Spectroscopically Determined Force Fields for Macromolecules. 2. Saturated Hydrocarbon Chains

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Received: February 11, 1998

Our methodology for producing a spectroscopically determined force field (SDFF) (i.e., a molecular mechanics energy function) that, in addition to structures and relative energies, reproduces vibrational frequencies to spectroscopic standards, has been extended from its previous implementation on the linear to include branched saturated hydrocarbon chains. To the ab initio force fields of the 14 stable conformers of *n*-pentane and *n*-hexane, we have now added those of the 7 stable conformers of isopentane, 3-methylpentane, and neopentane, plus specific force constants from a secondary set of branched molecules, to optimize the parameters of the SDFF. This SDFF reproduces 791 ab initio non-CH stretch frequencies with a root-mean-square deviation of 6.2 cm^{-1}. When applied to other molecules not in the optimization set, viz., cyclobutane, cyclohexane, isobutane, tri-*tert*-butylmethane, and tetra-*tert*-butylmethane, not only are ab initio as well as experimental geometries and frequencies well reproduced, but the correct (reassigned) tertiary CH stretching frequency in tri-*tert*-butylmethane is satisfactorily predicted. The larger frequency deviations for other modes of this molecule provide an unusual insight into sensitive features of the nonbonded interaction terms in the potential function.

Introduction

The need for spectroscopically accurate molecular mechanics (MM) energy functions for macromolecules is driven by two goals. First, we wish to be able to study the normal modes of different conformations of such molecules, and this requires that we have conformation-dependent force constants. The second derivatives of an accurate MM function provide the most natural way of obtaining such force constants. Second, it is obvious that the quality of MM and molecular dynamics (MD) predictions will be determined by the accuracy of the energy functions used in these simulations. Achieving spectroscopic in addition to structural and energetic accuracy in the energy function brings us closer to this goal.

For these reasons we have sought to develop an energy function that, in addition to reproducing structures and energies, inherently reproduces vibrational frequencies. We call this a spectroscopically determined force field (SDFF), and we have chosen to derive it from ab initio "data". We have shown[1,2] that MM parameters can be derived by analytical transformation from ab initio force fields, which avoids problems associated with least-squares-optimization methods. Redundancies can be dealt with appropriately,[3] and nonbonded parameters can be optimized straightforwardly.[4]

On the basis of a detailed ab initio analysis of *n*-pentane and *n*-hexane conformers,[5] we have implemented this procedure to produce an SDFF for the linear saturated hydrocarbon chain.[6] The value of such an energy function is illustrated by its ability to reproduce the experimental elastic modulus of polyethylene to about 1%. Development of an SDFF for alkenes has been initiated.[8]

In this paper we extend the saturated hydrocarbon SDFF to include branched chains. The procedure is the same as that previously used,[6] with the following modifications: a redundant coordinate basis replaces the previous nonredundant basis;[6] anharmonicity of bonds and angles is included explicitly, based on the observed variation in ab initio force constants with departures from equilibrium geometry; and an angle−torsion interaction term is included to account for the nonplanar structure of cyclobutane. The *n*-alkane results are, of course, included in the optimization.

Calculations

Ab Initio Force Fields. As in our previous study of the linear alkanes,[6] the SDFF for the branched alkanes was obtained by transformation[2] of scaled ab initio force fields of a set of conformers of representative molecules, followed by reduction in number and optimization of the parameters.[4,6] The primary set of molecules (and number of stable conformers) used in this procedure were *n*-pentane(4),[6] *n*-hexane(10),[6] 2-methylbutane(2) (isopentane), 3-methylpentane(4), and 2,2-dimethylpropane (1) (neopentane). To obtain specific force constants for other local structures than those represented by the above branched molecules, we performed ab initio calculations and SDFF transformations on a secondary series of molecules: 2,2-dimethylbutane, 2,2,4,4-tetramethylpentane, 2,3,3,4-tetramethylpentane, 2,2,3,4,4-pentamethylpentane, 2,2,3,3-tetramethylhexane, and 2,2,3,4-tetramethylhexane. These results showed that stretching and bending force constants in branched chains cannot be taken as constants independent of the number of hydrogens attached to the carbon atoms that make up the respective internal coordinates.

The ab initio force fields for the branched molecules in the primary set were obtained, as before,[6] at the HF/6-31G level, based on the previous scale factors[6] and a careful analysis of band assignments.[9] Relative energies of conformers, as before,[6] were obtained from MP2/6-31G* calculations. The 150 ex-

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S1089-5639(98)01105-0 CCC: $15.00

perimental frequencies below 1500 cm^{-1} of the 7 branched molecules are reproduced by the scaled ab initio force field with a root-mean-square (rms) error of 4.4 cm^{-1}.

Potential Energy Function. The potential energy function in our SDFF is defined in the following way:

$$V = {}^1/_2\sum_i F_{ii}(q_i - q_{i0})^2 + {}^1/_2\sum_i c_{i1}(q_i - q_{i0})^3 + {}^1/_2\sum_i c_{i2}(q_i - q_{i0})^4 + \sum_{i<j} F_{ij}\,(q_i - q_{i0})(q_j - q_{j0}) + \sum V_{\mathrm{tor}} + \sum V_{q,\mathrm{tor}} + \sum V_{\mathrm{tor,tor}} + \sum V_{nb} \quad (1)$$

The quadratic−cubic−quartic terms, and the standard type cross terms, are used for coordinates for which the potential energy has an approximately quadratic dependence. The torsion potential consists of the usual cosine terms,

$$V_{\mathrm{tor}} = {}^1/_2\sum V_N\,(1 \pm \cos N\varphi) \quad (2)$$

where φ is the torsion angle and $N = 1, 2, 3, 4,$ or 6. In the present force field it has been found that only the $N = 3$ term is needed. Cross terms where one of the coordinates is a torsion are given by

$$V_{q,\mathrm{tor}} = F_{q\varphi}(q - q_0)g(\varphi) \quad (3)$$

where q is a quadratic coordinate and

$$g(\varphi) = \frac{1}{N}\sin N(\varphi - \varphi_0) \quad (4)$$

in which N is the periodicity and φ_0 is the nearest intrinsic minimum of the torsion potential. If both of the interacting coordinates are torsions, the potential energy is defined by

$$V_{\mathrm{tor,tor}} = F_{\varphi\varphi}g(\varphi_i)g(\varphi_j) \quad (5)$$

These forms of $V_{q,\mathrm{tor}}$ and $V_{\mathrm{tor,tor}}$ automatically reflect the desired properties of cross terms that involve torsions,[6] i.e., that they should behave like ordinary quadratic cross terms for small torsion deformations, that the periodicity of the torsions should be accounted for, and that for deformations larger than $\pm\pi/2N$ the sign of the force constant should be reversed.

Some of the interaction force constants have explicit conformation dependence, i.e., the F_{ij} themselves depend on a torsion angle or deformation. This is the case for the next-nearest-neighbor (bond−angle and angle−angle) interactions where the interacting coordinates form a torsion angle. As in our previous force field,[6] the force constant then depends on that torsion angle according to

$$F_{ij} = F_0 \cos(\varphi) \quad (6)$$

Furthermore, as in that force field, the force constant for interaction between a torsion and its central bond (CC/XCCX) depends on the sine of the torsion angle deformation,

$$F_{ij} = F_0 \sin N(\varphi - \varphi_0) \quad (7)$$

This sine-modulation is also present in the (new) angle−torsion force constant for interaction between a torsion and an angle when the angle shares all its atoms with the torsion (CCC/XCCC).

The nonbonded potential accounts for electrostatic and van der Waals interactions by

$$\sum V_{nb} = \sum\left(\frac{1}{4\pi\epsilon_0\epsilon_r}\frac{Q_iQ_j}{r_{ij}} + \frac{A_iA_j}{r_{ij}^9} - \frac{B_iB_j}{r_{ij}^6}\right) \quad (8)$$

where r_{ij} is the distance between the ith and jth atoms, Q_i and Q_j are the partial charges on the ith and jth atoms, ϵ_0 is the permittivity of free space, ϵ_r is the dielectric constant (taken as one), and A_i and B_i are respectively the repulsive and attractive van der Waals parameters of atom i (the 9-6 was found to give better results than the 12-6 potential[6]). The summation runs over all atom pairs in positions 1,4 and higher. If the charges depend significantly on the values of the neighboring internal coordinates, i.e., charge fluxes are present, this must be taken into account when calculating the first and second derivatives of V_{nb}. Similarly, if the charges depend on the location of other charges (or dipoles) in the system, polarization may have to be taken into account. In the hydrocarbon force field, charge fluxes and polarization have minimal effect and have not been explicitly incorporated in the potential energy function. However, for more polar molecules these effects may not be negligible. The van der Waals parameters may also depend on conformation, but this is more difficult to explore because the effect on conformational energy is much smaller than for electrostatic interactions.

The following procedure was used to transform the scaled ab initio force constants into the MM format. Instead of the nonredundant coordinate basis that was used in our previous force field,[6] this time we used the conventional redundant basis where all six valence angles around the sp^3 hybridized carbon atoms are included. In the final force field, all torsion coordinates are also included, but in the SDFF transformation only one torsion per C−C bond was used. The inverse **B** matrixes, which are needed in the SDFF transformation but which are not automatically well defined in a redundant coordinate basis, were calculated using the method described by Pulay and Fogarasi.[10] In the SDFF transformation we used the same electrostatic and 9-6 Lennard-Jones nonbonded interaction parameters as in the previous force field.[6] The transformations produced a complete general MM valence force field for each of the molecules. These force fields were then truncated so that cross terms beyond interactions between coordinates centered on two adjacent chain atoms were left out. As a further simplification, average values were calculated for the remaining force constants.

The next step would be to optimize these force constants in a least-squares fit to the (scaled) ab initio vibrational frequencies, but in this case, because of the local redundancy in the angle coordinates at each sp^3 carbon atom, the angle-bending force constants as such are indeterminate, as are the interaction force constants involving these coordinates. Before a meaningful optimization can be done, therefore, appropriate constraints have to be applied.[3] Because the local symmetry of a group formed by a C(sp^3) atom and the four atoms attached to it depends upon the nature of those atoms, the constraints can be different in each case. At least six constraints are needed to make the angle force constants, as well as angle−angle interaction force constants within one group, determinate[3]. Three constraints can be used regardless of the local symmetry, viz., to set interactions involving angle coordinates which do not share a bond equal to zero. The nature of the other three constraints depends on the local symmetry.

For the methyl group, a good choice is the one suggested in ref 3, i.e., to assume that the interaction force constants CCH/CCH and HCH/HCH are equal. This allows the maximum number of degrees of freedom, which in this case, because of the 3-fold symmetry, means only two independent interaction force constants (i.e., F_1 = CCH/CCH = HCH/HCH and F_2 = CCH/HCH). When the redundancy transformation[3] was carried out, the values $F_1 = -0.33$ kcal/mol/rad^{-2} and $F_2 = 4.23$ kcal/mol/rad^{-2} were obtained. Since the former value is too small to be significant, this leaves only one independent angle−angle interaction force constant in the methyl group.

For the methylene group, sufficient constraints are obtained if CCH/CCC is required to be equal to CCH/CCH, CC bond shared in combination with the symmetry-based assumption that the diagonal force constants CCH are all equal. In this case, too, the maximum number of degrees of freedom is retained, leaving three independent interaction force constants, i.e., CCH/CCC = (CCH/CCH, CC bond shared), (CCH/CCH, CH bond shared), and CCH/HCH. All three are used in the final force field.

A branching site with one hydrogen and three carbon atoms attached to a common carbon atom has the same local symmetry as the methyl group, and thus has two independent angle−angle interaction force constants. With constraints equivalent to those used in the methyl group, these force constants are CCC/CCC = CCH/CCH and CCC/CCH, of which only the former was found to be significant in the final force field. In the case of a central carbon atom bonded to four other carbon atoms, there is obviously only one angle−angle interaction force constant (for angles that share a bond), i.e., CCC/CCC.

It should be noted that, in these as well as in other cases where redundant coordinates are involved, neither the interaction force constants nor the diagonal force constants are well defined without explicit mention of the constraints used in deriving them. Further, even seemingly similar force constants should be considered to be different parameters if they belong to groups of different local symmetry. This has generally not been taken into account in MM force field development. For example, in the parametrization of the CFF93 force field for alkanes, Hwang et al.[11] used three angle−angle interaction force constants in the methyl group, where only two are allowed (and only one needed), and four such force constants in the methylene group, where only three are allowed. They also combined force constants belonging to groups of different local symmetry. Consequently, the resulting parameters are associated with very artificial constraints.

The nearest-neighbor bond−angle interaction force constants at a C(sp^3) atom are also indeterminate in the redundant basis. An analysis, very similar to those described in ref 3 for diagonal force constants, reveals that, for each of the four bonds, a constant can be added to every interaction force constant involving the bond and one of the six angles. This is seen by forming a redundancy vector[3] $\mathbf{a}^t = (1\ 1\ 1\ 1\ 1\ 1\ 0)$, where the six 1 values represent the first-order redundancy relation for the angles and the 0 represents the bond, and calculating the redundancy matrix $\mathbf{ah}^t + \mathbf{ha}^t$, where $\mathbf{h}^t = (h_1, h_2, ..., h_7)$ is an arbitrary vector. The constant that can be added to the bond−angle interaction force constants without changing the potential energy in any way is then h_7. This means, if h_7 is chosen as the negative of one of these force constants, that force constant is eliminated. In the alkanes, however, it turns out that the force constants of all bond−angle cross terms where the interacting coordinates only share the central atom of the angle have values very close to one another. Thus, all these cross terms can be eliminated. Note that this may not always be the case, and that such force constants may sometimes have to be retained.

So far, only one torsion coordinate per C−C bond had been used. This, however, does not properly reflect the symmetry of, for example, ethane and neopentane. A transformation was therefore made to a coordinate basis in which all nine torsions per C−C bond were used. The affected parameters were transformed simply by dividing the original barrier height, the bond−torsion, and the angle−torsion interaction force constants by 9, and by dividing the torsion−torsion interaction force constant by 81. The 3-fold torsion potential is the same as in our previous force field, except that now all nine torsion coordinates associated with a C−C bond are explicitly used.

TABLE 1: Average Angle Force Constants[a] (at Intrinsic Equilibrium) and Angle−Angle Interaction Force Constants before (Indeterminate) and after (Determinate) the Redundancy Transformation

Angle

	indeterminate	determinate	force constant[b]
CCC	115.26	148.30	CH3−CH0−CH3
	96.00	126.19	CH2−CH1−CH2
	90.48	105.19	CH2−CH2−CH2
CCH	82.12	99.81	CH3−CH1−H
	76.00	94.89	CH2−CH2−H
	69.25	85.74	CH2−CH3−H
HCH	69.68	91.61	H−CH2−H
	66.53	80.23	H−CH3−H

Angle−Angle with Shared CC Bond

	indeterminate	determinate	center atom
CCC/CCC	−20.55	12.49	CH0
	−17.20	12.99	CH1
CCC/CCH	−21.79	2.16	CH1
	−19.08	−2.28	CH2
CCH/CCH	−21.17	−2.28	CH2
	−16.82	−0.33	CH3

Angle−Angle with Shared CH Bond

	indeterminate	determinate	center atom
CCH/CCH	−4.72	12.99	CH1
	−6.12	12.77	CH2
CCH/HCH	−11.45	8.95	CH2
	−10.88	4.23	CH3
HCH/HCH	−14.06	−0.33	CH3

Angle−Angle with Only Center Atoms Shared

	indeterminate	determinate	center atom
CCC/CCC	−33.04	0.0	CH0
CCC/CCH	−23.95	0.0	CH1
CCC/HCH	−18.31	0.0	CH2
CCH/CCH	−18.89	0.0	CH2
CCH/HCH	−15.11	0.0	CH3

[a] In units of kcal mol^{-1} rad^{-2}. [b] CH0, CH1, CH2, and CH3 denote carbon atoms that have 0, 1, 2, or 3 hydrogens attached, respectively.

Table 1 shows the results of some of the redundancy transformations, and the large differences between indeterminate and determinate force constants demonstrate the importance of using appropriate constraints.

After thus obtaining the force field in a determinate and symmetric form, some of the force constants were optimized in a least-squares fit to the (scaled) ab initio vibrational frequencies. In this connection, similar cross terms with values close to one another were combined in order to increase the stability of the optimization and to simplify the force field. For example, the next-nearest-neighbor (#2) angle−angle interaction force constants CCC/CCC#2 and CCC/CCH#2 were combined. Before the optimization, the rms frequency deviation for non-CH stretching vibrations was 9.1 cm^{-1} with individual deviations ranging from −27 to +24 cm^{-1} and with 78% of them within ±10 cm^{-1}. After the optimization, the rms deviation is 6.2

TABLE 2: Spectroscopically Determined Force Field for Saturated Hydrocarbons[a]

Diagonal Force Constants[b]

Bond Stretching

CC bonds	F_{ii}[c]	q_0[c]	c_1[c]	c_2[c]	CC bonds	F_{ii}[c]	q_0[c]	c_1[c]	c_2[c]	CC bonds	F_{ii}[c]	q_0[c]	c_1[c]	c_2[c]
CH3−CH3	640.5	1.526	−1100	1300	CH1−CH2	590.0	1.530	−1100	1300	CH0−CH2	560.0	1.539	−1100	1300
CH2−CH3	618.3	1.526	−1100	1300	CH1−CH1	590.0	1.530	−1100	1300	CH0−CH1	560.0	1.544	−1100	1300
CH2−CH2	620.2	1.528	−680	2100	CH0−CH3	560.0	1.539	−1100	1300	CH0−CH0	560.0	1.544	−1100	1300
CH1−CH3	595.0	1.530	−1100	1300										

CH bonds	F_{ii}	q_0	c_1	CH bonds	F_{ii}	q_0	c_1	CH bonds	F_{ii}	q_0	c_1
CH4−H	713.3	1.082	−1800	CH2−H	669.7	1.084	−1400	CH1−H	670.0	1.085	−1200
CH3−H	687.9	1.083	−1600								

Angle Bending

CCC angles	F_{ii}	q_0[d]	c_1	CCC angles	F_{ii}	q_0[d]	c_1	CCC angles	F_{ii}	q_0[d]	c_1
CH3−CH2−CH3	115.0	113.3	−40	CH3−CH1−CH3	131.0	111.6	−40	CH3−CH0−CH3	143.0	109.47	−40
CH2−CH2−CH3	110.0	113.0	−40	CH2−CH1−CH3	126.0	111.3	−40	CH2−CH0−CH3	135.0	109.47	−40
CH2−CH2−CH2	106.0	112.7	−40	CH2−CH1−CH2	121.0	111.3	−40	CH2−CH0−CH2	127.0	109.47	−40
CH1−CH2−CH3	100.0	112.1	−40	CH1−CH1−CH3	98.0	111.3	−40	CH1−CH0−CH3	123.0	109.47	−40
CH1−CH2−CH2	100.0	112.1	−40	CH1−CH1−CH2	92.0	111.3	−40	CH1−CH0−CH2	116.0	109.47	−40
CH1−CH2−CH1	100.0	112.1	−40	CH1−CH1−CH1	86.0	111.3	−40	CH1−CH0−CH1	108.0	109.47	−40
CH0−CH2−CH3	100.0	112.1	−40	CH0−CH1−CH3	99.5	111.3	−40	CH0−CH0−CH3	118.2	109.47	−40
CH0−CH2−CH2	100.0	112.1	−40	CH0−CH1−CH2	95.0	111.3	−40	CH0−CH0−CH2	110.0	109.47	−40
CH0−CH2−CH1	100.0	112.1	−40	CH0−CH1−CH1	90.0	111.3	−40	CH0−CH0−CH1	102.0	109.47	−40
CH0−CH2−CH0	100.0	112.1	−40	CH0−CH1−CH0	85.0	111.3	−40	CH0−CH0−CH0	94.0	109.47	−40

CCH angles	F_{ii}	q_0[d]	c_1	CCH angles	F_{ii}	q_0[d]	c_1	CCH angles	F_{ii}	q_0[d]	c_1
CH3−CH3−H	88.7	110.6	−30	CH3−CH2−H	93.8	109.3	−30	CH3−CH1−H	95.8	107.9	−30
CH2−CH3−H	85.9	110.6	−30	CH2−CH2−H	91.2	109.3	−30	CH2−CH1−H	93.2	107.9	−30
CH1−CH3−H	84.4	110.6	−30	CH1−CH2−H	89.7	109.3	−30	CH1−CH1−H	90.5	107.9	−30
CH0−CH3−H	81.6	110.6	−30	CH0−CH2−H	88.2	109.3	−30	CH0−CH1−H	87.9	107.9	−30

HCH angles	F_{ii}	q_0[d]	c_1	HCH angles	F_{ii}	q_0[d]	c_1	HCH angles	F_{ii}	q_0[d]	c_1
H−CH4−H	71.6	109.47	−30	H−CH3−H	80.2	108.3	−30	H−CH2−H	91.6	107.3	−30

Torsion

XCCX	3-fold barrier (V_3)	0.3010

Interaction Force Constants

Bond−Bond

	F_{ij}	shared atom		F_{ij}	shared atom		F_{ij}	shared atom
CC/CC	7.00	CH2	CC/CC	13.45	CH0	CH/CH	6.21	any C
	9.14	CH1	CC/CH	6.93	any C			

Bond−Angle

	F_{ij}	angle center atom		F_{ij}	angle center atom		F_{ij}	angle center atom
				Bond Shared				
CC/CCC	30.00	CH1 or CH2	CC/CCH	33.21	any C	CH/HCH	22.21	any C
	45.75	CH0	CH/CCH	17.11	any C			
				Only Angle End Atom Shared				
CC/CCC#2	−11.80	cosine modulation by CCCC torsion[e]				CC/CCH#2	−7.62	cosine modulation by CCCH torsion[e]

Bond−Torsion

	F_{ij}	
CC/XCCX	−1.07	torsion central bond shared, sine modulation by torsion deformation[f]

Angle−Angle

	F_{ij}	center atom		F_{ij}	center atom		F_{ij}	center atom
				Bond and Center Atoms Shared				
CCC/CCC	7.46	CH1	CCH/CCH	0.00	CH3	CCH/HCH	4.23	CH3
	4.90	CH0		−3.41	CH2, CC bond shared		6.53	CH2
CCC/CCH	0.00	CH1		8.97	CH2, CH bond shared	HCH/HCH	−3.46	CH4
	−3.41	CH2		7.46	CH1		0.00	CH3
				Bond Shared, Center Atoms Not Shared				
CCH/CCH#2	−14.78	cosine modulation by HCCH torsion[e]	CCC/CCH#2	−20.40	cosine modulation by CCCH torsion[e]	CCC/CCC#2	−20.40	cosine modulation by CCCC torsion[e]

Angle−Torsion

	F_{ij}			F_{ij}	
XCX/XCCX	0.538	only torsion arm shared[g]	CCC/XCCC	1.400	torsion arm and central bond shared, sine modulation by torsion deformation[f]
XCC/XCCX	0.306	only torsion central bond shared[g]			

Torsion−Torsion

	F_{ij}	
XCCX/XCCX	−0.01528	adjacent CC torsions

Nonbonded Parameters

atom	A	B	Q
C	177.00	30.51	−0.1e for each hydrogen attached
H	25.73	5.00	0.1e

[a] Units: energy in kcal/mol, length in angstroms, angle in radians, except as noted. [b] CH0, CH1, CH2, CH3, and CH4 denote carbon atoms that have 0, 1, 2, 3, or 4 hydrogens attached, respectively. [c] See eq 1. [d] Angle q_0 in degrees. [e] See eq 6. [f] See eq 7. [g] There is a sign choice associated with this force constant. If the vector product of the torsion arm and the torsion central bond has a positive component on the vector pointing from the angle center atom to the angle atom not shared with the torsion, the force constant is taken as positive.

cm^{-1}, the range is from −20 to +25 cm^{-1}, and 90% of the deviations are within ±10 cm^{-1}. The final force field is given in Table 2. The force constants in the table cover all alkanes that do not contain three-membered rings. (Such rings bring with them redundancies that directly interfere with the local internal coordinates and therefore require a special force field.)

The anharmonicities of the stretching and bending potentials were determined by least-squares fitting to SDFF-transformed force constant values as a function of bond length or angle. Given the cubic−quartic anharmonicity coefficients of the potential energy of an internal coordinate q_i, the force constant as a function of deformation is

$$F_i = F_{ii} + 3c_{i1}(q_i - q_{io}) + 6c_{i2}(q_i - q_{io})^2 \tag{9}$$

as seen by taking the second derivative of V with respect to q_i.

For $CH_2{-}CH_2$ bond stretching, it is interesting to note that the anharmonicity coefficient c_1 differs from that of the other C−C stretching potentials. Only for this force constant have we also directly determined the coefficient c_2 of the second-order term (whose important purpose in, for example, MD simulations, is to prevent dissociation of a bond). Since our c_1 values are close to those of CFF93,[11] for the other bond stretching force constants we have adopted the c_2 values of the CFF93 alkane force field[11] (transformed to our notation and slightly rounded off). For C−H stretching force constants we only use the linear corrections since these bonds generally are not strongly deformed. For angle force constants, we also use only linear corrections because no second-order trend can be seen in the data and, unlike bonds, large angles cannot cause a dissociation of the molecule. However, it is important to check that a spurious energy minimum is not created at π. This has been checked for all the angle bending energy terms in the current SDFF, and they were found to have a positive gradient for all positive deformations. In our opinion, it is not necessary to bring the gradient to zero at π for valence angles that do not take values close to π in normal MM and MD calculations. The time saved by skipping the quartic energy terms this would require is well worth the price of rarely occurring adverse effects that the discontinuity in the gradient may give rise to.

There is only one new type of cross term in the new SDFF compared to the old. This is the angle−torsion interaction where the angle shares the torsion central bond and one of the arms. This cross term was not included in the previous force field because it had too little impact on the vibrational frequencies of the linear alkanes. However, it becomes important at large angle deformations and is needed to reproduce the puckered geometry of cyclobutane.

Results and Discussion

The calculated geometries of the linear alkanes are almost identical to the ones presented earlier.[6] The energy minimized structures of the primary series of branched alkanes are also in excellent agreement with the ab initio HF/6-31G geometries. Table 3 shows the rms and maximum deviations between the SDFF and ab initio geometries. The bond lengths are within a few milliangstroms, the valence angles are well within 1°, and the torsion angles are within 3° of the ab initio values. In the secondary series there are larger deviations, even though the rms values are small. In particular, the bond deviation of 12 mÅ, which is for the 3-methyl C−C bond in 2,2,3,4,4-pentamethylpentane, is the largest discrepancy encountered in any of the molecules treated in this paper. The relative energies of conformers and barriers between them are also well reproduced, as can be seen in Figure 1 for 3-methylpentane. The 17 ab initio (MP2/6-31G*) relative energies of the molecules in the primary set are reproduced by the SDFF with an average deviation of 0.18 kcal/mol. The largest deviation, 0.6 kcal/mol, is for the g′g conformation of 3-methylpentane whose SDFF energy is 2.8 kcal/mol (above the tt conformation), whereas ab initio gives 3.4 kcal/mol. In regard to barriers between conformers, the SDFF generally gives lower values than ab initio but the discrepancies are no larger than ∼1 kcal/mol.

TABLE 3: SDFF Geometry Deviations from HF/6-31G for the Branched Alkanes

	rms	min	max	number
primary set				
bonds (mÅ)	1.3	−3.3	2.9	124
angles (deg)	0.2	−0.6	0.7	234
torsions (deg)	1.3	−2.8	2.9	288
secondary set				
bonds (mÅ)	2.7	−2.9	12.4	168
angles (deg)	0.4	−1.0	1.4	324
torsions (deg)	2.4	−6.0	4.7	432

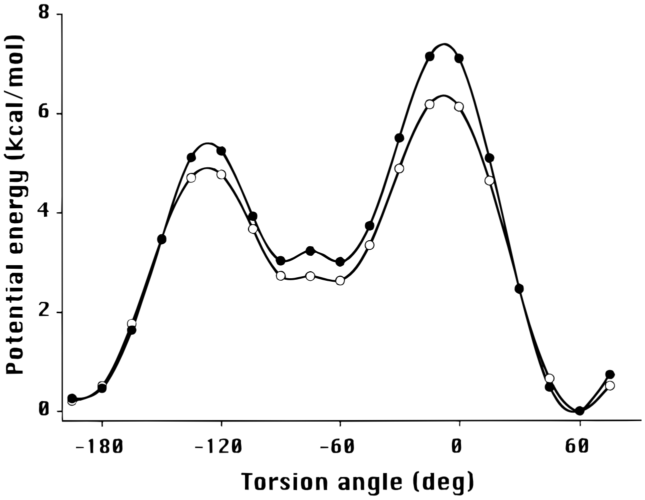

Figure 1. Comparison of ab initio MP2/6-31G* (solid circles) and SDFF (open circles) barriers for 3-methylpentane, tg to g′g to gg.

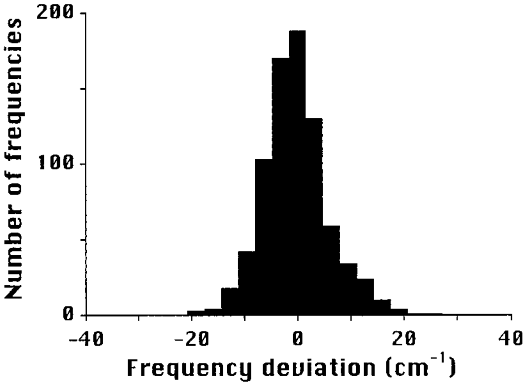

Figure 2. Histogram showing the distribution of differences between the SDFF and scaled ab initio non-CH stretching vibrational frequencies.

The SDFF vibrational frequencies are in excellent agreement with those given by the scaled ab initio force constants. The rms deviation for all 1071 frequencies is 7.0 cm^{-1}. The rms deviation for the 791 non-CH stretching vibrations is 6.2 cm^{-1} with 90% of the frequencies being within ±10 cm^{-1} of the (scaled) ab initio values. The histogram in Figure 2 shows the distribution of the non-CH stretching frequency deviations for all the molecules in the primary set.

TABLE 4: SDFF and ab Initio Results for Cyclobutane[a]

	CC	CCH_{eq}[b]	CCH_{ax}[c]	pucker[d] angle	rock[e] angle	barrier height	vibrational frequency
exptl[f]	1.552			27.9	6.2	1.5	199[g]
HF/6-31G	1.554	117.0	112.2	22.4	3.8	0.4	160[h]
HF/6-31G*	1.545	117.7	111.7	26.1	4.7	0.9	201[h]
HF/6-31G**	1.545	117.8	111.6	26.1	4.8	1.0	205[h]
MP2/6-31G*	1.545	118.4	111.0	30.8	5.8	2.3	254[h]
MP2/6-31++G**	1.546	118.5	110.8	31.7	6.0	2.7	263[h]
SDFF	1.540	117.7	111.7	25.5	4.7	1.9	280[h]

[a] Units: bond lengths in angstroms, angles in degrees, barrier heights in kcal/mol, and vibrational frequencies in cm^{-1}. [b] H_{eq} = equatorial H. [c] H_{ax} = axial H. [d] Defined as in ref 13. The CCC angle (θ_c) is related to the pucker angle (θ_p) by $\tan(\theta_c/2) = \cos(\theta_p/2)$. [e] Defined as in ref 13. [f] From ref 13. [g] Fundamental frequency[12,13] (i.e., uncorrected for anharmonicity). [h] Harmonic frequency.

We now discuss some more detailed results predicted by our SDFF for molecules that are not part of the primary or secondary sets.

Cyclobutane. By using a force field derived from a set of open chain molecules, we cannot expect to reproduce properties of small cyclic molecules as accurately. This is because the ring structures give rise to cross terms that are absent in the open chains. The normal modes are also bound to be different from their open chain counterparts, and thus their force constants do not influence the choice of average values in the SDFF. The most extreme example of this is cyclopropane which, because of the redundancies in the three-membered ring, requires its own force field. However, cyclobutane at least has the same internal coordinate setup at each carbon atom as the open chain molecules, and it should be possible to calculate a reasonable MM structure using a common force field. This turned out to be the case, although we had to add a general cross term type to the force field, i.e., the previously mentioned angle−torsion interaction where the angle is made up of the torsion central bond and one of the torsion arms. Without this cross term, the geometry of cyclobutane comes out planar. The larger the value of this force constant the larger is the nonplanarity of the carbon ring, as well as the barrier to inversion and the puckering vibrational frequency. The value 1.4 kcal/mol/rad^2 for the force constant was arrived at as a compromise, because it gives a barrier height of 1.9 kcal/mol, a puckering angle of 25.5°, and a puckering (harmonic) vibrational frequency of 280 cm^{-1}, which are in reasonable agreement with ab initio values, as shown in Table 4 (which also shows that these properties are fairly sensitive to the ab initio level and basis set used). The respective experimental values are 1.48 kcal/mol,[12] 27.9°,[13] and 199 cm^{-1} [12,13] (the latter undoubtedly reflecting the large anharmonicity of the potential[13]).

Cyclohexane. In the SDFF calculation of cyclohexane, the C−C bond length in the chair conformation is 1.537 Å, in good agreement with our HF/6-31G value of 1.535 Å and the experimental value of 1.536 Å.[14] Interestingly, an MP2/6-31G* calculation gives only 1.529 Å for this bond. The CCC bond angle is calculated to be 111.4°, in agreement with ab initio (111.4° with HF/6-31G, 111.2° with MP2/6-31G*) and experiment (111.4°[14]). The two different SDFF CCH angles are 109.2° (axial H) and 110.2° (equatorial H), very close to the ab initio values of 109.2° and 110.1° (HF) and of 109.1° and 110.3° (MP2). For the HCH angle, the SDFF value of 106.7° coincides with both HF and MP2, whereas the experimental value is 107.5°.[14] The SDFF value for the CCCC torsion angle is 55.1° compared with 54.9° and 55.6° given by HF and MP2, respectively. The experimental value is 54.9°.[14] The vibrational frequencies for the chair conformation are compared in Table 5 with the (scaled) HF/6-31G frequencies and with experiment.[15] The agreement is not as good as for the open chain molecules, but is still quite reasonable. The rms error for the non-CH stretching frequencies is 15.1 cm^{-1} for SDFF compared to ab initio or observed frequencies.

TABLE 5: Vibrational Frequencies (in cm^{-1}) of Cyclohexane

species	observed[a]	ab initio[b]	SDFF
A_{1g}	383	396	377
	802	794	807
	1157	1122	1149
	1451	1467	1458
	2853	2857	2876
	2938	2903	2911
A_{2g}		1170	1178
		1340	1337
E_g	425	440	434
	785	795	789
	1029	1032	1021
	1267	1269	1256
	1348	1339	1309
	1444	1449	1455
	2885	2855	2867
	2932	2899	2909
A_{1u}		1054	1050
		1100	1073
		1327	1337
A_{2u}	524	520	527
	1018	1034	1026
	1454	1461	1459
	2855	2856	2866
	2934	2911	2915
E_u	248	242	237
	862	848	863
	905	916	912
	1259	1260	1242
	1350	1350	1318
	1454	1451	1454
	2863	2853	2872
	2932	2896	2907

[a] From ref 15. [b] Scaled HF/6-31G.

SDFF and ab initio calculations were also done on the twisted boat conformation of cyclohexane and the geometry results were found to be in good agreement, as shown in Table 6. The energy difference between the two stable conformers was found to be 6.1 and 6.6 kcal/mol with the SDFF and MP2/6-31G*, respectively.

Isobutane. The 2-methylpropane (isobutane) molecule is of interest not only because there is detailed experimental information on its structure[16] and vibrational spectra,[15,17,18] but because it has been a base for comparison of geometry and frequency changes in more crowded molecules. As Table 7 shows, its SDFF geometry is in very good agreement with both ab initio and experimental results. The SDFF vibrational frequencies, given in Table 8, are also in good agreement with ab initio (scaled HF/6-31G) and experimental[15,17,18] frequencies, the rms deviation for non-CH stretching frequencies being 9.9 cm^{-1} with respect to the ab initio frequencies and 10.1 cm^{-1} with respect to the observed frequencies.

TABLE 6: Energy Minimized Geometry of Cyclohexane in the Twisted Boat Conformation[a]

	SDFF	HF/6-31G	MP2/6-31G*
C−C	1.535	1.533	1.527
	1.547	1.545	1.540
C−H	1.085	1.085	1.096
	1.086	1.086	1.097
	1.087	1.087	1.097
CCC	111.4	111.1	110.4
	111.9	112.2	111.8
CCH	108.8	108.9	108.8
	109.0	109.3	109.5
	109.1	109.9	110.1
	109.9	109.7	109.8
	110.0	110.0	110.2
	110.8	110.5	111.1
HCH	106.6	106.3	106.2
	106.8	106.4	106.4
CCCC	−63.6	−63.7	−65.7
	30.5	30.7	31.6

[a] Bond lengths in angstroms, angles in degrees.

TABLE 7: Energy Minimized Geometry of Isobutane[a]

	exptl[b]	SDFF	HF/6-31G	MP2/6-31G*
C_t-C_m[c]	1.535	1.531	1.534	1.528
C_m-H_m	1.113	1.084	1.086	1.096
		1.084	1.085	1.095
C_t-H_t	1.122	1.091	1.088	1.099
$C_mC_tC_m$	110.8	111.0	111.0	110.9
$C_mC_tH_t$	108.1	107.9	107.9	108.0
$C_tC_mH_m$	110.1	111.0	110.7	110.3
	111.4	111.2	111.2	111.2
$H_mC_mH_m$	106.5	107.8	107.8	107.9
	108.7	107.7	107.9	108.0

[a] Bond lengths in angstroms, angles in degrees. [b] From ref 16. [c] t = tertiary, m = methyl.

TABLE 8: Vibrational Frequencies (in cm^{-1}) of Isobutane

species	observed[a]	ab initio[b]	SDFF
A_1	433	425	428
	796	788	785
	1189	1191	1183
	1389	1389	1376
	1475	1474	1463
	2871	2881	2870
	2904	2900	2895
	2965	2963	2956
A_2		224	205
		939	957
		1449	1450
		2956	2951
E		271	259
	367	364	352
	913	909	905
	961	963	946
	1173	1176	1184
	1326	1327	1325
	1363	1366	1371
	1459	1454	1451
	1468	1467	1460
	2887	2891	2893
	2951	2950	2953
	2958	2962	2957

[a] From refs 15, 17, and 18. [b] Scaled HF/6-31G.

Because attention has been directed[19,20] to the tertiary CH stretch frequency, C_tH_t s, as well as its dependence on the C_tH_t bond length, $r(C_tH_t)$,[19] some comments are warranted here. We first note that, although this mode has been assigned to a band at 2904 cm^{-1} in isobutane,[15] several arguments do not lend support to this assignment, and in agreement with others[20] we also do not follow it.[9] For example, CH_3 to CD_3 deuteration experiments[17,18] show that this mode is at 2869 cm^{-1} in the liquid and at 2880 cm^{-1} in the gas, shifting to 2887 and 2896 cm^{-1}, respectively, in the $(CD_3)_3CH$ molecule (an effect due to the change in physical state and to any change in Fermi resonance interactions[21]). Furthermore, 2,2,3,3-tetramethylbutane has a band at 2906 cm^{-1},[15] although it has no C_tH_t group, making it unreasonable to assign this band to C_tH_t s in isobutane[15,19] or in other molecules. The next question is what force constant to choose for C_tH_t s. In contradistinction to a previous assignment,[20] and in view of our ab initio calculations on the various deuterated isotopomers,[9] we select the $(CD_3)_3$-CH molecule for this assignment because it has a pure C_tH_t s mode (this being a mixed mode in other molecules) and there is no possibility of Fermi resonances with C_tH_t bend modes (which are near 1300 cm^{-1}). Choosing the liquid frequency of 2887 cm^{-1} for this mode, we calculate the C_tH_t s mode in $(CH_3)_3CH$ at 2881 cm^{-1}. We attribute the shift to the observed band at 2869 (2871[15]) cm^{-1} to the proposed[17] Fermi resonance with the overtone of a CH_3 bend mode (although we would assign the overtone contribution to 2907 cm^{-1}, both in terms of its position and the similarity of its depolarization ratio to that of the 2869 cm^{-1} band;[17] the 2889 cm^{-1} band[17] is quite reasonably assigned to a CH_3 symmetric stretch mode predicted[9] at 2891 cm^{-1}).

The above assignment of the C_tH_t s frequency is in accord with its $r(C_tH_t)$ value. If we plot the ab initio values of $r(C_tH_t)$ against the C_tH_t s frequencies for isobutane and other molecules in the primary set, viz., 3-methylpentane, 1.0902 Å (2865 cm^{-1}), isopentane, 1.0892 Å (2871 cm^{-1}), and isobutane, 1.0882 Å (2881 cm^{-1}), we find that the result is a smooth curve with the expected inverse relationship between these quantities. This curve is a useful guide to the expected frequencies in other molecules with C_tH_t groups.

Tri-*tert*-butylmethane (tri-TBM). Tri-TBM is a highly crowded and strained molecule and has been much studied[19,20,22−25] because it can presumably provide a good test of a force field. In fact, it is claimed that "this molecule has presented one of the severest challenges to our understanding of the mechanics of molecules".[26] We will see that this is true in an unanticipated way.

The structure of tri-TBM has been determined by electron diffraction,[27,28] albeit under some geometrical constraints. As seen in Table 9, our SDFF reproduces the ab initio geometry quite well. The largest bond deviation (5 mÅ) is for one of the methyl C_q-C_m bonds. The SDFF value of 1.618 Å for the central C_t-C_q bond is very close to the HF/6-31G value of 1.620 Å, the experimental value being 1.611 Å. The largest angle deviation is for one of the methyl HCH angles, which is calculated to be 104.5° by the SDFF method, whereas the ab initio gives 106.5°. Most of the other angles are within 1° of the ab initio values, as evidenced by the low 0.6° rms deviation. For example, one of the $C_mC_qC_m$ angles, which is deformed by −7.7° to 101.8° (SDFF), is very close to the ab initio value of 101.9°. The SDFF torsion angles, which are deformed by up to 29°, are also close to the corresponding ab initio values. The largest deviation occurs for a $C_tC_qC_mH_m$ torsion, which is calculated by the SDFF to be −68.8°, whereas the ab initio gives −65.0°. The agreement with experiment is reasonable, though hard to assess because of the constraints and the average values given for the angles.

When it comes to the C_tH_t s frequency, the contrast between the predictions of our SDFF and those of other force fields

TABLE 9: Energy Minimized Geometry of tri-TBM[a]

	exptl[b]	SDFF	HF/6-31G
C_t-C_q[c]	1.611	1.618	1.620
C_q-C_m[d]	1.548 ave	1.544	1.547
		1.553	1.554
		1.565	1.560
C_m-H_m		1.077−1.087	1.073−1.086
C_t-H_t		1.088	1.087
$C_qC_tC_q$	116.0	115.5	115.3
$C_mC_qC_t$	113.0 ave	110.6	110.6
		114.1	114.3
		114.8	114.8
$C_mC_qC_m$	105.7 ave	101.8	101.9
		105.9	105.7
		108.8	108.7
$C_qC_mH_m$	114.2 ave	108.7	107.9
		109.1	109.1
		109.6	109.1
		111.4	110.8
		112.0	111.7
		112.1	112.0
		114.0	113.3
		114.3	114.2
		115.4	114.5
$C_qC_tH_t$	101.6	102.4	102.7
$H_mC_mH_m$		104.5	106.5
		105.1	106.7
		106.6	107.0
		106.7	107.2
		107.1	107.3
		107.2	107.8
		107.4	107.4
		108.3	108.2
		109.5	108.9
$\Delta(C_mC_qC_tC_q)$		−29.4	−30.0
		−25.8	−26.5
		−23.4	−24.2
		−10.1	−11.8
		−6.6	−8.3
		−4.1	−6.0
$\Delta(H_tC_tC_qC_m)$	10.8 ave	−19.7	−21.9
		−16.2	−17.4
		−13.7	−15.1
$\Delta(C_tC_qC_mH_m)$	18.0 ave	−8.8	−5.1
		−5.9	−3.4
		−3.8	−1.5
		−3.6	−1.0
		−2.9	−0.6
		−1.8	+0.7
		17.1	15.2
		18.8	17.3
		21.2	18.0

SDFF Geometry Deviations from HF/6-31G for tri-TBM

	rms	min	max	number
bonds (mÅ)	2.2	−2.6	4.9	40
angles (deg)	0.6	−2.0	0.9	78
torsions (deg)	2.3	−3.8	3.2	108

[a] Bond lengths in angstroms, angles in degrees. [b] From refs 27 and 28. [c] t = tertiary, q = quaternary. [d] m = methyl.

TABLE 10: Energy Minimized Geometry of tetra-TBM[a]

	SDFF	HF/6-31G
C_t-C_q[b]	1.683	1.690
C_q-C_m[c]	1.565	1.563
C_m-H_m	1.074−1.088	1.073−1.084
$C_mC_qC_t$	115.9	115.5
$C_mC_qC_m$	102.4	102.8
$C_qC_mH_m$	107.6	107.3
	114.0	113.3
	116.2	114.2
$H_mC_mH_m$	105.2	106.3
	105.4	106.7
	107.5	108.4
$\Delta(C_mC_qC_tC_q)$	−14.9	−14.0
$\Delta(C_tC_qC_mH_m)$	−11.5	−9.9
	−7.8	−7.0
	−5.5	−5.1

SDFF Geometry Deviations from HF/6-31G for tetra-TBM

	rms	min	max	number
bonds (mA)	2.9	−6.8	3.1	52
angles (deg)	1.0	−1.3	2.0	102
torsions (deg)	1.1	−1.9	1.1	144

[a] Bond lengths in angstroms, angles in degrees. [b] t = tertiary, q = quaternary. [c] m = methyl.

stands out. The ab initio calculation shows that $r(C_tH_t)$ = 1.0871 Å, a decrease from the $r(C_tH_t)$= 1.0882 Å of isobutane, and this is mirrored by the SDFF results, viz., 1.088 and 1.091 Å, respectively. The opposite prediction is made by CFF93: 1.118 Å for tri-TBM[26] and 1.116 Å for isobutane.[11] The longer $r(C_tH_t)$ for tri-TBM was supported by its supposedly lower C_tH_t s frequency,[19] but we believe that this assignment is incorrect. The scaled ab initio C_tH_t s frequency is found at 2898 cm^{-1}, which places tri-TBM exactly on the smooth bond length/frequency curve of the other molecules. Nor does the proposed assignment[19] of C_tH_t s to a band at 2868 cm^{-1} withstand close scrutiny. Deuteration to the C_tD_t molecule resulted in 64% deuteration by NMR,[29] yet the 2868 cm^{-1} band only decreases by about 13%.[29] On the other hand, a distinct shoulder at about 2895 cm^{-1} essentially disappears, and we believe that this band should be assigned to C_tH_t s, in agreement with the ab initio prediction.

The other ab initio CH_3 s frequencies span the range of 3075−2911 cm^{-1}, and a reasonable match can be made with observed frequencies,[29] although assignments in this region are obviously complicated by Fermi resonances.[21] Not unexpectedly because of overcrowding, CH_3 bend modes extend up to 1513 cm^{-1} (ab initio) and a medium intensity infrared band is found at 1503 cm^{-1}.[29] There is generally reasonable agreement between ab initio and observed[29] bands down to about 900 cm^{-1} (where spectra terminate[29]), although it is obviously difficult at this stage to make secure assignments in the absence of more extensive experimental information.

What is important to note is that the SDFF frequencies are (by our standards) in poor agreement with the ab initio frequencies: the rms error for non−CH s frequencies is 23.7 cm^{-1}. In some cases (CH_3 s) SDFF frequencies are lower than ab initio (up to 40 cm^{-1}) and in other cases (CH_3 bend) higher (up to 80 cm^{-1}). This clearly shows that this as well as all other energy functions do not properly account for the (probably nonbonded) potential when atoms get very close to one another, such as in overcrowded molecules. Whether the problem is associated with the repulsive van der Waals term or the electrostatic interaction remains to be determined, but it is obvious that agreement with vibrational spectra will be crucial in determining this correction.

Tetra-*tert*-butylmethane (tetra-TBM). For consistency, we calculated the ab initio energy minimized structure for this molecule as well. The SDFF calculation reproduces the ab initio structure quite well. The comparison in Table 10 shows that the bonds deviate from ab initio by about 3 mÅ, except for the central C_t-C_q bond for which the deviation is 7 mÅ. This bond is calculated to be 1.683 Å with SDFF and 1.690 Å with HF/6-31G. Allinger and co-workers obtained 1.725 Å with MM4,[25] but this is probably too long considering that higher levels (MP2) of ab initio generally have given shorter C−C bond lengths than HF. The bond angles are reproduced with an rms deviation of

1.0°. This time the biggest deviation is in one of the C_qC_mH angles, which is off by 2.0° (116.2° compared to 114.2°). However, the most deformed angles, i.e., $C_mC_qC_m$ deviate by only 0.4° from ab initio (102.4° compared to 102.8°). The torsion angles are less deformed in tetra-TBM than in tri-TBM and are reproduced by the SDFF to within 2°. Our calculations agree with MM4[25] in that the methyl groups bend away from the center of the molecule by about 6°, with the skeletal torsion angles twisted by 15° from their intrinsic equilibrium values.

Conclusions

Our implementation of the SDFF approach for developing MM energy functions for macromolecules[1,2] has been applied to branched saturated hydrocarbons with results that are comparable to those achieved for linear hydrocarbons.[6] We have therefore incorporated both types of molecules into a joint SDFF parameter set. The use of this function in MM and MD simulations is now also made somewhat more convenient by use of redundant internal coordinates. The high quality of this energy function is demonstrated by its excellent predictions of structures and vibrational frequencies of molecules not used in the parameter optimization. In particular, our SDFF gives results for isobutane and tri-*tert*-butylmethane that are consistent with ab initio calculations, which is not the case for other MM functions.[19,26]

The number of force constants is fairly large in this SDFF, mainly because the diagonal stretching and bending force constants turned out to depend on the number of hydrogens attached to each carbon atom. However, it is important to note that the speed of MM and MD calculations is not affected by the number of force constants, but by the number of energy terms. For angle−angle interactions, we have shown that the use of proper redundancy constraints helps keep the number of energy terms as small as possible.

The goal of the SDFF methodology is to produce an MM energy function that reproduces with high accuracy ab initio results, including vibrational frequencies. We believe that the latter requirement is the optimum criterion for the accuracy of the MM function. Our method achieves this because it uses a direct mathematical transformation from the (scaled to experimental frequencies) ab initio force field into the MM parameters, thereby avoiding a least-squares-fitting approach to determining the functional form of the energy function.[11] The method also gives direct information about the actual anharmonicities of the potential surface near its minima. The protocol is general for any macromolecular system and is now being implemented for the polypeptide chain.[30]

Acknowledgment. This research was supported by NSF Grants DMR-9627786 and MCB-9601006. Additional support was provided by the Air Force Research Laboratory/Materials & Manufacturing Directorate and by the Common High Performance Software Support Initiative of the Department of Defense High Performance Computing Program.

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