Conformation of the Bicyclo[2,2,2]octane System

By O. ERMER and J. D. DUNITZ*

(*Organic Chemistry Laboratory, Swiss Federal Institute of Technology,* 8006 *Zürich, Switzerland*)

WHETHER the bicyclo[2,2,2]octane system (I) possesses $D_{3h}(\bar{6}m2)$ or $D_3(32)$ symmetry has been much discussed. From the relatively large heats of hydrogenation of bicyclo[2,2,2]octene and bicyclo[2,2,2]octadiene, Turner, Meador, and Winkler[1] concluded that (I) possesses a twisted D_3 structure, a conclusion drawn also from certain strain-minimization calculations.[2] On the other hand, from analysis of the microwave spectra of 1-chloro- and 1-bromo-bicyclo[2,2,2]octanes, Nethercot and Javan[3] have estimated the angle of twist to be essentially zero ($0 \pm 4°$). The i.r. and Raman spectra of (I) also appear to be compatible with D_{3h} symmetry,[4,5] which is further supported by arguments and calculations based on strain considerations.[6,7] X-Ray analyses have been inconclusive; crystals of (I) itself are disordered,[8,9] while crystals of 1,4-dichlorobicyclo-[2,2,2]octane give a highly complex diffraction pattern indicative of a large super-cell.[10]

We have now determined the crystal structure of bicyclo[2,2,2]octane-1,4-dicarboxylic acid and find no significant deviation from D_{3h} symmetry in the carbon skeleton. The crystals are monoclinic, space group $P2_1/c$, $a = 6{\cdot}01$, $b = 16{\cdot}73$, $c = 10{\cdot}29$ Å, $\beta = 115{\cdot}08°$, $Z = 4$. Intensities of the X-ray reflexions were measured with Mo-K_α radiation with the aid of the Hilger–Watts 4-circle diffractometer Y290 controlled by a PDP-8 computer. About 1150 reflexions were observed. The analysis has led to the molecular parameters shown in the Figure, and it is unlikely that these will change significantly on further refinement

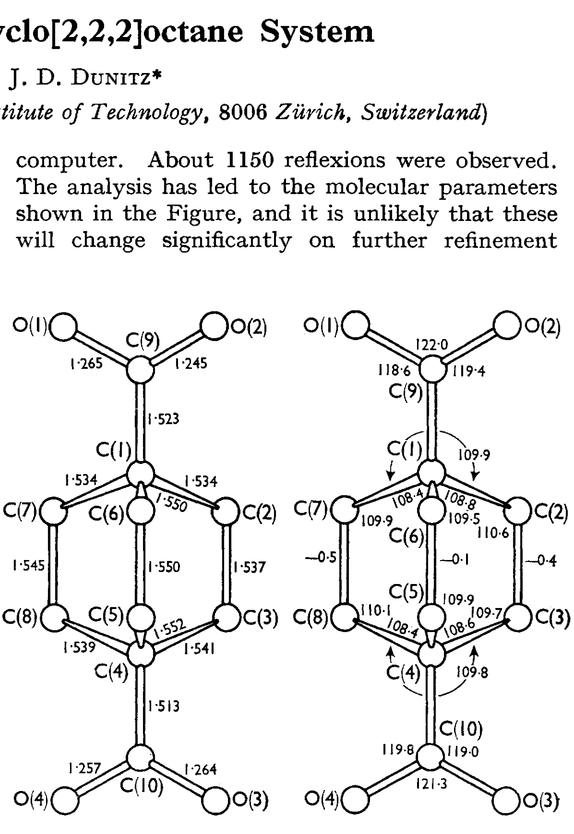

FIGURE. *Bond distances, angles and torsion angles in bicyclo*[2,2,2]*octane*-1,4-*dicarboxylic acid* (*estimated standard deviations*: *bond lengths* 0·007 Å, *bond angles* 30′, *torsion angles* 45′).

(present $R = 0{\cdot}066$, based on model with anisotropic thermal parameters for C and O atoms and is close to expected value based on estimated uncertainties in intensity measurements).

Within experimental error the molecule does not deviate from $C_{2v}(mm2)$ symmetry in the crystal. The mean values of chemically equivalent bond distances and angles of the bicyclo[2,2,2]-octane system in terms of D_{3h} symmetry are in good agreement with corresponding quantities calculated by Gleicher and Schleyer by a strain-minimization procedure[7] (Table). (It should, however, be remembered that the carbon skeleton with D_{3h} symmetry and given bond lengths is completely defined by specifying one of the angles; for equal bond lengths, $2 \cos \theta_1 = 3 \cos^2 \theta_2 - 1$.)

Comparison of mean values of observed molecular parameters with results of strain-minimization calculation by Gleicher and Schleyer (ref. 7).

	Calculated	Observed
C(1)–C(2)	1·540 Å	1·542 Å
C(2)–C(3)	1·543	1·544
C(1)–C(4)	2·592	2·597
C(2)–C(5)	2·944	2·946
∠C(2)–C(1)–C(7)	109·0°	109·0°
∠C(1)–C(2)–C(3)	109·9	110·0

In our analysis, the electron-density maxima corresponding to the carbon atoms of the methylene groups are almost spherical and not drawn out into ellipsoids (*cf.* the case of 1,4-diazabicyclo-[2,2,2]octane).[11] This would indicate that the apparent D_{3h} symmetry of the bicyclo[2,2,2]-octane skeleton observed in our case arises neither because of rapid interconversion of the two D_3-enantiomers, nor as a result of disorder from random occupation of the molecular sites by D_3-enantiomers, but corresponds to the stable conformation of the molecule.

Analysis of the anisotropic thermal ellipsoids in terms of the translational and rotational vibrations of the bicyclo-octane skeleton treated as a rigid body leads to an r.m.s. amplitude of 5·9 ± 0·2° for rotation about the three-fold axis.

This work was carried out with the financial support of the Schweizer Nationalfonds zur Förderung der wissenschaftlichen Forschung.

(*Received, March 26th,* 1968; *Com.* 375.)

[1] R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Amer. Chem. Soc.*, 1957, **79**, 4116.
[2] J. B. Hendrickson, *Chem. Eng. News*, 1961, **39**, 40.
[3] A. H. Nethercot and A. Javan, *J. Chem. Phys.*, 1953, **21**, 363.
[4] J. J. MacFarlane and I. G. Ross, *J. Chem. Soc.*, 1960, 4169.
[5] P. Brüesch and H. H. Günthard, *Spectrochim. Acta*, 1966, **22**, 867, 877.
[6] P. von R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, 1961, **83**, 2700.
[7] G. J. Gleicher and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1967, **89**, 582.
[8] J. Bauer, *Sbornik Vysoke Skoly Chem.-Technol. v. Praze*, 1957, 145 (*Chem. Abs.*, 1959, **53**, 1887d).
[9] P. Brüesch and H. H. Günthard, *Spectrochim. Acta*, 1966, **22**, 861.
[10] R. Grønback and J. D. Dunitz, unpublished results.
[11] S. Weiss, A. S. Parkes, E. R. Nixon, and R. E. Hughes, *J. Chem. Phys.*, 1964, **41**, 3759.