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MOLECULAR STRUCTURE OF TRIMESITYLMETHANE

John F. Blount*

Chemical Research Department, Hoffmann-La Roche Inc.
Nutley, New Jersey 07110

Kurt Mislow

Department of Chemistry, Princeton University
Princeton, New Jersey 08540

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The molecular structure of trimesitylmethane (1) is of unusual interest for two reasons. First, a full relaxation empirical force field calculation[1] has led to a ground state structure (a molecular propeller of C_3 symmetry) which features abnormally enlarged central C-C-C bond angles (117.7°). Second, when the same force field was employed in a study of the dynamics of enantiomerization (interconversion of right- and left-handed propellers), it was found[1] that the lowest-energy pathway corresponds to a "two-ring flip".[2] Although a large body of experimental work[3] is consistent with this conclusion, only one study has provided direct experimental evidence in support of this mechanism, and that for the case of a triarylborane.[4] No direct experimental evidence exists for the case of a triarylmethane or for any other system of the type Ar_3ZX. Consequently, the computational study[1] occupies a unique position of central importance in the conformational analysis of such systems, and a direct test of its quality would be highly desirable. The most obvious test is a comparison of the calculated ground state geometry[1] with the experimentally determined X-ray structure. The present paper reports the results of such a comparison.

Crystals of 1 are trigonal, space group $P\bar{3}$, with two molecules in a cell of dimension a = 13.127(6), c = 7.628(6) Å. The intensity data were collected on a Hilger-Watts four circle diffractometer. Of the 1560 accessible reflections (θ < 76°), 1184 were considered observed [$I > 2.5\sigma$ (1)]. The structure was solved by Patterson methods and was refined by full-matrix least squares. In the final refinement anisotropic thermal parameters were used for the carbon atoms and isotropic temperature factors were used for the hydrogen atoms. The final discrepancy index is 0.047 for the 1184 observed reflections.

In the crystal the trimesitylmethane molecules lie on crystallographic 3-fold axes. The methane carbons occupy the special positions at 1/3, 2/3, z; 2/3, 1/3, -z.[5] Thus the trimesitylmethane molecules possess C_3 point symmetry in the crystalline state. The helical conformation of *1* can be seen in the stereodrawing (Figure 1). The principal interatomic distances and angles in *1* are shown in Figure 2b. The dihedral angle between the reference plane (defined by the C_3 axis and one of the bonds to the central atom) and the plane of the six phenyl carbons of the corresponding mesityl is 37.7(3)°. The *rms* deviation of the six atoms comprising the phenyl ring from the best plane through these atoms is 0.017 Å. Deviations of other atoms from this plane are as follows: the methine hydrogen, 0.53; the central carbon C(10), -0.064; the *proximal* methyl carbon C(7), 0.093; the *para* methyl carbon C(8), -0.049; the *distal* methyl carbon C(9), 0.004 Å.

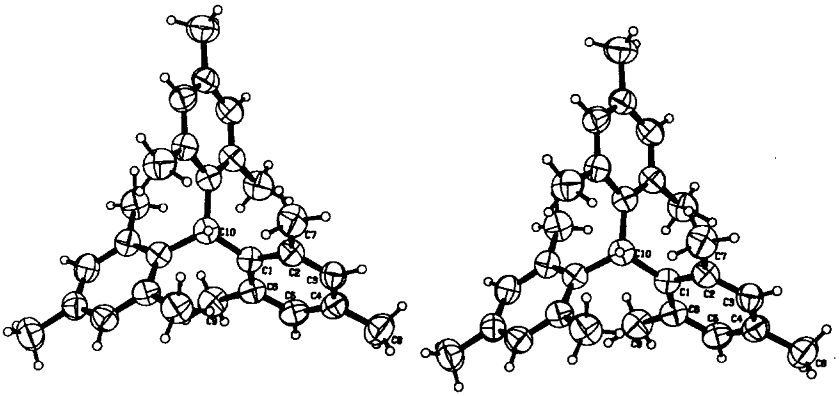

Figure 1. Stereoview and numbering scheme of trimesitylmethane (*1*). The thermal ellipsoids are scaled to 50% probability. The hydrogen atoms are shown as spheres of an arbitrary size.

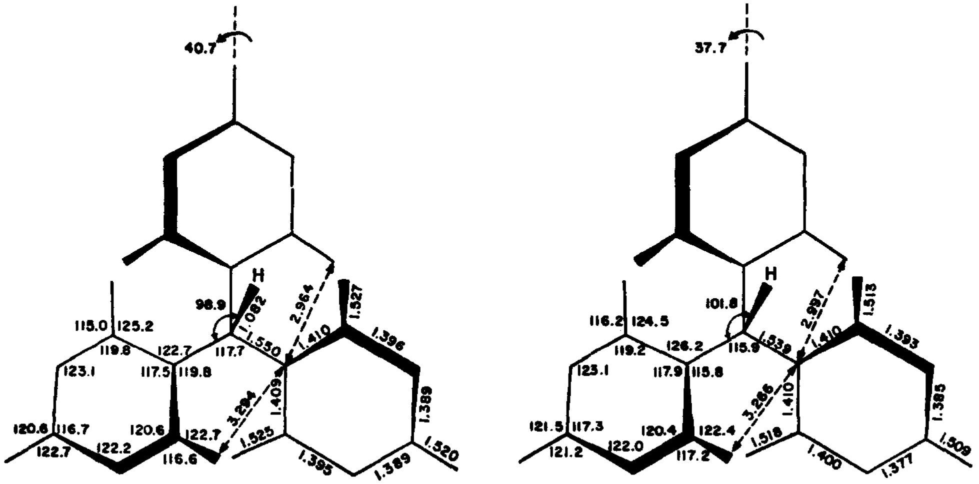

Figure 2. (a) Calculated[1] ground-state structure of trimesitylmethane (1) (left). (b) X-ray structural data for 1 (right); estimated standard deviations are 0.003 Å for distances and 0.2° for angles.

Comparison of bond lengths and bond angles in the calculated and X-ray structures (Figure 2) indicates satisfactory overall agreement between corresponding parameters. Also, the calculated value for the angle of twist of the molecular propeller (40.7°) is closely similar to that found by X-ray diffraction (37.7 ± 0.3°). However, although the calculated bond angle at the central carbon atom (117.7°) is quite comparable in magnitude to bond angles in similarly overcrowded systems,[6] it is significantly larger than the corresponding bond angle in the X-ray structure (115.9°). Similarly, the calculated[1] bond angle at the central carbon atom in triphenylmethane (114.4°) also exceeds the observed[9] average angle of 113°. Evidently, our computational scheme[1] affords reasonable values of molecular geometry with one exception: bond angle -- and to some extent bond length -- deformations at the central atom are consistently overestimated. Although it is not known to what extent these discrepancies can be attributed to crystal packing forces, which are not considered in our calculation, the deficiency appears to lie principally in the force field itself.[10] However, given the otherwise excellent agreement between bonding parameters, we see no need for corrective reparametrizations.

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References and Notes

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