Structure of Tri-*tert*-butylmethane. I. An Electron Diffraction Study

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Abstract: The molecular structure of tri-*tert*-butylmethane was investigated by gas-phase electron diffraction. Structure parameters clearly reveal the influence of the intermethyl repulsions present in the highly crowded molecule. The three innermost C–C bonds with lengths of 1.611 (5) Å are the longest reported for an acyclic hydrocarbon. The nine outer C–C bonds averaging 1.548 (2) Å are 0.015 Å longer than those in *n*-alkanes. A very low value of 101.6 (0.4)° was found for the C–C–H angle to the tertiary hydrogen, and the bond angles of the *tert*-butyl groups deviated appreciably from those normally encountered. Average values of 105.8 (0.2) and 114.2 (1.0)° for the outermost C_4–C_2–C_5 and C–C–H_{Me} angles, respectively, were derived by imposing local C_3 symmetry on the CC_3 and on the CH_3 segments of the *tert*-butyl groups. Optimal packing of the hydrogen protruberences of a given *tert*-butyl group into the hollows of adjacent groups is achieved according to the diffraction data, by twisting the *tert*-butyl groups and the methyl groups by 10° or more away from their staggered reference positions.

As part of a continuing program of structural research on hydrocarbon molecules[1,2] we report an investigation of tri-*tert*-butylmethane.[3] Precise structure studies have provided key information for the field of conformational analysis and the present, highly crowded molecule offered an unusually favorable opportunity for extending this information into the region of severe steric effects. Normal bond lengths, bond angles, and torsional angles in tri-*tert*-butylmethane would lead to an impossibly strained structure containing six pairs of hydrogen atoms closer together than 0.3 of their normal van der Waals contact distances. The distortions of the bond lengths, angles, and torsions induced sterically by these unavoidable gauche-gauche′ (GG′) interactions should be of potential value in formulating an improved model force field for hydrocarbon molecules.[4]

Unfortunately, the molecule tri-*tert*-butylmethane is too complex for a unique determination of its entire set of structure parameters to be carried out by gas-phase electron diffraction or spectroscopic methods alone. Neither does the substance readily yield well-ordered crystals suitable for analysis by X-ray diffraction.[5] It appeared profitable to bring to bear several rather diverse approaches in the resolution of the problem. Results are presented in two parts. Part I summarizes the information about mean distances, bond angles, and torsion angles that can be extracted directly from a conventional electron diffraction analysis. Part II considers the local steric displacements suffered by individual bonds, as gleaned by plausible interpretations of vibrational spectra and supplemental calculations by molecular mechanics. Part II also briefly assesses several model force fields for hydrocarbons.

Experimental Section

A sample of tri-*tert*-butylmethane was obtained from Professor M. Stiles and Dr. Hung-Hee Lee of the University of Michigan. The compound was purified by vapor-phase chromatography and its purity was checked by infrared analysis. The vapor pressure of tri-*tert*-butylmethane was estimated to be about 10 mm at 100°. The inlet system and the nozzle assembly were fitted with a jacket and heated with steam. Electron diffraction patterns were taken with the unit described previously.[6] The patterns were recorded on Kodak electron image plates at camera distances of 21 and 11 cm using an r^3 sector. The emulsion calibration[7] applied was of the form $2cA = (1 - e^{-2cE})$ with the constant c taken as 0.1. The diffraction data used in the structure analysis extended between $3.4 < s < 39.3$. Numerical values of the diffraction intensities and background functions are given in Tables A and B in the microfilm edition.[8]

Analysis of Data

Two plates taken at the 21-cm camera distance and three plates taken at the 11-cm camera distance were chosen for analysis. Experimental leveled intensities I_0 were corrected for extraneous scattering and showed an almost flat background function I_B. Halfway through the least-squares analysis,[9] which will be discussed in the next paragraph, it was found that in the overlapping region of s ($8.6 < s < 21.1$) the 11-cm camera distance data differed systematically from the 21-cm camera distance data. From a difference curve it was concluded that the sample used to take the 21-cm data was a mixture of tri-*tert*-butylmethane and air, owing to an overly cautious pumping out of the sample bulb with its very limited supply of sample. The composition was determined to be 67.9 mol % of $C_{13}H_{28}$ and 32.1 mol % of air, assuming a 4:1 ratio of nitrogen to oxygen. Throughout the least-squares analysis it was assumed that tri-*tert*-butylmethane possesses overall C_3 symmetry. Furthermore, a local C_3 symmetry was imposed upon the carbon skeleton of each *tert*-butyl group and upon each methyl group. The validity of this assumption will be discussed later. Initially the following four geometrical parameters were used to describe the molecule: $\langle r_g(\text{C–C})\rangle$; $\langle r_g(\text{C–H})\rangle$; $\delta(\text{C-2–C-1–C}'\text{-2}) = \beta(\text{C-1–C-2–C-5}) = \gamma(\text{C-2–C-5–H-8})$; $\Delta\tau(\text{H–C-1–C-2–C-5}) = \tau(\text{H–C-1–C-2–C-5}) - 60°$ (see Figure 1 for the numbering of the atoms).

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(1) See E. J. Jacob, H. B. Thompson, and L. S. Bartell, *J. Chem. Phys.*, 47, 3736 (1967).

(2) W. J. Adams and L. S. Bartell, *J. Amer. Chem. Soc.*, **92**, 5013 (1970), and references therein.

(3) Hung-Hee Lee, Thesis, The University of Michigan, 1971; H. Lee and M. Stiles, manuscript in preparation.

(4) For relevant references, see S. Lifson and A. Warshel, *J. Chem. Phys.*, **49**, 5116 (1968), and ref 1 and 2 above.

(5) C. E. Nordman, private communication, 1971.

(6) L. S. Bartell in "Physical Methods in Chemistry," A. Weissberger and B. W. Rossiter, Ed., 4th ed, Interscience, New York, N. Y., 1972. Also, L. S. Bartell, *Acta Crystallogr., Sect. A*, **25**, S76 (1969).

(7) R. C. Valentine, *Advan. Opt. Electron Microsc.*, 1, 180 (1966).

(8) Tables A, B, and C 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-94-5236. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(9) L. S. Bartell, D. A. Kohl, B. L. Carroll, and R. M. Gavin, Jr., *J. Chem. Phys.*, 42, 3079 (1965).

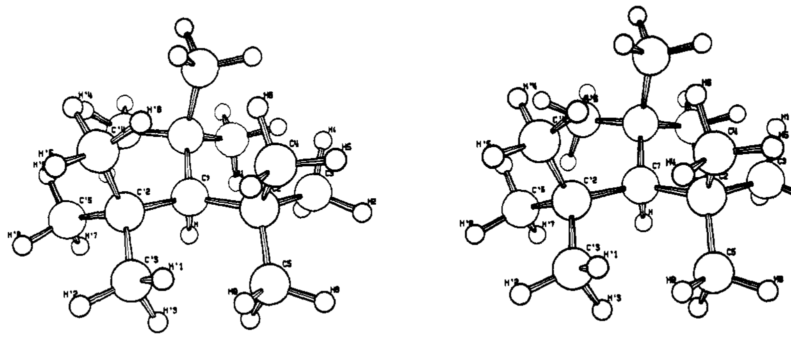

Figure 1. Stereoscopic view of tri-*tert*-butylmethane. The threefold axis runs along r(H-C-1). (Prepared with program ORTEP, C. K. Johnson, June 1965, Oak Ridge National Laboratory.)

Later, the theoretical model was made more flexible. While maintaining overall C_3 symmetry and local C_3 symmetry for the *tert*-butyl groups and the methyl groups, the structure parameters were increased to the following eight: r_g(C-2-C-5); $\Delta r = r_g$(C-1-C-2) $-$ r_g(C-2-C-5); $\langle r_g$(H-C)$\rangle$; α(H-C-1-C-2); β(C-1-C-2-C-5); γ(C-2-C-5-H-8); $\Delta\tau$(H-C-1-C-2-C-5) $=$ $\Delta\tau$(H-C-1-C-2-C-4) $=$ $\Delta\tau$(H-C-1-C-2-C-3); $\Delta\tau$ (methyl hydrogens where $\tau = \Delta\tau + 60$, 180, 300° except for methyl group C-5 where $\tau = -\Delta\tau + 60$, 180, 300°).

Analytical approximations to the elastic and inelastic scattering factors, as well as to the phase shifts, were taken from ref 10–12. Asymmetry constants a were assumed to be 2.0 Å^{-1} for all internuclear distances. Various shrinkage corrections were applied ranging from zero to those listed by Bartell and Kohl.[13] The corrections had no significant influence on the results.

The weight matrix used in the least-squares analysis of the experimental intensity function was diagonal with elements proportional to s^2. Effects of correlation between experimental measurements were included in the calculation of final standard deviations.[6] Background functions I_B were determined using the usual criteria. Before blending the experimental leveled intensities I_0 obtained from the two camera distances, all contributions due to hydrogen–hydrogen pair scattering and to air scattering were subtracted except for the contribution corresponding to the H···H 1,3-type distance at about 1.8 Å. Radial distribution functions (Figure 2) were calculated with the usual corrections.[12,14] The value of the Degard damping constant b used was 0.002.

Results and Discussion

If it is assumed that tri-*tert*-butylmethane has at most overall C_3 symmetry, the radial distribution function is composed of 275 different internuclear distances grouped into seven peaks not all of which are well resolved. Thirty-nine geometrical parameters are needed to define the most general model of this symmetry. The additional assumption of local C_3 symmetries in *tert*-butyl and methyl groups and equivalence of all C–H bond lengths reduces the number of geometrical parameters to eight. This simplification renders the problem tractable and provides a good starting point for the analysis. At the same time it obscures the significance of some of the parameters. Whereas the bond length r_g(C-1–C-2) and the bond angles α(H-C-1–C-2) or δ(C-2–C-1–C′-2) correspond to pure internal coordinates, each other parameter represents some kind of average value adjusted to fit the experimental data. The amplitudes of vibration for the 3.2-and 4.1 Å-nonbonded C–C distances found by imposing this simplified structural model are about 0.040 Å higher than those observed for n-alkanes.[15] This is contrary to the reasonable expectation of *lower* than normal amplitudes for individual pairs of atoms due to steric restrictions in vibrations. Therefore, we may infer that the spread of distances is not properly reproduced by the geometrically constrained model but that it is achieved, instead, by absorbing deficiencies of the model into the effective amplitudes of vibration. Moreover, the fluctuations of the residuals $s\Delta M(s)$ (Figure 3) in the range $3 < s < 20$ seem to be of a nonrandom nature when compared with the range $20 < s < 39$. This adds to the evidence that the model with local C_{3v} symmetry is too restricted and that more, though probably quite limited, information can be extracted from the experimental data. The standard deviations of the parameters, although corrected for correlation of experimental data,[6] should be considered a lower limit, because the effect of additional correlation due to the restrictions of the model and to interaction with systematic errors in intensity measurement is uncertain. Numerical values of the parameters and standard deviations are given in Table I. A matrix of correla-

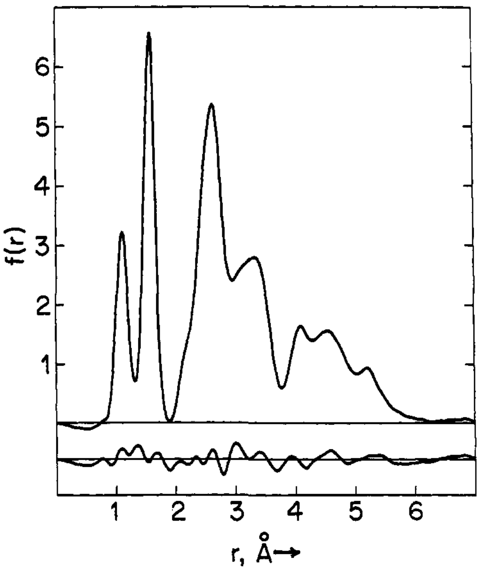

Figure 2. Experimental radial distribution function for tri-*tert*-butylmethane; $\Delta f(r) = f(r)_{\exp} - f(r)_{\text{calcd}}$.

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(15) R. A. Bonham, L. S. Bartell, and D. A. Kohl, *J. Amer. Chem. Soc.*, **81**, 4765 (1959).

Table I. Independent and Derived Structural Parameters[a] and Their Estimated Standard Deviations[b] for $C_{13}H_{28}$

r_g(C–H)	1.111 (3) Å	l_g(C–H)	(0.080 Å)[c]
r_g(C-2–C-5)	1.548 (2) Å	l_g(C···H, 2.18 Å)	(0.109 Å)[c]
Δr	0.063 (5) Å	l_g(C–C, 1.55 Å)	(0.055 Å)[c]
α(H–C-1–C-2)	101.6 (0.4)°	l_g(C···C, 2.6 Å)	0.080 (4) Å
β(C-1–C-2–C-5)	113.0 (0.2)°	l_g(C···C, 3.2 Å)	0.141 (19) Å
γ(C-2–C-5–H-8)	114.2 (1.0)°	l_g(C···C, 4.1 Å)	0.120 (14) Å
$\Delta\tau$(H-1–C-1–C-2–C-5)	10.8 (0.5)°	l_g(C···C, 4.6 Å)	0.104 (25) Å
$\Delta\tau$(methyl groups)	18.0 (6.0)°	l_g(C···C, 5.2 Å)	0.120 (20) Å
R(21 cm)[d]	1.03 (0.02)	$\sigma(I)/\langle I\rangle$	0.0025
R(11 cm)[d]	0.87 (0.02)		
r_g(C-1–C-2)	1.611 (5) Å		
δ(C-2–C-1–C′-2)	116.0 (0.4)°		
ϵ(C-4–C-2–C-5)	105.7 (0.2)°		
ζ(H-7–C-5–C-8)	104.3 (1.0)°		

[a] No shrinkage corrections. [b] The uncertainty in composition of the 11-cm data was not considered in the determination of the standard deviations. Results from the 11-cm data at various compositions did not differ from the present results by more than 3σ, except for $\alpha(100° < \alpha < 106°)$ and $\gamma(116° > \gamma > 110°)$. Least-squares standard deviations in parentheses are crude lower limits to be regarded with caution. See Table III of the following paper for a more complete analysis. [c] Values from ref 15, not varied. [d] Indices of resolution before 21-cm data and 11-cm data were blended.

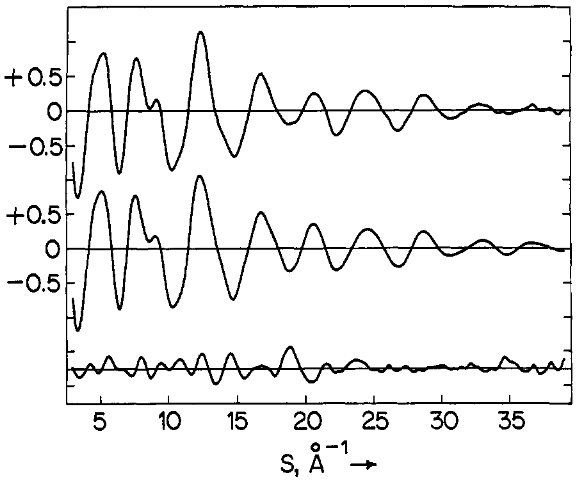

Figure 3. Experimental (upper curve) and calculated (middle curve) reduced molecular intensity functions $sM(s)$ for tri-*tert*-butylmethane. Bottom curve, $2 \times [sM(s)_{\text{exptl}} - sM(s)_{\text{calcd}}]$.

tion coefficients is given in Table C[8] of the microfilm edition.

The structural parameters present clear evidence for the intramolecular repulsions present in tri-*tert*-butylmethane. The bond length r_g(C-1–C-2) of 1.611 Å is longer than any other C–C bond length determined in an open chain hydrocarbon compound. It is 0.078 Å longer than the C–C bond length of 1.533 Å in *n*-alkanes.[13,15] This strain is induced primarily by the GG′ methyl–methyl interactions (C-5–C′-3, C-4–C′-4, etc). In less highly branched hydrocarbons where such conformations can be avoided it is usually assumed that GG′ conformations do not occur. Tri-*tert*-butylmethane cannot adopt a conformation that frees it of its GG′ conformations but it can relieve the attendant repulsions significantly by torsional displacements. In order to obtain an optimal fit of bumps into hollows the *tert*-butyl groups and methyl groups twist by 10° or more as shown in Table I.[16] Similar torsional deformations have been found in hexamethylethane,[17] in tetramethylethane,[17] and in tetrakis(trimethylsilyl)silane.[18]

Bonds of the type C-2–C-5 are subjected to much smaller stresses but are elongated, nevertheless, by about 0.015 Å on the average. Bond angles as well as bond lengths and torsional angles share in the steric deformations. Bond angles (C-1–C-2–C-5) and (C-2–C-5–H-8) are opened up to 113.0 and 114.2°, respectively. This deformation decreases the solid angle occupied by each methyl group and by the *tert*-butyl groups, thereby improving mutual avoidance of bulky neighboring groups. Inter-*tert*-butyl repulsions force the angle (C-2–C-1–C′-2) to open up to 116.2°.

More detailed information on the deformations undergone by the individual bonds and on the packing of the tightly meshed hydrogen atoms is deduced in the following paper, where inferences are drawn from a combination of diffraction and other data.

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(16) In the following paper, paper II, other least-squares minima with larger torsional displacements are found when the severe constraints of I are relaxed. Paper II also discusses the problem of torsional shrinkage effects which sometimes obscure measurements of torsional displacements.

(17) T. L. Boates, Thesis, Iowa State University, 1966.

(18) L. S. Bartell, F. B. Clippard, Jr., and T. L. Boates, *Inorg. Chem.*, **9**, 2436 (1970).