Structure of Tri-*tert*-butylmethane. II. Inferences Combining Electron Diffraction, Spectroscopy, and Molecular Mechanics[1]

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Abstract: A synergistic interaction of gas-phase electron diffraction, vibrational spectroscopy, and molecular mechanics has led to both a detailed structure of tri-*tert*-butylmethane and suggestions for improvements in model force fields. Of the two model force fields studied (Lifson and Warshel [CFF3] and Jacob, Thompson, and Bartell [JTB]), the crude unoptimized JTB field gave a better account of the structure of tri-*tert*-butylmethane than the highly optimized CFF3, apparently because the nonbonded interaction functions of the JTB field are more appropriate for the range of nonbonded distances present in this molecule. Evidence is presented that molecular mechanics calculations for strained hydrocarbons can be improved by including bond anharmonicity, neglected in the CFF3 and JTB fields. A simple formula is developed to correct bond lengths derived from harmonic bond potentials for effects of anharmonicity. A new scheme is introduced for interrelating C–H bond lengths and bond stretching frequencies. It indicates a methine C–H mean bond length (r_g) of 1.13 Å and a distribution of methyl C–H bond lengths from about 1.104 to 1.118 Å. The shortest C–H bond suffers strong repulsive interactions with each of two neighboring methyl groups sitting on an adjacent *tert*-butyl group (H···H distances slightly less than 2 Å). Methyl C–C–H bond angles are distributed over a range of 3°. *tert*-Butyl groups are rotated approximately 16° from staggered conformations. The clearest evidence of stress is found in the very low H_t–C_1–C_2 bond angle of 101.6 (0.4)° and in the remarkably long bond length C_1–C_2 of 1.611 (5) Å. The other C–C bond lengths are slightly long at 1.538, 1.548, and 1.558 Å. Calculations based on the JTB field, neglecting vibrational effects, suggested an isomerization energy (from n-$C_{13}H_{28}$ to $[(CH_3)_3C]_3CH$) of 33.5 kcal/mol and an activation energy for racemization of 16.0 kcal/mol. The nmr methine ^{13}C–H coupling constant (124 Hz) reported by Stiles and Lee is much higher than the value predicted by conventional hybridization models on the basis of the observed H_t–C_1–C_2 bond angle. Whether this result can be ascribed to bent bonds or to serious flaws in current interpretations of coupling constants is a question for further investigation.

Tri-*tert*-butylmethane, a saturated hydrocarbon molecule, is noteworthy because of the great intramolecular congestion arising from the packing of three bulky *tert*-butyl groups around a common tertiary carbon atom. Curiously, the manifestations of the anticipated overcrowding are not conspicuous in the available spectral properties of the molecule which appear to be, with one exception, quite normal.[2] The proton nmr spectrum shows singlets at 1.22 and 1.38 ppm with relative intensities 27 to 1. The carbon-13–methine proton coupling constant of 124 Hz is the same as that found for unstrained "sp^3-hybridized" C–H bonds. Three of the C–H-stretching frequencies, however, are quite high, at 3000, 3020, and 3038 cm^{-1}. Similar frequencies were observed previously in tri-*tert*-butylcarbinol.[3] It was hoped that a determination of the structure of tri-*tert*-butylmethane would lead to an explanation of the unusual vibrational spectrum and, more importantly, to an improved understanding of crowded molecules.

In paper I[4] the results of an electron diffraction study of tri-*tert*-butylmethane are described. Because of the complexity of the molecule, severe constraints on the parameters had to be introduced and the resulting molecular model does not account for all details of the experimental diffraction data. A further least-squares refinement with some of the constraints relaxed appeared to be feasible. Nevertheless, there are serious pitfalls in electron diffraction analyses carried out by exhaustive scanning in a multidimensional space of structural parameters as complex as that for tri-*tert*-butylmethane. Several slightly different molecular models may be expected to give comparably good fits between experimental and calculated diffraction intensities. The computer time for such an analysis is considerable and the inadequate discrimination between alternative solutions makes it desirable to use other sources of information. One possibility, as shown below, is to interpret the observed C–H frequencies of tri-*tert*-butylmethane in terms of the deformations of the various C–H bonds. Although this scheme cannot establish which bonds are the short ones and which are long, it adds to the information provided by electron diffraction, which yields only the average over all the bond lengths. Another possibility is to extrapolate to the present case the spectroscopic, thermodynamic, and structural information derived from other hydrocarbons and summarized in model force fields. Calculations based on such model force fields are known as "molecular mechanics."[5] Such calculations afford, in principle, the most detailed picture for they pinpoint exactly which of the bonds are short, which are long, and by how much. However, since the existing force field recipes were not constructed by a method known to assure reliable results for tri-*tert*-butylmethane, the results must be carefully checked for consistency with the infrared and diffraction results.

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(1) This work was supported in part by a grant from the National Science Foundation.

(2) H. Lee, Thesis, The University of Michigan, 1971. H. Lee and M. Stiles, manuscript in preparation.

(3) P. D. Bartlet and R. M. Stiles, *J. Amer. Chem. Soc.*, 77, 2806 (1955).

(4) H. B. Burgi and L. S. Bartell, *ibid.*, **94**, 5236 (1972).

(5) For a discussion of approaches and results, see J. E. Williams, P. J. Stang, and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.*, **19**, 531 (1968).

In recent years, the improved models of molecular force fields have made it possible to calculate the molecular structure of certain, less strained hydrocarbon molecules with an accuracy comparable to that of X-ray crystallography.[6] A corresponding calculation for tri-*tert*-butylmethane should be helpful in several respects. If the general features of the calculated and experimental structures agree, then the more extensive calculated model can serve as a guide to further refinements of the electron diffraction data. If certain details of the calculated and the experimental structures are found to be in significant disagreement, this would indicate deficiencies in the model force field and might lead to improved parameterization of such models. Extreme overcrowding places tri-*tert*-butylmethane in a range of stress hitherto unexplored for acyclic hydrocarbons and therefore makes it a particularly favorable case for study.

Model Force Field Calculations. The purpose of the present paper is to supplement a direct structural study with model force field calculations rather than to compare various fields. It seemed sufficient to apply two fields that were formulated by quite different approaches. One of them is the "consistent force field," CFF3, proposed by Lifson and Warshel.[7] This field is a particularly natural choice because, among all the model force fields published to date, it seems to have been optimized in the most objective manner. It was derived by a least-squares analysis in which some two dozen parameters were fitted to spectral, thermodynamic, and structural data of saturated hydrocarbon compounds. No molecules as strained as tri-*tert*-butylmethane were included in the parameter optimization procedure. As an alternative model the much simpler force field of Jacob, Thompson, and Bartell[8] (JTB) was selected which makes use of the valence components of the Urey–Bradley analyses of Schachtschneider and Snyder[9] together with a set of potential functions known to be balanced and "moderate."[5] Although the JTB force field was not adjusted to fit experimental energetic and structural trends in hydrocarbons, it was found to give a good account of observed variations in bond lengths and bond angles in acyclic hydrocarbons and a fair account of their isomerization energies. One difference between the CFF3 and JTB fields is that the former includes no anharmonic terms in the geminal nonbonded potential functions. On the other hand, the JTB field contributes strongly anharmonic terms in the geminal as well as nongeminal nonbonded potential functions which terms make the atoms progressively harder as they are forced closer together. This behavior, which makes bond angles resist extreme compression, might be important in highly crowded molecules.

For the purpose of structure calculations the potential energy of a molecule according to the CFF3 and JTB fields may be expressed as

$$V = \text{const} + {}^1/_2 \sum_i k_i(r_i - r_i^0)^2 + {}^1/_2 \sum_j k_j(\alpha_j - \alpha_j^0)^2 + {}^1/_2 \sum_k V_k(1 + \cos(\omega_k \tau_k)) + \sum_l V_{\text{nb}}(q_l) \quad (1)$$

where the variables r_i, α_i, and τ_i represent all the bond lengths, bond angles, and torsion angles in the molecule and the constants r_i^0 and α_i^0 are the corresponding reference values. The function $V_{\text{nb}}(q_i)$ represents the nonbonded interaction associated with the q_ith nonbonded distance. Minimization of the potential energy with respect to the independent structural variables yields the desired equilibrium structure. The potential energy constants and reference values for the CFF3 and JTB fields are given in ref 7 and 8.

For tri-*tert*-butylmethane there are 39 independent variables in a structure with C_3 symmetry. Table I lists the structural parameters derived from the two model force fields by minimization with respect to all 39 independent variables. From the individual calculated structural parameters, mean values were computed for comparison in Table II with the experimental parameters of paper I. Atomic numbering follows Figure 1.

Least-Squares Refinements of Electron Diffraction Intensities. In refinements designed to exhaust information not yet derived in paper I, the symmetry restrictions were relaxed by abandoning the local C_{3v} symmetry of the carbon skeleton of the *tert*-butyl groups. This introduced four additional angle parameters β(C-1–C-2–C-5) split into β_3(C-1–C-2–C-3), β_4(C-1–C-2–C-4), and β_5(C-1–C-2–C-5), and $\Delta\tau$(H-1–C-1–C-2–C-5) split into $\Delta\tau_{13}$(H-1–C-1–C-2–C-3), $\Delta\tau_{14}$-(H-1–C-1–C-2–C-4), and $\Delta\tau_{15}$(H-1–C-1–C-2–C-5). Local C_{3v} symmetry of the methyl groups was maintained and C–C bonds in the *tert*-butyl groups were all taken as equal. Least-squares refinement started from the parameters found for the constrained model and led to values given in Table III, column 4, with $\beta_4 > \beta_5 > \beta_3$. Since this ordering differs from that obtained by the model force fields, two other refinements were carried out with starting values of β_3 or β_5 chosen to be the largest β angles. The refinements in both cases led back to the results in column 4 unless β_3 or β_5 was constrained. Refinements corresponding to the constraints indicated by parenthesized values are given in columns 5 and 6. Correlation coefficients for the analysis in column 6 are given in Table A of the microfilm edition.[10] Another set of minima in least-squares refinements was found with $\Delta\tau$'s about 10° higher than in the previous series. Results for these minima paralleling runs 4–6 are shown in Table III, columns 1 through 3. Corresponding curves $s\Delta M(s) = sM(s)_{\text{exptl}} - sM(s)_{\text{calcd}}$ are shown in Figure A in the microfilm edition.[10] No model can be said to be unequivocally superior to the others based on

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(6) J. D. Dunitz, *Perspect. Struct. Chem.*, **2**, 1 (1968).

(7) S. Lifson and A. Warshel, *J. Chem. Phys.*, **49**, 5116 (1968). Note that a refinement not used in the present research was later introduced by Warshel and Lifson, *Chem. Phys. Lett.*, **4**, 255 (1969). It introduces a bend–bend interaction parameter which improves frequencies without altering structures appreciably.

(8) E. J. Jacob, H. B. Thompson, and L. S. Bartell, *J. Chem. Phys.*, **47**, 3736 (1967). One slight modification of the Jacob, Thompson, and Bartell procedure (JTB) was introduced in the present study. The calculations for tri-*tert*-butylmethane use the torsional potential V_3-$(1 + \cos 3\tau)$ whereas the original JTB calculations used parabolic fits to $V_3(1 + \cos 3\tau)$.

(9) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).

(10) Table A, Figure A, and derivation of eq 9 will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-5239. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Table I. Comparison of Tri-*tert*-butylmethane Structures Calculated by the CFF3 and JTB Model Force Fields. Also Listed Are the Corresponding Structure Parameters Calculated for Ethane by Each Model Force Field

Parameter[a]	CFF3[b]	JTB[c]
$r(\text{C–C})_{\text{ethane}}$	[1.533]	[1.534]
r(C-1–C-2)	1.569	1.595
$\bar{r}$(C-2–C-3,4,5)	1.528	1.552
(2–3), (2–4), (2–5)	+1, −10, +9	+0, −10, +10
$r(\text{C–H})_{\text{ethane}}$	[1.105]	[1.114]
$r(\text{C–H})_{\text{methine}}$	1.128	1.137
$\bar{r}(\text{C–H})_{\text{methyl}}$	1.100	1.111
(H-1), H-2), (H-3)	−3, +3, +3	−7, +7, +1
(H-4), (H-5), (H-6)	−3, +3, +1	−5, +7, −3
(H-7), (H-8), (H-9)	+2, +2, −8	+1, +5, −5
$\alpha(\text{H}_t\text{–C-1–C-2})$	100.9	102.4
$\bar{\beta}$(C-1–C-2–3,4,5)	114.7	112.5
(H-1,2,3), (H-1,2,4), (H-1,2,5)	+2.2, −0.7, −1.6	+1.1, +0.5, −1.7
$\angle(\text{HCC})_{\text{ethane}}$	[110.8]	[111.4]
$\bar{\gamma}(\text{HCC})_{\text{methyl}}$	111.4	112.4
(H-1), (H-2), (H-3)	+0.2, 0.0, −0.9	+1.6, −1.7, −0.6
(H-4), (H-5), (H-6)	+0.5, −0.2, −0.5	1.5, −2.0, 0.8
(H-7), (H-8), (H-9)	−1.0, +0.1, +1.6	−0.5, −1.0, +2.0
$\overline{\Delta\tau}$(*tert*-butyl)	+16.4	+15.8
(H-1,2,3), (H-1,2,4), (H-1,2,5)	−2.2, −0.4, +2.7	−1.9, −0.0, +1.9
$\overline{\Delta\tau}$(methyl 3)[d]	+4.4	+7.0
$\overline{\Delta\tau}$(methyl 4)[d]	+2.7	+5.4
$\overline{\Delta\tau}$(methyl 6)[d]	−15.0	−28.2

[a] Distances in ångström units or, for individual variations, thousandths of an ångström unit; angles, mean and individual variations, in degrees. [b] Lifson and Warshel force field and ethane results reported in ref 7. [c] Jacob, Thompson, and Bartell force field and ethane results reported in ref 8 with one additional correction. Since the C–C distances of the JTB field were systematically high by 0.006 Å, this amount was subtracted from each calculated C–C distance reported in Tables I–III. As a result structure parameters listed in tables and figures are not quite self-consistent. [d] Individual torsion angles in a given group varied a degree or two about the mean.

Table II. Observed and Calculated Average Structure Parameters[a] for Tri-*tert*-butylmethane

Parameter	Experimental Ed[b]	Calculated CFF3[c]	Calculated JTB[d]
$\bar{r}$(C–H)	1.111 (3)	1.100	1.112
$r(\text{C}_t\text{–C}_q)$	1.611 (5)	1.569	1.595
$\bar{r}(\text{C}_q\text{–C}_m)$	1.548 (2)	1.528	1.552
$\alpha(\text{H}_t\text{–C}_t\text{–C}_q)$	101.6 (0.4)	100.9	102.4
$\delta(\text{C}_q\text{–C}_t\text{–C}_q')$	116.0 (0.4)	116.5	115.5
$\bar{\beta}(\text{C}_t\text{–C}_q\text{–C}_m)$	113.0 (0.2)	114.7	112.5
$\bar{\epsilon}(\text{C}_m\text{–C}_q\text{–C}_m)$	105.8 (0.2)	103.8	106.2
$\bar{\gamma}(\text{C}_q\text{–C}_m\text{–H}_m)$	114.2 (1.0)	111.4	112.4
$\overline{\Delta\tau}(\text{H}_t\text{–C}_t\text{–C}_q\text{–C}_m)$	10.8 (0.5)	16.4	15.8
$\lvert\overline{\Delta\tau}\rvert$(methyl)[e]	18.0 (6.0)	7.4	13.5

[a] Subscripts t = tertiary, q = quaternary, m = methyl (primary). [b] Electron diffraction values derived under the constraints of paper I. Distances are mean r_g values in ångström units, angles in degrees. Least-squares standard deviations in parentheses are crude lower limits to be regarded with caution. [c] Consistent force field from ref 7. [d] Force field from ref 8 with C–C distances decreased 0.006 Å. See footnotes of Table I. [e] Average of absolute magnitude.

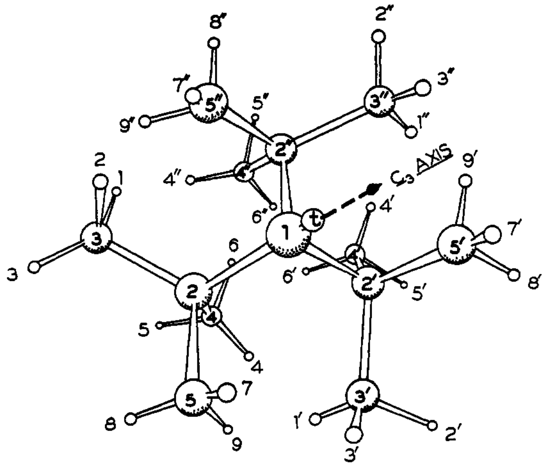

Figure 1. Atomic numbering for tri-*tert*-butylmethane. Note that atoms *n*, *n*′, and *n*′′ are equivalent in the C_3 symmetry structure.

the standard deviation of intensity only. Except at small scattering angles, residuals seem to be slightly more random in appearance and their distribution seems to be slightly more uniform for the curves 1, 2, and 6 than it is for curves 3, 4, and 5.

Treatment of Infrared Frequencies. The infrared-active C–H stretching frequencies in tri-*tert*-butylmethane are distributed over a significantly wider range[2] (≈170 cm^{-1}) than the corresponding frequencies in isobutane (≈70 cm^{-1} over the methyl frequencies, the splitting being due primarily to the difference in reduced mass between symmetric and asymmetric modes).[9,11] This indicates that the bonds in the more crowded molecule differ significantly in force constant from site to site, presumably because some bonds are shorter and hence stiffer than others owing to local stresses in the intramolecular environment. It is reasonable, then, to attempt to relate bond lengths to vibrational frequencies by some method and to interpret the vibrational spectrum in terms of a distribution in bond lengths over the molecule. Naturally, it is simpler to apply such a correlation by going from model bond length to calculated frequencies than by going from observed frequencies (which have not been decomposed into assigned modes) to calculated bond lengths. Therefore, vibrational frequencies were estimated from

(11) J. K. Wilmshurst and H. J. Bernstein, *Can. J. Chem.*, 35, 969 (1957). In certain respects the methine C–H stretch assignment of Wilmshurst and Bernstein looks more reasonable than the assignment of Schachtschneider and Snyder, ref 9. Therefore it was adopted for Figure 3.

Table III. Structure Parameters and Mean Amplitudes of Vibration for Tri-*tert*-butylmethane Corresponding to Various Least-Squares Minima (1–6) in Electron Diffraction Refinements with Relaxed Constraints[a]

Parameter	Least-squares minima 1	2	3	4	5	6	Molecular mechanics CFF3	JTB[b]
r_g(C–H)	1.111 (3)	1.111 (3)	1.112 (3)	1.108 (3)	1.108 (3)	1.109 (3)	1.100	1.112
$\bar{r}_g$(C-2–C-5)	1.548 (2)	1.548 (2)	1.548 (2)	1.547 (2)	1.548 (2)	1.548 (2)	1.528	1.552
$\bar{r}_g$(C-1–C-2)	1.624 (5)	1.622 (5)	1.623 (5)	1.607 (5)	1.601 (5)	1.603 (5)	1.569	1.595
Δr	0.076 (5)	0.074 (5)	0.075 (5)	0.060 (5)	0.053 (5)	0.055 (5)	0.041	0.044—
α(H–C-1–C-2)	104.3 (1.0)	102.2 (0.7)	101.7 (0.9)	101.9 (0.8)	101.7 (6)	101.5 (0.9)	100.9	102.4
β_3 (C-1–C-2–C-3)	111.8 (0.5)	110.3 (0.5)	[114.0]	111.6 (0.6)	111.2 (0.8)	[114.1]	116.9	113.7
β_4 (C-1–C-2–C-4)	116.6 (0.8)	113.4 (0.7)	113.8 (0.9)	113.4 (0.9)	113.0 (0.6)	112.9 (1.0)	114.0	113.1
β_5 (C-1–C-2–C-5)	109.8 (1.0)	114.9 (0.8)	110.5 (1.1)	112.4 (0.9)	[114.3]	111.7 (0.8)	113.1	110.8
$\bar{\beta}$	112.7	112.9	112.8	112.5	112.8	112.9	114.7	112.5
γ(C-2–C-5–H-8)	110.2 (0.7)	110.7 (0.7)	111.0 (0.8)	117.4 (0.9)	116.2 (1.0)	114.9 (1.2)	111.4	112.4
$\Delta\tau_{13}$(H–C-1–C-2–C-3)	19.7 (2.6)	19.8 (1.2)	18.2 (1.7)	12.0 (0.6)	9.9 (1.5)	12.2 (2.0)	14.2	13.9
$\Delta\tau_{14}$(H–C-1–C-2–C-4)	19.4 (0.8)	17.1 (0.9)	18.6 (1.0)	10.0 (0.9)	10.1 (0.7)	11.1 (1.8)	16.0	15.7
$\Delta\tau_{15}$(H–C-1–C-2–C-5)	26.6 (0.9)	24.8 (0.6)	22.8 (0.8)	8.6 (0.9)	7.6 (0.7)	8.2 (1.0)	19.1	17.6
$\overline{\Delta\tau}$	21.9	20.4	19.9	10.2	9.2	10.5	16.4	15.8
$\lvert\Delta\tau\rvert$(methyl groups)	(18.0)	(18.0)	(18.0)	(18.0)	(18.0)	(18.0)	7.4	13.5
l_g(C–H)	0.077 (3)	0.077 (3)	0.078 (3)	0.072 (3)	0.072 (3)	0.074 (3)		
l_g(C···H, 1.8 Å)	[0.109]	[0.109]	[0.109]	[0.109]	[0.109]	[0.109]		
l_g(C–C, 1.55 Å)	[0.055]	[0.055]	[0.055]	[0.055]	[0.055]	[0.055]		
l_g(C···C, 2.6 Å)	[0.075]	[0.075]	[0.075]	[0.075]	[0.075]	[0.075]		
l_g(C···C, 3.2 Å)	0.096 (13)	0.094 (8)	0.137 (16)	0.105 (9)	0.105 (8)	0.117 (13)		
l_g(C···C, 4.1 Å)	0.099 (12)	0.113 (10)	0.088 (15)	0.109 (9)	0.112 (10)	0.113 (11)		
l_g(C···C, 4.6 Å)	0.126 (31)	0.103 (22)	0.102 (25)	0.124 (29)	0.116 (30)	0.117 (32)		
l_g(C···C, 5.2 Å)	0.117 (25)	0.217 (30)	0.113 (35)	0.125 (16)	0.128 (17)	0.111 (20)		
R (average of plates)[c]	1.01 (2)	1.02 (2)	1.02 (2)	0.92 (2)	0.92 (2)	0.94 (2)		
$[\sigma(I)/\langle I\rangle]$[d]	0.0023	0.0021	0.0024	0.0020	0.0020	0.0022		

[a] Imposed constraints are in square brackets and least-squares standard deviations in parentheses. For comparison, calculated parameters from CFF3 and JTB fields are listed. [b] Parameters adjusted as in Table I. [c] Electron diffraction index of resolution. [d] Standard deviation in intensity divided by mean total intensity.

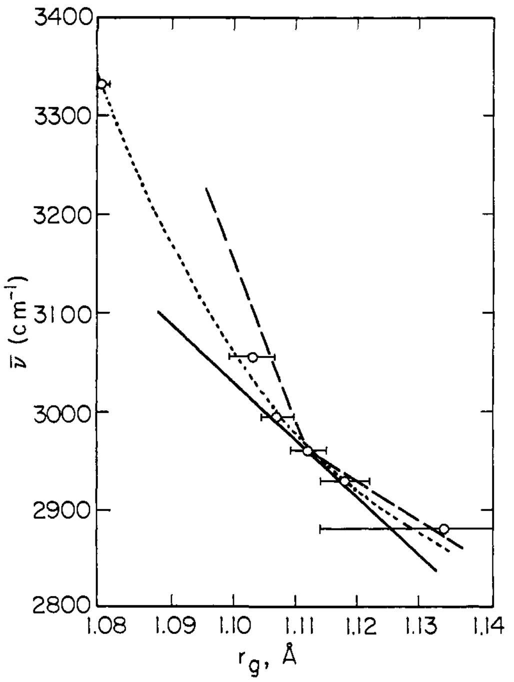

Figure 2. C–H stretching frequencies (averaged over normal modes) *vs.* mean (r_g) bond length. Points with esd error bars and the associated dotted curve represent experiment. Solid line represents Badger's rule. Coarse dashes represent nonbonded repulsion model of C–H bond collinear with perturbing atom (see text). Points, from left to right, refer to acetylene, ethylene, methane, ethane, methylene in propane ($\bar{\nu}$) and *n*-butane through *n*-heptane (r_g), and methine in isobutane ($\bar{\nu}$) and 2,3-dimethylbutane (r_g). Data from ref 11 and 12.

internuclear distances by two simple schemes: (a) a naive empirical relationship connecting frequency and bond length and (b) a calculation of frequencies based on three coupled oscillators perturbed by an asymmetric environment. The intramolecular nonbonded perturbations estimated from the JTB field are strong enough to make scheme a not much different from scheme b.

Summarized by the data points in Figure 2 are C–H frequencies[12] for a variety of molecules or groups within molecules averaged over all modes for the molecule (or group). These mean frequencies turn out to vary smoothly with bond length.[13] One justification for the observed trends is Badger's rule[14a] (solid line in

(12) Acetylene, methane, and ethane from G. Herzberg, "Infrared and Raman Spectra," Van Nostrand, Princeton, N. J., 1960. Ethylene from A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969). Propane from J. N. Gayles and W. T. King, *Spectrochim. Acta*, **21**, 543 (1965). Isobutane from ref 9 and 10.

(13) For consistency, only compounds with known mean (r_g) bond lengths were taken. Acetylene from B. D. Saksena, *J. Chem. Phys.*, **20**, 95 (1952), and corrected to r_g by L. S. Bartell, *Tetrahedron*, **17**, 177 (1962). Ethylene from L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, *J. Chem. Phys.*, **42**, 2683 (1965). Methane from L. S. Bartell, K. Kuchitsu, and R. J. deNeui, *ibid.*, **35**, 1211 (1961). Ethane from L. S. Bartell and H. K. Higginbotham, *ibid.*, **42**, 851 (1965). Methylene bond lengths derived in ref 8 from data in R. A. Bonham, L. S. Bartell, and D. A. Kohl, *J. Amer. Chem. Soc.*, **81**, 4765 (1959). Methine bond length derived in ref 8 from data in T. L. Boates, Thesis, Iowa State University, 1966. The methine bond length reported for isobutane by D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1519 (1960), is a microwave result of much greater *precision* than the diffraction result of ref 8, but its physical significance is quite uncertain as discussed in R. L. Hilderbrandt and J. D. Weiser, *J. Chem. Phys.*, in press, and R. L. Hilderbrandt, private communication.

(14) (a) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934); (b) P. M. Morse, *Phys. Rev.*, **34**, 57 (1929); L. S. Bartell, *J. Chem. Phys.*, **23**, 1219 (1955).

Figure 2), an empirical rule for diatomic molecules expressible as

$$\mathrm{d}k/\mathrm{d}r = -3k/(r - d) \qquad (2)$$

relating bond lengths, r, to force constants, k, *via* a parameter d which has a value of 0.335 Å for C–H bonds. In the event that polyatomic interaction constants are small, the *mean* frequencies are given quite accurately by the diatomic value

$$\bar{\nu} = [(4k/\pi^2)(m_C^{-1} + m_H^{-1})]^{1/2} \qquad (3)$$

An alternative point of view is exemplified by a model in which a C–H bond is compressed or expanded by the agency of nonbonded interactions. One such model which is easy to treat quantitatively is that of a C–H bond perturbed by a collinear atom Y. The position of the carbon atom is fixed. If the external atom Y is to the right of the C–H bond, the bond is compressed by nonbonded repulsions. If it is to the left, the bond is expanded. At a given distance R between the perturbing atom Y and the reference position of the bond hydrogen (at its unperturbed equilibrium distance r_e) the potential energy as a function of the displacement of the bond hydrogen is

$$V(x) = V_{CH}(x) + V_{nb}(r_{HY}) \qquad (4)$$

where $x = r_{CH} - r_e$ and $r_{HY} = R - x$. The equilibrium length of the perturbed bond is the length which makes the net first derivative $V'(x)$ equal to zero, and the effective force constant is the net second derivative

$$k(x_e) = V''(x_e) = V_{CH}''(x_e) + V_{nb}''(R - x_e) \qquad (5)$$

evaluated at x_e (the value of x for which $V' = 0$). Placing the perturbing atom at different values of R will lead to different equilibrium displacements, x_e, and to correspondingly different force constants, $k(x_e)$. If V_{CH} is represented by the Morse curve

$$V_{CH}(x) = (k_0/2)(x^2 - ax^3 + \ldots) \qquad (6)$$

where a is the conventional Morse asymmetry constant,[14b, 15] it can be shown by combining eq 5 with the equilibrium condition $V' = 0$ that the variation of the force constant, $k(x_e)$, with C–H bond length is

$$\mathrm{d}k/\mathrm{d}r = \mathrm{d}k/\mathrm{d}x \approx -3k_0[a + (V_{nb}''/3V_{nb}')] \qquad (7)$$

if R is not too great, where V_{nb}'' and V_{nb}' are evaluated at $(R - x_e)$. Since only the *ratio* of derivatives of V_{nb} is used, the result is not strongly dependent upon the function V_{nb} selected. For sake of comparing eq 7 with Badger's rule, V_{nb} was taken to correspond to H···H repulsions in the JTB field and a was assigned the value of 2.3 Å^{-1}, a mean of polyatomic C–H values deduced by various methods.[15] Note that, while V_{nb}'' may be expected to be positive in the region where V_{nb} is repulsive, V_{nb}' is positive when the C–H bond is being compressed and negative when it is being expanded. Hence, the simple collinear model imparts a nonphysical discontinuity to the slope of the frequency versus bond length curve. Nevertheless, as illustrated in Figure 2 where the ethane C–H bond is taken as the $x = 0$ reference, eq 7 gives a plausible representation of the empirical data. Indeed, if Badger's eq 2 and then onbonded formula 7, which err in opposite directions on the curvature at $x = 0$, are averaged, the resultant compromise fits empirical data to within experimental error. Frequencies calculated for the JTB structure of tri-*tert*-butylmethane from the empirical curve of Figure 2 are compared with observed frequencies in Table IV and found to be in reasonable agreement. Frequencies calculated on this basis for the CFF3 field are distributed fairly well about the mean but are about 100 cm^{-1} too high, not because the force field was intrinsically inferior but because the CFF3 reference length r_{CH}^0 was low. It seems to have been based on a type of vibrational average different from the true mean bond length[16] "r_g" whereas the r_g bond length for methane was built into the JTB field. Scheme b above was also carried out and the results for the JTB structure are given in Table IV. Since they are not greatly different from the results of scheme a, the method will not be discussed in detail. Suffice it to note that, according to the study of Schachtschneider and Snyder,[9] the coupling between different methyls in the *tert*-butyl group of isobutane is very small. Therefore, methyl groups were treated individually as systems of three coupled one dimensional C–H oscillators with force constants appropriate for isobutane and a coupling parameter sufficient to reproduce the observed 70-cm^{-1} split between the totally symmetric and doubly degenerate stretch modes. The individual C–H force constants were then perturbed by δk evaluated from the δr of the JTB structure using the dashed correlation curve of Figure 2 together with eq 3. The secular equations were solved to yield the frequencies of the perturbed methyls.[17] Because of the strength and asymmetry of the perturbations, the individual normal modes corresponded closely enough to individual bond vibrations to permit an assignment.

Table IV. Comparison of C–H Bond Lengths and Frequencies Calculated by the JTB Model Field[a] with Observed Frequencies and Lengths Estimated from the Observed Frequencies of Tri-*tert*-butylmethane

CH[b]	r_{CH}^{JTB}	ν_{calcd}(a)[c]	ν_{calcd}(b)[d]	ν_{obsd}[e]	$r_{CH}(\nu)$[f]
1	1.104	3057	3040	3038 w	1.10_5
9	1.105	3040	3025	3020 w	1.10_7
4	1.106	3028	3010	3000 w	1.10_9
6	1.108	3005	2990		
3	1.111	2970	2980	2960 s (br band)	1.11_2
7	1·112	2960	2980		
8	1.116	2940	2920		
5	1.118	2918	2920	2910 m	1.12_2
2	1.118	2918	2915		
t	1.137	2860		2868	1.13_2

[a] For sake of comparison with the 0.014 Å spread in C–H bond lengths calculated for methyl groups in tri-*tert*-butylmethane, we list the spreads of 0.002 and 0.0051 Å calculated for methyl groups in propane and hexamethyl ethane, respectively, by the JTB model field. [b] Identifying number of hydrogen. See Figure 1. [c] Calculated from r_{CH}^{JTB} by scheme a in text. [d] Calculated by scheme b in text. [e] From ref 2. [f] Estimated from observed frequencies according to Figure 2.

The following question deserves discussion. Since the CFF3 and JTB models both provide explicit force

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(15) K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.*, **36**, 2470 (1962); L. S. Bartell, K. Kuchitsu, and R. J. deNeui, *ibid.*, **35**, 1211 (1961); D. Herschbach and V. W. Laurie, *ibid.*, **35**, 458 (1961).

(16) K. Kuchitsu and L. S. Bartell, *ibid.*, **35**, 1945 (1961).

(17) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955.

fields for tri-*tert*-butylmethane, why are not the vibrational frequencies calculated directly from the model force fields without further approximation? Why is the above somewhat speculative and indirect method used? The answer is that the results of such a calculation would be of limited utility inasmuch as both fields leave out the vitally important anharmonic ingredient, the *a* parameter of eq 6 and 7. This parameter contributes the principal "Badger" component to the variation of $\bar{\nu}$ with r (*cf.* eq 2 and 7). Despite its vital role in frequency calculations, the bond anharmonicity has only a minor effect in structure calculations as discussed in a subsequent section. It would seem to be advantageous in future derivations of model force fields, designed to be consistent with spectral and structural data, to include a suitable bond anharmonicity.

Discussion of Results

Inferences from Electron Diffraction. The relatively good agreement between the experimental and calculated results listed in Table II lends credibility to the structure parameters derived for tri-*tert*-butylmethane. The largest discrepancy, namely the lengths of the most severely strained bonds (C-1–C-2), is probably indicative of a real deficiency in both model force fields and will be examined later. When the severe constraints imposed on the diffraction analyses corresponding to Table II are relaxed, the limitations on the remaining information not extracted in paper I are evident. It is apparent from Table III that there are a number of comparably good minima in the expanded parameter space and that the improvement in representation of the data is quite modest. It is pleasing, nevertheless, to find that several of the minima correspond fairly closely to the detailed deformations predicted by the model fields and that the rather large amplitudes of vibration encountered in the constrained analyses[4] are reduced to more normal values.[18,19] It seems fair to conclude that the combined approaches have established the three dimensional structure of the carbon skeleton of tri-*tert*-butylethane with an accuracy comparable to that obtained in conventional X-ray diffraction studies. Electron diffraction supplies the mean skeletal parameters and the model fields (Table I) agree on individual displacements from the mean. In the next section deformations of the individual methyl groups are discussed. Variations much too subtle for analysis by either X-ray or electron diffraction are found.

Before leaving the section on the diffraction analysis, some comment on the interpretation of the derived torsional displacements of the *tert*-butyl groups (Table III) is necessary. It has been noted in several places that so-called "torsional shrinkage effects"[18–20] stemming from torsional vibrations make groups appear to be displaced from their true equilibrium configurations. Such apparent mean displacements encountered in diffraction averages of instantaneous displacements are of the order of magnitude of root-mean-square torsional displacements or less. For the central bond in *n*-butane or a *tert*-butyl group sterically unhindered (with $V_3 \approx 3$ kcal/mol) the amplitude $\langle(\Delta\tau)^2\rangle^{1/2}$ should be of the order of 12° at room temperature.[18] Our conviction that the true internal rotation is at least 10° in tri-*tert*-butylmethane (*cf.* Table II) is reinforced by the semiquantitative evidence of steric hindrance provided by the model force fields. Both the CFF3 and the JTB fields yielded the very small value of 2.5° for $\langle(\Delta\tau)^2\rangle^{1/2}$ at room temperature, a value so much lower than the derived torsional displacement that the "shrinkage correction" should be negligible.

Comments on C–H Coupling Constant. Previous studies of ^{13}C–H coupling constants in nmr spectra of hydrocarbons have revealed a striking trend between the coupling constants and C–^{13}C–H bond angles.[21,22] This trend has been accounted for by changes in "hybridization." It was originally expected that the methine ^{13}C–H coupling constant of tri-*tert*-butylmethane would be significantly, perhaps dramatically, shifted from its "normal" 125 Hz value owing to the steric decrease of the central C–C–H angle. For example, model calculations by Hupbach, *et al.*,[22] predicted a value of about 75 Hz for a C–C–H angle of 100° (an angle similar to that found in tri-*tert*-butylmethane). If the value of 124 Hz reported for tri-*tert*-butylmethane is reliable, it is apparent that more realistic theoretical approaches are needed which use *bona fide* wave functions instead of simplified wave functions based on preconceived hybridizations. Perhaps the present result is an argument in favor of "bent bonds." It may be, also, that effects of bond length are significant in view of the greater than "normal" lengths of all bonds attached to the tertiary carbon. In the only published theoretical study of the dependence of coupling constants on bond length, Bartow and Richardson[23] found that the trends obtained with minimum basis sets were in the opposite direction from trends obtained with an extended basis set. Plainly, more work is needed before influences of structural variations upon coupling constants are understood.

Inferences from Vibrational Spectra. Infrared spectra provided firmer structural information than did nmr spectra. As shown in Table IV, the observed spread in C–H stretching frequencies is in good enough accord with the spread calculated by the JTB field that we may have some confidence in the calculated spread of C–H bond lengths. In particular, the bonds experiencing the strongest steric perturbations can be readily identified. The CFF3 field (Table I) predicted a comparable but somewhat smaller spread in distances with a pattern of deformations similar to but not identical with those of the JTB field. Since the actual values of the frequencies calculated for the CFF3 field are uniformly too high, corresponding with the fact that the mean C–H bond lengths from the CFF3 field are too low, we have not represented CFF3 in Table IV. Again, we emphasize that this discrepancy is not an essential flaw in the CFF3 force constants; it only reflects the low reference length r_{CH}^0.

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(18) R. A. Bonham and L. S. Bartell, *J. Amer. Chem. Soc.*, **81**, 3491 (1959).

(19) L. S. Bartell and D. A. Kohl, *J. Chem. Phys.*, **39**, 3097 (1963).

(20) A. McAdam, B. Beagley, and T. G. Hewitt, *Trans. Faraday Soc.*, **66**, 2732 (1970).

(21) For a review, see W. McFarlane, *Quart. Rev., Chem. Soc.*, **23**, 187 (1969).

(22) U. Hupbach, H. Frischleder, and H. Helbig, *Mol. Phys.*, **16**, 593 (1969).

(23) D. S. Bartow and J. W. Richardson, *J. Chem. Phys.*, **42**, 4018 (1965).

Unfortunately, no very precise C–H bond lengths of unequivocal interpretation are available for the $\bar{\nu}$ *vs.* r_g plot of Figure 2 in the region of the tertiary hydrogen. The smooth dotted curve associates a distance of 1.132 Å with the observed 2886 cm^{-1} frequency, in fair agreement with the distances 1.128 and 1.137 Å predicted by the CFF3 and JTB fields, respectively. Correcting the CFF3 reference $r_{CH}{}^0$ to fit ethane[12] would yield 1.135 Å.

When C–C frequencies and force constants are established from vibrational spectra, they will provide further valuable evidence concerning the structure.[23a]

Inferences about the Model Force Fields. From the previous discussion it is evident that the model force fields provide a convenient framework for the interpretation of the experimental data for they afford the only available *completely* detailed picture (be it right or wrong) of the structure. Since the model fields were not designed to treat the molecule tri-*tert*-butylmethane rigorously and since they are by their very nature simplified representations, it is worthwhile to comment on their possible shortcomings and improvement.

First, through quadratic terms, neither of the force fields employed contains enough interaction constants (stretch–stretch, stretch–bend, stretch–torsion, etc.) to make it a general force field, although the Urey–Bradley form introduces some interaction terms. Little is known quantitatively about the consequences of these omissions. Rough estimates based on the comprehensive study of hydrocarbon force fields by Schachtscheider and Snyder suggest that the structural consequences but not the spectroscopic consequences are minor, however.[24,25]

If the quadratic terms in the model fields fall somewhat short of a complete set, the cubic terms are scarcely represented at all. While this may cause little trouble when the model fields are used essentially to *interpolate* structural data in a given class of compounds, it may be important in *extrapolations* of the present sort where displacements are large. The only cubic terms represented in the CFF3 and JTB model fields are those stemming from the nonbonded interactions. As noted in a previous section, the JTB field introduces much stronger higher order terms than does the CFF3 field (which only contains such terms in nongeminal interactions). No Morse-like anharmonicity for bonds is included in either field. These facts account quite well for the comparisons in Table II where the experimental values of r(C–H), r(C-2–C-5), and of α, β, δ, and ϵ are intermediate between the two calculated values, though closer to the JTB field, and the highly stretched r(C-1–C-2) lies beyond both calculated values. Computations for cyclopentane, a molecule treated accurately by CFF3,[7] indicated that the JTB nonbonded interactions were somewhat too hard for small deformations from tetrahedral angles.[26] In the present highly deformed case, however, the results suggest that the CFF3 interactions may be insufficiently hard. Unfortunately, certain systematic difficulties[25] prevent an unequivocal determination of nonbonded interaction potentials even in such a highly optimized "consistent field" as that of Lifson and Warshel. At least the CFF3 interactions were derived from data including many hydrocarbons in contrast to the JTB interactions based on educated guesses[27] from benzene$\cdots$benzene and $H_2\cdots H_2$ interactions.

The discrepancy between the experimental and calculated r(C-1–C-2) bond length is in the direction to be expected from the neglect of the Morse-like bond anharmonicity. It is possible to estimate the magnitude of the anharmonic effect as follows. Let the C–C bond potential as a function of the C–C displacement $x = r - r_e$ be described by the expression

$$V(x) = V_{CC}(x) + V_{nb}(x) \tag{8}$$

analogous to eq 4, where $V_{CC}(x)$, the bond potential energy for unstrained compounds, is represented by $(k/2)x^2$ for the harmonically bonded CFF3 and JTB fields and by $(k/2)(x^2 - ax^3 + \ldots)$ for the desired anharmonic improvement. Let the displacements due to the perturbing potential V_{nb} be designated as x_h and x_a for the harmonic and anharmonic bond functions, respectively. Solving for the values of x that minimize $V(x)$ of eq 8, we find, letting the entire structure relax between the x_h and x_a solutions, that

$$(x_a - x_h) \simeq 3ax_h^2/\{2 - 6[a + (V_{nb}''/3V_{nb}')]x_h\} \tag{9}$$

as is proven in the Appendix of the microfilm edition,[10] where the assorted symbols correspond to those of eq 4–7.[28] Therefore it is a simple matter to estimate quite accurately the magnitude of the extra displacement $(x_a - x_h)$ suffered by anharmonic bonds from a knowledge of the displacement x_h already calculated by the CFF3 or JTB harmonic bond models. Note that the anharmonic correction, being proportional to the square of the displacement, is very small unless the displacement is large. Furthermore, the correction is practically insensitive to the perturbing potential $V_{nb}(x)$ since $V_{nb}(x)$ enters only as a *ratio* of derivatives and then only as a small correction[28] term in the denominator of eq 9. A representative value of $(V_{nb}''/3V_{nb}')$ is -1.5 Å^{-1},[27] and a is about 2 Å^{-1} for C–C bonds. Accordingly, the anharmonic correction $(x_a - x_h)$ for the deformation of the highly stretched C-1–C-2 bonds turns out to be 0.004 Å for the CFF3 field and 0.012 Å for the JTB field (using the calculated ethane bond length as an unstrained reference value of r_e).[29] The corrected model field lengths become 1.573 and 1.607 Å for the CFF3 and JTB fields in comparison with the experimental result of 1.611 Å in Table II. Therefore, at least for the JTB field, the anharmonic bond correction is adequate to account for the experiment.

[23a] Note Added in Proof. A recent reinterpretation of the structure of isobutane by R. L. Hilderbrandt (private communication, 1972), based primarily on microwave rotational constants corrected for vibrational effects, provides a new and better tertiary C–H bond length for Figure 2. The new point suggests a much smaller curvature in the $\bar{\nu}$ *vs.* r curve and a tertiary bond length in tri-*tert*-butylmethane about 0.01 Å shorter than the value obtained with the old point.

(24) A. Warshel and S. Lifson, *Chem. Phys. Lett.*, **4**, 255 (1969).

(25) L. S. Bartell, unpublished research. Note that L. S. Bartell and K. Kuchitsu, *J. Chem. Phys.*, **37**, 691 (1962), present evidence that the inference of nonbonded interactions from vibrational frequencies *via* a force field of the form of eq 1 in the text (CFF3 and JTB force fields) is susceptible of substantial error unless additional stretch–stretch interactions are included.

(26) W. J. Adams, H. J. Geise, and L. S. Bartell, *J. Amer. Chem. Soc.*, **92**, 5013 (1970).

(27) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).

(28) The term $6[a + V_{nb}''/3V_{nb}')]x_h$ expresses a correction for the influence of the shift $(x_a - x_h)$ in bond length upon the structure and thereby upon V_{CC} and V_{nb}.

(29) Note that r_e is not to be confused with the model field parameter r^0 of eq 1.

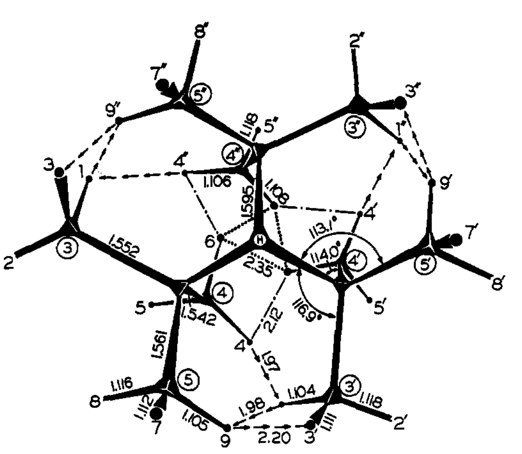

Figure 3. Network of close nonbonded interactions in tri-*tert*-butylmethane between *tert*-butyl groups. Internuclear distances calculated from JTB force field with corrections of Table I.

In assessing the model fields we observe that the CFF3 "consistent" field is often considerably superior to the JTB field when used directly to calculate vibrational frequencies because the frequencies were heavily weighted input data in least squares adjustments of field parameters.[7] On the other hand, the CFF3 field yielded a noticeably poorer structure result for tri-*tert*-butylmethane than did the JTB field. We suspect that when the nonbonded interaction functions of the CFF3 field, possibly the electrostatic components,[30] were adjusted to fit frequencies they absorbed effects of missing terms (interaction and anharmonic) and thereby misrepresented terms needed to fit structures of crowded molecules.[25] An investigation of this is being initiated in view of the utility of an improved model force field.

Concluding Comments about the Structure. A proper appreciation of the deformation undergone by tri-*tert*-butylmethane in the accommodation of its crowded *tert*-butyl groups can best be gained by examining a three-dimensional model. The stereoscopic view in paper I may also be helpful. Some insight can be derived by studying the rather tightly interwoven network of C–H bonds, with bumps fitting into hollows, that is illustrated in Figure 3. It is quite plain from this figure why the C–H bond variations are distributed as they are. An analysis to find which of the interactions bear the main burden of the stress depends upon the force field that is assumed to operate. For the JTB field the repulsive forces keeping the *tert*-butyl groups apart are comparable for the closest H···H and C···H contacts, C···C interactions being smaller. For the CFF3 field the nongeminal nonbonded forces are similar to those of the JTB field if electrostatic terms are neglected. When electrostatic terms are included, however, the C···C forces increase and C···H forces fall steeply or change sign; *tert*-butyl separations are maintained, according to the CFF3 field, by H···H and C···C repulsions. If the new Allinger force field[31] had been applied, the contacts would have been found to be borne almost entirely by H···H interactions.

The restriction of rotation of the *tert*-butyl groups is one obvious gauge of the steric environment. For small displacements this restriction was calculated assuming that only the torsional angle of one group varied during a torsional displacement. The CFF3 and JTB fields agreed closely, giving net torsional force constants 23 times and 25 times the ethane torsional constant, respectively. Whether the hindrance is sufficient to allow isolation of optical isomers is a problem worth further study. The activation energy for racemization was estimated as follows to be 16.0 kcal/mol, neglecting vibrations. Carbon atoms 5, 5′, and 5″ were set at successively smaller torsional angles, maintaining C_3 symmetry, and allowing all 38 remaining structure parameters to relax. Energies were calculated from the JTB field along the "reaction coordinate" until the mirror image of the starting structure was reached. It was found that two separate but equivalent reaction pathways were possible, neither one of them going through C_{3v} symmetry at the activated complex. Whether a reaction coordinate of lower symmetry exists that corresponds to a lower activation energy was not investigated. Another assessment of the intramolecular strain was carried out using the JTB field. It was found for this model field that the isomerization energy to transform n-$C_{13}H_{28}$ (all trans conformation) into tri-*tert*-butylmethane is 33.5 kcal/mol, neglecting vibrational energy. The zero point energy of the C–H stretches alone would add perhaps another 2 kcal/mol to this isomerization energy. The probable heat capacity differences would perhaps add yet another 12 or more kcal/mol to the isomerization energy at room temperature. Whether the implied JTB strain energy has any quantitative merit is uncertain but it does provide a target for further research.

In summary, tri-*tert*-butylmethane furnishes an especially opportune illustration of a case where electron diffraction, vibrational spectroscopy, and molecular mechanics are individually insufficient for a precise structure analysis but are mutually augmentative. The initial hope that a structural investigation of the crowded molecule would extend previous knowledge of intramolecular force fields and thereby help to improve molecular mechanics was indeed realized. It appears that further research on the thermochemistry and vibrational spectroscopy of the present unusual molecule would be profitable. Of particular significance in view of the very small CCH_t bond angle was the surprisingly "normal" nmr coupling constant for the methine C–H bond.[2] According to model calculations,[22] a much lower value of J_{CH} was expected. This anomaly points the way to a reexamination of the status of hybridization and bent bonds. A definitive resolution of this problem might materially sharpen our concepts of directed valence.

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(30) When electrostatic terms are reduced, the modified CFF3 structure becomes more like the experiment and like the JTB structure.

(31) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.*, 93, 1637 (1971).