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THE STRUCTURE OF BICYCLO-[2,2,2]-OCTENE 2,3 ENDO-DICARBOXYLIC ANHYDRIDE

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The conformation of bicyclo-[2,2,2]-octane and its derivatives is a subject of considerable recent interest and discussion (1, 2, 3, 4, 5, 6, 7, 8, 9). In connection with this argument, the structure of bicyclo-[2,2,2]-octene 2,3 endo-dicarboxylic anhydride $C_{10}H_{10}O_3$ has been determined by X-ray diffraction.

Crystals of the substance (m.p. 146°) were obtained by Diels-Alder reaction of cyclohexadiene with maleic anhydride. They are monoclinic, space group P $2_1/c$, with $\underline{a}$ = 6.534 (±0.004), $\underline{b}$ = 10.480 (±0.001), $\underline{c}$ = 12.184 (±0.001) Å, β = 96.37° (±0.02°) and four molecules per unit cell. These data were obtained by Cohen's back reflexion method, as described by Buerger (10), using Cu K_α radiation (λ_1=1.54051, λ_2=1.54433 Å) at a room temperature of 21°C. The effective radius of the camera (an ordinary Weissenberg) was determined by mounting the film according to Straumanis technique.

The standard deviations were taken from the sum of the residuals, according to Whittaker and Robinson (11). The measured density is 1.43 g cm^{-3} and the corresponding calculated value is 1.427.

The structure was solved by direct methods and refined by least-squares.

At the present stage of the refinement, the R index is 0.083 on 1262 observed independent reflexions. Anisotropic temperature factors for carbon and oxygen atoms were used in the last cycles of least-squares. The uncertainty of the bond distances (not involving H atoms) is about 0.01 Å and of bond angles is less than 1°: the most salient details of the molecular geometry are reported in Figure 1. The molecular symmetry (non crystallographic) is very close to m.

In the bicyclo-octene nucleus, most of the angles centered on sp^3 carbon atoms are almost tetrahedral; their values are very close to the corresponding bicyclo-octane data, as reported by Ermer and Dunitz (8). The angle C(3)-C(4)-C(8) and the corresponding one centered on C(1) are somewhat smaller than normal: the deformation is however definitely minor than for 5-norbornene-2,3-endo-dicarboxylic anhydride (12, 13), where these angles are 98°. A similar observation can be drawn about the angles centered on sp^2 carbon atoms C(5) and C(6), which are showing a significant deviation from 120°; in the corresponding norbornene compound, their value is 108°.

The atoms C(1), C(2), C(3) and C(4) are all coplanar within the experimental uncertainty; the same situation occurs for the other two planes C(1), C(4), C(5), C(6) and C(1), C(7), C(8) and C(4). This excludes any significant twisting from 'eclipsed' configuration around the C(1)-C(4) axis. The dihedral angles between the first plane and the other two are 122° and 116°, respectively.

The bond distances in the bicyclo-octene nucleus are all normal; the geometry of the anhydride group is very close to the situation observed for 5-norbornene 2,3-endo-dicarboxylic anhydride and for succinic anhydride (12, 13, 14, 15), except for a slightly higher deviation (up to 0.06 Å) of the oxygen atoms from the plane of C(2), C(3), C(9) and C(10), which are themselves coplanar within the range of experimental error. The direction

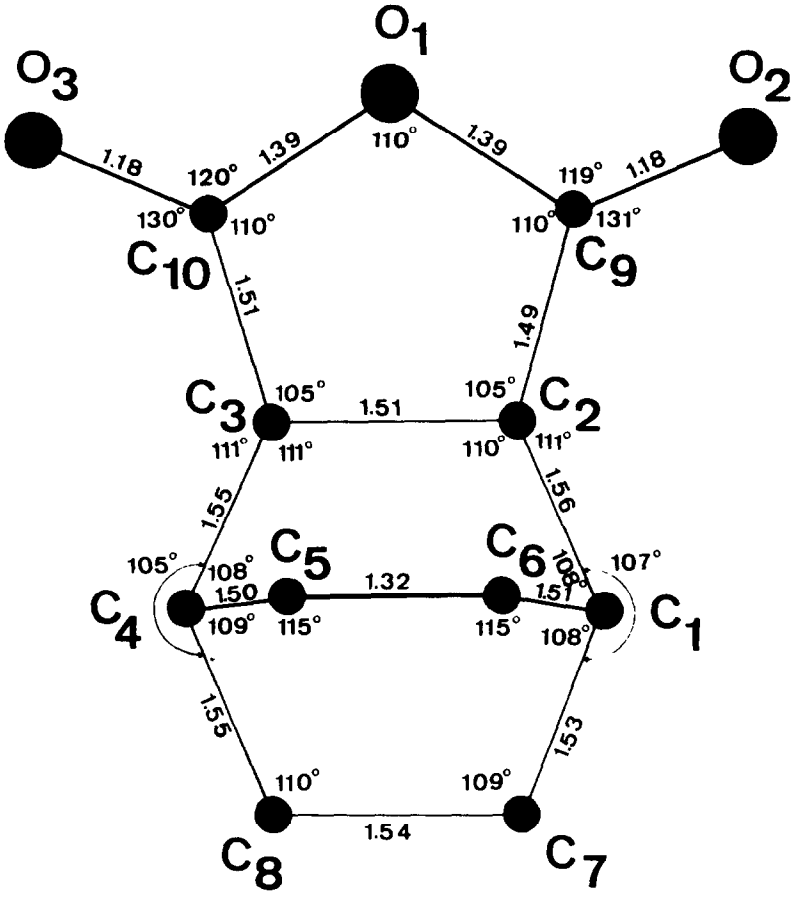

Fig.1 - Bond distances and angles in bicyclo-[2,2,2]octene 2,3 endo-dicarboxylic anhydride. The molecule is seen along the direction corresponding to the maximum moment of inertia.

of this displacement is opposite for O(1) with respect to O(2) and O(3), which are shifted out of the plane towards the bicyclo-octene nucleus.

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