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Representations of Molecular Force Fields. 2. A Modified Urey–Bradley Field and an Examination of Allinger's Gauche Hydrogen Hypothesis

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Abstract: A modified Urey–Bradley force field for hydrocarbons, designated MUB-2, has been constructed for application in the field of "molecular mechanics". The initial aim of this research was to incorporate as realistic nonbonded potential energy functions as are presently possible in a pairwise additive formulation in order to investigate the plausibility of Allinger's new gauche-hydrogen interaction basis of conformational analysis. The resultant force field, derived from Kochanski's $H_2 \cdots H_2$ quantum calculations and various experimental observations, yielded an energy for H···H interactions similar to that of Allinger's field at the crucial 2.6 Å internuclear distance for vicinal hydrogens. Nevertheless, considered in its entirety, it supported the conventional interpretation rather than Allinger's, for reasons that are discussed. Field MUB-2 was designed to be nominally of the "consistent force field" type though it is too sparing in parameters to reproduce vibrational and thermochemical quantities with high accuracy. It gives an excellent account of structures and structural trends in the cases it has been applied to, being superior in these cases to alternative published fields. It gives a fair account of isomerization energies, being inferior to several more optimized fields containing a greater number of adjustable parameters than does MUB-2. It gives correct magnitudes of vibrational frequencies but poor splittings due to its neglect of certain interaction constants. One area in which MUB-2 outperforms alternative fields for molecular mechanics is exemplified in its successful semiquantitative prediction of certain unknown force constants for ethane that were later calculated by ab initio molecular orbital methods. These constants include a variety of bend and stretch-bend couplings, harmonic and anharmonic, which are not represented in the other fields, and which stem in MUB-2 from geminal H···H and C···H nonbonded interactions. The new field is far from a fully optimized field but it furnishes useful clues and guidelines for future advances in molecular mechanics.

I. Introduction

In studies of conformational analysis there has been widespread use of the "molecular mechanics" potential energy minimization method.[1] Many different model force fields have been proposed in attempts to get a satisfactory analytical representation but in no sense has a final, accepted force field emerged. This is because so little is known about force fields that not even for a molecule as simple as *ethane* are the true potential constants known from experiments![2] Therefore, by necessity, all proposed fields are greatly simplified representations containing only a fraction of the parameters allowable in a general representation. Adding to the difficulty is the fact that, when attempts are made to refine parameters in these simplified fields by comparisons of calculated quantities with experiment, high parameter correlations, in addition to the aforementioned systematic errors of truncation, prevent the derivation of a reliable and uniquely appropriate set of potential constants. Different workers with different points of view adopt strikingly different force fields. In many comparisons the results of the different force fields are in fair agreement.

Naturally, the above situation has led to diverse interpretations of trends in molecular properties. One of the more intriguing recent interpretations is Allinger's challenge to the popular idea that gauche conformations are destabilized relative to anti because of 1···6 hydrogen repulsions between gauche methyl or methylene groups.[3] Allinger maintains that the gauche destabilizations instead stem in large measure from 1···4 (vicinal) interactions between hydrogens bonded to the carbons forming the axis of internal rotation.

Since gauche destabilization is one of the cornerstones of conformational analysis and since new theoretical information[2,4] has become available since Allinger's 1973 field was constructed, it seemed timely to test Allinger's assertion that his conclusions are not dependent on the exact parameterization of the force field. It was clear from the outset that his conclusions were not consistent with the reasonably successful force field MUB-1[5] (sometimes referred to as JTB). It was of great interest to find whether his conclusions were compatible with a new force field constructed on a firmer basis than the MUB-1 force field, with new theoretical constraints built in to uncouple the otherwise highly correlated nonbonded interaction functions that are so crucial in tests of Allinger's hypothesis.

The new force field, which we designate as MUB-2, is not intended to be a final or even a fully optimized field within its own limited framework. It is certainly inferior to, for example, the CFF (consistent force field) of Ermer and Lifson[6] in representing vibrational frequencies. It is likely to have as rational a basis as presently exists, however, for assessing the role of H···H interactions in molecular mechanics. For this reason it is worthwhile to describe the construction of the model. The key points are outlined in section II and details are given in

Appendix A of the microfilm edition. Various structural and energetic consequences of the model are presented in section IV to illustrate its merits and flaws.

II. Construction of Model Force Field

(A) **Form of Force Field.** In view of the effectiveness of the unoptimized MUB-1 field,[5] a modified Urey-Bradley (UB) field containing only two freely adjusted parameters, it was decided to use the same form but to augment it with several new interactions. The expression adopted for the potential energy is:

$$V_{\text{total}} = \sum_{\text{stretches}} \tfrac{1}{2}K_{ij}(r - r^0)_{ij}{}^2 + \sum_{\text{bends}} \tfrac{1}{2}H_{ik}(\alpha - \alpha^0)_{ijk}{}^2 + \sum \sum_{l \neq m} \tfrac{1}{2}k_{lm}{}'(\phi_l - \phi_l{}^g)(\phi_m - \phi_m{}^g) + \sum_m \tfrac{1}{2}V_3{}^m(1 + \cos 3\tau_m) + \sum_n V_n{}^{nb}(r_n) + V_{\text{Morse}} + V_{\text{st}} \tag{1}$$

where the first three terms on the right-hand side represent a major part of the quadratic variation of potential energy with respect to changes in the stretching or bending internal coordinates ϕ_l. The displacements $(\phi_l - \phi_l{}^0)$ and $(\phi_l - \phi_l{}^g)$ signify respectively displacements relative to "reference" values $\phi_l{}^0$ and "unstrained" values $\phi_l{}^g$ of bond lengths and angles. Only in severely strained molecules do the interactions involving $\phi_l{}^g$ have any consequence in calculations of molecular structure and strain energy, but the need for parameter $\phi_l{}^g$ in a UB field in addition to $\phi_l{}^0$ is discussed in the microfilm edition. Constants K_{ij} and H_{ik} are UB bond stretching and bond bending force constants and the $k_{lm}{}'$ represent components of the off-diagonal elements of the force constant matrix that are not ascribable to the nonbonded interaction energy. Of the many possible $k_{lm}{}'$, only the CH/CH stretch-stretch constant k_{rr} found to be significant in an earlier paper[7] on modified UB fields was included. The fourth term in eq 1 is a conventional contribution from the torsions τ_m. Nonbonded interactions are represented by nonbonded potential energy functions of the usual, simplified form considered to depend only upon nonbonded distances, r_n, and to be expressible as a pairwise sum over nonbonded interactions $V_n{}^{nb}(r_n)$. Geminal nonbonded interactions are explicitly included in this field in accordance with its Urey-Bradley nature.[8] The symbol V_{Morse} represents the anharmonic bond stretching correction of form:

$$V_{\text{Morse}} = -\Sigma\tfrac{1}{2}[Ka(r - r^g)^3]_{ij} \tag{2}$$

A final, anharmonic stretch-torsion term

$$V_{\text{st}} = \Sigma\tfrac{1}{2}K_{\text{st}}(r - r^g)_l(1 + 3\cos\tau)_m \tag{3}$$

is included to allow for the inference from ab initio calculations that C-C bonds are longer in eclipsed conformations than in staggered.[9] Numerical values of the potential constants in the MUB-2 field are listed in Table I.

(B) **Interpretation of Derived Structures.** There has been a certain looseness in the meaning of the structures, frequencies of vibration, and thermodynamic quantities calculated from model force fields. Two principal sources of trouble arise. First, until comparatively recently, real molecular force fields (which are intrinsically anharmonic) have been fitted in the mean by quadratic approximations which neglect many quadratic terms as well as all higher-order terms. Frequencies calculated from the quadratic model force fields are not supposed to represent harmonic oscillator frequencies calculated from the true quadratic components of the actual force fields.[10] Second, effects of molecular vibrations have been neglected in calculating structure and they have often been neglected in calculating thermodynamic quantities. A truly rigorous treatment of the whole problem is impractical at present, partly because not enough molecular information is available and partly because simple compensations can be made that are good enough for many purposes.

Now that anharmonic components are beginning to be included in force fields to account for certain trends, it is necessary to say a few words about the meaning of derived structure parameters. Since atoms vibrate with a substantial amplitude ($\approx$0.1 Å) and since chemists like to study trends in bond lengths at the thousandths of an ångström unit level, it is clear that the method of averaging implicit in a reported "bond length" is crucial.[11,12] Suffice it to say here that the commonest types of bond lengths reported are equilibrium lengths (r_e), thermal average lengths (r_g), distances between thermal average atomic positions (r_α), and "spectroscopic" lengths (r_0 or r_s).

Of these, r_e is the theorist's favorite, for it corresponds to the structure with minimum potential energy. Unfortunately, r_e is available for only diatomic and a handful of triatomic molecules. The mean length r_g is often 0.01 to 0.02 Å longer than r_e. Gas-phase electron diffraction yields r_g quite directly and, in favorable cases, provides an accuracy of a few thousandths of an ångström unit or better. The parameter r_α is most naturally associated with x-ray studies and may be a hundredth of an ångström unit shorter than r_g. "Spectroscopic" averages, while often more precise experimentally than diffraction averages, are much more complex averages which can range in value from less than r_e to greater than r_g. Spectroscopic frequencies can be, and occasionally are, interpreted with the aid of a normal coordinate treatment in terms of r_α or r_g structures.

Since r_g is one of the simplest direct gauges of bond length, differing from r_e by approximately[11]

$$r_g - r_e = (3a/2)\langle(r - r_g)^2\rangle \tag{4}$$

Table I. Parameters of MUB-2 Force Field[a]

Bond stretching: $V(r) = \tfrac{1}{2}K(r - r^0)^2 - \tfrac{1}{2}Ka(r - r^g)^3$

Bond	K	r^0	a	r^g
C-H	3.85	1.0203	2.0	1.1068
C-C	2.34	1.166	2.0	1.534

Angle bending: $V(\theta) = \tfrac{1}{2}H(\theta - \theta^0)^2$

Angle	H	θ^0, radians
C-C-C	0.629	1.910 63
C-C-H	0.322	1.910 63
H-C-H	0.350	1.910 63

Torsional:[c] $V(\tau) = \tfrac{1}{2}\sum_{i=1}^{9} V_3(1 + \cos 3\tau_i)$

$V_3 = (2.154 \times 10^{-2})/9$ mdyn − Å for any dihedral angle

Nonbonded: $V(d) = Ae^{-\alpha d} - Bd^{-6}$

Nonbonded distance type	A	B	α	Δ
H···H[b]	14.72	0.3333	3.4	0.117
C···H[b]	135.4	1.076	3.75	0.117
C···C	502.2	2.779	3.75	

Stretch-torsion: $V(r,\tau) = \tfrac{1}{2}K_{\text{st}}(r - r^g)(1 + \cos 3\tau)$

$K_{\text{st}} = -7.125 \times 10^{-2}$ mdyn $\quad r^g = 1.534$ Å

[a] All units are such that energies are in units of mdyn Å, angles in radians, and distances in ångström units. [b] The hydrogens are foreshortened by a distance Δ as explained in the text. The potential functions are for the foreshortened distances. [c] The contribution to the potential energy from a torsion around a given carbon-carbon bond is taken as the sum of contributions from all nine dihedral angles across that bond.

(where the Morse "anharmonicity constant" a is identified in eq 2), we shall use it as a basis of comparison in the following. We follow the standard practice of seeking the structure which will minimize the potential energy [V_{total} of eq 1]. In principle, such a structure should correspond to r_e lengths. In practice we adopt the inconsistent practice of fixing the reference lengths [r^0 in eq 1] to make the minimum energy bond lengths correspond as closely as possible to r_g, not r_e. This simplification is reasonable since a and $\langle (r - r_g)^2 \rangle$ of eq 4 are quite constant for a given type of bond and, at ordinary temperatures, $(r_g - r_e)$ is not markedly temperature dependent. This simplification saves performing a tedious perturbation treatment to deduce anharmonic vibrational wave functions in order to establish the expectation values of internuclear distances.[12]

(C) Selection of Parameters for the Force Field. (1) Nonbonded Potential Constants. These constants are the weakest links in conventional model force fields (including the present one), for it is becoming clear that pairwise additive functions are incapable of giving a proper representation of interatomic forces. Their pattern of success and failure in anharmonic as well as harmonic interactions is discussed elsewhere.[2,13] Since they have some utility it is premature to dismiss them without replacing them with a better formulation as economical in parameters, however, and for the purposes of this paper, we adopt as realistic a compromise as is feasible.

In the testing of Allinger's hypothesis,[3] the most crucial parameters in the force field are the H···H interactions. Allinger's gauche hydrogen interpretation is in no small measure related to the fact that his hydrogen atoms in formulations of recent years have been effectively larger than those proposed by many others, and his carbon atoms have been smaller.[3,14] For example, at the 2.4 Å foreshortened H···H distance that is so important in gauche hydrogen interactions, Allinger's nonbonded destabilization potential energy[3] is *fourfold* higher than that of the MUB-1 field. At the time the present study was initiated, the most rational, least biased assessment of H···H interactions appeared to be that implicit in Kochanski's treatment[4] of the H_2···H_2 system by the perturbative procedure of Musher and Amos.[15] Evidence that Kochanski's results are physically reasonable is the good agreement between Kochanski's interaction energies averaged over orientations and the experimental interaction energies reported by Farrar and Lee[16] and Dondi et al.[16] The fact that the H···H nonbonded energy *at* 2.4 Å, inferred from our curve-fitting of Kochanski's work, agreed with Allinger's 2.4 Å value stimulated the present research.

Kochanski's H_2···H_2 interaction energies were computed at four orientations of one molecule relative to the other and at close intervals over a range from 4 through 10 au. We assumed that the interaction energies could be accounted for, approximately, by pairwise interactions between "nonbonded" hydrogens following the modified Buckingham potential energy (per pair):

$$V_{\text{HH}} = A \exp(-\alpha r) - B(r + b)^{-6} \qquad (5)$$

and, further, we adopted Williams' scheme of "foreshortening" in which interaction centers in bonds to hydrogen atoms are moved a distance Δ toward the bond center away from the protons.[17,18] Because of our reluctance to impose a rigid weighting in least-squares fits of precipitously falling points giving a nonrandom pattern of residuals, we used a trial and error procedure to find reasonable values for the parameters A, α, B, b, and Δ. Since the inclusion of parameter b did not seem to improve the fit markedly, b was set equal to zero and V_{HH}, V_{CC}, and V_{CH} were all reduced to simple Buckingham functions but with C-H bonds foreshortened by the same value of Δ as are H-H bonds.

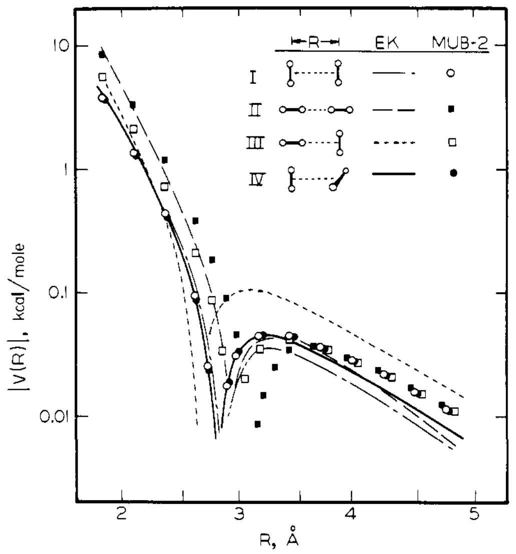

Figure 1. Comparison between H_2···H_2 interaction energies as calculated at four orientations by E. Kochanski and as represented by the MUB-2 pairwise additive Buckingham potential functions with foreshortening. The right-hand lobes of the curves correspond to negative values of $V(r)$.

Figure 1 illustrates the degree to which Kochanski's calculated interactions can be represented by our analytical approach. Plainly the interatomic forces cannot be satisfactorily accounted for by pairwise interactions. They depend strongly on bond orientations. Values of A, α, and Δ that reproduce energy curves for orientations I and IV and yield satisfactory energies for orientations II and III at 2 Å separations make the atoms much too repulsive at 3 Å for orientations II and III. To simulate the entire set of Kochanski's results with Buckingham-like parameters, it would be necessary to introduce an orientation dependence in the B constant to account for the great augmentation of dispersion forces in orientation III. Our choice of Buckingham parameters (Table I) is based on a compromise heavily favoring orientations I and IV.

The repulsions between geminal hydrogen atoms according to our inferences from Kochanski's work are of the order of those predicted by Mulliken[19] many years ago but *much* larger than those deduced from Urey-Bradley analyses of experimental spectra (see Table AI in the microfilm edition). This discrepancy is believed to be an artifact of the standard UB method, as discussed briefly in the microfilm edition and in more detail elsewhere.[2,7]

No source of information comparable to Kochanski's work was available for establishing C···C and C···H interactions. The selection of a set of functions compatible with our H···H function and other information is described in the microfilm edition. Suffice it to say here that the other information included published Urey-Bradley F values (see Table AI in the microfilm edition),[20,21a,22] intermolecular nonbonded functions of Williams,[18] estimates of B by Pitzer and Catalano,[23] the C-C-C angle in *n*-alkanes,[24] and the energy of isomerization of *n*-butane to isobutane.[25] Results are listed in Table I.

In studies of structure the most direct insight into deformations is gained through an examination of the *forces* acting in the deformations rather than through the *potential energies*. Nonbonded forces, then, are plotted in Figure 2 for the H···H, C···H, and C···C functions determined above. These are compared with the forces corresponding to Allinger's (1973) force field,[3,4] Ermer and Lifson's[6] force field, the MUB-1 force field,[5] the crystal structure parameters of Williams,[18] Boyd's field,[26] and Schleyer's force field[1] which is a modification of Boyd's field. The reasonably close agreement between all force fields (except Boyd-Schleyer) in the case of C···H interactions

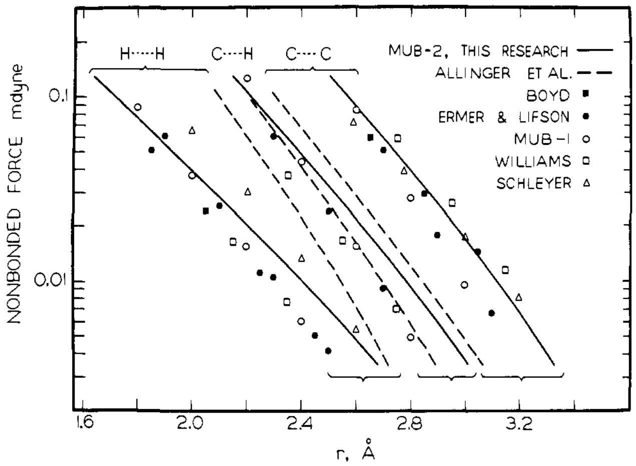

Figure 2. Nonbonded force curves, $-\partial V(r)/\partial r$, corresponding to various nonbonded potential energy functions. The abscissa represents distance between interaction centers, not internuclear distances. To avoid confusion, the Boyd and Schleyer (modified Boyd) points for C···H interactions are not shown, for they fall in the H···H region, lying almost on top of the Schleyer H···H points. For no other sets of functions do the C···H curves depart so markedly from the mean of C···C and H···H curves expected according to commonly invoked combining relations.

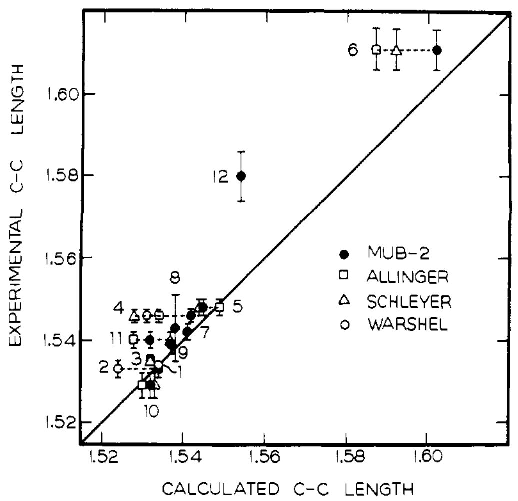

Figure 3. Comparison of experimental and calculated C–C bond lengths. The vertical error bars correspond to $\pm\sigma$. Points which represent fits of the same bond length by different force fields are joined by dotted lines. The numbers refer to the following molecules: (1) ethane; (2) *n*-butane; (3) isobutane; (4) cyclopentane; (5) tri-*tert*-butylmethane (C(2)–C(5)); (6) tri-*tert*-butylmethane (C(1)–C(2)); (7) hexamethylethane (end bond); (8) tetramethylethane (central bond); (9) tetramethylethane (end bond); (10) methylcyclohexane; (11) adamantane; (12) hexamethylethane (central bond).

is striking. The aforementioned tendency of Allinger's hydrogens to be large and carbons to be small, however, is apparent, if the consensus arrived at by the other diverse approaches to the problem is significant. Previous representations of Allinger[14] had H···H and C···C force curves spaced even more closely together. These systematic differences between Allinger's fields and others may be partly related to the fact that Allinger's potentials are shaped by Hills' parameterization for *rare-gas* atoms[27] and partly to the importance Allinger attaches (not unreasonably) to accounting for the axial-equatorial isomerization energy for methylcyclohexane (as discussed later). Certainly the specific Allinger trends evident in Figure 2 are at the heart of the gauche hydrogen hypothesis.

(2) **Other Potential Constants.** A set of Urey-Bradley and k_{lm}' force constants was selected to make the net MUB-2 potential surface simulate the experimental UB surface of Schachtschneider and Snyder[20] (SS) despite the appreciable differences between the nonbonded functions of the two fields. Adjustments were made in the K_{ij} and H_{ik} constants to compensate for these differences. For simplicity, the MUB-2 K_{ij} and H_{ik} values from specific bond type (e.g., methyl, methylene, and methine) were averaged and given common values. The associated reference lengths r_{ij}^0 and r_{ij}^g and angles, α_{ijk}^0, were similarly assigned common values for a given type of link, independent of the nature of the adjacent bonds. Furthermore, for the saturated molecules treated, all of the α^0 values were taken to be 109.47 . . . °, the simplest possible value.

In various representative applications of eq 1 the anharmonic potential functions included probably contribute less than some of the quadratic interaction constants left out of MUB-2. It seemed advantageous to include them, nevertheless, to permit the testing of certain conjectures about anharmonic effects in crowded molecules.[28] Preliminary calculations confirm their utility in accounting for the distribution of C–H stretching frequencies in tri-*tert*-butylmethane.[29]

(3) **A Subsequent Modification.** A program to calculate frequencies rigorously when foreshortened potential functions of the sort adopted in MUB-2 are used was not developed until the structural and energetic computations were completed. It was found that modest changes in the force constants could improve calculated frequencies somewhat. Such changes altered the structures and isomerization energies very little in the cases that were checked. Since the figures and tables in the text correspond to the MUB-2 field described in previous sections, it is the MUB-2 (unoptimized) parameters that are listed in Table I. The potential constants modified to secure better frequencies are discussed and listed in Appendix B of the microfilm edition under the designation MUB-2′.

III. Energy Minimization and Frequency Calculation

Many of the geometry and isomerization energy calculations neglecting vibrations were carried out with the computer program DIPSY VI by Jacob,[5] modified to include the functions of eq 1, Section IIA. DIPSY VI employs a Gauss-Newton minimization procedure. A few of the computations made use of a modified version of Boyd's program.[26] The remainder of the (Newton-Raphson) potential minimization, frequency, and thermodynamic calculations were performed with the aid of a program by R. L. Hilderbrandt modified to include foreshortening and the anharmonic corrections of eq 2 and 3. Frequency calculations corresponded to classical, infinitesimal vibrations and used anharmonicity only in the calculation of second derivatives of V_{total} at the potential minimum.

IV. Comparison of Calculated and Experimental Results

(A) **Structures.** Comparisons between calculated and observed structures are summarized in Figures 3–6 with error bars representing estimated standard deviations. It should be noted, on the one hand, that there is not a completely satisfactory error analysis procedure in the electron diffraction experiments. On the other hand, it should be recalled that the only agency spreading the calculated points out was the nonbonded environment (or, the case of cyclopentane, the torsion arising from ring closure constraints). Quantum chemistry does not rule out more specific interactions than were included in the MUB-2 field. All in all, then, the agreement between observed and calculated structure parameters is remarkable. Setting r_{CH}^0 and r_{CC}^0 guarantees an exact fit of r_{CH} for methane and a fair fit of r_{CC} for ethane, but in no way builds in the observed trends. Setting all angle reference values at the tetrahedral angle guaranteed neither a fit of specific angles nor a correct prediction of the trends. The physically plausible

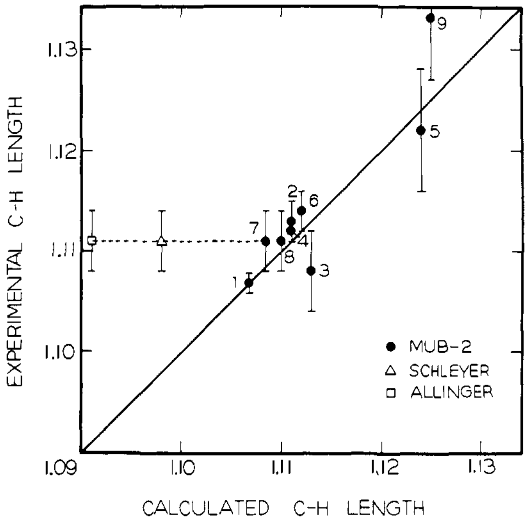

Figure 4. Comparison of experimental ($\pm\sigma$) and calculated C-H bond lengths. Points which represent fits of the same bond length by different force fields are joined by dotted lines. The numbers refer to the following molecules: (1) methane; (2) ethane; (3) *n*-butane; (4) isobutane (methyl), tetramethylethane (methyl); (5) isobutane (tertiary); (6) cyclopentane; (7) tri-*tert*-butylmethane; (8) hexamethylethane; (9) tetramethylethane (tertiary).

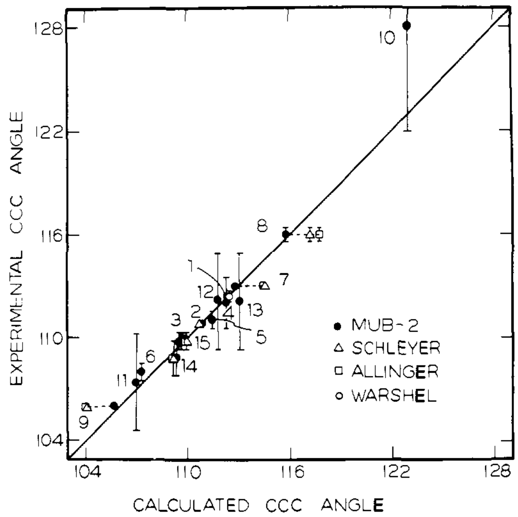

Figure 5. Comparison of experimental ($\pm\sigma$) and calculated CCC angles. Points which represent fits of the same angle by different force fields are joined by dotted lines. The numbers refer to the following molecules: (1) *n*-butane; (2) isobutane; (3) tetramethylethane (Me-C-Me); (4) tetramethylethane (C-C-Me); (5) hexamethylethane (C-C-Me); (6) hexamethylethane (Me-C-Me); (7) tri-*tert*-butylmethane (Ct-C-Me); (8) tri-*tert*-butylmethane (C-Ct-C); (9) tri-*tert*-butylmethane (Me-C-Me); (10) di-*tert*-butylmethane (C(2)-C-C(2′)); (11) di-*tert*-butylmethane (C-C(2)-C(3)); (12) di-*tert*-butylmethane (C-C(2)-C(4)); (13) di-*tert*-butylmethane (C-C(2)-C(5)); (14) adamantane (Ct-Cs-Ct); (15) adamantane (Cs-Ct-Cs).

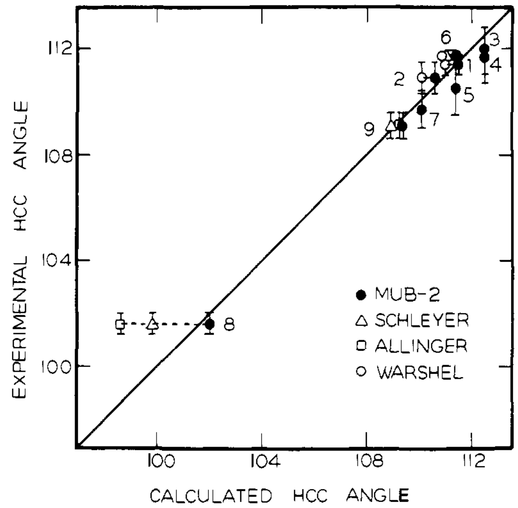

Figure 6. Comparison of experimental ($\pm\sigma$) and calculated HCC angles. Points which represent fits of the same angle by different force fields are joined by dotted lines. The numbers refer to the following molecules: (1) ethane; (2) *n*-butane; (3) di-*tert*-butylmethane; (4) hexamethylethane; (5) tetramethylethane; (6) cyclopentane; (7) methylcyclohexane; (8) tri-*tert*-butylmethane; (9) adamantane.

nonbonded functions governed the deformations of angle from the tetrahedral value.

A few structure trends calculated by other force fields are available. These are included in Figures 3-6 for comparison. Points labeled "Warshel" correspond to unpublished computations by Warshel based in the force field of ref 21b. For the particular cases for which we had corresponding data (and most notably for the highly strained case of tri-*tert*-butylmethane), the MUB-2 field results are somewhat more accurate than the others. Not plotted in Figure 3 are the rather scattered points corresponding to the case of norbornane. As discussed in the microfilm edition, MUB-2 results are in significantly better agreement with observations than are the results of the other fields represented in Figure 3.

Another gauge of model fields is the puckering amplitude (q) of cyclopentane. In terms of the puckering definition of Pople and Cremer,[30] the electron diffraction[31] and Lifson and Warshel[21a] CFF amplitudes are both 0.42 Å. The MUB-2 field, however, yields only 0.36 Å.

(B) Isomerization Energies. A potential energy function of the form of eq 1 should be able, if valid, to account for changes in energy with changes in conformation. It is less clear that it should be expected to yield geometric isomerization energies because it has nothing whatsoever in it to distinguish between primary, secondary, and tertiary bonds except for nonbonded interactions. The degree to which the MUB-2 force field reproduces rotational isomerization energies and barrier heights is illustrated in Tables II and III, and geometric isomerization energies are given in Table IV for gas-phase, vibrationless molecules at 0 K. Comparisons with results from other model force fields[32,33] and experiment show that MUB-2 can account, approximately, for geometric isomerization energies at 0 K as well as for conformational energy differences, although it appears to have characteristic defects. For example, ($E_{\text{axial}} - E_{\text{equat}}$) for methylcyclohexane is low. It should be mentioned that the geometric isomerization energies in Table IV corresponding to Schleyer's and Allinger's fields are taken out of context. Schleyer[32] and Allinger[33] include additional *bond* or *group increments* intended to correct motionless, 0 K, energies to heats of formation at 25 °C. These extra parameters not included in MUB-2 contain not only zero-point energies and changes of enthalpy with temperature, but also effects of bond type (e.g., methyl vs. methylene vs. methine). Apparently, MUB-2 has built into it naturally, with fewer parameters than most force fields, at least a crude accounting of bond type; this accounting, whether or not its physical interpretation is correct, originates from the geminal nonbonded interactions.

V. Examination of Gauche Hydrogen Hypothesis

The standard explanation of why gauche *n*-butane has a higher energy than the anti conformer is, as expressed by Eliel et al.:[34] "In the *gauche* form there are the following individual *gauche* interactions: Me···Me, 2 Me···H and 3 H···H. The corresponding interactions in the *anti* form are 4 Me···H and 2 H···H, the difference being an Me···Me and an H···H inter-

Table II. Experimental and Calculated Rotational Isomerization Energies[a]

	Exptl	MUB-2, for vibrationless molecule[b]	MUB-2, for vibrating molecule,[b] 0 K
n-Butane	0.63 ± 0.2,[c] 0.76 ± 0.1[d]	0.54	0.63
n-Pentane (TT → TG)	0.63 ± 0.2, 0.52 ± 0.07[d]	0.60	
Tetramethylethane	±0.2,[e] 0.17 ± 0.2[f]	−0.28	−0.28
2-Methylbutane	±0.2[e]	0.49	
Methylcyclohexane	1.78 ± 0.15[g]	0.95	1.03
1,3-Dimethylcyclohexane	1.96 ± 0.3[h]	1.03	1.09

[a] All energies are in kcal/mol and represent gauche–trans or axial–equatorial energy differences. [b] The quantities for the vibrationless molecules do not contain computed zero-point energy differences, while those for the vibrating molecules do contain these differences. [c] Reference 24. The tabulated value represents $\Delta G°$ per conformation from anti to one (of two) gauche configurations in the *gas* phase. [d] N. Sheppard and G. J. Szasz, *J. Chem. Phys.*, **17**, 86 (1949). The tabulated value represents $\Delta H°$ in the *liquid* phase. [e] N. Sheppard and G. J. Szasz, *J. Chem. Phys.*, **17**, 93 (1949). The spectroscopic studies reported here indicate that the enthalpy difference between the two (liquid phase) isomers is 0.2 kcal/mol or less, but do not establish which isomer has the higher enthalpy. [f] T. L. Boates, Thesis, Iowa State University, 1966. The tabulated value has the same significance as that in footnote *c*. [g] Reference 36. [h] E. J. Prosen, W. H. Johnson, and F. D. Rossini, *J. Res. Natl. Bur. Stand.*, **39**, 173 (1947).

Table III. Experimental and Calculated Barriers to Hindered Internal Rotation[a]

	Exptl	MUB-2	Allinger	Schleyer[b]
Ethane	2.93 ± 0.03[c]	(3.0)		(2.8)
Propane	3.33 ± 0.02[d]	3.60		2.9
n-Butane (H eclipses Me)	3.72,[e] 4.2 ± 0.4[f]	4.03	2.94	
n-Butane (Me eclipses Me)	6.10,[e] 6.7 ± 0.4[f]	6.10	4.55	5.8
Neopentane	4.3[g]	4.15		

[a] All energies are in kcal/mol and are the differences between the energies of the eclipsed and staggered forms of the molecule. [b] The Schleyer force field contains special barrier parameters to distinguish between the end atoms of τ_{ijkl}. The Allinger force field and MUB-2 do not. [c] S. Weiss and G. E. Leroi, *J. Chem. Phys.*, **48**, 962 (1968) (from torsional frequencies). [d] E. Hirota, C. Matsumura, and Y. Morino, *Bull. Chem. Soc. Jpn.*, **40**, 1124 (1967) (from microwave data). [e] K. Ito, *J. Am. Chem. Soc.*, **75**, 2430 (1953) (estimates from thermodynamic data). [f] J. E. Piercy and M. G. S. Rao, *J. Chem. Phys.*, **46**, 3951 (1967) (from ultrasonic data). [g] K. S. Pitzer and J. E. Kilpatrick, *Chem. Rev.*, **39**, 435 (1946) (from entropy calculation).

Table IV. Computed and Experimental Geometrical Isomerization Energies[a] for Vibrationless Molecules and Zero-Point Energy Differences[a]

	Exptl isomerization energy[b,i]	MUB-2 isomerization energy	Allinger isomerization energy	Schleyer isomerization energy	Exptl zero-point energy difference	MUB-2′[l] zero-point energy difference	Exptl zero-point energy
n-Butane	0.0. . .	0.0. . .	0.0. . .	0.0. . .	0.0. . .	0.0. . .	80.62[c]
Isobutane	1.39 ± 0.7	1.30	2.32	0.28	0.24	0.24	80.38[c]
n-Pentane	0.0. . .	0.0. . .	0.0. . .	0.0. . .	0.0. . .	0.0. . .	98.32[c]
Isopentane	0.63[d] ± 0.7	0.44	0.76	−0.88	0.71	0.21	97.61[c]
Neopentane	3.49[d] ± 1.0	3.73	4.80	0.79	1.02	0.72	97.30[c]
n-Hexane	0.0. . .	0.0. . .	0.0. . .	0.0. . .	0.0. . .	0.0. . .	116.02[e]
2,2-Dimethylbutane	2.91 ± 1.0	1.78	3.02	1.59	0.83	0.63	115.19[f]
Tetramethylethane	(1.0) ± 2.0	−0.21[j], 0.07[k]	1.06	0.29			(115.2)[g]
Ethylcyclohexane	0.0. . .	0.0. . .					
cis-1,3-Dimethylcyclohexane	2.38[h] ± 0.7	2.70					
trans-1,3-Dimethylcyclohexane	0.42[h] ± 0.7	1.67					

[a] All energies are in kcal/mol. The Allinger and Schleyer values are taken out of context (see text). Heats of formation of 0 K were, except where noted, taken from F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," w tables. All energy differences listed are energy(*n*-alkane) − energy(isomer). [b] The experimental isomerization energies listed have been corrected for zero-point energy differences. [c] Reference 23. [d] New experimental $\Delta H_f°$ for *n*-pentane, isopentane, and neopentane given by G. Pilcher and J. D. M. Chadwick, *Trans. Faraday Soc.*, **63**, 2357 (1967). The Pitzer corrections to 0 K were used. [e] Calculated from zero-point energy of *n*-pentane on the basis of the increment per CH_2 unit of 17.7 kcal/mol given in ref 23. [f] T. L. Allen, *J. Chem. Phys.*, **31**, 1039 (1959). [g] Zero-point energy of tetramethylethane ≃ zero-point energy of 2,2-dimethylbutane. [h] Experimental energies (corrected to 0 K) from E. J. Prosen, W. H. Johnson, and F. D. Rossini, *J. Res. Natl. Bur. Stand.*, **39**, 173 (1947), minus 0.700 kcal, approximate zero-point energy difference for *n*-pentane − isopentane, *n*-hexane − isohexane, etc. (this seemed appropriate given the difference in the two structures). [i] The uncertainties given may be regarded as lower limits, as they are Pitzer's estimates for the $\Delta H_f°$ (0 K) for the branched compounds and do not reflect the uncertainties in $\Delta H_f°$ (0 K) for the *n*-alkanes. [j] Energy(*n*-hexane) − energy(*trans*-tetramethylethane). [k] Energy(*n*-hexane) − energy(*gauche*-tetramethylethane). [l] MUB-2′ is a minor modification of MUB-2 which yields better vibrational frequencies than does MUB-2 (for details, see Appendix II, microfilm edition). Other results obtained using MUB-2′ are essentially the same as those obtained when MUB-2 is used.

Table V. Components of Gauche-Anti Isomerization Energy in *n*-Butane, Neglecting Vibrations, According to Various Force Fields (kcal/mol)

	Fully relaxed structure			Rigid internal rotation[a]	
Interaction	MUB-1[b]	MUB-2[c]	NLA[d]	MUB-2	NLA
Vicinal[e]					
Gauche H···H only	0.06	0.46	0.56	0.43	0.49
All gauche	−0.07	−0.07	0.35	0.03	0.24
Gauche and anti	−0.07	−0.11		−0.01	0.24
Me···Me[f]					
All C···H, H···H		0.61		1.58	2.18
Shortest H···H	0.25	0.37	0.26	0.88	2.14
Valence deformation[g]		0.56	0.43	0.00	0.00
All other nonbond.[h]		−0.53		−0.41	−0.15
Total	0.43	0.54[i]	0.69	1.16	2.27

[a] All structure parameters from MUB-2 anti structure except for C-C-C-C torsion = 60°. [b] Reference 5. [c] This research. [d] Reference 3. [e] 1-4 interactions across central C-C bond. [f] Excluding 1-4 C···C interaction which is counted in the previous entry. [g] In the case of MUB-1 and MUB-2, the geminal nonbonded contributions are included as "valence deformations" for purposes of comparison because in non-UB fields such interactions are included in the "valence constants". [h] Interactions over and above vicinal interactions across central C-C, Me···Me, and geminal 1-3 interactions. [i] 0.63 at 0 K including calculated zero-point energies.

action in the *gauche* form versus 2 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 the instability of the *gauche* form of butane may be ascribed entirely to the Me···Me interaction . . ." Allinger's new hypothesis[3] is that it is principally the gauche H···H interactions rather than the Me···Me interaction that destabilize the gauche conformer. To assess whether molecular mechanics calculations support this interpretation, and support it independently of the exact parameterization of the model fields as Allinger suggests, we have carried out computations with two alternative fields besides Allinger's. The first is the MUB-1 field which contains nonbonded potentials[35] which have been invoked in a wide variety of published studies. The second is the present MUB-2 field. Now, chemists commonly suppose that the Me···Me repulsions in the conventional interpretation stem largely from the methyl hydrogens protruding toward each other in the gauche form. Seldom is it suggested that the 1-4 C···C interaction is dominant. In the present study of the gauche H···H hypothesis it seems reasonable to lump all 1-4 interactions together, and consider the C···C and C···H as well as the H···H. After all, these interactions all play equivalent roles whether or not their magnitudes are similar. If the gauche H···H interactions really provide the preponderant part of the isomerization energy (gauche-anti), then the lumped-together 1-4 contributions should reflect the fact. If, on the other hand, the 1-4 H···H contributions are individually large but are balanced by competing 1-4 C···C and C···H interactions, there is nothing special about the H···H interactions and the gauche hydrogen hypothesis has little utility. It is too early to decide unequivocally what is true but it is easy to test whether the hypothesis holds for all plausible potential functions, as claimed.[3]

Table VI. Energies of Interaction Across the Central C-C Bond in *n*-Butane (kcal/mol)

Rotamer[a]	MUB-2	Allinger
Gauche-type Interactions		
Anti		
Two H···H	0.30 each	0.26 each
Four H···Me	0.46 each	0.07 each
Gauche (unrelaxed)		
Two H···H	0.33 each	0.32 each
One H···H	0.37	0.38
Two H···Me	0.39 each	0.01 each
One Me···Me	1.74	2.03
Anti-type Interactions		
Anti		
Two H···H	0.03 each	−0.07 each
One Me···Me	−0.25	−0.24
Gauche (unrelaxed)		
One H···H	0.03	−0.07
Two H···Me	−0.07 each	−0.15 each

[a] Based on MUB-2 structural parameters for anti rotamer except for the C-C-C-C torsion in the gauche rotamer which is taken as 60°. Here the Me···Me interactions *include* the vicinal C···C interactions (excluded in Table V).

The results presented in Table V favor Allinger's new hypothesis only when Allinger's field is used and only, then, in the relaxed structure decomposition. The MUB-1 field makes the 1-4 H···H interactions trivial in the first place, apparently because, at the crucial 2.4 Å distance where the competing dispersion forces and repulsive forces are fortuitously comparable in magnitude, a nonoptimum parameterization accidentally reduced the net energy to too low a value. Note that this apparent deficiency in *energy* is less conspicuous in the *force* curve $(-\partial V/\partial r)$ illustrated in Figure 2. In contrast to the MUB-1 field, the MUB-2 field gives gauche 1-4 energies similar to Allinger's in the 2.4 Å range. Nevertheless, as shown in Table V, where the MUB-2 1-4 energies (gauche only or gauche plus anti) are lumped together, they stabilize gauche more than anti and therefore fail to support Allinger's hypothesis. If it is not the 1-4 interaction, what *is* responsible for selectively destabilizing the gauche conformer? The values in Tables V and VI confirm that the Me···Me interactions contribute heavily, as popularly thought. The situation is complicated, however, by effects of molecular relaxation in the *gauche* form in response to the stress imparted by the Me···Me forces. Here Allinger's field and the MUB-2 field are in substantial agreement that valence deformations in relaxation contribute about 0.5 kcal/mol, an amount by itself accounting for most of the isomerization energy. Clearly, however, this consequence of relaxation to increase Me···Me clearances and thereby to reduce the total energy cannot be considered the primary *cause* of the gauche destabilization. In the MUB-2 field, at least, the nonbonded interactions not already included in the above categories (largely from the H···Me interactions) *stabilize* gauche relative to anti by 0.5 kcal/mol, undoing half of the [Me···Me plus valence deformation] total. Relaxation effects so redistribute the molecular energy that interpretations of causes of the conformational energy difference from final "energy components" are specious. Individual components are changing in first order while the total energy changes in second order as molecular deformations allow the energy to reach a minimum value. Therefore, rather widely varying distributions of energy components can imply similar total energies.

An alternative and more direct way to test the Allinger gauche hydrogen hypothesis is to look at energy contributions prior to molecular relaxation. That is, if it is really the 1-4 interactions across the central C-C bond which destabilize gauche, the effect should show up most strongly if the anti conformer is twisted around to gauche without altering any bond lengths, bond angles, or torsions except that about the central C-C bond. The results of applying this model are presented in Tables V and VI where the anti structure parameters of the MUB-2 field are used, and gauche is formed by a torsional displacement to $\tau_{CCCC} = 60°$. Both the MUB-2 and Allinger 1-4 nonbonded functions are applied to the structures specified above. Again, the results of lumping all 1-4 interactions together (Table V) as well as the more usual breakdown into Me···Me, Me···H, and H···H interactions (Table VI) fail to suggest that gauche hydrogen interactions overbalance the others markedly. The gauche Me···Me repulsions clearly dominate, even with Allinger's potential functions. Other interactions, rather than being negligible (as in Eliel's account[34]), seem, instead, to be more or less balanced.

As further examples consistent with his gauche hydrogen hypothesis, Allinger cited the cases of 2,3-dimethylbutane and methylcyclohexane. Various kinetic effects were also considered but these are beyond the scope of the present paper. The fact that the difference in energy between gauche and anti conformations of 2,3-dimethylbutane is apparently much less than that for *n*-butane was interpreted as favoring the gauche hydrogen interpretation. But the MUB-1 and MUB-2 models which are in accord with the conventional butane interpretation give, for vibrationless 2,3-dimethylbutane, the very low values of only 0.10 and −0.28 kcal/mol, respectively, for E(gauche) − E(anti). The relative stability of gauche in this molecule as compared with *n*-butane seems to stem from the freedom of *gauche*-2,3-dimethylbutane to relax.[3,5]

The MUB-2 force field is less successful than Allinger's field in accounting for the high difference in energy (1.8 ± 0.15 kcal/mol)[36] between axial and equatorial methylcyclohexane. Allinger achieves an energy difference of 1.6 kcal/mol, whereas the MUB-2 field yields only 1.0 kcal/mol ($\Delta H°$ at 298 K). But Schleyer et al. obtain an even better isomerization energy (1.8 kcal/mol) than does Allinger, and with C···C and H···H nonbonded potential forces similar to those of MUB-2. Therefore, highly repulsive H···H interactions are not a sine qua non for the methylcyclohexane case.

VI. Discussion

A model force field of lasting merit should have predictive value in treating vibration frequencies, structures, and thermodynamic properties. The MUB-2 field is of utility only as an interim compromise according to these criteria since its prime role is to model certain steric components of a force field while neglecting the effects of truncation of the set of force constants adopted. The field, through the action of these steric components, is successful in reproducing semiquantitatively a variety of quadratic stretch-bend interactions neglected in more conventional CFF formulations or represented by a number of individually adjusted parameters. Furthermore, it reproduces with the same steric components a series of anharmonic couplings that are entirely missing from all other CFF formulations for general hydrocarbons.[36] These couplings are discussed elsewhere.[2] The field yields vibrational frequencies that are much less accurate than those derived from the CFF fields of Lifson and co-workers[6,21] (which were adjusted explicitly to fit frequencies) but it gives roughly the correct magnitudes (see microfilm edition). A prime rationale of the present approach is that it is reasonable to force plausible nonbonded interactions (including geminal) into a truncated field instead of adjusting nonbonded interaction parameters to compensate for neglected potential constants in frequency calculations.

Apropos of the last point, it was found, as expected, that an appreciable k_{rr} (CH/CH interaction) constant was needed to moderate the stretch-stretch components of our strong H···H interactions. Although k_{rr} appreciably influences frequencies, its presence or absence had an absolutely insignificant effect on the *structure* of gauche and anti butane and it was taken as zero in the structure calculations represented in Figures 3-6. Perhaps the most significant interaction neglected completely in the MUB-2 field is a bend-bend interaction designated as $k_{\psi\psi'} - k_{\psi\psi'\beta}$ in ref 2 and most easily envisioned as a C-C bond flexibility parameter.[38]

Although the MUB-2 force field is not as accurate as the CFF in reproducing frequencies, it is at least as accurate in reproducing structures and structural trends in the series of molecules selected for Figures 3-6. This is true even though the new field assigns but a single reference value ϕ^0 and force constant to a given type of internal coordinate (C-C, C-H, ∠C-C-C, ∠C-C-H), irrespective of the adjacent bonds.

Obviously, an improved fitting of frequencies and structural parameters could be obtained if the MUB-2 field adjusted reference angles instead of setting them 109.47 . . . ° and if it adjusted reference lengths and force constants to reflect in more detail the molecular environment, as do nearly all other model fields. But the present study is more concerned with interpreting large effects than with fitting small ones, and simplicity of force field offers advantages for this.

The primary diagnosis of concern in the present paper was of those conformational energies interpreted by Allinger in terms of his gauche hydrogen hypothesis.[3] In this our results were clear. The degree to which gauche hydrogen interactions account for the gauche-anti energy difference does, after all, depend critically upon the parameterization of the force field.[39] No support for the gauche hydrogen hypothesis was provided by MUB-2 even though H···H interactions in MUB-2 were *equal to or greater than* (depending on bond orientations) Kochanski's ab initio H···H interactions.[4] Until even more definitive nonbonded interaction functions become available, we provisionally conclude that the conventional interpretation of the conformational energy difference is correct.[39]

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Supplementary Material Available: Appendix A describing details of the construction of force field MUB-2 and structure results for norbornane, and Appendix B presenting field MUB-2′, frequencies calculated via MUB-2′, and a brief discussion of neglected constants and uncertainties (15 pages). Ordering information is given on any current masthead page.

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Trends in Molecular Properties by the Method of Structural Fragments. Bond Angles in Triatomic Molecules, Pyramidal Inversion Barriers, and Singlet-Triplet Energy Differences

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Abstract: The recently suggested method of structural fragments is employed in this article to provide trends in bond angles, pyramidal inversion barriers, and singlet–triplet energy differences in carbenes and related electron-deficient species. No experiments or calculations need be performed. Instead, one merely counts the number of electrons in the appropriate fragments. Relative ionization potentials and electron affinities for the fragments are sometimes required, but intuition based on electronegativity trends usually suffices. The concepts of relative σ or π richness and of relative porosity or blockedness are thus introduced as natural extensions of the method described earlier. Analysis of the σ or π rich and porous or blocked fragment needed for reconstruction of the molecule then allows comparison of the species of interest with other compounds which are related either isoelectronically or by the loss or gain of electrons.

In two recent articles we introduced the method of structural fragments as a nonempirical, noncalculational procedure for predicting the molecular geometry of ground[2] and excited state[3] species. We now wish to show how this method may be employed to provide trends in bond angles, pyramidal inversion barriers, and singlet–triplet energy differences in carbenes and related electron-deficient species with no loss of generality or conceptual simplicity.

Let us briefly review the method of structural fragments as applied to the molecular geometry of ground state triatomic molecules. The triatomic molecule is mentally dissociated into diatomic and atomic fragments. The diatomic fragment is chosen to have either four or ten valence electrons and to therefore be isoelectronic with BH or CO, and to be labeled σ rich. Alternatively, if it has either eight or fourteen electrons and it is isoelectronic with HF or F_2, it is labeled π rich. In turn, if the remaining atomic fragment has a closed shell electron configuration or is but one electron short, it is labeled blocked; if not blocked, it is labeled porous. The geometry prediction is then made through the simple rules: σ rich + porous → linear, σ rich + blocked → bent, π rich + blocked → linear, π rich + porous → bent. For example, we recognize H^+ as porous but H and H^- as blocked. As such, we are not surprised that BeH_2, formed from the σ-rich BeH^- and porous H^+, is linear while BH_2, formed from the σ-rich BH and blocked H, is bent.[4] The lowest lying singlet state ($^1A_1$) of CH_2[5] is also bent since it may

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