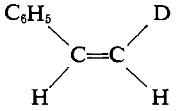
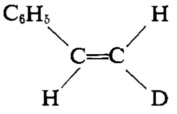
water and bisulfite and dried ($MgSO_4$), and pentane again was removed at ambient pressure. The residue had a styrene:phenylacetylene ratio of 1:2 (glpc). Attempted distillation led to extensive polymerization. Preparative glpc separation on 10.3 g of product, half of which consisted of material other than styrene and phenylacetylene, led to a mixture of 2.25 g of the latter in the ratio of 1:2.40 (glpc). The ratio of the highest field vinyl signals to the middle group of vinyl signals in the nmr spectrum (Figure 2) indicates that the styrene is *ca.* 80% monodeuterated. The presence of



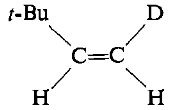
would transform the remaining methylene hydrogen signal at highest field from a doublet of doublets into a doublet by removing the small splitting resulting from the geminal coupling constant. That this is not observed indicates stereochemical purity (>95%) of the styrene as



***erythro*-(1,2-Dibromoethyl-2-*d*)Benzene (1b).** The styrene-phenylacetylene mixture described above was brominated in CS_2 solution. A methanol solution of the material obtained upon removal of CS_2 was cooled to −40°, and solid which separated was collected. Charcoal treatment followed by two recrystallizations from methanol gave 0.808 g of pure dibromide, mp 73°.

3,3-Dimethylbutyne-1-*d*. A mixture of 20 g of 3,3-dimethylbutyne, 50 ml of pyridine (dried over BaO, stored over CaH_2), 50 ml of D_2O, and 0.658 g of sodium methoxide was shaken in a sealed tube for 4 days. The acetylene was isolated by simple distillation. Examination of the infrared spectrum showed the appearance of a new band at 2580 cm^{-1} and a decrease in intensity of the old one at 3320 cm^{-1}, with a ratio of intensities of 8.71:2.02. (This leads to an approximate value of 81% t-Bu-C$\equiv$CD.) A broad band centered at 960 cm^{-1} is absent in undeuterated material. From the cracking pattern of the acetylene, comparison of the mass 67–66 pair in t-Bu-C$\equiv$CH and the 68–67 pair in the above samples shows that the sample is 82.4% t-Bu-C$\equiv$CD.

3,3-Dimethyl-*cis*-1-*d*-butene-1. A solution of BF_3 in diglyme was prepared by mixing 350 ml of BF_3-Et_2O with 500 ml of diglyme and pumping on the stirred mixture at 0° for 2 hr. Diborane, generated by addition of $NaBH_4$ to the diglyme solution of BF_3, was bubbled into a solution of 14.5 g of t-Bu-C$\equiv$CD in 145 ml of THF until all the acetylene was reacted (as evidenced by vpc examination of the reaction mixture). Acetic acid (70 ml) was added and the solution was permitted to remain overnight. After addition of water the mixture was extracted several times with $CHCl_3$. The organic extract was washed with 5% Na_2CO_3 and water and dried overnight. This material then was distilled slowly through a Heli-Pak column to give a dilute chloroform solution of olefin.[15] A sample of pure olefin was obtained by preparative vapor phase chromatography (20-ft silicone oil column at 53°) and its nmr spectrum was examined. The observed proton-proton coupling constant of 10.6 cps and deuteron-proton coupling of 2.59 cps, corresponding to a proton-proton coupling of 16.9 cps, establish the configuration of the olefin as



Integration of the vinyl proton area *vs.* the t-butyl proton signal in the deuterated compound and comparison of this ratio with that observed in undeuterated olefin showed the olefin was 78.5–85.9% monodeuterated and that 98.3–103.1% of the deuteriums were in the terminal methylene position.

***threo*-1,2-Dibromo-3,3-dimethyl-1-*d*-butane (2a).** The olefin-chloroform distillate was treated with bromine at −60° until the bromine color persisted. The solution was shaken with 5% bisulfite, washed with water, and dried ($MgSO_4$). After evaporation of chloroform the residue was distilled through a short column to afford 4.28 g of dibromide, bp 58–60° (5 mm). Examination by vpc indicated a purity of 92%, with four other materials comprising the remaining 8%.

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(15) Evidently protonolysis of the organoborane is not complete at room temperature. Addition of acetic acid to the pot when olefin was barely detectable in the distillate was followed almost immediately by a tenfold increase of olefin concentration in distillate.

Studies in Magnetic Nonequivalence. A Model for Conformational Analysis of Acyclics from Spin-Coupling Constants

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Contribution from the Central Basic Research Laboratories, Esso Research and Engineering Co., Linden, New Jersey, and the Department of Chemistry, University of Connecticut, Storrs, Connecticut. *Received July 8, 1965*

Abstract: A much simplified model is presented to account for conformational (rotational) isomerism in acyclic molecules. The model assumes (1) a $\cos^2 \phi$ dependence of the vicinal coupling constant, (2) an equilibrium dihedral angle near 65°, (3) that conformers with a bulky group *gauche* to two other such groups are energetically highly unfavorable. One can then develop equations relating the conformational equilibrium constant to the two vicinal coupling constants in 1,2-disubstituted and 1,1,2-trisubstituted ethanes. Several tests for our model are mentioned; results of conformational analysis of several systems are presented and discussed.

In the previous two papers we have qualitatively related the results of spectral analysis of several compounds of the type XCH_2CHYZ to rotational isomerism in these molecules and have also presented evidence which, we feel, establishes with reasonable certainty the most stable conformer in two such molecules. In this paper we shall present a model which we use in conformational analysis of acyclics using nmr data, we shall attempt to critically examine it, and we shall discuss the results of our conformational analyses with regard to those factors determining conformational equilibria. The meaning of our statement, made in the first of these three papers, that our model represents a "zeroth-order" approximation to the solution of this problem will become abundantly clear as the approximations and assumptions used are discussed.

Briefly, if in the molecules XCH_2CHYZ we assume (1) that $J = J_0 \cos^2 \phi$ satisfactorily describes the angular dependence of vicinal coupling constants, (2) the equilibrium dihedral angle between *gauche* substituents in trisubstituted acyclics is 65°, (3) the mole fraction of that conformer with X *gauche* to both Y and Z is sufficiently small to be neglected, then the ratio of the other two conformers is

$$\frac{n}{n'} = \frac{(J/J') - 0.180}{1 - 0.180(J/J')}$$

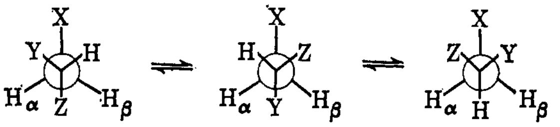
where J, J' are the two vicinal coupling constants.

Dihedral Angular Dependence of Vicinal Coupling Constants. Theoretical elaboration of vicinal proton–proton spin-coupling constants based on a Fermi contact interaction mechanism predicts an angular dependence such that the minimal coupling constant occurs when the dihedral angle between coupled protons is about 90°, with the coupling rising (unsymmetrically) on either side of 90° to its maximal value at $\phi \pm 0°, 180°$.[1,2] Ample verification of the qualitative aspects of the angular dependence of vicinal couplings is available.[3] Further, several workers[4] have claimed that the angular dependence is accurately described by $J = A + B \cos^2 \phi$, which is the form originally cited by Karplus,[1] with $A << B$. This means that *empirically* the angular dependence of vicinal couplings seems, at least in some cases, to be satisfactorily described by $J = J_0 \cos^2 \phi$. We shall assume the latter form of the angular dependence of vicinal coupling constants, dropping the constant term of the Karplus equation because it is small and because the present treatment is only approximate. However, further examination reveals several flaws. Perhaps foremost is the well-known result that the values of A and B calculated by Karplus[1] give values of J far lower than those observed. Recent temperature-dependent studies[5] also suggest that if the correct form of the angular dependence is $J = A + B \cos^2 \phi$, then $|B/A| \sim 6$ compared to the theoretical[1] value of 30 and other empirical values larger than 6. In addition even the empirical confirmation of the latter form requires one set of constants A, B, for $0 \leq \phi \leq 90°$ and another different set for $90 \leq \phi \leq 180°$.[4] This seems to confirm the skew character of the J *vs.* ϕ curve, a skewness which is absent in $J = J_0 \cos^2 \phi$. Still more recently[6] Karplus has emphasized the approximate nature of his earlier work which led to the $J = A + B \cos^2 \phi$ relation. The foregoing should make it apparent that our assumption of the functional dependence $J = J_0 \cos^2 \phi$ is tenuous.

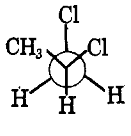
Potential Minimum in 1,1,2-Trisubstituted Ethanes. Their Equilibrium Conformation. For molecules in which one group has a threefold axis and the other a plane of symmetry, *e.g.*, $CH_3\text{-}CH_2X$, all available evidence points to a potential barrier adequately described by $V = (V_0/2)(1 + \cos 3\phi)$,[7] where ϕ is the dihedral angle between substituents. This means that the potential minimum corresponds to a dihedral angle of 60°, leading to the perfectly staggered rotamer.

With less symmetrical molecules some other dihedral angle might correspond to the energy minimum. Structural studies on more complicated molecules are sparse but the halides seem to present systematic deviations. Morino and Kuchitsu[8] tabulate values for $CH_2Cl\text{-}CH_2Cl$, $CHCl_2\text{-}CH_2Cl$, $CH_2OH\text{-}CH_2Cl$, and $CH_2OH\text{-}CH_2OH$ in which ϕ is reported to be near 70°. Although these authors report $\phi = 59 \pm 5°$ for the *gauche* form of $CH_3CH_2CH_2Cl$, a recent microwave investigation favors a value near 70°.[9] Microwave spectroscopic study leads to a dihedral angle of 63 ± 4° in the *gauche* form of $CH_3CH_2CH_2F$[10] but one near 70° for FCH_2CH_2Cl.[11] A dihedral angle of 66° has been found for that conformer of isobutyl chloride in which chlorine is *gauche* to one methyl but *trans* to the other.[12] Thus the available information suggests that for the molecules reported in our first paper a dihedral angle near 65° is appropriate. As we shall show below, the per cent composition of the equilibrium conformer mixture as given by our method is not very sensitive to small deviations from 60° in the dihedral angle. Hence our assumption of $\phi = 65°$ is valid *within the framework of our model.*

Conformers with Two *gauche* Interactions Are Highly Disfavored. In the equilibrium established by the rotational isomers, it is the qualitative notion of the organic chemist that the amount of conformer III present will be negligible because X is *gauche* to two (bulky) groups Y, Z, whereas in conformers I and II, X is *gauche* to only one of these groups. It is claimed that Raman spectral examination of $CH_3CHClCH_2Cl$ demonstrates that the conformer corresponding to III is of "...much higher energy than the other two."[13] Infrared examination of $CH_2Cl\text{-}CHCl_2$ demonstrated that conformer III is some 2 kcal mole^{-1} higher in energy than the enantiomorphic conformers I and II.[14]



I II III



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

[2] H. Conroy, *Advan. Org. Chem.*, 2, 265 (1960).

[3] For example, see the graph on page 311 of ref 2.

[4] *Cf.* R. J. Abraham and W. A. Thomas, *J. Chem. Soc.*, 3739 (1964), and references cited therein.

[5] H. S. Gutowsky, G. G. Belford, and P. E. McMahon, *J. Chem. Phys.*, 36, 3353 (1962).

[6] M. Karplus, *J. Am. Chem. Soc.*, 85, 2870 (1963).

[7] D. J. Millen, *Progr. Stereochem.*, 3, 138 (1962).

[8] Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, **28**, 175 (1958).

[9] T. N. Sarachman, *ibid.*, **39**, 469 (1963).

[10] E. Hirota, *ibid.*, **37**, 283 (1962).

[11] This is quoted as ref 4 by Hirota.

[12] G. H. Pauli, F. A. Momany, and R. A. Bonham, *J. Am. Chem. Soc.*, **86**, 1286 (1964).

[13] S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press Inc., New York, N. Y., 1954, p 70.

[14] J. Powling and H. J. Bernstein, *J. Am. Chem. Soc.*, **73**, 1815 (1951).

Some data to the contrary are suggested by the positions of equilibrium in, *e.g.*, $CH_3CH_2CH_2F$, where the conformer with fluorine *gauche* to methyl is favored[10] by 0.47 ± 0.31 kcal mole^{-1}, and in *n*-propyl chloride, where the comparable conformer is favored[8] by 0.3 ± 0.2 kcal mole^{-1}. Such stabilization of *gauche* orientations has been suggested to be unique to methyl–halogen interactions.[15] It is significant that the conformer corresponding to III is *not* the most stable one in *sec*-butyl chloride, but is disfavored by 0.41 ± 0.16 kcal mole^{-1} even though there exists the opportunity for two stabilizing *gauche* methyl–chlorine interactions.[12] Since in no case do we have a methyl–halogen interaction, the meager data available support our assumption that the mole fraction of conformer III is sufficiently small to be neglected.[16]

We now can develop expressions relating observed coupling constants to conformational equilibrium. Since the conformational equilibrium is established in a time fast compared to the nmr measurement, the observed vicinal coupling constants, $J_{\text{H-H}\alpha} \equiv J_\alpha$, $J_{\text{H-H}\beta} \equiv J_\beta$, will be weight averaged over the conformers according to their mole fraction, n_i, Thus

$$J_\alpha = n_\text{I}J_t + n_\text{II}J_g + n_\text{III}J_g$$

$$J_\beta = n_\text{I}J_g + n_\text{II}J_t + n_\text{III}J_g$$

where J_t, J_g are the vicinal couplings between *trans* and *gauche* hydrogens, respectively. From the difference

$$J_- \equiv |J_\alpha - J_\beta| = |(n_\text{I} - n_\text{II})(J_t - J_g)| \qquad (1)$$

it is apparent that the difference in observed vicinal coupling constants is a very sensitive function of the imbalance in population of conformers I and II. If $J_t - J_g \sim 10$, then a change in J_- of 1 cps can be caused by n_I, n_II each changing by only 0.05. From the sum

$$J_+ \equiv |J_\alpha + J_\beta| = (n_\text{I} + n_\text{II})(J_g + J_t) + 2n_\text{III}J_g \quad (2)$$

it can be seen that we have a test of the assumption that $n_\text{III} \sim 0$. If it is valid, then J_+ should be independent of changes in conformer equilibrium. (However, the converse is *not* true, *i.e.*, invariance of J_+ does *not* demonstrate that $n_\text{III} \sim 0$.) We could then expect J_+ to be both solvent independent and temperature independent subject to the requirement that the individual couplings J_g, J_t be solvent and temperature independent.

Continuing with the assumption that $n_\text{III} \sim 0$ and introducing the functional dependence $J = J_0 \cos^2 \phi$ (which requires that J_g, J_t be of the same sign)

$$J_\alpha = J_0(n_\text{I} \cos^2 \phi_t + n_\text{II} \cos^2 \phi_g)$$

$$J_\beta = J_0(n_\text{I} \cos^2 \phi_g + n_\text{II} \cos^2 \phi_t)$$

where ϕ_t, ϕ_g are the dihedral angles characterizing *trans* and *gauche* protons in conformers I and II. Note that we assume J_t, J_g retain the same values in all three conformers as a consequence of the $\cos^2$ dependence of J. If $J_\alpha/J_\beta = r$, then since $n_\text{I} + n_\text{II} = 1$ we find

$$n_\text{I} = \frac{\cos^2 \phi_g - r \cos^2 \phi_t}{(r + 1)(\cos^2 \phi_g - \cos^2 \phi_t)} \qquad (3)$$

$$\frac{n_\text{I}}{n_\text{II}} = K = \frac{\cos^2 \phi_g - r \cos^2 \phi_t}{r \cos^2 \phi_g - \cos^2 \phi_t} \qquad (4)$$

For $\phi_g = 65°$, $\phi_t = 185°$

$$n_\text{I} = \frac{1.220(r - 0.180)}{r + 1}$$

$$K = \frac{r - 0.180}{1 - 0.180\,r}$$

We can see numerically that the values for n_I are not particularly sensitive to small deviations in ϕ. In Table I we give values of n_I $(\phi = 65°)/n_\text{I}$ $(\phi = 60°)$ calculated for representative values of r, the ratio of the observed vicinal couplings. At the extreme, values of n_I differ by only 7% and as the ratio decreases to values near those actually observed the difference is near 5%.

Table I. Numerical Effect of Value of Dihedral Angle

n_1 $(\phi = 65°)/n_1$ $(\phi = 60°)$	r	K $(\phi = 65°)/K$ $(\phi = 60°)$	n_I/n_II $(\phi = 60°)$	n_I/n_II $(\phi = 65°)$
0.93	4	0	∞	
0.94	3	0.55	11 (92:8)	6 (86:14)
0.94	2.5	0.70	6.0 (86:14)	4.2 (81:19)
0.95	2	0.81	3.5 (78:22)	2.8 (72:28)
0.97	1.5	0.90	2.0 (67:33)	1.8 (64:36)

Since the vicinal coupling constants can be evaluated to about 0.1 cps, the inherent mean square error in r can be evaluated from

$$r = \frac{J_1 \pm \epsilon_1}{J_2 \pm \epsilon_2}$$

$$\delta r = \sqrt{\left[\left(\frac{\partial r}{\partial J_1}\right)\epsilon_1\right]^2 + \left[\left(\frac{\partial r}{\partial J_2}\right)\epsilon_2\right]^2} = \sqrt{\left(\frac{\epsilon_1}{J_2}\right)^2 + \left(\frac{r\epsilon_2}{J_2}\right)^2}$$

which leads to an error in n_I, K of

$$\delta n_\text{I} = \frac{1.440}{(r + 1)^2}\delta r$$

$$\delta K = \frac{0.9676}{(1 - 0.180r)^2}\delta r$$

This shows that the error in K increases rapidly with increasing values of r. However, for $r \sim 2.5$, $J_2 \sim 5$, at $0 = 65°$, where $K = 4.22$

$$\delta r = 0.054$$

$$\delta n_\text{I} = 0.006$$

$$\delta K = 0.17$$

Therefore, the precision inherent to this method is, at least at the present stage of development, far better than the uncertainties introduced by the various approximations.

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(15) G. J. Szasz, *J. Chem. Phys.*, **23**, 2449 (1955).

(16) A qualitative argument also can be offered on the basis of the results of our previous paper (M. Buza and E. I. Snyder, *J. Am. Chem. Soc.*, **88**, 1161 (1966)) where it was shown that both $C_6H_5CHBrCH_2Br$ and *t*-BuCHBrCH$_2$Br exist largely in one conformer corresponding to I or II, respectively. If the other of these conformers II (or I) is of no higher energy than III, then the relatively small remaining mole fraction of species must be distributed between conformers II (or I) and III. Since the total $n_\text{II} + n_\text{III}$ is small, then n_II itself must be small.

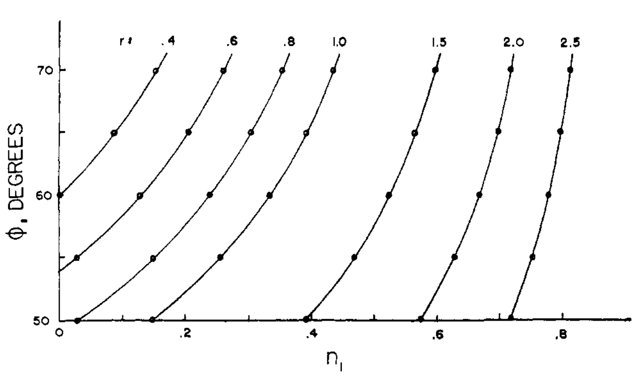


Figure 1. Dependence of mole fraction *trans* conformer (n_I) on dihedral angle (ϕ) for different values of r (eq 5).

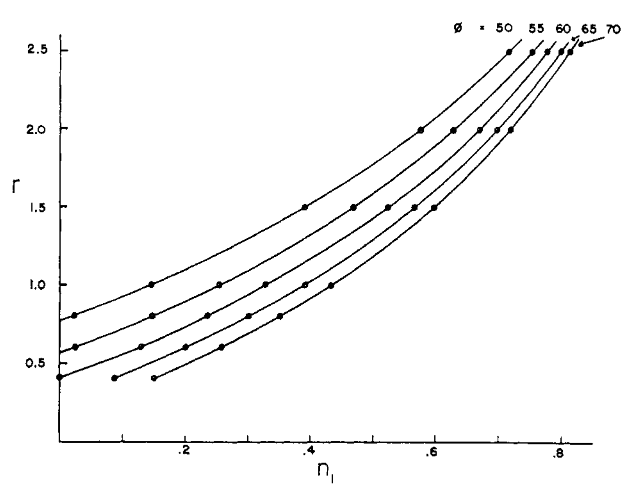
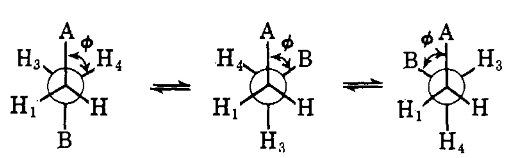


Figure 2. Variation of mole fraction *trans* conformer (n_I) with r as a function of dihedral angle (ϕ).

This model transforms advantageously to systems having the symmetry properties of an A_2X_2 spin system. Such a system as ACH_2CH_2B can be generally represented as



I II III

If conformer I has but a single energy minimum, then $\phi = 60°$ by symmetry. The angles ϕ in the remaining conformers must be equal since II and III are mirror images. We can then write (assuming $J = J_0 \cos^2 \phi$)

$$J_\alpha \equiv J_{13} = J_0[n_I \cos^2 60 + n_{II}[\cos^2(120 - \phi) + \cos^2(120 + \phi)]]$$

$$J_\beta \equiv J_{14} = J_0[n_I(\cos^2 180 - \cos^2 \phi) + \cos^2 \phi]$$

$$n_I = \frac{0.5r[\cos^2(120 - \phi) + \cos^2(120 + \phi)] - \cos^2 \phi}{1 - \cos^2 \phi - r[0.25\text{–}0.5\,[\cos^2(120 - \phi) + \cos^2(120 + \phi)]]} \tag{5}$$

where $r = J_\beta/J_\alpha$

$$K = \frac{n_I}{2n_{II}} = \frac{n_I}{1 - n_I} \tag{6}$$

$$\frac{n_{II}}{n_I} = 2e^{-\Delta E/RT}, \Delta E = RT \ln 2K$$

Figure 1 shows how n_I varies with r for different values of ϕ; Figure 2 shows the dependence of n_I on ϕ at constant r.

Note that transformation of our model to A_2X_2 systems no longer requires the assumption that $n_{III} \sim 0$. The latter systems also possess the advantage that their conformational equilibrium has been investigated by means other than nmr spectroscopy and comparisons are possible between our results and those of others. An important feature of this model applied to A_2X_2 systems is that the coupling constant between *gauche* protons (J_g) not only differs according to the conformer (*e.g.*, I and II) but also different values of J_g may appear in the same conformer (*e.g.*, II or III) when the dihedral angle ϕ is different from 60°. Previous workers have always made the simplifying assumption that all J_g values were equal.[5,17]

A test for the model presented can be afforded by studying the temperature dependence of the nmr spectral parameters. This has been done for three- and four-spin systems by Gutowsky[5] and such an approach had been explicitly considered earlier for A_2X_2 systems by Sheppard and Turner.[18a] Should the model survive this test, its chief value would reside in affording (approximate) values of the conformational equilibrium constant through spectral examination at a single temperature. The assumption for three-spin systems that $n_{III} \sim 0$ can be tested as described above. Subsequent discussion (*vide infra*) will show that the choice of a dihedral angle near 60° does not influence the results in an important way.

Consequences of Assumptions Used. Restricting consideration of our model to applications in A_2X_2 systems the consequences of several of our assumptions can be assessed. These relate to (1) values of the dihedral angle chosen and (2) the functional dependence of the vicinal coupling on the dihedral angle. Figures 1 and 2 attempt to describe the dependence of n_I on ϕ, as r varies. For values of $r \sim 2$ and $\phi \sim 60°$, it happens that ΔE changes by only 0.01 kcal per degree change in ϕ. Consequently, our choice of a value for ϕ is not critical—at least for the systems contained in Table III.

If we permit J to vary with ϕ as $J = A + B\cos^2 \phi$ we can write $n_I' = n_I + C$ where n_I' is the value calculated from the three-parameter equation, above, n_I is obtained from eq 5, and C is a correction term of the form

$$C = \frac{A(r - 1)}{B[1 - \cos^2 \phi - r(0.25 - 0.5[\cos^2(120 - \phi) + \cos^2(120 + \phi)])]} \tag{7}$$

If $A/B = S < 0^1$, then eq 5 *overestimates* n_I by an

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(17) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **84**, 743 (1962).

(18) (a) N. Sheppard and J. J. Turner, *Proc. Roy. Soc.* (London), **A252**, 506 (1959). (b) We would like to thank Dr. George Whitesides (Massachusetts Institute of Technology) for communicating these results and for permission to cite them prior to their publication.

Table II. Conformational Energy Differences for $(CH_3)_3CCH_2CH_2X$

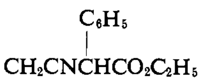
X	ΔE,[a] kcal mole^{-1}	ΔE[b]	ΔE[c]	ΔE[d]
Cl	0.99	0.99	1.05	1.02
Br	1.30	1.17	1.30	1.26
CN	0.75	0.76	0.75	0.76
CO_2CH_3	0.99	0.91	0.95	0.94
CO_2H	0.99	0.95	1.02	0.99
C_6H_5	1.68	1.40	1.69	1.58
$Si(CH_3)_3$	2.30	2.04	*e*	3.42

[a] G. Whitesides, private communication. These data were obtained from analysis of the temperature dependence of the vicinal coupling constants. [b] From eq 5. [c] From eq 5 and 7, $\phi = 60°$, $S = A/B = 0.075$. [d] From eq 5 and 7, $\phi = 62°$, $S = 0.05$. [e] The value for n_I was greater than unity.

amount largely dependent on $|S|$, r, for ϕ near 60°. Conversely a positive value of S implies that use of (5) underestimates n_I. However, for any one compound in a series of solvents the *difference* in correction terms should approximately vanish, since changes in S and ϕ should be small for most compounds. Hence (5) seems to be most valid when examining solvent effects on the conformational equilibrium. Since $\delta\Delta E = K\delta n_I/n_I(1 - n_I)$, calculations show that even if n_I is underestimated by as much as 0.1 mole fraction this gives rise to an error in the difference of ΔE values of only about 0.1 kcal mole^{-1} when n_I changes by 0.4 mole fraction about a mean of 0.6 mole fraction.

Recent experiments by Whitesides[18b] permit the most extensive comparison of energy differences derived *via* (5) and those obtained by a completely independent method. Such comparisons (Table II) show that the ΔE values afforded by these two methods differ on the average by only 7%, an agreement which we consider most gratifying. Further, the ΔE calculated by our model is consistently *lower* than those obtained by Whitesides, *i.e.*, eq 5 seems to underestimate n_I. Using a three-parameter equation, the average difference, neglecting the last entry, could be reduced to 2% using $\phi = 60°$, $S = 1/13.3$, or 3% using $\phi = 62°$, $S = 1/20$. However, we feel that use of the three-

Table III

Compound	Solvent	r[a]	J_+[b]	n_I	K	ΔE (25°), kcal mole^{-1}	δn_1	Errors[c] δk	$\delta(\Delta E)$
$CH_2BrCHBrCO_2H$	C_6H_6	2.445	15.40	0.802	4.05	0.833	0.007	0.195	0.028
	$CHCl_3$	2.582	15.69	0.818	4.49	0.895	0.007	0.228	0.030
	CH_3CN	2.704	15.37	0.831	4.92	0.949	0.007	0.272	0.033
	Acetone	2.343	15.38	0.789	3.74	0.786	0.007	0.171	0.027
$CH_2BrCHBrCO_2C_2H_5$	C_6H_6	2.536	15.70	0.813	4.33	0.874	0.007	0.215	0.029
	Neat	2.386	15.54	0.794	3.87	0.806	0.007	0.179	0.027
	CCl_4	2.665	15.76	0.827	4.78	0.932	0.007	0.252	0.031
	CH_3CN	2.242	15.27	0.776	3.46	0.739	0.007	0.151	0.026
	CH_3COCH_3	2.532	15.33	0.812	4.32	0.872	0.007	0.219	0.030
	$C_6H_5NO_2$	2.326	15.40	0.787	3.69	0.778	0.007	0.167	0.027
$CH_2ClCHClCO_2H$	C_6H_6	1.523	13.27	0.649	1.85	0.366	0.008	0.068	0.022
	$CHCl_3$	1.571	13.47	0.660	1.94	0.394	0.008	0.071	0.022
$CH_2ClCHClCO_2C_2H_5$	C_6H_6	1.589	13.72	0.664	1.97	0.405	0.008	0.072	0.022
	$CHCl_3$	1.565	13.75	0.659	1.93	0.391	0.008	0.069	0.021
	CCl_4	1.682	14.19	0.683	2.16	0.457	0.007	0.079	0.022
	Neat	1.409	13.30	0.622	1.65	0.297	0.008	0.058	0.021
$CH_2BrCHBrC_6H_5$	CCl_4	2.074	16.14	0.751	3.02	0.659	0.007	0.115	0.023
	$CHCl_3$	1.900	16.18	0.723	2.61	0.572	0.007	0.092	0.021
	CH_3COCH_3	1.810	15.85	0.707	2.42	0.526	0.007	0.082	0.020
	CH_3CN	1.923	15.99	0.727	2.67	0.584	0.007	0.096	0.021
$CH_2ClCHClC_6H_5$	C_6H_6	1.187	14.26	0.562	1.28	0.147	0.007	0.040	0.018
	CCl_4	1.261	14.45	0.583	1.40	0.200	0.007	0.044	0.018
$CH_2BrCHOHC_6H_5$	CH_3COCH_3	1.577	11.93	0.661	1.95	0.398	0.009	0.081	0.025
	$CHCl_3$	2.124	12.31	0.759	3.15	0.683	0.009	0.161	0.030
$CH_2OHCHIC_6H_5$	$CHCl_3$	1.029	14.59	0.510	1.04	0.025	0.007	0.031	0.018
	CH_3CN	1.163	14.77	0.554	1.24	0.129	0.007	0.037	0.018
$CH_2BrCHBrC(CH_3)_3$	C_6H_6	3.489	12.39	0.899	8.89	1.302	0.009	0.981	0.065
	CCl_4	3.006	12.34	0.860	6.16	1.083	0.009	0.504	0.048
	CH_3CN	4.161	12.49	0.941	15.86	1.647	0.010	2.90	0.108
	CH_3COCH_3	3.754	12.55	0.917	11.02	1.430	0.009	1.443	0.078
$CH_2BrCHBrCN$	Neat	1.370	14.48	0.612	1.58	0.272	0.007	0.050	0.019
	C_6H_6	1.905	15.02	0.724	2.63	0.575	0.007	0.100	0.022
$CH_2ClCHClCN$	Neat	1.263	12.20	0.584	1.40	0.201	0.008	0.052	0.022
	C_6H_6	1.376	12.88	0.614	1.59	0.276	0.008	0.057	0.021
	CH_3COCH_3	1.396	11.55	0.619	1.63	0.289	0.009	0.066	0.024
	CH_3CN	1.372	11.28	0.613	1.58	0.274	0.009	0.064	0.024
 $\overset{C_6H_5}{\overset{\vert}{CH_2CNCHCO_2C_2H_5}}$	C_6H_6	1.077	15.06	0.527	1.11	0.064	0.007	0.032	0.017
	CH_3CN	1.079	14.80	0.527	1.12	0.065	0.007	0.033	0.017
	$CHCl_3$	1.008	14.92	0.503	1.01	0.007	0.007	0.029	0.017
	CCl_4	1.013	14.98	0.505	1.02	0.011	0.007	0.030	0.017

[a] $r = J_\alpha/J_\beta$, where J_α, J_β are the two vicinal couplings with $J_\alpha > J_\beta$; values of J come from Table I of our previous paper: *J. Am. Chem. Soc.*, **88**, 1155 (1966). [b] $J_+ \equiv |J_\alpha + J_\beta|$. [c] Errors are calculated assuming errors of 0.1 cps in each vicinal coupling.

Table IV. Conformational Equilibria in 1,2-Disubstituted Ethanes

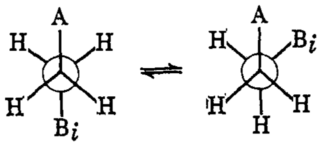
Compound[a]	Solvent	r^b	n_t	K^c	ΔE^d (27°), kcal mole^{-1}	ΔE (lit.)
$BrCH_2CH_2Br^e$	Neat	1.964	0.687	2.199	0.883	0.75[f]
	n-Hexane, 1:3	2.215	0.742	2.879	1.043	0.94[f]
	CH_3NO_2	1.684	0.617	1.613	0.698	0.39[f]
$ClCH_2CH_2Cl^e$	Neat	1.125	0.440	0.786	0.269	0.0[g]
	n-Hexane, 1:3	1.423	0.542	1.182	0.513	0.39[f]
$ClCH_2CH_2Br^h$	Neat	1.515	0.570	1.324	0.580	0.49[i]
	CH_3CN, 1:1	1.254	0.486	0.947	0.381	
$ClCH_2CH_2OH^h$	Neat	0.709	0.261	0.353	−0.208	−0.95[i]
	CCl_4, 1:2	0.668	0.240	0.316	−0.274	
	Acetone, 1:1	0.807	0.308	0.444	−0.070	
$BrCH_2CH_2OH^h$	Neat	0.814	0.311	0.451	−0.061	
	$CHCl_3$, 1:1	0.768	0.289	0.407	−0.122	
	CS_2, 1:1	0.835	0.320	0.471	−0.036	
	Acetone, 1:1	1.000	0.391	0.643	0.150	
$CH_3OCH_2CH_2OH^h$	Neat	0.622	0.216	0.275	−0.356	
	CCl_4, 1:1	0.553	0.178	0.217	−0.498	
	D_2O, 1:1	0.548	0.175	0.213	−0.509	
	Acetone, 1:1	0.656	0.234	0.305	−0.295	
$ClCH_2CH_2OCOCH_3^h$	Neat	0.681	0.246	0.327	−0.253	
	CCl_4, 1:1	0.735	0.273	0.376	−0.170	
$CH_3OCH_2CH_2OCOCH_3^h$	Neat	0.549	0.176	0.213	−0.508	
	CCl_4, 1:1	0.556	0.180	0.219	−0.492	
	Acetone, 1:1	0.544	0.173	0.209	−0.520	
$CH_3COCH_2CH_2CO_2H^h$	$CHCl_3$, 1:1	0.814	0.311	0.451	−0.061	
	D_2O, 1:1	0.743	0.277	0.384	−0.158	
$CH_3OCH_2CH_2CO_2C_2H_5^h$	Neat	0.788	0.299	0.426	−0.096	
	$CHCl_3$, 1:1	0.808	0.308	0.445	−0.070	
	CH_3OH, 1:1	0.752	0.282	0.392	−0.145	
	CF_3CO_2H, 2:3	0.738	0.275	0.379	−0.166	

[a] Calculations were performed for ϕ(eq 5) = 65°. [b] A value of $r \geq 0.944$ signifies that the *trans* conformer is favored. [c] K = mole fraction of *trans* conformer/mole fraction of *gauche* conformer. [d] $\Delta E = E_g - E_t = 1.372 \log 2K$. [e] N. Sheppard and J. J. Turner, *Proc. Roy. Soc.* (London), **A252**, 506 (1959). [f] See Table II of preceding reference. [g] Reference 13, p 41. [h] R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, **7**, 165 (1964). [i] N. Sheppard, *Advan. Spectry.*, **1**, 296 (1960).

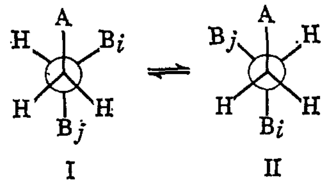
parameter equation is presently only an exercise in curve fitting, although as more data become available they might serve to define the latter equation.

Results

Values of the conformational equilibrium constant, K, calculated by eq 4 from our data for three-spin systems[19] are collected in Table III. Similar values for A_2X_2 symmetry systems are presented in Table IV. If one adopts the simplified notion that effects responsible for determining conformational equilibria are additive, then the results for three- and four-spin systems are related in the following way.



trans *gauche*



I II

Let (K, L) = interaction energy between groups K, L when *gauche*

$$\Delta_{t-g}{}^{A-B} = (E_t - E_g)_{ACH_2CH_2B};\ \Delta_{I-II}{}^{A-B_2B_1} = (E_I - E_{II})_{ACH_2CHB_1B_2}$$

Then

$$\Delta_{t-g}{}^{A-B_1} = 2(B_1, H) + 2(A, H) + 2(H, H) - [(A, B_1) + (B_1, H) + 3(H,H)]$$

$$\Delta_{t-g}{}^{A-B_2} = 2(B_2, H) + 2(A, H) + 2(H, H) - [(A, B_2) + (A, H) + (B_2, H) + 3\,(H, H)]$$

$$\Delta_{t-g}{}^{A-B_1} - \Delta_{t-g}{}^{A-B_2} = [(B_1, H) - (B_1, A)] - [(B_2, H) - (B_2,A)] = [(B_1, H) - (B_2, H)] - [(B_1, A) - (B_2, A)]$$

But

$$\Delta_{I-II}{}^{A-B_2B_1} = [(B_2, A) + (B_2, H) + 2(B_1, H) + (H, H) + (A, H)] - [(B_1, A) + (B_1, H) + 2(B_2, H) + (H, H) + (A, H)] = [(B_2, A) - (B_1, A) - [(B_2, H) - (B_1, A)] = \Delta_{t-g}{}^{A-B_1} - \Delta_{t-g}{}^{A-B_2}$$

Therefore if the model is correct we have a built-in test for additivity of conformational effects.[20]

Table III shows that the values of J_+ are relatively solvent insensitive (a total variation of less than 0.5 cps) for such systems as $CH_2BrCHBrCO_2R$ (R = H, C_2H_5), $BrCH_2CHBrC_6H_5$, and $BrCH_2CHBr$-*t*-Bu. Such invariance is required by our model (eq 2) so long as

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(19) E. I. Snyder, *J. Am. Chem. Soc.*, **88**, 1155 (1966).

(20) This is inherently an approximation since the dihedral angle between groups in, say, the *t* conformer is different from that of the *g* conformer. In general one would expect, *e.g.*, (A,H) = (A,H) + δ where $\delta \rightarrow 0$ as $\phi \rightarrow 60°$.

$n_{\mathrm{III}} \sim 0$, although the solvent dependence[21] of J_t, J_g themselves could lead to variation in J_+ even when $n_{\mathrm{III}} = 0$. Furthermore, replacement of the bulky Br by the smaller Cl leads to wider (0.9 cps) variation in J_+, explicable on the basis of an expected relaxation of the requirement $n_{\mathrm{III}} \sim 0$. Finally, when the groups become sufficiently small so that the energy of that conformer with two *gauche* interactions (other than hydrogen–hydrogen) becomes comparable to that of conformers with but one *gauche* interaction, as in $ClCH_2CHClCN$—the linear CN group may be considered to have a small van der Waal's energy[22]—then $n_{\mathrm{III}} \neq 0$ and the variation in J_+ becomes large, as observed (1.6 cps). Thus the whole range of observations is at least qualitatively reasonable.

Inspection of Table III also shows that the conformer distribution is modestly solvent dependent. In most cases the variation in ΔE is under 0.2 kcal mole^{-1}. The direction of variation is but weakly related to solvent dielectric, since in some cases ΔE changes with solvent in the order CH_3COCH_3, C_6H_6 (or $CHCl_3$), CH_3CN. The data of Table III show somewhat greater solvent variation in ΔE, to be expected of 1,2-disubstituted ethanes, but even here the largest change is only about 0.3 kcal mole^{-1}. A somewhat better correlation with dielectric constant of the medium seems to hold. Because other work[23] reports a much greater change in ΔE with solvent it seems that this aspect of conformational isomerism might need to be reexamined.

The last column of Table IV contains the conformer energy difference obtained by other workers for 1,2-disubstituted ethanes and provides, so far as we know, the only available tests of our method based on published data. In some cases agreement is quite good (to within 0.1 kcal mole^{-1}) whereas in others differences up to 0.7 kcal mole^{-1} are noted. Unfortunately the limited range of data over which comparisons are possible does not permit, at this time, a meaningful, unambiguous test.

Since we do not unequivocally know the identity of the most stable conformer in most systems included in the tables, it is difficult to assess the importance of the several factors governing conformational equilibrium. The data seem to demonstrate the importance of steric effects, *i.e.*, interactions associated with the "size" of an atom or group of atoms. The effect of dipole–dipole repulsions is not easily determined from these data. Since it is reported[24–26] that the *gauche* conformer of $ClCH_2CH_2O_2CC_2H_5$, $CH_3OCH_2CH_2O_2CC_2H_5$ and $CH_3COCH_2CH_2CO_2H$ and its ester is the more stable one, it appears that additional factors might also need to be considered. Hopefully examination of a large number of compounds will eventually permit compilation of interaction energies for acyclics similar to the A values of cyclics.[27]

Although our initial paper in this series[19] dwelled on the origin of magnetic nonequivalence of CH_2 groups, our subsequent work has merely used this nonequivalence, in the chemical shift sense, as a probe to delve into the realm of rotational isomerism. The spectrum of $C_6H_5C(CO_2C_2H_5)HCH_2CN$ is of interest in that the two vicinal coupling constants are equal, or nearly so, whereas the chemical shift between the methylenes remains large. That is, the methylenes are equivalent in the spin-coupling sense, but nonequivalent in the chemical shift sense. The identity of the two vicinal couplings might be interpreted as indicative of a statistical conformer distribution (hence nonequivalence arising from an asymmetric magnetic field, independent of conformer distribution), but eq 1 clearly shows this result merely requires $n_{\mathrm{I}} = n_{\mathrm{II}}$, *i.e.*, the mole fractions of the two conformers with but one *gauche* interaction are equal. An unambiguous test for the origin of magnetic nonequivalence would seem to reside in examination of the nmr spectrum of the series, $ACH_2C{\equiv}C\text{-}CXYZ$. Because the barrier to rotation of the methyl group in acetylenes is so low (under 0.1 kcal mole^{-1}),[28] the energy difference between conformers is necessarily negligible. Therefore if one observes nonequivalent methylene groups in these compounds the nonequivalence must necessarily arise from a magnetic asymmetry. The converse, that absence of nonequivalence precludes magnetic asymmetry as the origin of nonequivalence, is clearly invalid, so the experiment is meaningful *only* if nonequivalence is observed.

Another system suitable for distinguishing between the origins of nonequivalence is $p\text{-}XC_6H_5(p\text{-}YC_6H_5)C(C_6H_5)CH_2Z$. If X, Y are sufficiently small, all conformers should be equally populated. Large differences in the magnetic properties of X and Y might then lead to observation of magnetic nonequivalence of the CH_2 groups if magnetic asymmetry is responsible.

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(21) E. I. Snyder, *J. Am. Chem. Soc.*, **85**, 2624 (1963); G. M. Whitesides, J. J. Grocki, D. Holtz, H. Steinberg, and J. D. Roberts, *ibid.*, **87**, 1058 (1965).

(22) N. L. Allinger and W. Szkrybalo, *J. Org. Chem.*, **27**, 4601 (1962); B. Rickborn and F. R. Jensen, *ibid.*, **27**, 4606 (1962).

(23) A. Wada, *J. Chem. Phys.*, **22**, 198 (1954).

(24) M. Buza and E. I. Snyder, ref 16.

(25) R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, **7**, 165 (1964).

(26) Because this result, if correct, would be extremely important to the subject of rotational isomerism, we are currently attempting confirmation by stereospecific dideuteration (*cf.* the method of ref 24).

(27) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 8.

(28) V. W. Laurie and D. R. Lide, *J. Chem. Phys.*, **31**, 939 (1959).