Representations of Molecular Force Fields. 3. On Gauche Conformational Energy

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Abstract: A heretofore neglected class of potential functions in molecular mechanics is the set of onefold and twofold barrier functions associated with the individual HCCH, HCCC, and CCCC dihedral angles about C–C single bonds. It is suggested that these functions may be transferable from structure to structure and that they may contribute significantly to the difference in energy ΔE_g between gauche and anti conformations even though they cancel identically in such molecules as ethane. In the simplest approximation, the onefold and twofold contributions can be lumped together into a single parameter $\Delta V_g^{\mathrm{intr}}$, which is applicable to the prototype cases of *n*-butane, 2-methylbutane, 2,3-dimethylbutane, and methylcyclohexane. Prior to the introduction of the new parameter the most frequently used force fields relied on physically implausible imbalances between nonbonded interactions in order to obtain reasonable ΔE_g values. The new parameter suffices to bring calculated and experimental values into close agreement when taken together with balanced interactions in the force field MUB2.

I. Introduction

Molecular mechanics is developing into a well-established technique for estimating molecular properties.[1] Its reliability, of course, is no better than that of the force fields incorporated into its potential energy minimization procedure. Dozens of model force fields with widely differing parametrizations have been introduced to account for various properties. No universally successful recipe has been found, and all of the more successful formulations suffer systematic defects in certain areas. The purpose of this paper is to draw attention to just one of the problems encountered in treatments of hydrocarbon groups and to propose a possible resolution. The problem is the source of the difference in energy (hereinafter called ΔE_g) between gauche and anti conformations, and its proper representation in model fields; ΔE_g depends strongly on the C–C environment.

In *n*-alkane chains ΔE_g has traditionally been ascribed to steric interactions between methyl or methylene groups although Allinger et al.[2] have recently proposed, instead, that it originates from the repulsive 1,4-interactions between gauche vicinal hydrogens. All of the more actively applied force fields in molecular mechanics are based on Hooke's law forces in bond stretching and bond bending deformations, threefold barrier functions to describe torsions about single bonds, and nonbonded interactions to keep atomic clearances reasonable. In some cases, other interactions or empirical correction parameters are included as well, but the burden of representing ΔE_g has always fallen on the interactions between nonbonded atoms. This limitation is artificial, needlessly restrictive, and leads to the following trouble.

Force fields relying solely on short-range nonbonded repulsions to produce ΔE_g tend to underestimate its magnitude if the repulsive potential functions invoked form a moderate, balanced set. This is because, by flexing slightly, most gauche structures can avoid close, strongly destabilizing nonbonded contacts more remote than 1,4-interactions. Examples of formulations with this deficiency that are reasonably successful otherwise are the modified Urey–Bradley fields MUB1[3] and MUB2.[1a,4] How pervasive this deficiency is when fields with potential functions comparable to those in MUB1 and MUB2 are applied to a prototype series of molecules including *n*-butane, 2-methylbutane, 2,3-dimethylbutane, and methylcyclohexane was not fully appreciated at the time the fields were formulated (1974 and earlier) because accurate experimental values of ΔE_g had not been established. Two force fields which account quite well for rotational isomerization in *n*-butane and methylcyclohexane are Allinger's[1c,2,5] and Schleyer's.[1b] Allinger achieves large ΔE_g values by invoking what seem to be disproportionately large H···H repulsions, while Schleyer's strategem is to make his C···H repulsions considerably smaller (in comparison with H···H and C···C) than is consistent with any of the popular combining laws.[6] That the above two schemes should enhance ΔE_g is evident from the following considerations.

Steric interactions which are not easily avoided by internal rotations are the vicinal interactions across the C–C bond undergoing the anti to gauche transformation. In this transformation two gauche C···H interactions per C–C bond disappear and one gauche H···H and C···C pair are produced. Hence, in Schleyer's field, two weak interactions are replaced by two moderately strong ones whereas, in Allinger's field, two moderate interactions are replaced by one modest and one very strong one. Because these two expedients appear to be questionable on physical grounds and because a more balanced pattern of H···H, C···H, and C···C interactions offers other advantages, it is worthwhile to investigate alternative ways of achieving satisfactory ΔE_g values. One natural approach is discussed in the following.

A. Low-Order Barrier Components. First, we shall show the plausibility of introducing into the barrier function of ethane some low-order components which give rise to observable effects when ethane is distorted. Then we shall demonstrate that, in molecules possessing lower symmetry than ethane, low-order components over and above those associated with conventional steric effects may play a role in destabilizing gauche conformations.

Ethane's high symmetry precludes the possibility of a torsional potential energy with Fourier components of lower order than threefold. This by no means signifies that it is inappropriate to associate substantial onefold and twofold functions $V_n(\tau_{ij}) = V_n^0(1 + \cos n\tau_{ij})/2$, $n = 1, 2, \ldots$, with individual torsional sequences H_iCCH_j in ethane. It simply means that the sum over all pairs τ_{ij} vanishes except for $n = 3, 6, \ldots$. That it is reasonable and even profitable to assign V_1 and V_2 components to individual torsional angles τ_{ij} is suggested by several arguments. First, it has often been noted that proton–proton electrostatic repulsions account closely (when slightly screened) for ethane's barrier if rigid internal rotation of the framework is assumed.[7] Proton–proton repulsions (unscreened) yield onefold and twofold barriers per H_iH_j pair of 35 and 3.7 kcal/mol, respectively. Secondly, extended Hückel molecular orbital calculations can be decomposed into H_iCCH_j interactions, indicating onefold components with

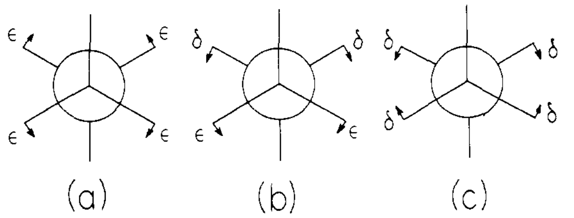

Figure 1. Newman projections of molecular deformations that are (a) *n*-butane-like, (b) 2-methylbutane-like, and (c) 2,3-dimethylbutane-like.

barriers of about 3 kcal/mol and twofold with barriers perhaps 0.2 times as large.[8] Although the extended Hückel method is far from rigorous, illustrative calculations based on it have been given serious consideration in explanations of ethane's barrier to internal rotation.[9] The short-range forces characteristic of the molecular orbital result probably model the molecular physics more satisfactorily than do the long-range electrostatic monopole results. That the Hückel result is more than a trivial artifact of an oversimplified quantum mechanical decomposition is hinted at by the following. Observe that the D_{3d} equilibrium symmetry of the molecule is lost, making onefold and twofold components allowed in the overall torsional function, if the HCH dihedral angles of the individual methyls are forced into fixed deformations as in Figure 1. It turns out that deviation from a threefold function, as calculated directly by EHMO theory for case b in Figure 1 with distorted methyl groups,[10] is reproduced approximately by the sum of the individual H_iCCH_j one- and twofold components if the components[8] are *derived from structures with symmetric* (C_{3v}) *methyl groups*! [Configurations a and c in Figure 1 were not tested numerically.] This suggests the approximate transferability of one- and twofold barrier components from structure to structure. Implications of transferability are discussed in the next section.

B. Model with One- and Twofold Barrier Components. Because of the threefold form of the ethane torsional potential it became traditional in molecular mechanics to introduce the "intrinsic" ("nonsteric") part of the barrier function about C–C bonds in terms of simple threefold components calculated either for a key dihedral angle or summed over all nine dihedral angles about a given bond. However, any factor destroying the threefold symmetries about the carbon atoms opens up the possibility of a more complicated torsional potential. Deformations of bond angles as in Figure 1 or the replacement of H atoms by C atoms can spoil the exact cancellation of one- and twofold barrier components that occurs in ethane. Let us take both distortion and substitution factors into account in the following model.

Assume that individual X_iCCY_j barrier components V^{XY} can be written as sums of one-, two-, and threefold functions with

$$V^{HH}(\tau_{ij}) = \sum_{n=1}^{3} A_n \cos n\tau_{ij} \qquad (1a)$$

$$V^{CH}(\tau_{ij}) = \sum_{n=1}^{3} B_n \cos n\tau_{ij} \qquad (1b)$$

and

$$V^{CC}(\tau_{ij}) = \sum_{n=1}^{3} C_n \cos n\tau_{ij} \qquad (1c)$$

where τ_{ij} is reckoned from the s-cis configuration and the A_n, B_n, and C_n are half the *n*-fold barriers. Assume that the individual groups at each end of a C–C bond participate in internal rotations as rigid bodies with fixed deformations (δ and ϵ) as illustrated in Figure 1. Assume, finally, that the total barrier function is the sum of the nine $V^{XY}(\tau_{ij})$ component functions. Express the individual τ_{ij} in terms of the deformations δ and ϵ and the intergroup dihedral angle τ reckoned from the symmetric conformation, apply appropriate trigonometric identities, and sum the V^{XY}. The results, after expanding and discarding terms higher than first-order in δ and ϵ, are for the *n*-butane-like case:

$$\begin{aligned} V(\tau) = {} & \{(2B_1 - A_1 - C_1) + 12^{1/2}(B_1 - A_1)\epsilon\} \cos \tau \\ & + \{-(2B_2 - A_2 - C_2) + 48^{1/2}(B_2 - A_2)\epsilon\} \cos 2\tau \\ & + \{-(4B_3 + 4A_3 + C_3) + 0\epsilon\} \cos 3\tau \end{aligned} \qquad (2a)$$

for the 2-methylbutane-like case:

$$\begin{aligned} V(\tau) = {} & \{-(2B_1 - A_1 - C_1) - 3^{1/2}[(B_1 - A_1)\epsilon \\ & - (B_1 - C_1)\delta]\} \cos \tau + \{(2B_2 - A_2 - C_2) \\ & - 12^{1/2}[(B_2 - A_2)\epsilon - (B_2 - C_2)\delta]\} \cos 2\tau \\ & + \{-(5B_3 + 2A_3 + 2C_3) + 0\epsilon + 0\delta\} \cos 3\tau \end{aligned} \qquad (2b)$$

and for the 2,3-dimethylbutane-like case:

$$\begin{aligned} V(\tau) = {} & \{(2B_1 - A_1 - C_1) - 12^{1/2}(B_1 - C_1)\delta\} \cos \tau \\ & + \{-(2B_2 - A_2 - C_2) - 48^{1/2}(B_2 - C_2)\delta\} \cos 2\tau \\ & + \{-(4B_3 + A_3 + 4C_3) + 0\delta\} \cos 3\tau \end{aligned} \qquad (2c)$$

If *A*, *B*, and *C* are taken to be equal, the model corresponds to distorted ethane and all of the above terms cancel, except for threefold terms, through terms linear in δ and ϵ. The small quadratic terms surviving in distorted ethane are

$$\begin{aligned} V(\tau)_{\text{quad}} = {} & 3\epsilon\delta(A_1 \cos \tau - 4A_2 \cos 2\tau) \\ & - 27(\delta^2 + \epsilon^2)A_3 \cos 3\tau \end{aligned} \qquad (3)$$

for the Figure 1b case, and the Figure 1a and Figure 1c cases are reproduced by setting $\delta = -\epsilon$. For δ and ϵ values of a few degrees, the one- and twofold terms of eq 3 may be a few small calories per mole according to EHMO computations. Therefore eq 3 is not likely to be important in molecular mechanics.

Clearly, the illustrative model embodied in eq 2 implies a substantial "nonsteric" contribution to gauche destabilization if there is a moderate imbalance in the A_n, B_n, and C_n barrier values. Estimates of the "nonsteric" contributions to ΔE_g, taking τ(asymm) = 120° (from symm) and τ(symm) = 0°, are then, for the *n*-butane case:

$$\begin{aligned} V(120°) - V(0°) = {} & \tfrac{3}{2}\{(A_1 + C_1 - 2B_1) \\ & + 12^{1/2}(A_1 - B_1)\epsilon\} - \tfrac{3}{2}\{(A_2 + C_2 - 2B_2) \\ & - 48^{1/2}(A_2 - B_2)\epsilon\} \end{aligned} \qquad (4a)$$

for the 2-methylbutane case ($\Delta E_g \equiv E_{\text{symm}} - E_{\text{asymm}}$):

$$\begin{aligned} -[V(120°) - V(0°)] = {} & \tfrac{3}{2}\{(A_1 + C_1 - 2B_1) \\ & + 3^{1/2}[(A_1 - B_1)\epsilon - (C_1 - B_1)\delta]\} - \tfrac{3}{2}\{(A_2 + C_2 - 2B_2) \\ & - 12^{1/2}[(A_2 - B_2)\epsilon - (C_2 - B_2)\delta]\} \end{aligned} \qquad (4b)$$

and for the 2,3-dimethylbutane case:

$$\begin{aligned} V(120°) - V(0°) = {} & \tfrac{3}{2}\{(A_1 + C_1 - 2B_1) \\ & - 12^{1/2}(C_1 - B_1)\delta\} - \tfrac{3}{2}\{(A_2 + C_2 - 2B_2) \\ & - 48^{1/2}(C_2 - B_2)\delta\} \end{aligned} \qquad (4c)$$

To the present approximation, the difference between axial and equatorial methylcyclohexane is just twice eq 4b, because two C–C bonds undergo anti to gauche rotations. Possible magnitudes associated with the above one- and twofold contributions are discussed in the next section.

II. Discussion

Many alternative interpretations of barriers to internal rotation have been advanced. Those which have survived into the period of successful ab initio quantum calculations of barriers still admit the possibility of one- and twofold compo-

Table I. Differences in Energy, ΔE_g (kcal/mol), between Gauche and Anti Conformations According to Various Force Fields

Molecule	Obsd	MUB2[a]	MUB2 + 0.36	WA[b]	WA + 0.20	EAS[c]	WL[d]	B[e]
n-Butane	0.966 (50)[f]	0.540	0.900	0.69	0.89	0.93	0.7	0.72
2-Methylbutane	0.809 (50)[f]	0.484	0.847	0.55	0.75	0.78		
2,3-Dimethylbutane	0.054 (30)[f]	−0.277	0.083	−0.14	0.06	−0.03		
½(Methylcyclohexane)	0.890 (75)[g]	0.477	0.837	0.80	1.00	0.92	0.9	0.62

[a] Reference 1a. [b] Reference 2 and private communication. [c] Reference 1b and private communication. [d] Reference 16. [e] Reference 17. [f] Reference 14 uncertainties in parentheses. [g] Reference 15 uncertainty in parentheses.

nents. Sovers et al.[11] attribute ethane barriers to repulsive interactions between electron pairs localized in C–H bond orbitals that are analogous to the closed-shell repulsion between a pair of helium atoms. The asymmetry of C–H bonds would presumably yield all terms, beginning with onefold, in a Fourier representation of bond–bond interactions. The electrostatic monopole and dipole models of Lowe and Parr[7,12] also can be expanded in such terms. Molecular orbital descriptions by Lowe[9] and by Radom et al.[13] draw special attention to conjugative and hyperconjugative interactions transmitted via π orbitals of the carbons in the C–C bond. These interactions may contribute to the barrier by orientation-dependent π delocalization or by net covalent antibonding between vicinal atoms originating from occupied high-lying π molecular orbitals. Such descriptions are suggestive of significant twofold barrier components as well as onefold.

A clue that a molecular mechanics model with one- and twofold barriers may be of practical significance is provided by the simplicity with which it accounts for ΔE_g values without requiring the seemingly artificial assumptions of some previous force fields. In order to reduce the model to its most primitive form, let us assume that the small δ and ϵ deformations found in hydrocarbons (0.02–0.04 rad) allow us to neglect the deformation corrections in eq 4a–4c. Then the one- and twofold barrier contributions to ΔE_g all reduce to:

$$\Delta V_g^{\mathrm{intr}} \approx \tfrac{3}{2}\{A_1 + C_1 - 2B_1 - A_2 - C_2 + 2B_2\} \qquad (5)$$

where $\Delta V_g^{\mathrm{intr}}$ may be envisioned as an "intrinsic" component to be added to the "steric" contribution to ΔE_g. Most noteworthy is the fact that the *n*-butane, 2-methylbutane, 2,3-dimethylbutane, and the half-methylcyclohexane cases all reduce to the same result and that, to this order of approximation, it is unnecessary to know the individual one- and twofold contributions separately in order to estimate ΔE_g. An assessment of $V(\tau)$, which is needed for a calculation of the relaxed gauche structure, does require a breakdown into the one- and twofold contributions, however (or the neglect of one).

In view of the fact that $\Delta V_g^{\mathrm{intr}}$ has been reduced to a single parameter, common to all the cases considered here, it is of special interest to observe that the differences between the experimental[14,15] and calculated ΔE_g values *are* approximately constant over the series of molecules when the calculations are carried out by the "balanced" field MUB2. The ΔE_g values themselves are widely scattered and the constancy of the error in the calculated values had not been apparent when MUB2 was formulated and applied. This is because we had accepted an earlier unpublished value of $\Delta E_g \approx 0$ for 2-methylbutane and other available ΔE_g values were in error by as much as several hundred calories. As is shown in Table I, a value of $\Delta V_g^{\mathrm{intr}} \approx 0.36$ kcal/mol brings calculated MUB2 results into agreement with experiment virtually to within experimental error if vibrationless energies are computed. A slightly different value would be needed if vibrational effects were included in calculations. A value of 0.36 kcal/mol can be obtained with a very modest imbalance between the individual one- and twofold potential barriers. Available Allinger[2] (large H···H), Schleyer[1b] (small C···H), Warshel-Lifson,[16] and Boyd[17] ΔE_g values are also included in Table I for comparison. It can be seen that the Allinger (1973 field) results are also improved by adding a constant amount to each, although this amount is smaller (≈0.20 kcal/mol)[18] because of the aforementioned differences in nonbonded parametrization.

No doubt it is fortuitous that the addition of a single parameter corrected all MUB2 and Allinger ΔE_g values as well as it did. The original field parameters were not adjusted with any such goal in mind. It is worth mentioning that this extra parameter does not make MUB2 more extravagant of parameters than the other force fields, since the Allinger[5] and Schleyer[1b] fields need four extra parameters to reproduce the geometric isomerization energies that are accounted for reasonably well with no additional parameters just by the MUB2 pattern of nonbonded interactions.[1a,19]

The Warshel-Lifson force field[16] invokes no specific parameter $\Delta V_g^{\mathrm{intr}}$, yet it successfully reproduced butane and methylcyclohexane with a set of short-range nonbonded potentials roughly comparable to those in MUB2. What it does invoke additionally, instead, are partial changes on hydrogens and carbons to be taken into account for interactions between pairs of atoms more remote than geminal (1,3) nonbonded pairs. These electrostatic charges are introduced with an intent different from that in models designed to reproduce the entire barrier to rotation. In the barrier model, like charges were distributed. In the Warshel-Lifson models, H and C atoms bear opposite charges. Warshel-Lifson electrostatic interactions seem to play a role somewhat similar to that of the one- and twofold barriers proposed in the present work. In the case of *n*-butane, for example, the Warshel-Lifson Coulomb terms contribute 0.39 kcal/mol to ΔE_g, a value strikingly close to that of our $\Delta V_g^{\mathrm{intr}}$. This close comparison does not mean that the essence of the electrostatic corrections is identical with that of the present one- and twofold corrections. A simple sum over only the vicinal (1,4) electrostatic interactions across *n*-butane's central C–C bond yields a value an order of magnitude larger (5 kcal/mol) than the total Warshel-Lifson electrostatic value including the methyl hydrogens. What the pattern is in other molecules has not been investigated.

Whether the electrostatic or one- and twofold approach is more effective is not yet known. Certainly electrostatic interactions must exist and Williams[20] has found them helpful in intermolecular interactions. Nevertheless, it is not obvious that charges as high as +⅓ on carbon atoms are appropriate for hydrocarbons and that dielectric constants should be taken as unity independent of conformation and the intervening material. Moreover, although the electrostatic model may account quite well for many observed properties, they can cause troubles in molecules different from those in the set from which the charge parameter was derived. For example, in tri-*tert*-butylmethane, a molecule with methyl groups crowded close together, CFF3[21] gave a substantially better structure when the charges were turned off than when they were included.[22]

It is premature to attempt to compare definitively the merits of various types of force fields for molecular mechanics or to put into full perspective the role of one- and twofold barrier components. The aim of this paper is simply to point out a legitimate, but heretofore neglected, aspect of molecular force fields which should be taken carefully into account by designers of future force fields.

Acknowledgment. This research was supported by a grant from the National Science Foundation. Thanks are due to Professors Allinger and Schleyer for supplying unpublished results listed in Table I. After this paper was completed it was discovered that Professor Allinger, in independent research, has developed ideas somewhat parallel to those expressed herein.

References and Notes

(1) See, for example, the following references reviewing various aspects of the field: (a) S. Fitzwater and L. S. Bartell, *J. Am. Chem. Soc.*, **98**, 5107 (1976); (b) E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *ibid.*, **95**, 8005 (1973); (c) N. Allinger, *Adv. Phys. Org. Chem.*, **13**, 1 (1974); (d) J. D. Dunitz and H. B. Burgi, *MTP Int. Rev. Sci.*, in press; (e) C. Altona and D. H. Faber, *Fortschr. Chem. Forsch.*, **45**, 1 (1974); (f) O. Ermer, *Struct. Bonding (Berlin)*, **27**, 161 (1976).

(2) D. H. Wertz and N. L. Allinger, *Tetrahedron*, **30**, 1579 (1974).

(3) E. J. Jacob, H. B. Thompson, and L. S. Bartell, *J. Chem. Phys.*, **47**, 3736 (1967).

(4) Note that ref 1a contains several numerical errors. The first, kindly pointed out by Professor K. Mislow, is that the reported torsional barrier parameter V_3 (per nine dihedral angles) should be decreased by 0.366 kcal/mol as should the propane and butane values in Table III; the MUB2 neopentane result should read 4.46 kcal/mol. Finally, the *R* scale in Figure 1 was inadvertently moved about ¼ Å to the right of the correct position.

(5) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Am. Chem. Soc.*, **93**, 1937 (1971).

(6) For various combining rules and discussions of their successes and failures, see C. H. Chen, P. E. Siska, and Y. T. Lee, *J. Chem. Phys.*, **59**, 601 (1973); K. V. Mirskaya, *Tetrahedron*, **29**, 679 (1973); K. G. Spears, *J. Chem. Phys.*, **57**, 1842 (1972); R. J. Good and C. J. Hope, *ibid.*, **55**, 111 (1971); W. C. Stwalley, *ibid.*, **55**, 170 (1971).

(7) See, for example, J. P. Lowe and R. G. Parr, *J. Chem. Phys.*, **44**, 3001 (1966).

(8) L. S. Bartell, unpublished research. The essence of the decomposition is as follows. The total electronic energy of molecules, in the extended Hückel approximation, can be expressed as the sum $\sum_{i,j} E_{ij}$ over atom-atom terms. Although the individual E_{ij} can be apportioned between diagonal and off-diagonal terms in an infinite number of ways, the simplest formulation, and one which is plausible for nonpolar molecules, is to assign E_{ij} the value $\sum_{r,s} (H_{ir,ir} + H_{js,js})(K - 1)n(i_r,j_s)/2$, where K is the empirical extended Hückel constant and $n(i_r,j_s)$ is the Mulliken overlap population between orbitals r and s. See R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963). In the case of a molecule such as ethane, the $E_{ij}(\tau)$ values between hydrogens at opposite ends of the molecule vary during torsional displacements. These variations reflect not only the changes in "classical nonbonded interactions" with changing internuclear distance, but also the changing hyperconjugative and other "through bond" interactions discussed in section II. Therefore, by subtracting the MUB2 nonbonded interactions from the $E_{ij}(\tau)$ values of H_iCCH_j sequences, a barrier function can be calculated which can be decomposed into one-, two-, and threefold components.

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(18) Professor Allinger suggests that a better number to optimize his overall results would be 0.10 kcal/mol (private communication).

(19) It should be noted that the quantity $\Delta V_g^{\mathrm{intr}}$ naturally arises in geometric isomerization energies, also. For example, the one- and twofold barrier components contribute $+\frac{2}{3}$ units of $\Delta V_g^{\mathrm{intr}}$ in the transformation from *anti-n*-butane to isobutane, +1 units in *n*-pentane to isopentane, and $+\frac{4}{3}$ units in *n*-pentane to neopentane and *n*-hexane to 2,3-dimethylbutane (in all cases between conformers with the greatest number of anti CCCC interactions). These changes are so much smaller than the uncertainties in isomerization energies summarized in ref 1a, however, that it is too early to tell whether the new parameter helps or hurts here.

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(21) S. Lifson and A. Warshel, *J. Chem. Phys.*, **49**, 5116 (1968).

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Conformational Analysis. 125. The Importance of Twofold Barriers in Saturated Molecules[1,2a]

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Abstract: The use of twofold barriers in force field calculations in molecules of the type XCH_2CH_2Y can significantly improve the results in many cases as is shown for X, Y = F, OH; F, OAc; and Cl, OH in particular, and these results are applied to 5-substituted-1,3-dioxanes. It is pointed out that for butane (X = Y = methyl) a small twofold term can be used to improve hydrocarbon calculations in at least three of the currently used force fields. With Bartell's 1976 field (MUB2), such a twofold term permits calculation of a more accurate gauche-anti energy difference. With Schleyer's 1973 field (EAS) it will permit a stronger (intuitively desirable) C···H repulsion. With our 1973 field (MMI) it will permit smaller hydrogens. It is suggested that this kind of term, which is theoretically fully justifiable, will permit improvement as well as substantial convergence of these three force fields.

The difference in energy between the gauche and anti conformations of butane is one of the cornerstones of conformational analysis. The standard textbook explanation for this energy difference is exemplified by the following:[3]

"*n*-Butane illustrates the first factor which determines the relative stability of conformational isomers, namely, steric repulsion. In the gauche form there are the following individual gauche interactions: Me-Me, two Me-H, and three H-H. The corresponding interactions in the anti form are four Me-H and two H-H, the difference being an Me-Me and an H-H interaction in the gauche form vs. two Me-H interactions in the anti form. Evidently the sum of the former two interactions exceeds the sum of the latter two. In this particular case it appears that the Me-H and H-H interactions are energetically negligible and that the instability of the gauche form of butane may be ascribed entirely to the Me-Me interaction taken to be 0.8 kcal/mol."

Earlier we discussed an alternative view of the gauche interaction, based on the results of our 1973 force field (MMI).[4] We would like to further discuss the question here.