but there is no reason to assume from the available data that J(trans) and J(cis) are identical.

This work represents an attempt to create a theoretical explanation for the long-range coupling phenomena in system **1**. Besides the inherent interest of the problem, a successful rationalization of the empirical data may be helpful for the evaluation of the usefulness of such data for stereochemical assignments.

The mechanisms determining this type of coupling are exceedingly complex. The disparity between long-range coupling constants in 2,5-dihydrofuran and tetrahydrofuran have been discussed[2] in terms of the symmetry properties of the molecular orbitals. It was concluded that the differences between cis and trans H–H coupling could be attributed to the lone pairs on oxygen in addition to contributions from the σ and π electrons. In that study it was not possible, on the basis of symmetry arguments alone, to say anything theoretically about the directions and magnitudes of these effects.

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[1] To whom correspondence should be directed at the University of Arizona.

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The present investigation presents theoretical results for coupling over the dual path in five-membered rings based on finite perturbation theory[23] and semiempirical INDO (intermediate neglect of differential overlap) wave functions.[24] Since this method offers no simple conceptual basis for interpreting the relevant mechanisms, the theoretical and experimental results are investigated by means of qualitative arguments which make use of the symmetry of the molecular orbitals and the appropriate energy level diagrams. These results emphasis the importance of the substituent X in **1** on the homoallylic coupling constant as well as the four-bond path, H–C–X–C–H, and it is concluded that it is the substituent effect on homoallylic coupling which has the major effect on the difference between the cis and the trans coupling constants.

I. Theoretical Formulation

(A) Theoretical Calculations by Finite Perturbation Theory in the INDO Approximation. Calculations of long-range H–H coupling constants are based on finite perturbation theory[23] and semiempirical wave functions in the INDO approximation of unrestricted self-consistent-field molecular orbital (SCF–MO) theory.[24] The finite-perturbation method (FPT) for coupling constants is performed by adding the contact perturbation of magnitude

$$\eta_{\mathrm{H}} = (8\pi/3)\gamma_{\mathrm{H}}\phi_{\mathrm{H}}{}^2(\mathrm{H}) \qquad (1)$$

to the diagonal element for the s orbital of proton H in the Fock matrix corresponding to electrons of α spin. This term is subtracted from the corresponding element of the Fock matrix for electrons of β spin. Thus, the contact perturbation has the effect of inducing a small spin density, $\rho_{\mathrm{h}'}$, throughout the molecular electronic system. The coupling constant can be obtained from the spin density

$$J_{\mathrm{HH}'} = h(4\beta)^2\gamma_{\mathrm{H}}\gamma_{\mathrm{H}'}\phi_{\mathrm{h}}{}^2(\mathrm{H})\phi_{\mathrm{h}'}{}^2(\mathrm{H}')[\rho_{\mathrm{h}'}(\eta_{\mathrm{H}})/\eta_{\mathrm{H}}] \qquad (2)$$

where $\rho_{\mathrm{h}'}(\eta_{\mathrm{H}})$ is the diagonal element of the spin-density matrix corresponding to the 1s orbital which is centered on proton H′, β is the Bohr magneton, γ_{H} is the magnetogyric ratio of the proton, and $\phi_{\mathrm{h}}{}^2(\mathrm{H})$ is the 1s orbital density at proton H. The spin-density matrix is computed as the difference between the α- and β- spin components of the density matrix. Because the spin density is exceedingly small in these systems, the spin-density matrix must be known with great accuracy to calculate coupling constants from eq 2. The usual energy criterion for convergence of the SCF iterations is changed[23] to the requirement that the root-mean-square difference between successive density matrices

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

be less than 10^{-9}.

A number of theoretical studies of contact nuclear spin–spin coupling have made use of sum over excited states methods. In the scheme of Pople and Santry[25] the coupling constant is obtained as a sum over occupied and unoccupied MO's

$$J_{\mathrm{HH}'} = -h^{-1}(16\pi\beta\hbar/3)^2\gamma_{\mathrm{H}}\gamma_{\mathrm{H}'}\phi_{\mathrm{h}}{}^2(\mathrm{H})\phi_{\mathrm{h}'}{}^2(\mathrm{H}') \times \sum_{\substack{i,\mathrm{occ}\\ j,\mathrm{unocc}}} (\epsilon_j - \epsilon_i)^{-1}c_{i\mathrm{h}}c_{i\mathrm{h}'}c_{j\mathrm{h}}c_{j\mathrm{h}'} \qquad (3)$$

where $c_{i\mathrm{h}}$ and $c_{j\mathrm{h}'}$ are the coefficients of the 1s atomic orbitals h and h′ in the *i*th occupied and *j*th unoccupied MO's with energies ϵ_i and ϵ_j, respectively. If SCF wave functions are used in eq 3, the method corresponds to one approximation to the first-order Hartree–Fock perturbation equations.[26,27] This method has been called[26] the "uncoupled" Hartree–Fock approximation and, in general, leads to poor results for polarizabilities[27] and nuclear spin–spin coupling constants.[28] In the same terminology[26,27] the finite-perturbation method conforms to the "coupled" Hartree–Fock method.

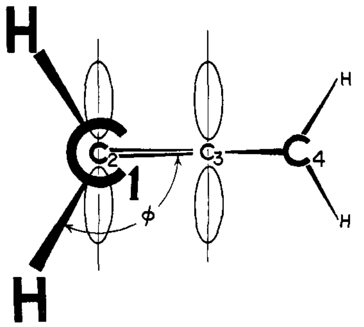

Figure 1. A fragment of the *cis*-2-butene molecule; the dihedral angle ϕ is measured from the C_1–C_2–C_3 plane.

Calculated coupling constants in this study were based on the semiempirical INDO approximation.[24,29] The integral parameterization in this scheme is discussed in ref 24. Valence s-orbital densities are semiempirical ones from ref 23. Molecular coordinates were based on representative bond lengths and bond angles from the compilations of Sutton.[30] All computations were performed on a Control Data Corporation 6400 digital computer.

(B) Substituent Effects on Homoallylic Coupling Constants. Previous theoretical calculations[31,32] of homoallylic coupling constants were based on the σ–π configuration-interaction mechanism and six electron molecular fragments consisting of the π bond and the two C–H bonds containing the coupled nuclei. The calculated semiempirical valence-bond (VB) results[32] are given by

$${}^5J_{\mathrm{HH}'}{}^{\pi} = 4.99 \sin^2 \phi \sin^2 \phi' \qquad (4)$$

where ϕ and ϕ' are the dihedral angles of the C–H bonds measured from the C_1–C_2–C_3 and C_2–C_3–C_4 planes, respectively, as depicted in Figure 1. According to eq 4, the cis ($\phi = 120°$, $\phi' = 120°$) and trans ($\phi = 120°$, $\phi' = 240°$) coupling constants should be identical in sign and magnitude (2.81 Hz). Recently, it has been

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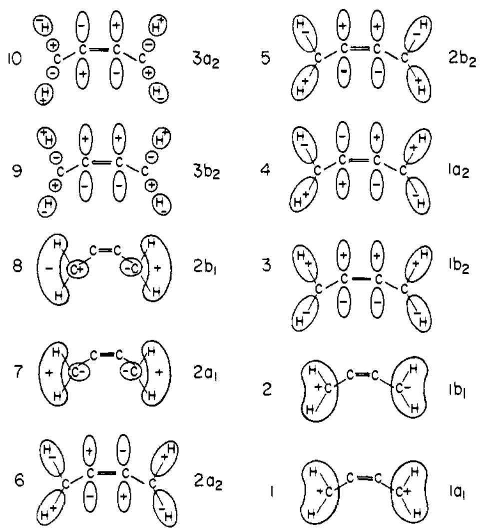


Figure 2. Nodal behavior and symmetry designations for the molecular orbitals of a ten-electron fragment of the *cis*-2-butene molecule.

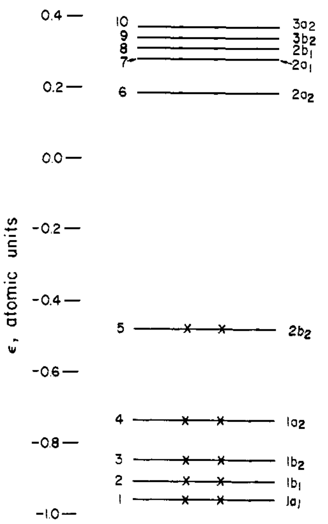


Figure 3. Molecular orbital energies for the ten-orbital fragment of the *cis*-2-butene molecule.

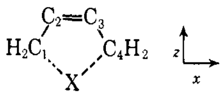
suggested[33] that the cis and trans homoallylic coupling constants may not have equal magnitudes. In fact, the theoretical SCF-MO results in the next section give inherently different values for these coupling constants. For example, in *cis*-2-butene, the calculated cis and trans (cis and trans are defined so as to maintain a situation analogous to $J_{2,5}$ and $J_{2,5'}$ in system **1**) coupling constants are found to be +2.83 and +3.17 Hz, respectively. These differences can be rationalized most simply by means of symmetry arguments of the type proposed by Barbier, Gagnaire, and Vottero.[2]

There appears to have been no previous general theoretical discussion of substituent effects on homoallylic coupling constants. A qualitative analysis is presented here which is completely analogous to those which have been used to discuss geminal[34] and long-range H-H coupling over four bonds.[35,36]

The qualitative analysis of substituent effects on homoallylic coupling constants is based on the ten-electron fragment of the *cis*-2-butene molecule in Figure 1. The fragment consists of eight electrons in two CH_2 groups and the two electrons of the double bond. The nodal behavior of the molecular orbitals is depicted in Figure 2. Each of the MO's is labeled by the appropriate irreducible representation for the C_{2v} symmetry group for the *cis*-2-butene molecule. The ordering of the MO energies in Figure 3 is based on the calculated INDO results for *cis*-2-butene.

The sign of the contribution to the cis and trans coupling constants of each term in the perturbation sum in eq 3 is just opposite to the sign of the product of the coefficients of the 1s atomic orbitals, h and h′. These signs are entered in the second and third columns of Table I for each of the transitions from occupied to unoccupied MO's which correspond to opposite signs for ^5J(cis) and ^5J(trans). The ordering of the excitations in the first column of the table correspond to increasing energy separation as inferred from Figure 3.

Now consider the effect of introducing an electron-withdrawing group, **X**, linked to carbon atoms C_1 and C_4 in such a way that the C_{2v} symmetry is preserved.



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Electron density will be withdrawn from the bonding region of the symmetric MO, $1a_1$, which is depicted in Figure 2. This will result in a decrease in the 1s atomic orbital coefficients. The 1s coefficients of the other MO's of this symmetry will be increased accordingly and the coefficients of the other MO's will be unchanged because of orthonormality. The substituent will have a much smaller effect on the coefficients of

Table I. Changes in the Magnitudes of the Homoallylic Cis and Trans Coupling Constants Due to an Inductive or a Hyperconjugative Substituent Bonded to the C_1 and C_4 Carbon Atoms

			Sign change			
	Sign[b] of		X, inductive[c]		X, hyperconjugative[c]	
Transition[a]	^5J(cis)	^5J(trans)	^5J(cis)	^5J(trans)	^5J(cis)	^5J(trans)
5 → 7	−	+	> −	> +	< −	< +
5 → 8	+	−	...	...	< +	< −
4 → 7	+	−	> +	> −	...	...
4 → 8	−	+	...	...	...	...
2 → 6	−	+	...	...	...	...
3 → 7	−	+	> −	> +	< −	< +
1 → 6	+	−	< +	< −	...	...
3 → 8	+	−	...	...	< +	< −
2 → 9	−	+	...	...	> −	> +
2 → 10	−	+	...	...	...	...
1 → 9	−	+	< −	< +	> −	> +
1 → 10	+	−	< +	< −	...	...

[a] Only those transitions which have opposite signs for the contributions to the cis and trans coupling constants are included. Transitions are listed in order of increasing energy separation. [b] Signs were based on eq 3 where the signs of the coefficients follows from the irreducible representations for the C_{2v} symmetry group. [c] A case in which the substituent would be expected to have little or no effect is indicated by an ellipsis.

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(33) D. J. Atkinson and M. J. Perkins, *Tetrahedron Lett.*, 2335 (1969).

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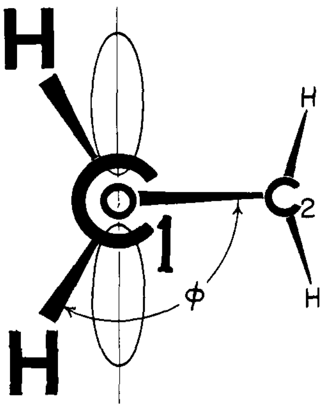

Figure 4. A fragment of the dimethyl ether molecule; the dihedral angle ϕ is measured from the C_1–O–C_2 plane.

the $1b_1$ MO, because only the $2p_x$ atomic orbital of X is of the proper symmetry for interacting with this MO. In columns four and five of Table I are entered the changes which are expected in the values of ^5J(cis) and ^5J(trans) due to the introduction of an electron-withdrawing substituent. By counting up the number of increases and decreases in each column, it may be reasonably concluded that the introduction of an electron-withdrawing group, X, should lead to less positive values of the cis coupling and more positive values of the trans homoallylic coupling constant.

The introduction of an hyperconjugative substituent, X, in **5** would have the major effect of reducing the electron density about the four hydrogen atoms in the antisymmetric MO's $1b_2$ and $2b_2$. The coefficients of the 1s orbitals in these MO's will be decreased, whereas those in the $3b_2$ MO will be increased. With the same kinds of arguments which were used for the case of an inductive substituent, it follows that the hyperconjugative substituent will affect those transitions which have differing signs for the contributions to the cis and trans coupling constants as given in the last two columns of Table I. From these values it appears, therefore, that the overall effect of the introduction of an hyperconjugative substituent should also be to give less positive values of the cis coupling and more positive values of the trans coupling. The trends which are predicted for inductive and hyperconjugative substituents in this section are qualitatively consistent with the calculated results based on finite perturbation theory to be discussed in section II.

(C) Dependence of Long-Range Coupling over Four Bonds in H–C–X–C–H on the Nature of X. Long-range H–H coupling over four bonds in H–C–X–C–H has been investigated theoretically for the case in which X denotes a carbon atom.[35–38] The conformational dependence of this type of coupling apart from substituent effects is quite complex, exhibiting both positive and negative signs, depending on the orientations of the bonds containing the coupled nuclei. This type of coupling is predicted and found to have its maximum (positive sign) value in the all-trans or "W" conformation. The most recent calculations,[38] which are based on finite-perturbation theory and INDO wave functions, indicate that positive values occur only for a narrow range of dihedral angles near the all-trans orientation of the coupled protons.

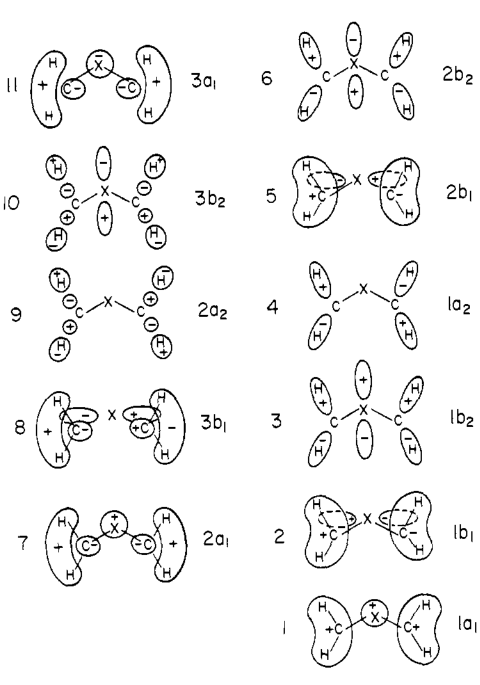

Figure 5. Nodal behavior and symmetry designations for the molecular orbitals of an 11-orbital fragment of the dimethyl ether molecule.

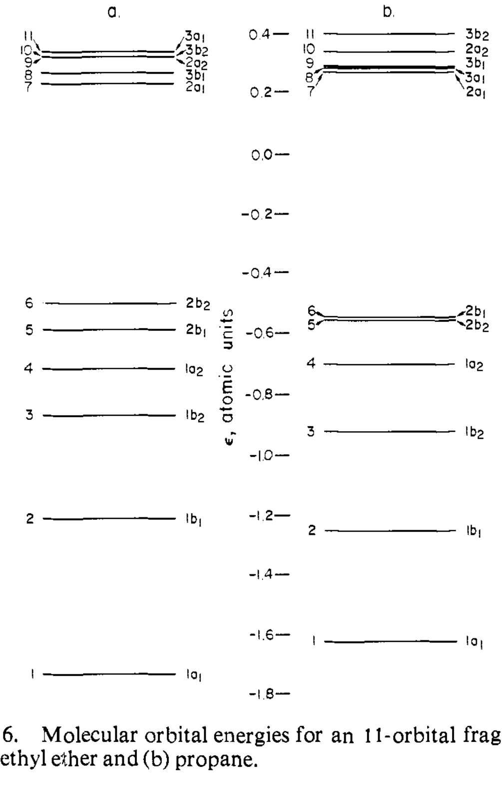

Figure 6. Molecular orbital energies for an 11-orbital fragment of (a) dimethyl ether and (b) propane.

The effect of substituents on propanic coupling constants have also been discussed[35,36] by means of crude qualitative arguments of the type used in the preceding section. The theoretically calculated results,[38] which should provide a better criterion, indicate that inductive substituents at either the C_1 or C_2 carbon atom should lead to positive shifts of $^4J_{HH'}$ from the propane value. However, hyperconjugative

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(37) M. Barfield, *J. Chem. Phys.*, 41, 3825 (1964).

(38) M. Barfield, *J. Amer. Chem. Soc.*, 93, 1066 (1971).

substituents at the central and terminal carbon atoms of propane are expected to give positive and negative shifts, respectively. There is not a great amount of experimental data in substituted propanes to test these predictions; however, for substituted propenes these predictions are reasonably consistent with the experimental data.[38]

Now consider an 11-orbital fragment of the dimethyl ether molecule in the conformation depicted in Figure 4. The fragment consists of four C-H bonds and 2s, $2p_x$, and $2p_y$ atomic orbitals on oxygen. The nodal behavior of the MO's and their C_{2v} symmetry designations are given in Figure 5. The ordering of these MO's based on the INDO results for dimethyl ether is given in Figure 6a. For comparison, analogous data for propane are given in Figure 6b.

The shifts in the cis and trans values of $^4J_{HH'}$ due to an increase in the inductive or hyperconjugative character of X are determined by means of arguments which are almost identical with those given in the preceding section. From the results tabulated in Table II, it can be seen that if X is more inductive, then the cis coupling constant should be more negative and the trans coupling constants should be less negative. A hyperconjugative group, X, would have the opposite effect. The applicability of these predictions will be discussed in the next section.

Table II. Changes in the Magnitudes of ^4J(cis) and ^4J(trans) in the Fragment CH_2–X–CH_2 on the Nature of the Group X

			Sign change[c]			
			X, inductive		X, hyper-conjugative	
Transition [a]	Sign[b] of ^4J(cis)	^4J(trans)	^4J(cis)	^4J(trans)	^4J(cis)	^4J(trans)
6 → 7	−	+	> −	> +	< −	< +
6 → 8	+	−	. . .	. . .	< +	< −
6 → 11	−	+	> −	> +	< −	< +
5 → 9	−	+	. . .	. . .	. . .	. . .
5 → 10	+	−	. . .	. . .	> +	> −
4 → 7	+	−	> +	> −	. . .	. . .
4 → 8	−	+	. . .	. . .	. . .	. . .
4 → 11	+	−	> +	> −	. . .	. . .
3 → 7	−	+	> −	> +	< −	< +
3 → 8	+	−	. . .	. . .	< +	< −
3 → 11	−	+	> −	> +	< −	< +
2 → 9	−	+	. . .	. . .	. . .	. . .
2 → 10	+	−	. . .	. . .	> +	> −
1 → 9	+	−	< +	< −	. . .	. . .
1 → 10	−	+	< −	< +	> −	> +

[a] Only those transitions which have opposite signs for the cis and trans coupling constant contributions have been included in the table. Transitions have been listed in order of increasing energy separation. [b] Signs of the contributions follow from eq 3. [c] A case in which the substituent would be expected to have little or no effect is indicated by an ellipsis.

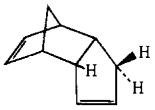
II. Results and Discussion

Calculated coupling constants for a series of molecules, which are relevant to this investigation, are entered in Table III. All calculated values were obtained by means of the finite-perturbation theory and INDO wave functions as described in section IA. The calculated values for propane (item 1 of Table III) were reported previously.[38] In this case ^4J(cis) = ^4J(120°, 120°) and ^4J(trans) = ^4J(120°, 240°), where the dihedral angles are measured as in Figure 4. The available experimental data are included in Table III for comparison.

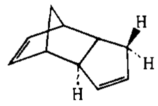
Table III. Comparison of Calculated Cis and Trans Coupling Constants in Representative Molecules with the Available Experimental Data

	Calculated results		Experimental	
Molecule	J(cis), Hz	J(trans), Hz	J(cis), Hz	J(trans), Hz
(1) Propane	−0.12[a]	−0.29[a]	. . .	. . .
(2) Dimethylamine[b]	−1.06	0.38	. . .	. . .
(3) Dimethyl ether[c]	−0.72	0.81	. . .	. . .
(4) Tetrahydrofuran[d]	−0.95	0.91	<0.3[e]	<0.3[e]
(5) *cis*-2-Butene[f]	2.83	3.17	. . .	. . .
(6) Cyclopentene[g]	2.78	4.92	. . .	. . .
(7) Cyclopentene[h]	1.78	4.38	2.2[i]	3.8[i]
			2.2[i]	3.1[i]
			+1.80[j]	+1.77[j]
			+2.16[j]	+2.02[j]
			+1[j]	+2[j]
			+2[j]	+2[j]
(8) 2,5-Dihydropyrrole[k]	−3.68	4.73	±4.5[l]	±7.0[l]
			±3.5[m]	±7.5[m]
			±4.0[m]	±7[m]
			±3.76[n]	±5.81[n]
			±3.0[n]	±7.2[n]
(9) 2,5-Dihydrofuran[o]	2.52	7.51	±0.4[p]	±4.0[p]
			±0.4[p]	±3.5[p]
			±0.9[q]	±4.0[q]

[a] M. Barfield, Table II of ref 38. [b] r(C—N) = 1.474 Å, ∠CNC = 112.2°, ∠CNH = 112.2°. [c] r(C—O) = 1.417 Å, ∠COC = 111° 37′. [d] r(C—O) = 1.43 Å, r(C—C) = 1.54 Å, ∠CCC = 105° 23′. [e] Reference 2. [f] r(C=C) = 1.337 Å, r(C—C) = 1.54 Å, ∠C=C—C = 120°. [g] r(C=C) = 1.337 Å, r(C—C) = 1.54 Å, ∠C=C—C = 120°. This structure corresponds to removal of two H atoms from *cis*-2-butene and insertion of a CH_2 group with the carbon atom 1.54 Å from C_1 and C_4. [h] r(C=C) = 1.34 Å, r(C—C) = 1.54 Å, ∠C=C—C = 112° 6′, ∠=C—C—C = 103° 40′, ∠C—C—C = 109° 28′. [i] Data from ref 20 for structures **6** and **7**.

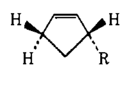


6

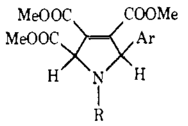


7

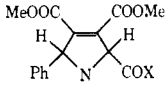
[j] Experimental; from the unpublished work of Knorr[19] for A,



A

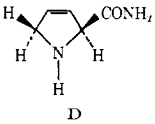


B

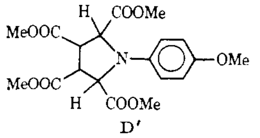


C

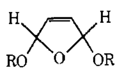
where R denotes COOMe, CN, Ph, and H, respectively. [k] r(C=C) = 1.337 Å, r(C—C) = 1.54 Å, r(C—N) = 1.474 Å, ∠C=C—C = 120°. This structure corresponds to removal of two H atoms from *cis*-2-butene and insertion of an N–H group with the N atom 1.474 Å from C_1 and C_4. [l] Data from ref 6 for B. [m] Data from ref 8 for C, where X = OEt, –N(Et$_2$). [n] Data from ref 3 for D and D′. [o] r(C=C) = 1.34 Å, r(C—C) = 1.54 Å, r(C—O) = 1.43 Å, ∠C=C—C = 109°, ∠CCC = 106°, ∠COC = 110°. [p] Data from ref 2 for E, where R = –Me, –COMe. [q] Data from ref 3 for F.



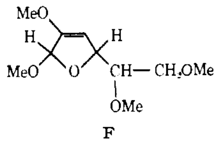
D



D′



E



F

Replacement of the methylene group of propane with an N–H group and an oxygen atom gives dimethylamine and dimethyl ether, respectively, (items 2 and 3 in Table III). In both of these cases ^4J(cis) is shifted to more negative values and ^4J(trans) is shifted to more positive values. These are just the trends which were predicted for an inductive substituent in section IC. Electron donation as by lone pairs in p-type orbitals would be expected to have the same effect. An interesting feature of the results for the first three items in Table III is that the N–H group has a greater effect on the cis coupling (more negative), whereas the oxygen has the greatest effect on the trans coupling (more positive). Some experimental values of $^4J_{HH'}$ have been reported[39] for molecules of this type; however, the methyl groups will be undergoing rotation about the C–X bonds such that the calculated data cannot be easily compared with the experimental results. The slight differences between the calculated values for dimethyl ether and tetrahydrofuran (item 4) could be attributed to several factors which include contributions along the five-bond path and changes in the geometry associated with the four-bond path.

For *cis*-2-butene (item 5 in Table III) the values of ^5J(cis) and ^5J(trans) differ by only 0.34 Hz, and both values are close to the VB theoretical result of 2.81 Hz obtained from eq 4. It is unlikely that a difference of this magnitude could be detected experimentally in molecules of uncertain geometry.

Now consider the attachment of the group X to carbon atoms C_1 and C_4 of the *cis*-2-butene fragment depicted in Figure 1. The calculated results in Table III for five-membered rings are all based on the assumption of planar geometry, since there is little information regarding ring puckering in these compounds. In cyclopentene (items 6 and 7 in Table III), it is reasonable to assume that small negative contributions to the two coupling constants arise *via* the four-bond paths as in propane. The coupling is dominated, therefore, by the homoallylic coupling mechanism, and the differences between J(cis) and J(trans) must surely be due to the substituent effect on the homoallylic coupling. For both conformations of cyclopentene (items 6 and 7 in Table III) the cis coupling and the trans coupling are less positive and more positive, respectively, than the *cis*-2-butene value. This is consistent with the predictions of section IB for the case in which X is an electron-withdrawing and/or hyperconjugative group.

In the first calculation on cyclopentene (item 6 in Table III) the geometry assumed for the $H_2C—HC=CH—CH_2$ portion of the molecule is identical with that used in the calculations for *cis*-2-butene to minimize changes in geometry. In the second calculation, the C–C–C angle is assumed to be tetrahedral to emphasize the connection with the structural features of the propane calculations. On the basis of these results, it is clear that the introduction of a methylene substituent has a substantial effect on the trans homoallylic coupling constant. Apparently the difference between the cis and trans coupling constants is not entirely an artifact of the assumed geometry, since the latter changes only slightly in the two sets of calculations. Experimental data[20] for *endo*- and *exo*-tricyclo[5.2.1.0^{2,6}]deca-3,8-dienes **6** and **7**, respectively, provides evidence for inherently unequal J(cis) and J(trans). (Structures **6** and **7** are given in footnote *i*, Table III.) Furthermore, on the basis of other coupling constants in the system, planar five-membered rings are indicated.[20] On this basis the agreement with the calculated values (item 7 in Table III) is quite good. The other experimental values were obtained for highly substituted cyclopentene derivatives of uncertain geometry.

Relative to the *cis*-2-butene results, cyclopentene, 2,5-dihydropyrrole, and 2,5-dihydrofuran (items 6–9 in Table III) all exhibit less positive cis and more positive trans H–H coupling constants. These trends are qualitatively consistent with the predictions of section IB for an inductive substituent and with experimental data, but the trends within the series are puzzling. The sign reversal noted for 2,5-dihydropyrrole is completely unexpected and is in conflict with the meager experimental data.[4,5] Relative sign studies appear not to have been given for any of the derivatives of 2,5-dihydrofuran for which coupling constant data are available.

Acknowledgments. This work was supported in part by a grant from the National Science Foundation. Services of the University of Arizona Computer Center are gratefully acknowledged.

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[39] H. Dreeskamp, K. Hildenbrand, and G. Pfisterer, *Mol. Phys.*, 17, 429 (1969).