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 Thanks are due to Professors Allinger and Schleyer for supplying unpublished results listed in Table I. After this paper was completed it was discovered that Professor Allinger, in independent research, has developed ideas somewhat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).

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(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.

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(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(8) L. S. Bartell, unpublished research.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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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.

Currently much attention is being directed toward the problem of developing force fields which are suitable for the calculation of molecular properties.[5] We would like to discuss here the general problem with specific reference to three of the force fields which are typical of those in current use for hydrocarbons. These force fields are referred to in the following as MUB2, EAS, and MMI. There are many other force fields currently in use for studying properties of hydrocarbons which have not been considered in the present work, but as far as is known to the present authors, they would fall near to one of the above three (or somewhere in between) with respect to the properties to be discussed.

After analyzing the output from our force field (MMI) we concluded in 1974[4] that the *gauche*-butane energy was not, according to our force field, due in the main to the interactions between the methyls as had been previously assumed, but was rather due to the interactions between the gauche hydrogens. There are only two such interactions in the anti conformation, and three in the gauche conformation. There is some ambiguity in how one decides what the energy is "due to". After the molecule has relaxed, there is some uncertainty in deciding what it was that caused the relaxation in the first place. However, for the interpretation we used with MMI, the single most important contribution to this energy difference in the relaxed molecules could be attributed to this gauche-hydrogen interaction. We had tried various kinds of modifications of this force field, and had always gotten the same qualitative result. We therefore suggested that all force fields would find this interaction "to be at least important if not dominating".

In Schleyer's force field (EAS) an analysis of the data (kindly provided by Professor Schleyer) showed that the interaction between the gauche hydrogens was not the dominating cause of the gauche–trans butane energy difference, but it was important. More recently, Professor Bartell has commented that with MUB2 the gauche-hydrogen effect is not a major contributor to this energy difference.[6]

In our own force field (MMI) we placed one constraint on the parameter variation permitted which was intentional and one which was unintentional, to which our conclusions regarding the gauche hydrogen effect can be traced. The intentional restraint concerned the *gauche*-butane interaction energy. Our feeling was that this had to be calculated reasonably accurately. If it was not, then conformational analysis, as the organic chemist knows and uses it, would be impossible. We therefore limited our considerations to force-field parameter sets which gave this number rather accurately. While the gauche–anti butane energy difference was not too accurately known at the time, the axial–equatorial energy difference for methylcyclohexane (which is to a good approximation the same quantity twice over) was, and we have used it as a measure of the *gauche*-butane interaction. The conformational energy of axial methylcyclohexane is experimentally 1.7 kcal/mol in the liquid phase or 1.9 kcal/mol in the gas phase. MMI gives the value of 1.6 kcal/mol. EAS also gives a satisfactory value, while MUB2 gave a value of only 1.0 kcal/mol. Thus we did not regard MUB1 (or MUB2) as satisfactory for our purposes, as it avoided big hydrogens by simply calculating too small an energy difference.

The unintentional constraint which we placed on our force field involved the van der Waals interaction between carbon and hydrogen. We took this to be a mean of the van der Waals interactions between hydrogens and between carbons. Explicitly, the energy parameters (ϵ in the Hill equation[7]) were geometric averages, and the van der Waals radii were arithmatic averages. While intuition, previous experience, and available theories seemed to indicate that this should be approximately true, in an empirical method one is not constrained to precisely follow such a relationship. In EAS, the *gauche*-butane problem was solved in part by making the C–H interaction very much weaker than the mean of the other two. It is not only the H–H interaction which determines this *gauche*-butane energy, but rather it is more the size of the H–H interaction relative to the C–H interaction. Instead of making the H–H interaction big, one can achieve the same result by making the C–H interaction small. This possibility was not considered by us when we wrote our 1974 paper. Schleyer has used it successfully, however, and it seems to work well.

We (among others) reached the conclusion some time ago that none of these three force fields was wholly satisfying. They each calculate molecular structure very well, although not perfectly. EAS[5c] and MMI[5a] also give very reasonable (but not as good as one would desire) heats of formation for a broad selection of hydrocarbons. Thus we have continually sought ways to improve these force fields, and at the same time maintain the constraint that the *gauche*-butane problem be dealt with in a satisfactory way.

In concurrent studies being carried out on halides, and especially on compounds which contain two or more polar groups in a vicinal orientation, we noticed that the available parameters for MMI did not permit us to fit the facts as well as we desired. There is a good deal of information available on conformational energies of 5-substituted-1,3-dioxanes,[8] for example, and these numbers simply could not be fit within the parameter constraints then in use.

In a consideration of other *kinds* of parameters (as opposed to just different values for parameters) that one might use in a force field, the following became apparent:

For saturated compounds, a threefold torsional term is commonly used to give the ethane-type sinusoidal barrier that is required. With alkenes, it is generally found that one- and twofold torsional terms are required.[5a] In a molecule like ethane, one- and twofold terms are unobservable due to symmetry. In butane, however, there is a priori no reason why one cannot have one- and twofold torsional terms. In fact, in recent papers by Pople and his colleagues[9] they have shown that in general, torsion in small molecules (including butane) can be well represented by the sum (Fourier series) of one-, two-, and threefold torsional terms. Pople's use of torsion is different from ours, however. In his use of torsion, he is aiming at reproducing the total change in energy of the molecule upon rotation. In our use of torsion, we are concerned with only that portion of the energy change which is not already accounted for through other interactions, particularly van der Waals. In the terminology of organic chemistry, onefold and threefold terms in saturated compounds are attributed to steric effects, that is, the direct interaction between two groups. A twofold barrier in butane, for example, does not seem explainable in terms of steric effects, but rather in terms of electronic effects.[9,10] Pople and coworkers have discussed[9] the effect in the case of 1,2-difluoroethane. One fluorine tends to withdraw electrons, leaving a low electron density at the attached carbon. The other carbon gives a hyperconjugative response, which corresponds to resonance of the following type:

$$\mathrm{FCH_2CH_2F} \leftrightarrow \overset{-}{\mathrm{F}}\,\mathrm{CH_2{=}CHF}\,\overset{+}{\mathrm{H}} \leftrightarrow \overset{+}{\mathrm{H}}\,\mathrm{FHC{=}CH_2}\,\overset{-}{\mathrm{F}}$$

A cooperative resonance effect (in both directions) is only possible when the fluorines have a 90° dihedral angle, so that both pairs of 2p π orbitals can be simultaneously involved. Thus a negative V_2 term results, and the bond order between the carbons increases. With butane a negative V_2 term (but smaller) is also found, and a parallel explanation can be offered. One might expect the V_2 terms to be large in general when there are vicinal electronegative groups.

The chemist will quickly recognize these resonance forms discussed above as unusual, and would not expect them to be of major importance. As is shown below, they have a combined effect of <2 kcal/mol in all cases studied. Thus while not of

Table I. Torsional Parameters to be Added to the 1973 Force Field (MMI)

Linkage	V_1	V_2	V_3
OCCO	0.00	−0.80	0.53
OCCF	0.00	−1.40	0.53
OCCCl	0.00	0.20	0.53
OCCBr	0.00	0.30	0.53
$OCCC_{sp}$	0.00	−0.40	0.53

major importance in bonding, they are large enough to be significant in determining conformational behavior. We have explicitly included twofold barriers in our earlier force field of the anomeric effect,[11] and this was also consistent with ab initio calculations.[12]

As examples of the importance of V_2 terms in dealing with vicinal dipolar substituents, we will discuss the OCCF system, represented by 2-fluoroethanol and its acetate, and also by 5-fluoro-1,3-dioxane. For fluoroethanol the gauche form (OCCF) is more stable than the anti by more than 2.0 kcal/mol in the gas phase[13] and from 1.35 to 2.07 kcal in solution in different solvents,[14,15] depending on polarity. For the corresponding acetate where the effect of hydrogen bonding is eliminated, the gauche form is also stable, by 1.5 kcal[16] (for $D = 4.81$, estimated for a 1:1 solution in chloroform). Using the values in the original MMI program, assuming the V_3 constant is 0.53 (as it is for HCCH, CCCH, and CCCC), it is found that the calculated gauche conformation is not nearly stable enough in any of the above (by about 1.4 kcal/mol in each case). Also, 5-fluorodioxane was calculated to have the equatorial conformation more stable than the axial (by 0.21 kcal/mol), while experimentally the axial is stable by 1.22 kcal in acetonitrile ($D = 37.5$). A substantial improvement in fitting the facts was noted if for the grouping FCCO, $V_2 = -1.4$ kcal/mol, whereupon the axial conformation of the 5-fluorodioxane is now calculated to be stable by 2.17 kcal/mol, and fluoroethanol is calculated to have the gauche conformation stable by 1.75 kcal ($D = 1$), and the gauche form of the acetate is more stable by 1.33 kcal/mol.

It is generally found that small (usually negative) values for V_2 for the system XCCY greatly improve the fit to experiment. The numerical values of V_2 are generally in the range of 1 kcal/mol. Thus they are small but, especially considering that such a term comes in twice in a compound like 5-halodioxane, these are by no means negligible quantities. The values for some common systems are summarized in Table I.

In our efforts to find ways to improve MMI in the longer range, we have also considered a twofold torsional term as one of the parameters to be optimized in the case of the CCCC linkage. There is no reason why one cannot have twofold terms in the case of CCCH or HCCH linkages, or onefold terms in all of these cases.

We have recently developed a further improved force field for alkanes,[18] which we call MM2, in which a small twofold torsional term for butane is used as described above. This permits the hydrogens to be softer than they were in MMI, and there is other evidence that this is desirable.[6] The actual methylcyclohexane energy is at the same time kept large (in fact, it is increased). The main purpose of this manuscript is to point out to others the usefulness of such a twofold torsional term as a general feature of force fields. Theory certainly permits such a term, indeed it seems to demand such a term.[9] Because of the correlation between parameters, the magnitude of such a term may or may not be significant in a given force field or for a given set of compounds. It is of small importance for hydrocarbons in our 1973 force field, but will clearly be much more important in a hydrocarbon field which uses small or soft hydrogens such as MUB2. With the advent of a twofold torsional term in butane, the "gauche-hydrogen effect" per se can become less important in our force field. The methyl-methyl repulsion originally assumed to be the only important cause of the *gauche*-butane interaction is not, however, in MM2. Rather, the gauche-hydrogen effect, the low order torsional terms (V_1 and V_2), and the methyl-methyl repulsion are all significant contributors to the total interaction energy.

Acknowledgment. After this work was complete, the authors were informed by Professor L. S. Bartell of recent work in which he had independently reached the conclusion that one- and twofold barriers in hydrocarbons promised to remedy the principal deficiencies of existing force fields. The present authors appreciate receiving this information, and Professor Bartell's willingness to have our respective papers published simultaneously.

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