J. Am. Chem. Soc. **1996,** *118,* 3759−3760 3759

On the Reinterpretation of the Experimental Structure of a Molecular Standard: Tri-*tert*-butylmethane by CFF93 Molecular Mechanics and Quantum Mechanics

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Received October 11, 1994

The advent of modern theoretical techniques is beginning to allow us to achieve an unparalleled understanding of molecular architecture. Tri-*tert*-butylmethane, whose structure is shown in Figure 1, is a classic molecule of unusual properties which has intrigued and challenged chemists for over 20 years. In a pioneering electron diffraction study in 1971, Bartell and Burgi attempted to solve the structure of this highly strained molecule in order to illuminate its properties and explain its unsual vibrational spectra.[1a] The resulting structure was indeed one of the most strained molecules known, with a C−C bond length in excess of 1.61 Å (*cf.* 1.53 Å) and tetrahedral angles strained from their standard values of 109.5° to values ranging from as low as 100° to over 115°. However, because of the limited resolution of the electron diffraction, in order to solve this structure, severe approximations had to be made. Thus, it was assumed not only that the molecule had overall C_3 symmetry but also that the individual *tert*-butyl groups were constrained to C_{3v} symmetry. This problem was pointed out by Bartell and Burgi in their initial paper where they noted[1a] "...this adds to the evidence that the model with local C_{3v} symmetry is too restrictive and that more, though probably quite limited, information can be extracted from the experimental data."

In a second paper,[1b] the authors made an attempt to relax the local *tert*-butyl C_{3v} symmetry and included the carbon backbones of the *tert*-butyl groups in their refinements. However, they were still constrained to assuming local C_3 symmetry of the methyl groups, and the C−C bonds in the *tert*-butyl group were all taken as equal. With this approximation they found six local minima in the refinement space which could be separated into two classes, all of which gave roughly equal agreement with the data: one class was characterized by a twist of the *tert*-butyl groups by roughly 10° as in the original constrained study, while in the second the *tert*-butyl groups were rotated by roughly 20°. In addition, the two classes of structures differed in most of the additional characteristic features which have made this molecule so unique and interesting, for example, the Ct−Cq bond length, which in one class of structures, as in the original, was roughly 1.61 Å while in the second class it was even more strained to 1.624 Å. In their paper, the authors stressed that "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...." Although they highlight the large (16°) calculated *tert*-butyl rotations from the staggered conformation, a preference for any of the refined ED structures was not expressed. As noted, this molecule has presented one of the severest challenges to our understanding of the mechanics of molecules and has been included as a test of virtually every molecular energy surface and form developed in the literature.[1b−8]

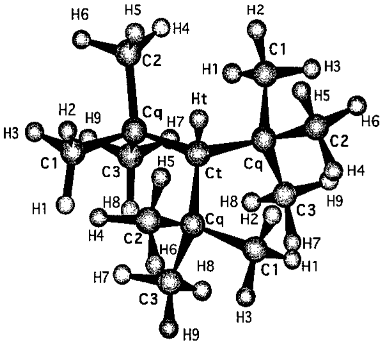

Figure 1. Structure of tri-*tert*-butylmethane as optimized by HF/6-31G*. The structure has three *tert*-butyl groups related by C_3 symmetry, *i.e.*, all methyl groups labeled 1 etc. are symmetry related. There is no symmetry between the methyl groups inside a *tert*-butyl group. All symmetry-independent geometries (bonds, angles, and torsions) are presented in Table 1 according to the atom labels shown here.

Here we show that with modern tools of high-level quantum and molecular mechanical calculations, including Hartree−Fock, density functional theory, and class II force fields, together with the available experimental data, we can finally assign a unique structure to tri-*tert*-butylmethane. In doing so we elucidate some of the long sought after features and trends in this molecule which are indeed special (such as H−C−C angles of approximately 101°). We can also assess the validity of the remaining approximation in the electron diffraction study, i.e., that of C_3 symmetry about the methyls.

Table 1 summarizes the results of the experimental studies and compares these with structures calculated from the quantum mechanical and molecular mechanics methods. One of the ironies of the study is that, in fact, it is the second set of structures, as demonstrated in Table 1, which turns out to be closer to the correct structure for this unusual molecule. Thus, unfortunately, we have been in the position of comparing our calculated results of many years with the "wrong" [2,4−8] experimental data. The geometrical parameters of representatives of the two solutions to the electron diffraction refinement space are given in Table 1 along with Hartree−Fock, BLYP, and ACM nonlocal density functionals[9,10] and the results of the class II force field.[11−16] As can be seen from this table, the agreement among the very different theoretical methods is remarkable. For example, all theoretical methods indicate a whole spectrum of large C_qC_mH angle values, as opposed to the single values assumed in the refinement. The trends in the values of these angles as calculated by different methods are virtually identical. (Note that the shorter C−H bond lengths obtained in the Hartree−Fock results are a well-known characteristic of the Hartree−Fock approximation.)[17] The most significant finger-

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Table 1. Two Experimental Models of Tri-*tert*-butylmethane[a] Compared with Those Calculated by Hartree−Fock, Density Functional Theory and Class II Molecular Mechanics

	expt		QM structures			
			Hartree−Fock	density functional		
	I[b]	II[c]	HF/6-31G*	DFT/BLYP	DFT/ACM	CFF93[h]
I. Representative Bonds[g] (Å)						
Ct Cq	1.611(5)	1.622(6)	1.616	1.639	1.609	1.630
⟨Cq C⟩	1.548(2)	1.548(2)	1.550	1.567	1.547	1.555
Cq C1			1.550	1.568	1.548	1.555
Cq C2			1.555	1.572	1.552	1.563
Cq C3			1.554	1.562	1.542	1.548
⟨C H⟩	1.111(3)	1.111(3)	1.083	1.100	1.092	1.112
Ct Ht			1.086	1.104	1.098	1.118
C2 H4			1.075	1.092	1.085	1.106
C3 H9			1.086	1.103	1.095	1.114
variation[d]			0.011	0.012	0.013	0.012
II. Representative Angles[g] (deg)						
Cq Ct Ht	101.6(4)	102.2(7)	102.6	102.6	102.7	102.3
Cq Ct Cq′	116.0(4)	115.7	115.4	115.4	115.3	115.6
⟨Ct Cq C⟩	113.0(2)	112.9	113.4	113.2	113.3	113.7
Ct Cq C1		114.9(8)	114.4	114.7	114.6	114.2
Ct Cq C2		110.3(5)	110.7	110.4	110.6	111.8
Ct Cq C3		113.4(7)	115.0	114.5	114.6	115.2
⟨C Cq C⟩	105.8(2)	105.8	105.2	105.5	105.3	104.8
C1 Cq C2			101.6	101.9	101.7	100.6
C2 Cq C3			108.6	108.9	108.8	108.4
⟨Cq C H⟩	114.2(1.0)	110.7(7)	111.6	111.4	111.5	112.3
Cq C1 H1			114.4	114.3	114.4	114.4
Cq C1 H3			108.0	107.9	107.8	109.9
Cq C2 H4			114.9	114.5	114.8	115.8
Cq C3 H9			109.2	109.3	109.2	109.8
H1 C1 H2			108.7	108.7	108.8	108.8
H1 C1 H3			106.4	106.7	106.6	104.5
H2 C1 H3			106.9	107.0	106.9	106.5
III. Representative Torsions[e,g] (Twist Angle, deg)						
⟨Ht Ct Cq C⟩	10.8(5)	20.4	17.7	18.2	18.1	16.4
Ht Ct Cq C1		24.8(6)	15.0	15.6	15.4	13.4
Ht Ct Cq C2		19.8(12)	20.9	21.2	21.2	20.0
Ht Ct Cq C3		17.1(9)	17.3	17.9	17.7	15.7
Cq Ct Cq2 C4			24.3	24.9	24.5	23.1
Cq Ct Cq2 C6			26.6	27.2	26.8	25.4
Cq Ct Cq2 C5			30.2	30.5	30.3	29.7
⟨Ct Cq C H⟩	18.0(60)	(18.0)	6.6	5.4	5.5	8.7
⟨Ct Cq C2 H⟩[f]			15.7	13.0	13.3	16.5
Ct Cq C1 H2			0.8	0.1	0.0	4.1
Ct Cq C1 H3			3.4	2.7	2.6	5.9
Ct Cq C2 H4			16.9	13.9	14.3	18.5
C1 Cq C2 H4			18.8	16.2	16.4	20.1
C1 Cq C3 H7			8.6	8.1	8.1	11.3
C2 Cq C1 H1			4.5	3.5	3.7	8.5
C2 Cq C1 H2			0.2	0.6	0.6	4.0
C3 Cq C1 H1			2.3	2.8	2.8	1.2
C3 Cq C2 H4			9.7	7.4	7.5	10.5
short H···H contacts (Å)			1.97 2.00	1.94 2.03	1.91 1.98	2.04 2.07

[a] The atoms are labeled according to Figure 1. Only symmetry-independent parameters are listed. Brackets denote averages over symmetrically distinct parameters. [b] The ED structure reported in ref 1. [c] An alternative experimental structure (model 2 of Table III of ref 1b) with fewer constraints than those employed for structure A. [d] Difference between the shortest (C2−H4) and the longest (Ct−Ht) C−H bond. [e] Expressed as the deviation from the nearest staggered configuration, i.e., twist angle = $|\tau - (\pm 60° \text{ or } \pm 180°)|$. [f] Only those of the type 2 methyl (C2) are averaged (the experiment assumes a local C_3 symmetry). [g] The complete list is given in the supporting information. [h] Class II molecular mechanics.

print, however, is the twist angle of the *tert*-butyl groups, the $H_tC_tC_qC$ torsion angle. As Bartell noted, the two classes of structures differed by some 10° (approximately 10° versus 20° in the two gas-phase ED refined structures, respectively). The angles from the theoretical methods cluster about 17° with the class II force field at the low end (16.4°) and the DFT methods at the high end (18°), clearly in closer agreement with the second class of structures. The averges clearly indicate that the *tert*-butyl groups in tri-*tert*-butylmethane are significantly more distorted by the strong nonbond steric interactions than inferred from the first class of structures until now accepted as the experimental structure.[2,4−8]

The trends in these highly distorted internals provide us with still more data to challenge our understanding of forces and mechanics of molecules. All theoretical methods indicate a large range of values for distortions in the *tert*-butyl group with the largest torsion twist of ∼20° corresponding to methyl group two and significantly smaller twists of methyl groups one and three (∼15° and 17°, respectively). We note that these values, although in the same range of values indicated by the restrained refinement, differ quantitatively and in order of distortion. In fact, in their molecular mechanics calculations,[1b] Bartell and Burgi obtained similar results (∼14°, 16°, and 18° torsion twists of the *tert*-butyl groups). Thus, as hypothesized by Bartell and Burgi,[1] the symmetry constraints in the refinement have serious consequences for the final values of the intervals. Given the remarkable agreement by the very different theoretical methods, it appears that these values provide a truer picture of the structure of tri-*tert*-butylmethane. The correspondence with experiment and the confluence of these high-level theories give us confidence that we are indeed beginning to be able to probe the true mechanics of the molecule. Thus, having achieved qualitative agreement of all methods with the key fingerprints deduced from experiment, we can go on to look at such things as the torsions of the methyl groups themselves. Here we see that whereas experiment had to constrain these to assume C_3 symmetry, and a single average value of ∼18° was obtained, from the theoretical results we note that not only does the average value appear to be much smaller (some 10° smaller) but there is significant variation among the methyls, a variation range of some 20°. From these results, it is not surprising that the details of the refined structure with these constraints vary.

In conclusion we see that modern theoretical methods, including quantum mechanical, Hartree−Fock, and density functional as well as molecular mechanical using class II force fields, have now reached a level where they can be used to probe the structure and mechanics of organic molecules to an extent surpassing low-resolution experimental techniques and enhancing the information obtained from the latter. These techniques are clearly more powerful when used in concert and inspire a much greater degree of confidence than any individual technique used on its own. Clearly, the most powerful combination is that of modern theoretical methods used in conjunction with experiment. Nevertheless, modern theoretical methods can give us an insight into the structural details and intramolecular forces operating in molecules that has hitherto been unachievable by experimental methods and previous generation theoretical methods.

Acknowledgment. This work was supported by the Consortium for Research and Development of Potential Energy Functions and a grant from the Advanced Technology Program of the National Institute of Standards and Technology.

Supporting Information Available: Complete listing of experimental and calculated bonds, angles, and torsions for tri-*tert*-butylmethane (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA9433176