Urey–Bradley Force Field, Valence Force Field, and ab Initio Study of Intramolecular Forces in Tri-*tert*-butylmethane and Isobutane

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Abstract: The relationship between intramolecular forces, molecular geometry, and vibrational frequencies as reflected in tri-*tert*-butylmethane (TTBM) and isobutane was investigated using empirical force field and ab initio calculations. The strong intramolecular forces in TTBM and the resulting large deviations in its physical properties from normal values make it an ideal system for this study. Isobutane, which consists of a *tert*-butyl group, but is not as overcrowded as TTBM, serves as a good model for comparison. Studying TTBM with the more recent Urey-Bradley (UBCFF) and valence (VCFF) consistent force fields pointed to the need for the inclusion of an anharmonic bond stretching potential in both force fields and a stretch–bend interaction term in the VCFF. Ab initio calculations verified the results of the empirical force fields and showed how close nonbonded hydrogen–hydrogen interactions compress the C_m–H_m bond and raise its effective force constant. They also showed how the increased 1–3 geminal interactions induced by closing the H_t–C_t–C_q bond angle stretch the C_t–H_t bond and lower its effective force constant. The modified force fields leave the calculated structures essentially unchanged, but result in dramatic improvement in the vibrational frequencies, particularly in the VCFF. Thus, both shifts toward higher frequencies and lower frequencies due to overcrowding were accounted for to within 10 cm^{-1} or less. The root mean square deviation of the CH stretching frequencies was reduced from 26.7 to 7.9 cm^{-1} in isobutane and from 39.0 to 4.7 cm^{-1} in TTBM.

I. Introduction

The structure of tri-*tert*-butylmethane (TTBM) was determined experimentally by Bürgi and Bartell[1,2] using the method of gas electron diffraction. They also calculated[2] the equilibrium structure of the molecule using the Urey–Bradley consistent force field (UBCFF) developed by Lifson and Warshel[3] and the simpler force field of Jacob, Thompson, and Bartell[4] (JTB). The latter gave better agreement with the experimental values.

As can be seen from the experimental structure,[1] represented in stereo in Figure 1, TTBM is a highly crowded molecule. Six pairs of nonbonded hydrogens are less than 2 Å from one another. The closeness of nonbonded atoms causes strong repulsions which distort the structure of TTBM in a number of ways (in the following C_t, C_q, and C_m denote the tertiary, quaternary, and methyl carbons): (1) The C_t–C_q bond is highly stretched (1.611 Å compared to 1.533 Å in *n*-butane,[5] 1.535 Å in isobutane[6]). (2) The *tert*-butyl and methyl groups are twisted from their staggered conformations, by 11 and 18°, respectively. (3) The C_q–C_t–C_q bond angles are opened (116° compared to 111.5° in cyclohexane,[7] 110.8° in isobutane[6]). (4) The angles between neighboring methyl groups and between neighboring hydrogens of the same methyl group are closed.

Other manifestations of crowding are evidenced in the spectral properties of TTBM. There are three C–H stretching frequencies, at 3000, 3020, and 3038 cm^{-1},[8] which are much higher than usual (e.g., in both *n*-butane and isobutane the highest frequency is 2965 cm^{-1} [9,10]). The frequencies are also distributed over a wider range (170 cm^{-1})[8] than usually found in alkanes.

Since the original presentation of the UBCFF[3] used by Bartell and Bürgi,[2] the consistent force field has been further developed and modified. The UBCFF has been extended to intermolecular interactions, with a significant modification of the representation of nonbonded interactions and other energy functions.[11] Subsequently, the Urey-Bradley force field was replaced by a generalized valence force field (VCFF).[12]

In the present study we used the more recent force fields UBCFF and VCFF. We compared the structure and frequencies of isobutane, which contains one *tert*-butyl group, with those of the highly crowded TTBM. This provided more insight into the effects of the interactions between the different *tert*-butyl groups.

An analysis of the discrepancies between calculated and experimental geometry and vibrational frequencies, guided by ab initio molecular orbital calculations on model compounds, led to two essential modifications. One was the representation of the bond-stretching potential by the anharmonic Morse function in both the UBCFF and VCFF. The other was the introduction of a CH–CCH stretch–bend interaction term in the VCFF. We found that anharmonicity accounted successfully for the dependence of the C–H frequency on the CH equilibrium bond length. Thus, nonbonded repulsions shorten the CH bond and the stretching frequency goes up. On the other hand, the stretch–bend interaction extends the C_t–H_t bond upon the opening of the C_q–C_t–C_q bond angle and thus shifts the frequency down.

The calculated structure of TTBM is capable of giving more details of the results of overcrowding than can be obtained from electron diffraction, in particular the nature of the deviation from local C_3 symmetry of the CH_3 and *tert*-butyl groups. However, the extreme extension of the C_t–C_q bond could be obtained only in part by the VCFF, and not at all by the UBCFF, and introducing a Morse function did not improve the results. On the other hand, the large shifts to higher frequency of the C–H stretching vibrations caused by overcrowding were well accounted for by the introduction of anharmonicity through the Morse potential, while the strong shift to lower frequency of the C_t–H_t stretching vibration was shown to depend upon a combination of the anharmonicity and the 1–3 stretch–bend interactions.

A number of ab initio calculations were carried out on model compounds in order to help understand the causes of the large spread in C–H stretching frequencies in TTBM. They showed how the nonbonded interactions between closely situated methyl hydrogens raised the effective force constants and thus the vibrational stretching frequencies of these compressed bonds. Ab initio calculations also showed that the 1–3 interactions between C_q and H_t atoms are indeed responsible for the stretching of the C_t–H_t bond and for the corresponding low frequency shift of its vibration upon closure of the H_t–C_t–C_q angle. The calculations involved the evaluation of C_t–H_t bond distances and their effective force constants as a function of H–C–C bond angle and molecular environment.

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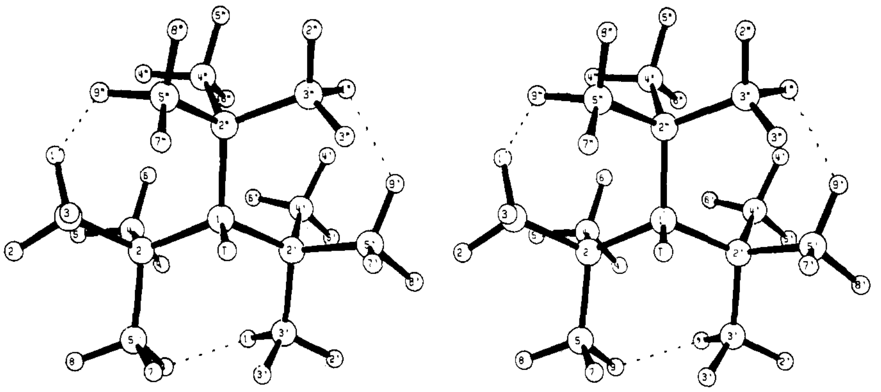


Figure 1. Stereoscopic view showing the atomic numbering of TTBM. Note that atoms *n*, *n*′, and *n*″ are equivalent in the C_3 symmetry structure. The axis of symmetry is along H_t–C_t. Dotted lines indicate the strong nonbonded interactions between the close $H_{9''}$–H_1, H_9–H_1, and $H_{9'}$–$H_{1''}$ pairs of atoms. (Program prepared with program ORTEP, C. K. Johnson, Oak Ridge National Laboratory, June 1965.)

Table I. The Morse Parameters[a] Used in the M-UBCFF

bond	D, kcal mol^{-1}	α, Å^{-1}	b_0, Å
C–C	88.0	1.302 (0.002)	1.482 (0.006)
C_m–H_m	108.6	1.718 (0.003)	1.095 (0.001)
C_t–H_t	106.7	1.679 (0.003)	1.087 (0.003)

[a] The standard deviation of optimized parameters is given in parentheses.

II. Method

A model force field is a set of energy functions of internal coordinates and interatomic distances that may be used to calculate the various properties of molecules. The molecular equilibrium conformation is calculated from the force field by minimizing the total energy of the molecule as a function of its atomic coordinates. The normal modes of vibration of the molecule are derived by calculating the eigenvalues and eigenvectors of the matrix of second derivatives of the energy of the molecule at its calculated equilibrium conformation. The UBCFF[11] was derived by a least-squares optimization over thermodynamic, structural, and spectral data of normal and cyclic (but not branched) alkanes. The VCFF[12] included alkenes as well as alkanes. For further details see ref 11 and 12.

In the modified UBCFF (M-UBCFF), the parameters α and b_0 of the Morse potential, $D[1 - e^{-\alpha(b-b_0)}]^2 - D$, were optimized using a linearized least-squares method[13] to achieve the best fit between calculated and experimental quantities, and the values of D were taken from bond dissociation energies.[14] The remainder of the parameters were taken directly from the UBCFF of Warshel and Lifson.[11] The resultant parameters are listed in Table I.

In the modified VCFF (M-VCFF) the parameters α and b_0 of the Morse potential were chosen such that the second derivative of the Morse potential at its minimum point b_0 was equal to the second derivative of the harmonic potential, i.e., $2D\alpha^2 = K_b$; D was again taken from experiment.[14] The VCFF Morse potential of C_t–H_t was equal to that of C_m–H_m. The reasons for this are given in the Discussion.

The final form of the valence force field used here is given in eq 1.

$$\begin{aligned} V = {} & \sum\{D_b[1 - e^{-\alpha_b(b-b_0)}]^2 - D_b\} \\ & + \tfrac{1}{2}\sum H_\theta(\theta - \theta_0)^2 + \tfrac{1}{2}\sum H_\phi\,(1 + s\cos n\phi) \\ & + \sum\sum F_{bb'}\,(b - b_0)\,(b' - b_0') + \sum\sum F_{\theta\theta'}\,(\theta - \theta_0) \\ & \times (\theta' - \theta_0') + \sum\sum F_{b\theta}\,(b - b_0)(\theta - \theta_0) + \sum\sum f_{\theta\theta'} \\ & \times \cos\phi(\theta - \theta_0)(\theta' - \theta_0') + \sum\epsilon[2(r^*/r)^9 - 3(r^*/r)^6] \end{aligned} \quad (1)$$

Table II, adapted from ref 12, defines the potential energy parameters in the M-VCFF (as well as the harmonic stretching terms) in graphical form, and gives their values.

III. Results and Discussion

Structural Aspects. The results of the original and modified force field calculations on the structure of isobutane are presented in Table III together with the experimental results.[6]

These results serve as a test of the force fields as no molecules with tertiary carbons were included in the data set used to derive the force fields.

The results of the calculations on the structure of TTBM along with the experimental results[1] are given in Table IV. The agreement between the force field calculations and the electron diffraction experiments is not as good as in isobutane. However, the experiment could not yield the detailed structure and some, although not all, of the deviations may result from the fact that the calculations are more accurate than the experiment. The electron diffraction data were analyzed with the assumption that the methyl groups possessed local C_3 symmetry and that all C_q–C_m bonds were equivalent, whereas calculation of the molecular structure using any of the force fields UBCFF, VCFF, or JTB indicates that TTBM has only overall C_3 symmetry (i.e., equivalence of the three *tert*-butyl groups), and that, in fact, the overcrowding of the molecule imposes a different distortion on each of the various internal coordinates *within* a *tert*-butyl group. For example, all the force fields (including JTB[2]) indicate that C_2–C_5 is the longest and C_2–C_4 is the shortest among the C_q–C_m bonds (see Figure 1 for identification of bonds), thus reflecting the different environments of these three distinct bonds. Similarly, all the force fields predict that the three methyl torsion angles are quite different, the average absolute deviations from staggered positions being about 10, 5, and 22°, respectively (see Table IV), while the analysis of the electron diffraction yielded a single value of 18°. In addition, all five force fields referred to, as well as three others,[15] predict that the three H_t–C_t–C_q–C_m torsion angles will have an average deviation from staggered position of about 15°, whereas the experimental electron diffraction value is about 11° or, using alternative assumptions in the least-squares refinement, about 20° (Table III of ref 2).

One of the most outstanding results of the overcrowding is the large stretching of the C_t–C_q bond to 1.611 Å, as compared to the unstrained value of 1.53–1.54 Å. This result of the electron diffraction is supported by the recent X-ray structure of the TTBM derivative, tri-*tert*-butylmethyl *p*-nitrobenzoate, in which the three C_t–C_q bond lengths have values of 1.64, 1.61, and 1.61 Å, respectively.[16] It has been suggested by Bartell and Bürgi that the lack of anharmonicity in the UBCFF bond stretching potential may be the cause for the low value of the calculated stretching. To our surprise, the modification of the force field by the use of a Morse function for bond stretching resulted in a minor increase of 0.006 Å of the C_t-C_q bond length in the M-VCFF, and a similar *decrease* in the M-UBCFF. In order to understand the underlying forces responsible for the stretching we have partitioned the force acting along the C_t-C_q bond at the equilibrium geometry of the unmodified force field into its various terms. The corresponding quantities are also calculated for the C_t-H_t bond in order to compare the mechanism of stretching of these two bonds. These results are presented in Table V.

As is seen from the table, the large positive force along the C_t-C_q bond resulting in its elongation is due solely to the nonbonded repulsions, as expected from the overcrowding. It is opposed by essentially two terms: the bond stretching potential and the 1-3 interactions ($F_{\text{stretch bend}}$ in VCFF and $F_{\text{Urey-Bradley}}$ in UBCFF), the former of which constitutes only ~60% in the VCFF, while the latter is predominant in the UBCFF. Thus from consideration of the contributions to the total force it follows that the discrepancy between the observed and calculated bond length may be due either to an underestimate of the nonbonded repulsion or to an overestimate of the 1-3 interactions.[17]

The linear dependence of the bend-stretch term on θ (which arises from a Taylor expansion truncated at second order) may break down at large deviations of θ. On the other hand, as suggested by Bartell and Bürgi,[2] there is some indication that the nonbonded interactions may be too soft. A computer experiment in which the "6-9" nonbonded function of the VCFF was replaced by a "6-12" potential derived from fitting the intermolecular properties of crystals[18] was carried out. In the minimized structure of TTBM which resulted from this experiment, the C_t-C_q bond length was 1.645 Å. (The C_q-C_m bonds were stretched by only ~0.02 Å.) This indicates the possibility of reconciling the deviation in C_t-C_q bond length with a reasonable nonbonded potential (without introducing errors in the C_q-C_m bonds), and the desirability of reexamining the entire set of molecules treated previously, together with additional strained molecules and crystal properties.

Finally, the stretching of C_t-H_t as well as the spread of C-H distances in TTBM also belongs to this discussion on structural aspects. However, the experimental data are scarce, and these structural properties are intimately related to the vibrational properties of TTBM and isobutane. Thus, they will be discussed below in relation to the vibrational frequencies.

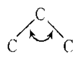
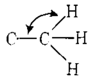
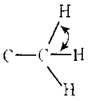
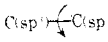
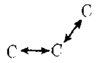
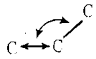
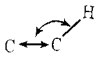
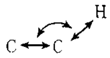
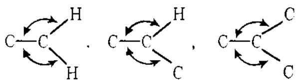
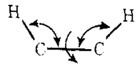
C-H Stretching Vibrational Modes. The effect of overcrowding on the C-H stretching frequencies of TTBM may be clearly observed in Table VI. The spread in the experimental frequencies is 170 cm^{-1} (from 3038 to 2868 cm^{-1}). Bartell and Bürgi[2] attributed the wide range to the possibility that, in more crowded molecules such as TTBM, bonds differ significantly in effective force constants from site to site owing to stresses on these bonds caused by the local intramolecular environment. The C-H stretching frequencies of isobutane are given for comparison in Table VII. In this case, the spread is only 86 cm^{-1} (from 2965 to 2879 cm^{-1}).

It is seen from Tables VI and VII that the Morse potential improves the calculated C-H stretching frequencies significantly in both isobutane and TTBM. Furthermore, it accounts for both the high-frequency and low-frequency shifts in TTBM as compared to isobutane. This remarkable feature deserves a detailed analysis.

High-Frequency Shift of the C_m-H_m Stretching Modes. The effective force constant of the Morse potential, $\partial^2 V_m/\partial b^2$, depends on b, increasing as b decreases in the range of interest. Therefore, those C_m-H_m bonds which are compressed by the strong nonbonded repulsions in TTBM are shifted to higher stretching frequencies.

In order to understand what are the underlying forces responsible for these shifts to higher frequency in TTBM, an analysis was made of the contributions to the force along the shortest C_m-H_m bond (C_5-H_9) in the M-UBCFF and the M-VCFF and the result is given in Table VIII. The results show that in both force fields the bond is compressed primarily by the nonbonded forces. In Table IX, the contribution of each energy term in the force field to the diagonal second derivative $\partial^2 V/\partial b^2$ (i.e., the effective force constant) is given. The table shows how compression of the bond from its average value by nonbonded forces results in raising the effective bond-stretching force constant in the anharmonic force field (and thereby the value of the C-H stretch frequency) over the corresponding value in the harmonic force field.

Table II. Optimized Force Field Parameters[a] Defined in Graphical Form

	I. Diagonal Terms	
	bond stretch (Morse potential)	
D_R, b_{0R}, α_R	C↔C	88., 1.526, 1.915
D_r, b_{0r}, α_r	C↔H	108.6, 1.105, 1.771
	bond stretch (harmonic)	
K_R, b_{0R}	C↔C	645.3 (10.9), 1.526 (0.003)
K_r, b_{0r}	C↔H	681.5 (2.4), 1.105 (0.003)
	angle bend	
H_ω, ω_0		93.2 (5.1), 110.5 (0.2)
$H_\beta, [\beta_0]$		88.8 (1.1), (112.4)
H_α, α_0		79.0 (0.9), 106.4 (0.6)
	torsion	
$H_{\phi R}$		2.845 (0.122)
	II. Cross Terms	
F_{RR}		28.5 (7.3)
$F_{R\omega}$		60.2 (6.0)
$F_{R\gamma}$		38.4 (2.0)
$F_{r\gamma}$[b]	(i) 	12.6
$F_{\gamma\gamma}$		−7.9 (1.1)
$f_{\gamma\omega}$		−10.5 (1.4)
	III. Nonbonded Interactions	
r^*HH	H···H	3.632 (0.032)
ϵ_{HH}		0.004 11 (0.000 42)
r^*CC		3.518 (0.041)
ϵ_{CC}	C···C	0.1658 (0.0262)

[a] Units of the potential constants are kcal mol^{-1}, Å, and rad for energies, lengths, and angles, respectively. Reference lengths and angles are given in Å and deg, α_R and α_r in Å^{-1}. Dependent reference angles are given in square brackets; standard deviations are given in parentheses. See ref 12 for further details. [b] This cross term was not included in the VCFF, but, as discussed below, was subsequently found to be very effective when the anharmonic bond stretching function was introduced.

Table III. Calculated and Experimental Isobutane Structures[a]

parameters	exptl[b]	UBCFF	M-UBCFF	VCFF	M-VCFF
$b(C_t-C_m)$	1.535 ± 0.001	1.523	1.527	1.540	1.542
$\bar{b}(C_m-H_m)$[c]	1.113 ± 0.002	1.106	1.099	1.106	1.106
$b(C_t-H_t)$	1.122 ± 0.006	1.115	1.103	1.107	1.110
$\alpha(C_m-C_t-C_m)$	110.8 ± 0.2	109.0	108.8	109.2	109.2
$\gamma(H_t-C_t-C_m)$	108.1 ± 0.2	109.9	110.2	109.7	109.7
$\beta(C_t-C_m-H_m)$	110.1 ± 0.3	111.1	111.1	113.2	113.2
$\beta(C_t-C_m-H_{m'})$[c]	111.4 ± 0.4	110.8	110.9	112.5	112.5
$\delta(H_m-C_m-H_{m'})$	106.5 ± 1.7	108.1	108.0	106.1	106.1
$\delta(H_{m'}-C_m-H_{m''})$	108.7 ± 1.1	107.9	107.9	105.8	105.8

[a] Units: lengths in Å, angles in deg. t = tertiary, m = methyl. [b] From ref 6. [c] Both experiment and calculation showed that the methyl has a plane of symmetry through $C_t-C_m-H_m$ so that $H_{m''}$ is equivalent to $H_{m'}$.

Table IV. Calculated and Experimental Structure[a] of TTBM

parameters[b]	exptl[c]	UBCFF	M-UBCFF	VCFF	M-VCFF
$\bar{b}(C-H)$	1.111 (0.003)	1.103	1.096	1.104	1.104
$b(C_t-H_t)$		1.125	1.116	1.106	1.114
$\bar{b}(C_m-H_m)$		1.101	1.093	1.104	1.103
C_3-H_1		1.098	1.091	1.101	1.100
C_3-H_2		1.103	1.096	1.107	1.107
C_3-H_3		1.102	1.095	1.106	1.106
C_4-H_4		1.100	1.093	1.101	1.100
C_4-H_5		1.106	1.099	1.106	1.107
C_4-H_6		1.099	1.092	1.102	1.102
C_5-H_7		1.102	1.095	1.106	1.106
C_5-H_8		1.102	1.095	1.106	1.106
C_5-H_9		1.092	1.085	1.099	1.098
$\underline{b}(C_t-C_q)$	1.611 (0.005)	1.544	1.538	1.572	1.578
$\bar{b}(C_q-C_m)$	1.548 (0.002)	1.539	1.542	1.557	1.559
C_2-C_3		1.542	1.546	1.562	1.566
C_2-C_4		1.522	1.526	1.539	1.538
C_2-C_5		1.552	1.555	1.569	1.574
$\alpha(H_t-C_t-C_q)$	101.6 (0.4)	103.5	103.5	104.2	104.2
$\underline{\delta}(C_q-C_t-C_{q'})$[d]	116.0 (0.4)	114.8	114.7	114.2	114.2
$\bar{\beta}(C_t-C_q-C_m)$	113.0 (0.2)	115.0	115.2	114.1	114.1
$C_1-C_2-C_3$		115.6	115.8	114.2	114.0
$C_1-C_2-C_4$		116.9	117.0	116.9	116.9
$C_1-C_2-C_5$		112.6	112.8	111.3	111.2
$\bar{\epsilon}(C_m-C_q-C_{m'})$[e]	105.8 (0.2)	103.3	103.1	104.3	104.4
$C_3-C_2-C_4$		104.1	103.9	105.2	105.4
$C_3-C_2-C_5$		99.9	99.7	99.4	99.4
$C_4-C_2-C_5$		105.9	105.7	108.2	108.3
$\bar{\gamma}(C_q-C_m-H_m)$	114.2 (1.0)	111.6	111.6	113.9	113.9
$C_2-C_3-H_1$		111.6	111.6	115.6	115.7
$C_2-C_3-H_2$		110.9	110.9	111.8	111.7
$C_2-C_3-H_3$		111.3	111.3	113.6	113.5
$C_2-C_3-H_4$		112.0	112.0	115.6	115.6
$C_2-C_3-H_5$		110.5	110.5	111.6	111.6
$C_2-C_3-H_6$		112.5	112.5	114.7	114.7
$C_2-C_3-H_7$		110.6	110.7	113.4	113.3
$C_2-C_3-H_8$		111.1	111.2	112.5	112.4
$\underline{C_2}-C_3-H_9$		113.6	113.6	116.5	116.5
$\overline{\Delta\tau}(H_t-C_t-C_q-C_m)$[f]	10.8 (0.5)	13.7	13.7	16.4	16.4
$(H_t-C_1-C_2-C_3)$		10.6	10.7	12.5	12.3
$(H_t-C_1-C_2-C_4)$		13.7	13.8	15.8	15.9
$(\underline{H_t}-C_1-C_2-C_5)$		16.7	16.7	20.9	21.0
$\overline{\Delta\tau}(C_t-C_q-C_m-H_m)$[f]	18.0 (6.0)	13.2	12.9	11.5	11.4
$(C_1-C_2-C_3-H_1)$		13.1	12.9	11.6	11.6
$(C_1-C_2-C_3-H_2)$		10.0	9.2	7.7	7.9
$(C_1-C_2-C_3-H_3)$		9.5	9.3	5.5	5.7
$(C_1-C_2-C_4-H_4)$		7.2	7.0	6.3	6.2
$(C_1-C_2-C_4-H_5)$		5.7	5.5	4.4	4.3
$(C_1-C_2-C_4-H_6)$		5.7	5.5	3.3	3.2
$(C_1-C_2-C_5-H_7)$		−21.2	−21.1	−19.7	−19.4
$(C_1-C_2-C_5-H_8)$		−21.9	−21.8	−20.9	−20.6
$(C_1-C_2-C_5-H_9)$		−24.3	−24.1	−24.1	−23.8

[a] Units: lengths in Å, angles in deg. [b] See Figure 1 for the numbering of parameters. t = tertiary, q = quaternary, m = methyl. [c] From ref 1, with estimated errors in parentheses. Since the experimental model assumed local C_3 symmetry for *tert*-butyl and methyl groups, the appropriate calculated values are averaged to facilitate comparison (cf. discussion in text). [d] The angle δ is dependent upon α, but is included for convenience. [e] The angle ϵ is dependent upon β, but is included for convenience. [f] $\tau = \Delta\tau + 60, +180, -60$.

Table V. Force (kcal mol^{-1} $Å^{-1}$) along the C_t-C_q and C_t-H_t Bonds at the Equilibrium UBCFF and VCFF Geometries. Effect of Anharmonicity

bond	equilibrium coordinates	force field	F_{total}	$F_{stretch}$	$F_{nonbond}$	F_{elec}	$F_{Urey\text{-}Bradley}$	$F_{stretch\text{-}stretch}$	$F_{stretch\text{-}bend}$
C_t-C_q	VCFF	VCFF	0	−29.9	+49.1			−5.3	−13.9
C_t-C_q	VCFF	M-VCFF[a]	+3.7	−26.2	+49.1			−5.3	−13.9
C_t-C_q	UBCFF	UBCFF	0	−11.9	+53.3	−1.3	−40.1		
C_t-C_q	UBCFF	M-UBCFF	−4.4	−16.3	+53.3	−1.3	−40.1		
C_t-H_t	VCFF	VCFF	0	−0.8	+0.8				
C_t-H_t	VCFF	M-VCFF[a]	0	−0.8	+0.8				
C_t-H_t	UBCFF	UBCFF	0	−14.5	+1.3	−2.6	+15.8		
C_t-H_t	UBCFF	M-UBCFF	−6.6	−21.1	+1.3	−2.6	+15.8		

[a] The force here is calculated without the inclusion of cross term i (see Table II).

Table VI. Calculated and Experimental Frequencies (cm^{-1}) of Tri-*tert*-butylmethane

	calcd[b]				
exptl[a]	UBCFF	M-UBCFF	VCFF	M-VCFF[c]	M-VCFF[d]
3038	2983	3052	2999	3027	3028
3020	2973	3009	2986	3017	3018
3000	2970	3005	2983	3003	3002
	2967	2985	2979	2987	2984
	2964	2982	2977	2969	2963
2960	2956	2975	2968	2963	2958
2910	2906	2926	2898	2903	2908
	2902	2915	2891	2890	2897
	2893	2911	2884	2884	2890
2868[e]	2933	2833	2945	2936	2864
rmsd[f]	41.6	18.5	39.0	28.3	4.7

[a] Reference 8. [b] Only the nondegenerate frequencies are given. For the most part, the corresponding degenerate frequencies are within 1 or 2 cm^{-1} of these, the largest difference being 5 cm^{-1}. [c] The M-VCFF without the proposed stretch-bend cross term $F_{r\gamma}$ (see text and cross term i in Table II). [d] The complete M-VCFF, including the stretch-bend cross term $F_{r\gamma}$. [e] This frequency has been assigned in ref 8 to be a pure C_t-H_t stretching mode. Therefore, it is compared with the corresponding pure C_t-H_t stretching mode determined by each force field. [f] Root mean square deviation between the experimental and the nearest calculated frequencies.

Ab Initio Calculation of the Relationship between Nonbonded Strain and Frequency Shifts in C–H Bonds. In order to verify that such a nonbonded compression can indeed lead to a shift to higher frequencies, a simulation of this effect has been carried out using ab initio molecular orbital calculations. Using the GAUSSIAN 70 program[19] with an extended 4-31G basis set,[20] the energy of an isolated methane molecule was minimized with respect to C–H bond length, and the effective force constant of this unperturbed C–H bond was determined. The calculation was carried out again using two methane molecules, separated by an $H_3CH \cdots HCH_3$ distance of 1.94 Å, the distance between the C_3–H_1 and $H_{9''}$–$C_{5''}$ methyl hydrogens in TTBM, i.e., the closest nonbonded $H \cdots H$ distance. (In this calculation, $C–H \cdots H–C$ was collinear, and the two CH_3 groups were eclipsed when viewed along this line.) The energy was minimized about the optimized methane C–H bond distance, and the effective force constant evaluated. The frequencies were obtained from the relationship $\nu = (2\pi)^{-1}(K_f/\mu)^{1/2}$ after the force constants were scaled by the factor of 0.83 as suggested by Blom et al.[21] to account for the intrinsic error in the relative 4-31G ab initio energies and geometries, and the quadratic function from which the force constants are determined. The results, presented in Table X, show that the compression of the C–H bond resulting from the nonbonded force upon it from another C–H group indeed raises the frequency significantly.

Low-Frequency Shift of the C_t–H_t Stretching Mode. The C_t–H_t stretching frequency showed different behavior than that of C_m–H_m. It is 36 cm^{-1} lower in TTBM than in isobutane. In the UBCFF, the frequency is shifted down upon introduction of the Morse potential by 100 cm^{-1}, overshooting

Table VII. Calculated and Experimental Frequencies (cm^{-1}) of Isobutane

exptl[a]		calcd			
		UBCFF	M-UBCFF	VCFF	M-VCFF
A1	2965	2994	2980	2983	2968
	2904[b]	2956	2944	2954	2909
	2879	2891	2884	2883	2881
	1468	1473	1482	1467	1466
	1389	1405	1415	1404	1396
	1189	1150	1160	1175	1173
	796	867	884	832	801
	433	447	448	437	437
A2		2963	2956	2977	2964
		1459	1469	1446	1445
		972	975	1002	1003
		214	216	229	239
E	2958	2968	2960	2982	2968
	2951	2966	2959	2980	2966
	2879	2895	2888	2884	2882
	1475	1470	1479	1465	1463
	1459	1464	1473	1448	1447
	1365	1420	1429	1399	1393
	1330	1302	1313	1314	1302
	961	964	971	985	981
	913	891	908	937	912
	367	377	379	355	354
		241	242	262	262
rmsd					
C–H stretch		26.7	18.3	26.7	7.9
all the rest		34.4	35.2	19.0	15.6
total		32.3	30.9	21.7	13.8

[a] Reference 10. [b] C_t–H_t stretch.

Table VIII. Force (kcal mol^{-1} $Å^{-1}$) along the C_5–H_9 Bond at Equilibrium. Effect of Anharmonicity

force field	Δb, Å[a]	F_{total}[b]	$F_{stretch}$	$F_{nonbond}$	F_{elec}	$F_{Urey\text{-}Bradley}$
M-UBCFF	−0.009	0	6.17	−3.50	−1.00	−1.67
M-VCFF	−0.006	0	3.80	−3.80		

[a] Δb is defined as $b(C_5\text{–}H_9) - b_0(C_m\text{–}H_m)$ (see Tables I and II). [b] The total force along the bond is zero at the equilibrium conformation. $F = -\partial V/\partial b$, $F_{bond} = -\partial V_{bond}/\partial b$, etc.

Table IX. Contribution of Each Energy Term to the Effective Force Constant (kcal mol^{-1} $Å^{-2}$) of the C_5–H_9 Bond

force field	DDV_{total}[b]	$DDV_{stretch}$	$DDV_{nonbond}$	DDV_{elec}	$DDV_{Urey\text{-}Bradley}$
UBCFF	694.3	621.3	6.8	0.1	66.1
M-UBCFF	734.3	661.6	6.8	0.2	65.7
VCFF	686.9	681.5	5.4		
M-VCFF[b]	707.3	701.8	5.5		

[a] $DDV = \partial^2 V/\partial b^2$, $DDV_{stretch} = \partial^2 V_{stretch}/\partial b^2$, etc. [b] DDV is calculated here without the inclusion of cross term i (see Table II).

Table X. Ab Initio Calculation of the Effect of Nonbonded Interactions on Frequency[a]

system	$b(C_m\text{–}H_m)$	H···H	K_f(calcd)	K_f(scaled)	ν
CH_4	1.081		846.1	702.2	2983
$H_3CH\cdots HCH_3$[b]	1.075	1.94	860.9	714.5	3009
$H_3CH\cdots HCH_3$[c]	1.075	1.94	874.5	725.8	3033

[a] Units: lengths and distances in Å, force constants in kcal mol^{-1} $Å^{-2}$, frequencies in cm^{-1}. [b] The force constant was determined by varying only one C–H bond length. [c] The force constant was determined by varying both the interacting C–H bond lengths symmetrically.

Table XI. Contribution of Energy Terms to the Effective C_t–H_t Force Constant[a]

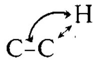
force field	frequency	DDV_{total}[b]	$DDV_{stretch}$	$DDV_{nonbond}$	DDV_{elec}	$DDV_{Urey\text{-}Bradley}$
UBCFF	2933	691.5	572.7[c]	−0.4	−0.1	119.3
M-UBCFF	2833	645.4	527.6	−0.4	−0.1	118.3
VCFF	2945	680.6	681.5	−0.9		
M-VCFF[d]	2936	676.5	677.4	−0.9		

[a] Units: frequency in cm^{-1}, force constant in kcal mol^{-1} $Å^{-2}$. [b] $DDV = \partial^2 V/\partial b^2$, $DDV_{stretch} = \partial^2 V_{stretch}/\partial b^2$, etc. [c] The harmonic force constant for the tertiary C–H bond C_t–H_t was assumed to be the same as that for the secondary C–H bond in ref 11. [d] DDV is calculated here without inclusion of cross term i (see Table II).

the experimental value by 35 cm^{-1}. But introduction of anharmonicity into the bond stretching potential of the VCFF leaves the C_t–H_t stretching frequency essentially unaffected. The underlying molecular forces responsible for this remarkable difference between the two anharmonic force fields were revealed through analysis of the force along the C_t–H_t bond (Table V) and of its effective force constant $\partial^2 V/\partial b^2$ (Table XI).

As seen from Table V, there is a significant contribution from the Urey-Bradley 1-3 term tending to stretch the C_t–H_t bond, and indeed $b(C_t\text{–}H_t)$ as calculated by UBCFF is the largest C–H bond in Table IV. The effective stretching force constant of the Morse potential decreases when the C_t–H_t bond is extended, just as it increases when the C_m–H_m bond is compressed. As is seen in Table XI, this is due solely to the anharmonic Morse term $DDV_{stretch}$, which decreases from 572.7 in the UBCFF to 527.6 in the M-UBCFF while $DDV_{Urey\text{-}Bradley}$ is unaffected. Thus, the decrease in frequency in the UBCFF upon introducing anharmonicity is due to a combination of the 1-3 "$C_q \cdots H_t$" repulsive interactions which stretch the C_t–H_t bond, and the anharmonicity which results in a lower effective force constant for the stretched bond.

Now the reason for the absence of a shift in this bond on introducing anharmonicity in the VCFF becomes clear. There is no analogous 1–3 interaction correlating the C_t–H_t bond length with the C_q–C_t–H_t angle. Thus, the bond is only slightly stretched (Table V), and therefore the effective force constants and consequently the frequencies are almost the same in the VCFF and Morse modified VCFF (Table XI). This phenomenon has implications for the significance of the experimentally determined C_t–H_t bond length, the nature of the coupling between bond lengths and angles, and the need for an additional term in the VCFF force field to account for this coupling. With regard to the latter, it is of interest to note that a



(i)

cross term was not included in the VCFF. Califano points out[22] that all cross terms involving a stretching of the C–H bond may usually be neglected, but that this approximation is by no means justified a priori.[23] Indeed, the above analysis shows that such a cross term can be quite important when coupled with an anharmonic stretching potential like the Morse potential.

Such a term was, therefore, introduced into the M-VCFF, involving a single additional constant ($F_{r\gamma}$ in Table II). The results are seen by comparing the two last columns of Table VI, and also by inspection of the isobutane frequencies in Table VII. It is seen that the combination of the Morse and stretch bend potentials produced the best fit to vibrational frequencies.

We have found that *no* harmonic force constant can simultaneously account for the C_t–H_t frequencies in both isobutane and TTBM, even if introduced especially for that mode of vibration. The best fit simply lowers both frequencies by

Table XII. Ab Initio Calculation of the Effect of 1-3 Interactions on Frequency[a]

molecule	$b(C_t-C_q)$	$\theta(H_t-C_t-C_q)$	$b(C_t-H_t)$	K_f(calcd)	K_f(scaled)	ν
isobutane	1.535	108.1	1.086	802.5	666.0	2906
isobutane	1.611	101.6	1.091	768.8	638.1	2844
triethynylmethane[b]	1.535	108.1	1.082	834.9	693.0	2964
triethynylmethane	1.611	101.6	1.085	816.2	677.4	2930

[a] Units: lengths in Å, angles in deg, force constants in kcal mol^{-1} Å^{-2}, frequencies in cm^{-1}. [b] b(C≡C) = 1.204 Å, b(≡C—H) = 1.056 Å.

about the same amount. Only when anharmonicity and the C-C-H cross terms were taken into account did a *single* bond stretching force constant account correctly for the properties of primary and tertiary C-H bonds, as well as for the difference between isobutane and TTBM, as noted above. In addition, as shown in Table VII, the other M-VCFF calculated frequencies in isobutane are brought into better agreement with experiment. Thus, the new modified anharmonic valence force field (M-VCFF) seems to give better insight into the nature of the C-H bonds and their interactions than the previous force fields. Specifically, it would appear that the use of different force constants for similar bonds such as different C-H groups may have masked the effects of bond-stretching anharmonicity and stretch-bend interaction, and thus this approximation fails when the environment of the bond is changed significantly. Further support for this conclusion is given both by the ab initio calculations on ethane by Bartell et al.[23] which show that the CH-CCH stretch-bend cross term seems to have a significant nonzero value, and by the ab initio "computer experiments" described below which we carried out on isobutane.

Ab Initio Calculation of the Coupling between C-C-H Angle Bending and the C-H Stretching Frequency. In order to further support the proposal that it is indeed the variation in the 1-3 interaction on closing the C-C-H angle that stretches the C_t-H_t bond, thus lowering the frequency, as opposed to another mechanism, for example, the nonbonded forces as is the case for the C_t-C_q bond, or different harmonic force constants, several ab initio molecular orbital calculations were carried out. We used the same basis set and followed the same procedure as described above.

The first experiment was the calculation of the energy of isobutane as a function of C_t-H_t bond lengths, keeping all other internal coordinates at their experimental values.[6] The results are presented in the first row of Table XII. The minimum energy was found at a C_t-H_t bond length of 1.086 Å and the effective force constant was found to be 802.5 kcal mol^{-1} Å^{-2}. The corresponding stretching frequency of 2906 cm^{-1} is in excellent agreement with the experimental value of 2904 cm^{-1} for C_t-H_t in isobutane. The calculation was repeated using the experimental coordinates of TTBM for the C_t-C_q bond length (1.611 instead of 1.535 Å), and the H_t-C_t-C_q angle (101.6 instead of 108.1°). The results are given in the second row of Table XII. This experiment shows that closing the H_t-C_t-C_q angle will cause the C_t-H_t bond to stretch even without the other strong nonbonded interactions that exist in TTBM. In addition, the molecular orbital calculations indicate that stretching this bond will reduce the effective force constant and thus the vibrational frequency of this mode, in agreement with the conclusions drawn from the force field calculations.

To further check whether the stretching of the C_t-H_t bond may be caused by the 1-3 interaction between H_t and C_q even in the absence of nonbonded repulsion of the methyl hydrogens, an additional computer experiment was carried out with the hypothetical molecule triethynylmethane, $(HC{\equiv}C)_3CH$, which has no close nonbonded atoms. The C_t-C_q bond length and C_q-C_t-H_t bond angle were taken to be the same as in the first and second rows of Table XII. The results are given in the third and fourth rows, respectively. This experiment shows that the stretching of the bond is indeed effected by the 1-3 "$C_q \cdot\cdot\cdot H_t$" interactions which can be represented by the cross term $\sum K_{b\theta}(b - b_0)(\theta - \theta_0)$. Closing the bond angle H_t-C_t-C_q causes the C_t-H_t bond to stretch and, for an anharmonic potential, decreases its effective force constant, thus lowering its vibrational frequency.

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