when N_2O is added to a solution of O_2 in *n*-pentane prior to irradiation.

Increased pentyl radical formation in the presence of N_2O will result in enhanced yields of pentenes, formed according to reaction 5. Moreover, pentene formation in nonradical processes, for example, reaction 10, is also affected by N_2O. This is evident from the observed decrease in *cis*-pentene-2 yield when N_2O is added to solutions of oxygen in *n*-pentane, as shown in Table IV. The observed increase in pentene-1 formation when N_2O is added to these solutions cannot be due to the formation of free pentyl radicals in reactions 25 and 26. However, it can be explained by reaction 25, if the radicals formed in this reaction have a finite probability of reacting with each other within the liquid cage to form pentene and H_2O. The formation of H_2O, with a *G* value of about 2, has been observed in the presence of N_2O.

Hydrogen formation is reduced when N_2O is added to *n*-pentane. This decrease is smaller than the yield of N_2, which is formed simultaneously, as is shown in Figure 6. Similar observations were made in the radiolysis of solutions of N_2O in cyclohexane.[9,11] It may indicate that dissociative electron capture (reaction 23) is a more efficient process than hydrogen formation following parent ion–electron recombination.[31] It may also be partly due to additional modes of decomposition of N_2O.

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(31) This interpretation is consistent with observed increases in hydrogen yield when HI or HCl is added to cyclohexane: P. J. Horner and A. J. Swallow, *J. Phys. Chem.*, 65, 953 (1961); J. R. Nash and W. H. Hamill, *ibid.*, 66, 1097 (1962).

A Nuclear Magnetic Resonance Study of Steric Effects in the 2-Butenes[1]

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Abstract: The 60-Mcps proton nmr spectra of *cis*- and *trans*-2-butene are reported and analyzed. A semiempirical method has been used to construct a potential energy surface representing the steric interaction between the methyl groups of the *cis* isomer, and this surface has been used to interpret the vicinal coupling constants. It is found that the barrier restricting rotation about the carbon–carbon single bonds is not of the simple threefold type, and that the preferred conformation is skewed from that in which a methyl proton eclipses the carbon–carbon double bond. The values of the *trans* and *gauche* vicinal couplings determined in this study, $J_t = 10.0 \pm 1.0$ cps and $J_g = 3.7 \pm 0.2$ cps, are in good agreement with those reported by other workers.

In a former paper,[3] we reported on a nuclear magnetic resonance study of steric effects in *cis*- and *trans*-1,4-dichloro-2-butenes. It was found in that case that the analysis was complicated by inseparable contributions from both skewing and population effects, so that only a lower limit to the magnitude of the steric interaction was inferred.[4] The parent compounds, *i.e.*, *cis*- and *trans*-2-butene, present no such complicating factors, however. Thus, it is possible in this case to identify changes in the nmr parameters directly with skewing effects, which have their origin in the strains produced by intramolecular steric interactions. We report the result of our study of *cis*- and *trans*-2-butene in the present paper.

As in our former work, so in this case also we rely upon the marked angular dependence of the proton–proton vicinal couplings across carbon–carbon single bonds to interpret the effect. Of course, rapid rotation of the methyl groups about the carbon–carbon single bonds is to be expected, and the observed coupling is interpreted as a rotational average. The average is weighted by the relative stability of the various configurations, however, so that, if a skewing does take place, a different rotational average should be observed.

There is good reason to believe that in the *trans* isomer the preferred orientation of the methyl group is that for which one of the protons is *trans* to an adjacent vinyl proton.[3,5] The fact that a rather strong steric interaction is to be expected if such an orientation persisted in the *cis* isomer can be appreciated by observing the model of Figure 1, which is constructed to scale for the experimentally observed[6] (although perhaps not quanti-

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(1) Based in part on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Author to whom inquiries should be addressed: University of California, Los Alamos Scientific Laboratory, Los Alamos, N. M. 87544.

(3) H. G. Hecht and B. L. Victor, *J. Am. Chem. Soc.*, 89, 2532 (1967).

(4) In ref 3, an error was made in defining the equilibrium. The correct expression should be $\Delta F = -RT \ln [p_I/(1 - 2p_I)]$ which leads to $\Delta H_{trans} = -650$ cal/mole and $\Delta H_{cis} \rightarrow -\infty$. Thus, no limit at all can properly be established. We wish to thank S. S. Butcher for calling this error to our attention in a private communication.

(5) M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, 85, 1899 (1963); H. J. M. Bowen, A. Gilchrist, and L. E. Sutton, *Trans. Faraday Soc.*, 51, 1341 (1955); A. A. Bothner-By and H. Günther, *Discussions Faraday Soc.*, 34, 127 (1962); D. R. Herschbach and L. C. Krisher, *J. Chem. Phys.*, 28, 728 (1958).

(6) L. O. Brockway and P. C. Cross, *J. Am. Chem. Soc.*, 58, 2407 (1936).

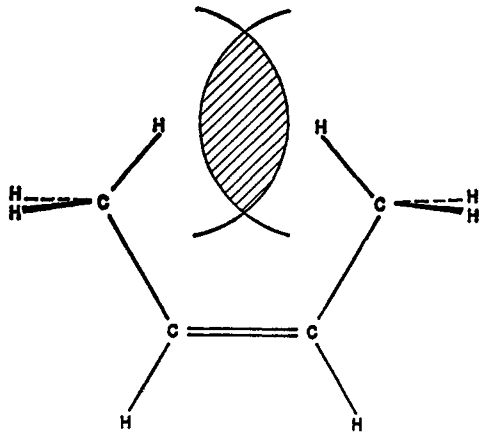

Figure 1. Model of *cis*-2-butene constructed to scale for C=C, 1.38 Å; C—C, 1.54 Å; C—H, 1.06 Å; ∠CCC, 120°; ∠CCH, 109.5°. The van der Waals radius is taken to be 1.2 Å.

tatively accurate) bond distances (C=C, 1.38 Å; C—C, 1.54 Å; C—H, 1.06 Å) assuming a van der Waals radius for the protons of 1.2 Å.[7] The region of strong interaction (represented by the shaded area) is rather large, and it is anticipated that the steric repulsion will be lessened by a skewing to a new equilibrium conformation. This in turn results in a different rotationally averaged vicinal coupling constant.

The spectra are of the $X_nAA'X_n'$ type, whose features have been discussed for the case $J_{XX'} = 0$ in a series of papers by Harris and coworkers,[8-10] the most recent of which[10] discusses the case of deceptive simplicity. There is another type of deception which can occur in this case, however. If one ignores the cross-coupling and assumes that the spectra are a superposition of two spectra of the AX_3 type, a first-order analysis can be made which reproduces the salient features of the spectra quite well. This probably accounts for the 4.5-cps vicinal coupling assigned to both the *cis* and *trans* compounds by Pople, Schneider, and Bernstein[11] in early work. By now the effects of magnetic inequivalence are well known, particularly in A_2B_2 spectra,[12] the result of which is that certain degeneracies are removed so that a complete analysis can be made. It turns out that the assumed first-order coupling is really an approximation of $|J_{AX} + J_{AX'}|$ (it would be equal of $J_{XX'} = 0$), and that a complete analysis must be made to derive the correct coupling constants.

Experimental Section

Cylinders of gaseous *cis*-2-butene and *trans*-2-butene were purchased from the Matheson Co., Inc. Both were specified as CP grade with a minimum purity of 99.0%. The boiling points are low (1° for the *cis* and 2.5° for the *trans*), but, by sealing the samples in tubes at low temperatures, it was possible to observe the nmr spectra of the neat liquids up to room temperature. The sample tubes, containing a sealed capillary of benzene as a reference standard, were prepared by attaching them to a vacuum system which was evacuated and flushed out with nitrogen gas. The gases were then admitted into the system and condensed into the sample tubes at liquid nitrogen temperature. The sample tubes were then sealed under vacuum, assuring the exclusion of oxygen.

The spectra were recorded using a Varian A-60 nmr spectrometer operating at room temperature. Some low-temperature spectra were observed as well, but no temperature-dependent effects were noted.

The spectra were calibrated by side-banding with a Hewlett-Packard Model 202 C audiooscillator monitored by a Hewlett-Packard Model 524 C electronic counter. The peak positions within a given multiplet were thus determined within a probable error of ±0.05 cps relative to the center. The chemical shifts of the centers of multiplets are determined with less accuracy but are thought to be accurate to within ±0.01 ppm.

Theoretical spectra were synthesized using an IBM 7030 (STRETCH) computer. The program was written in FORTRAN II language using standard procedures. Because of the very large core storage available on the STRETCH computer (98K), it was not necessary to resort to symmetry factoring to handle these eight-spin systems. By appropriate variation of the parameters, the features of the experimental spectra were sufficiently well reproduced that we feel that the uncertainties in the parameters determined are largely a result of calibration error, *i.e.*, ±0.01 ppm in the chemical shifts and ±0.05 cps in the coupling constants.

Results and Discussion

The chemical shifts and coupling constants determined in this study are listed in Table I, and the experimental and calculated spectra are shown in Figures 2 and 3. The labeling is in terms of the $X_3AA'X_3'$ notation, and the magnetic field calibration is in cycles per second from the benzene external standard.

Table I. Chemical Shifts and Coupling Constants of *cis*- and *trans*-2-Butene

	ν_A, ppm[a]	ν_X, ppm[a]	J_{AX}, cps	$J_{AX'}$, cps	$J_{XX'}$, cps	$J_{AA'}$, cps
trans	6.00	2.25	6.58	−1.66	1.61	14.00
cis	6.58	2.75	6.42	−1.41	1.15	7.85

[a] Relative to a benzene external standard, uncorrected for bulk susceptibility.

$J_{AX'}$ and $J_{XX'}$ are allylic and homoallylic coupling constants, whereas $J_{AA'}$ represents the *cis* and *trans* proton coupling across the carbon–carbon double bond. The values determined for these parameters are all quite normal,[13] and they will not be discussed further at this time.

The small but significant difference in the vicinal coupling constants (6.42 cps for *cis*-2-butene and 6.58 cps for *trans*-2-butene) reflects the skewing of the methyl groups in the *cis* isomer from the conformation favored in the *trans* isomer. We will first discuss a model for the steric interaction and then show that the model predicts coupling parameters which are in accord with those reported by other workers.

This problem has been treated by Hill[14] using the method of Westheimer and Mayer,[15] but we choose a more empirical approach which lends itself readily to physical interpretation (*cf.* Woolfenden and Grant[16]). The treatment should be regarded as rather qualitative, because of the approximations involved.

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(7) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948.

(8) R. K. Harris, *Can. J. Chem.*, 42, 2275 (1964).

(9) R. K. Harris and C. M. Woodman, *Mol. Phys.*, 10, 437 (1966).

(10) E. G. Finer and R. K. Harris, *ibid.*, 12, 457 (1967).

(11) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

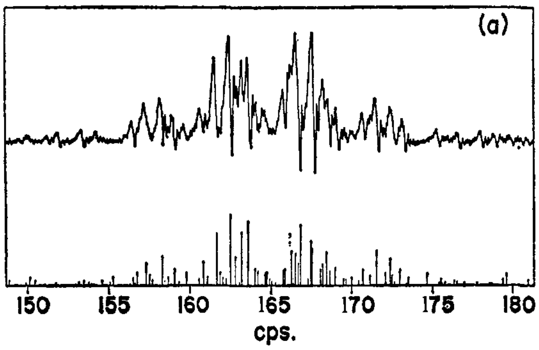
(12) D. M. Grant and H. S. Gutowsky, *J. Chem. Phys.*, 34, 699 (1961); D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *ibid.*, 38, 470 (1963); R. C. Hirst and D. M. Grant, *ibid.*, 40, 1909 (1964).

(13) S. Sternhell, *Rev. Pure Appl. Chem.*, 14, 15 (1964).

(14) T. L. Hill, *J. Chem. Phys.*, 16, 938 (1948).

(15) F. H. Westheimer and J. E. Mayer, *ibid.*, 14, 733 (1946).

(16) W. R. Woolfenden and D. M. Grant, *J. Am. Chem. Soc.*, 88, 1496 (1966).



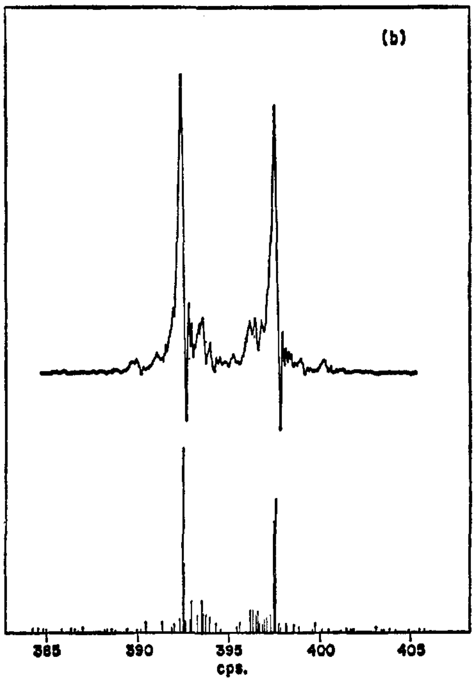
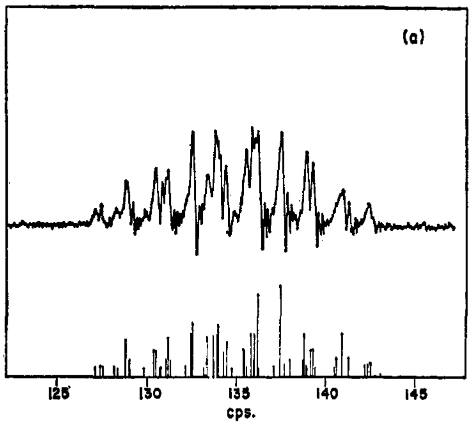


Figure 2a. Experimental and calculated 60-Mcps nmr spectrum of *cis*-2-butene: vinyl protons.
Figure 2b. Experimental and calculated 60-Mcps nmr spectrum of *cis*-2-butene: methyl protons.



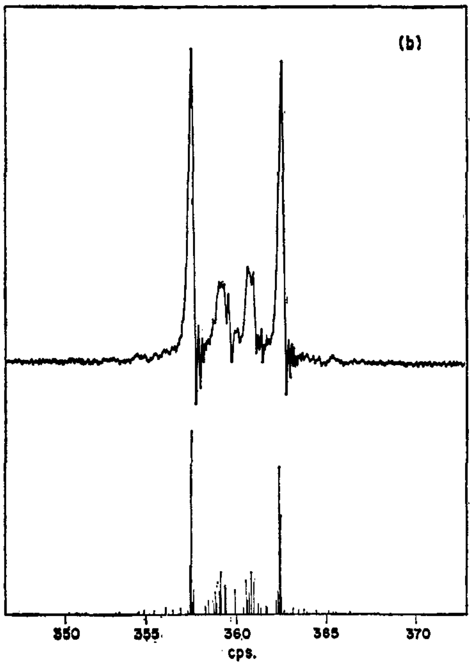


Figure 3a. Experimental and calculated 60-Mcps nmr spectrum of *trans*-2-butene: vinyl protons.
Figure 3b. Experimental and calculated 60-Mcps nmr spectrum of *trans*-2-butene: methyl protons.

It might be supposed that protons which are forced into close proximity become directly bonded to a certain extent by exchange forces. If such an interaction were to take place, a larger coupling between methyl groups in the *cis* isomer would be observed. An examination of the $J_{XX'}$ values of Table I shows that this is not a significant effect, so the methyl protons can safely be regarded as nonbonding with respect to one another. We may then adopt the Mason and Kreevoy[17] function for the nonbonded repulsion energies between protons in methyl groups.

$$V_{ij} = 3.7164 \times 10^3 \exp(-3.0708r_{ij}) - 89.52/r_{ij}^6 \quad (1)$$

$$(r_{ij} \geq 1.8 \text{ Å})$$

This expression, which was derived by fitting to the potential function for the $^3\Sigma$ state of H_2 calculated by Hirschfelder and Linnett,[18] gives the potential energy in kcal/mole for the pair-wise interaction between protons i and j, in terms of their separation, r_{ij}, in angstrom units. The total repulsive interaction potential is

$$V_r = K\sum_{i=1}^{3}\sum_{j=1}^{3} V_{ij} \quad (2)$$

where K is an empirical constant which should fall within the range 0.5–1.0. Following Woolfenden and Grant,[16] we choose $K = 0.75$ which compensates in part for the neglect of proton–carbon repulsions.

A complete calculation of the potential energy surface for the rotating methyl groups must include the rotational barrier about the carbon–carbon single bonds as well. Thus we write for the total potential energy

$$V = V_r + V_{b1} + V_{b2} \quad (3)$$

where it is assumed that V_{bi} is of the form

$$V_{bi} = (V_0/2)(1 - \cos 3\,\phi_i) \quad (i = 1, 2) \quad (4)$$

ϕ_1 and ϕ_2 are generalized coordinates representing the angle of rotation of the two methyl groups (see Figure 4); these two parameters of course also determine all the r_{ij}'s necessary for the evaluation of V_r. Thus, we

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[17] E. A. Mason and M. M. Kreevoy, *J. Am. Chem. Soc.*, 77, 5808 (1955).

[18] J. O. Hirschfelder and J. W. Linnett, *J. Chem. Phys.*, 18, 130 (1950).

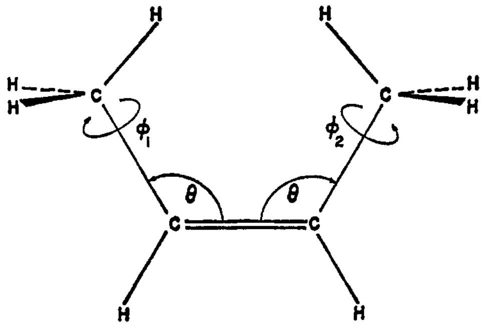

Figure 4. Coordinates used for the calculation of the potential energy of the sterically interacting methyl groups of *cis*-2-butene.

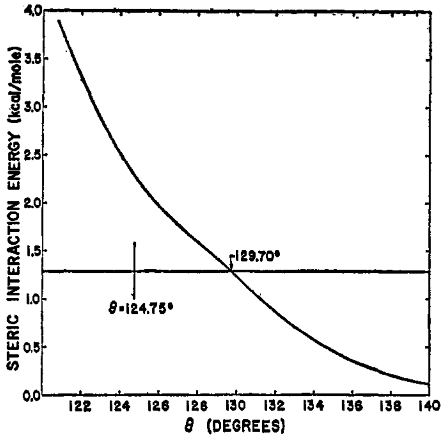

Figure 5. Steric repulsion between methyl groups of *cis*-2-butene calculated from eq 5 as a function of θ.

can construct a potential energy surface in terms of just these two coordinates as parameters.

A reasonable choice for the V_0 of an unperturbed methyl group adjacent to a double-bonded carbon atom seems to be about 1.950 kcal/mole.[19-21] We have adopted this value for the barrier in all of the subsequent calculations, assuming that it is not greatly altered by the conformational changes dictated by the steric repulsions.

As pointed out by Skinner,[22] there are two mechanisms by which the steric repulsion in compounds of this type may be relieved. The first, as mentioned above, consists of a twisting of the interfering methyl groups from the assumed orientation (changes of ϕ_1 and ϕ_2), and the second increases the C=C—C bond angle (change of θ) as shown in Figure 4. In propylene the angle is found to be 124.75°,[21] so that it appears that a 4.75° variation from the value for pure sp^2 hybridization is required just to satisfy energetic requirements in the absence of steric strain. Thus, we take 124.75° to be a *lower limit* for this angle.

We have derived an estimate of θ in the following manner. The steric repulsion between the methyl groups is given by

$$\langle V_r \rangle = \int_0^{2\pi/3}\int_0^{2\pi/3} V_r e^{-V}\,d\phi_1 d\phi_2 \bigg/ \int_0^{2\pi/3}\int_0^{2\pi/3} e^{-V}\,d\phi_1 d\phi_2 \quad (5)$$

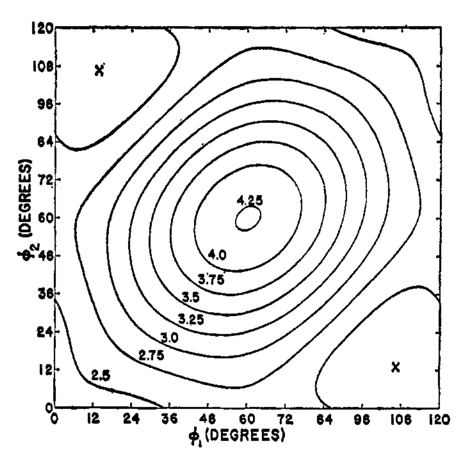

Figure 6. Potential energy surface for methyl groups of *cis*-2-butene.

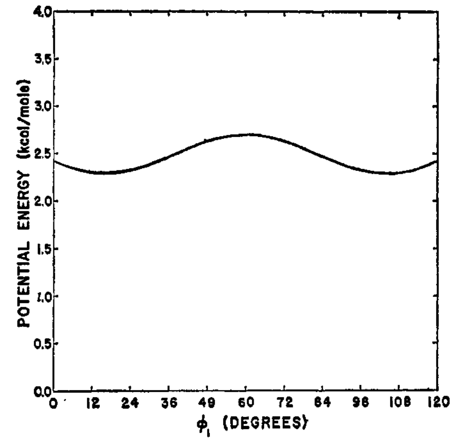

Figure 7. Calculated barrier restricting rotation of a methyl group in *cis*-2-butene.

The integrals occurring in eq 5 have been evaluated by a 16-point Gaussian quadrature using Legendre polynomial weighting functions for various values of θ, using the appropriate bond lengths,[6] and assuming a tetrahedral angle for the methyl protons. The result is shown as the curve of Figure 5. The experimental repulsion energy as determined from heats of formation is 1.288 kcal/mole,[23] which leads to a value for θ of 129.70°. This value is assumed in the subsequent calculations.

Having thus determined θ, it is possible to construct a potential energy surface in ϕ_1, ϕ_2, V space. The result is shown in Figure 6. The surface is of course periodic in both ϕ_1 and ϕ_2, with a periodicity of $2\pi/3$.

It is of interest to note that the most stable conformation (point of minimum potential) is not $\phi_1 = \phi_2 = 0°$, but corresponds approximately to the positions marked with crosses on Figure 6. Pitzer[24] has stated that for a single bond adjacent to a double bond, a threefold barrier is expected unless the two sides of the planar group become equivalent, in which case a much lower sixfold barrier results. Making the admittedly poor assumption of a threefold barrier, Kilpatrick and Pitzer[20] found a barrier of 0.45 kcal/mole by fitting to

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(19) L. Guttman and K. S. Pitzer, *J. Am. Chem. Soc.*, 67, 324 (1945).

(20) J. E. Kilpatrick and K. S. Pitzer, *J. Res. Natl. Bur. Std.*, 37, 163 (1946).

(21) D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, 27, 868 (1957).

(22) H. A. Skinner, *J. Chem. Soc.*, 4396 (1962).

(23) A. P. I. Research Project 44, "Selected Values of Properties of Hydrocarbons," National Bureau of Standards, Washington, D. C., 1944–1946, Table 8w (Part 1).

(24) K. S. Pitzer, *J. Chem. Phys.*, 5, 473 (1937).

the thermochemical data. Tracing out a trajectory across our potential energy surface as a function of one of the ϕ angles gives the result shown in Figure 7. It will be observed that the potential function is intermediate between the pure threefold and sixfold limits, but it can be roughly approximated by a threefold barrier with a restricting potential of about 0.4 kcal/mole. Thus, the features of the potential energy surface we have constructed seem to be in good accord with the thermochemical data. It remains only to show that the observed vicinal coupling constants agree as well.

The parameters which characterize vicinal coupling, J_t (for the *trans* conformation) and J_g (for the *gauche* conformation), have been discussed a great deal, particularly where both carbon atoms have sp^3 hybridization. It appears that in the sp^2–sp^3 case the couplings are not much different.[25,26] Ordinarily, these parameters can be determined quite readily because the potential energy barriers restricting rotation are sufficiently large that only a few discrete conformations contribute significantly. The situation here is obviously quite different, since the steric interaction has decreased the potential energy barrier to such an extent that many conformations may be expected to make significant contributions (see Figure 7). We have accordingly used a more general procedure which appropriately weights all conformations; *i.e.*, the average vicinal coupling constants have been calculated from

$$\langle J_V\rangle = \int_0^{2\pi/3}\int_0^{2\pi/3} J(\phi_i)e^{-V}\,d\phi_1 d\phi_2 \Big/ \int_0^{2\pi/3}\int_0^{2\pi/3} e^{-V}\,d\phi_1 d\phi_2 \qquad (6)$$

where, again, a Gaussian quadrature has been used to evaluate the integrals. Ranft[27] has shown theoretically that the angular dependence of sp^2–sp^3 vicinal coupling is similar to that for sp^3–sp^3 hybridization. Furthermore, it has been shown by Batterham, *et al.*,[28] and Okuda, *et al.*,[29] that a Karplus-type equation[30] with modified coefficients gives an excellent account of the experimental data. Thus we have taken $J(\phi_i)$ to be

$$J(\phi_i) = \begin{cases} J_1 \cos^2 \phi_i - 0.28 \text{ cps} & 0° \le \phi_i \le 90° \\ J_2 \cos^2 \phi_i - 0.28 \text{ cps} & 90° \le \phi_i \le 180° \end{cases} \qquad (7)$$

where $J_2 = J_t + 0.28$ cps and $J_1 = 4(J_g + 0.28)$ cps. Using eq 7 in eq 6, the average vicinal coupling constants were calculated for both the *cis* and *trans* compounds as a function of J_g and J_t (V_r was set equal to zero in the *trans* case, of course). The experimental values for each compound can be obtained for any number of combinations of J_g and J_t, but fitting to both simultaneously requires that J_g = 3.7 ± 0.2 cps and J_t = 10.0 ± 1.0 cps (see Figure 8). These values are in good agreement with those obtained by other workers for similar compounds, as can be seen by an inspection of Table II.

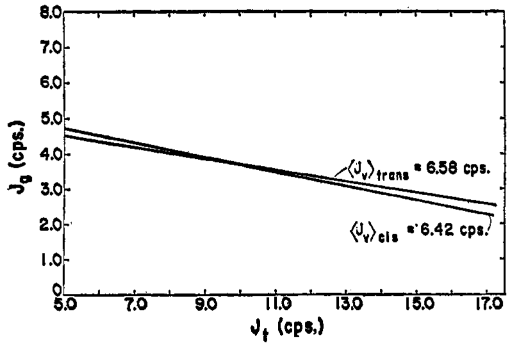

Figure 8. Calculated average vicinal coupling constants for *cis*- and *trans*-2-butene as a function of J_g and J_t.

Table II. Values of J_g and J_t for Vicinal Coupling across Carbon(sp^2)–Carbon(sp^3) Atoms

Compounds	J_g, cps	J_t, cps	Ref
Cyclohexene and cyclopentene	1–3	~16	*a*
Alkylethylenes	3.7	11.6	*b*
3-Fluoropropenes	−2.2–+0.3[e]	6.8–8.3[e]	*c*
$CH_2{=}CHCH_2Cl$	2.4[e]	13.4[e]	*d*
$CH_2{=}CHCHCl_2$	2.5[e]	9.6[e]	*d*
$CH_2{=}CHCH_2OCH_3$	2.8[e]	11.5[e]	*d*
$CH_2{=}CHCH(OCH_3)_2$	1.8[e]	10.3[e]	*d*
2-Butenes	3.7 ± 0.2	10.0 ± 1.0	This work

[a] A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961). [b] A. A. Bothner-By, C. Naar-Colin, and H. Günther, *ibid.*, **84**, 2748 (1962). [c] A. A. Bothner-By, S. Castellano, and H. Günther, *ibid.*, **87**, 2439 (1965). [d] A. A. Bothner-By, S. Castellano, S. J. Ebersole, and H. Günther, *ibid.*, **88**, 2466 (1966). [e] An electronegativity correction such as discussed by A. A. Bothner-By and H. Günther [*Discussions Faraday Soc.*, **34**, 127 (1962)] and by A. A. Bothner-By [*Advan. Magnetic Resonance*, **1**, 195 (1966)] should be applied here.

Thus, although only a small difference in the vicinal coupling constants is observed in this pair of compounds, this difference does reflect quite an altered weighting of conformations. The fact that both thermochemical and nmr data are in good accord with the potential energy surface we have constructed suggests that it is essentially correct. The approximations involved in the above semiempirical treatment are sufficiently crude that only a qualitative significance should be attached to it, however. A quantitative account must await more refined computational techniques. The implications of such skewing effects as we have discussed here, as they effect chemical structure and reactivity where exact geometric relationships between the atoms of the involved molecules are important, are of great significance and are worthy of further pursuit.

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(25) A. A. Bothner-By and H. Günther, *Discussions Faraday Soc.*, 34, 127 (1962).

(26) A. A. Bothner-By, C. Naar-Colin, and H. Günther, *J. Am. Chem. Soc.*, 84, 2748 (1962).

(27) J. Ranft, *Ann. Phys.*, 9, 124 (1962).

(28) T. J. Batterham, K. H. Bell, and U. Weiss, *Australian J. Chem.*, 18, 1799 (1965).

(29) S. Okuda, S. Yamaguchi, Y. Kawazoe, and K. Tsuda, *Chem. Pharm. Bull. Japan*, 12, 104 (1964).

(30) M. Karplus, *J. Chem. Phys.*, 30, 11 (1959).