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THE STRUCTURE OF
5-NORBORNENE-2,3-EXO-DICARBOXYLIC ANHYDRIDE

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In the sequence of studies about the conformation of norbornene derivatives, the structure of 5-norbornene 2,3-endo dicarboxylic anhydride $C_9H_8O_3$ was determined by X-ray diffraction (1). A comparison of this structure with the one of the exo isomer was considered to be useful; further interest derives from a series of kinetic studies on the mechanism of the endo-exo transformation (2).

The crystals of the substance are orthorhombic, space group $P2_12_12_1$ with $\underline{a}$ = 7.985 ± 0.002, $\underline{b}$ = 7.630 ± 0.005, $\underline{c}$ = 12.770 ± 0.002 Å and four molecules per unit cell. These data were obtained by Cohen's back reflection method,as described by Buerger (3), using CuK_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 deviation was taken from the sum of the residuals, according to Whittaker and Robinson (4). The measured density is 1.42 and the calculated value is 1.401 g cm^{-3}.

The orientation of the molecule with respect to crystallographic axes was obtained by angular scanning of the three-dimensional Patterson synthesis

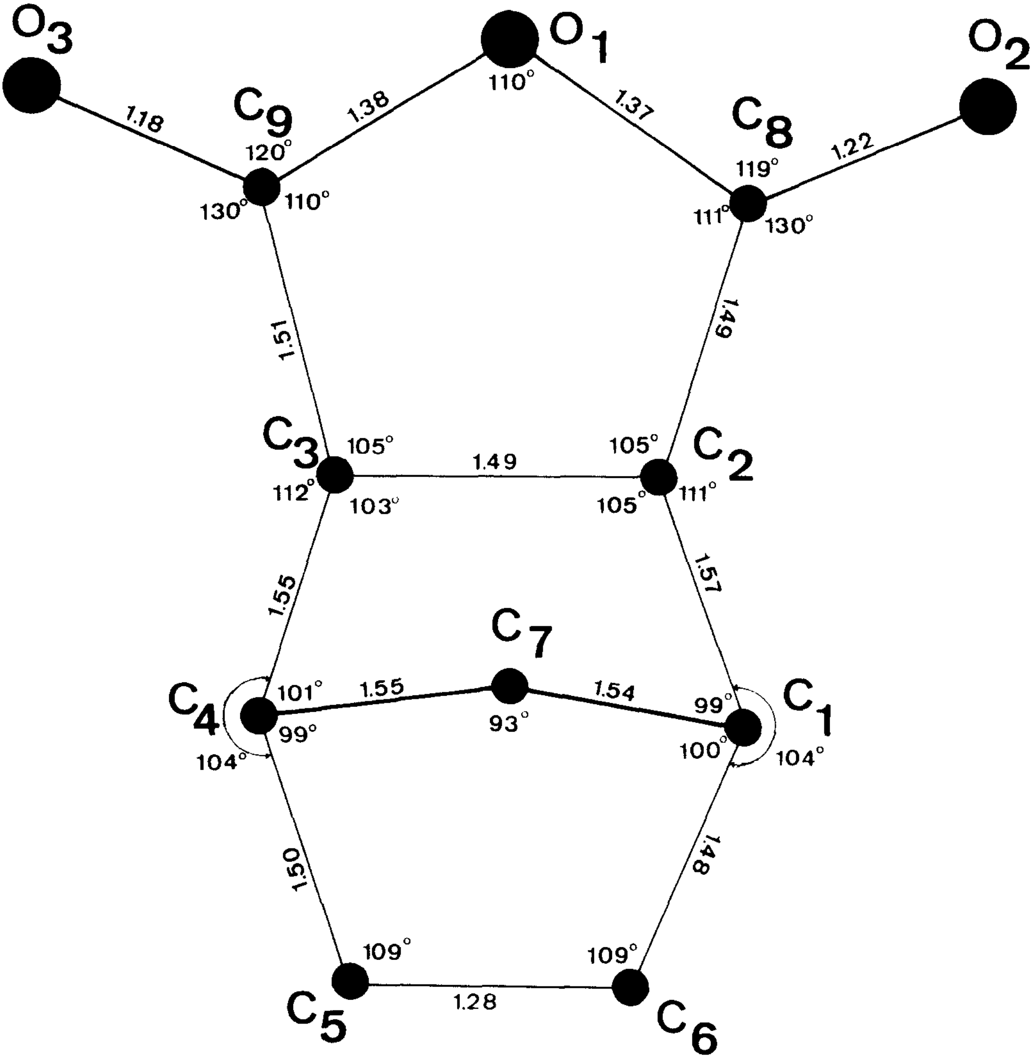

Fig.1 - Bond distances and angles in 5-norbornene-2,3 exo-dicarboxylic anhydride. The molecule is seen along the direction corresponding to the maximum moment of inertia. The uncertainty is ± 0.01 Å for bond distances and ± 1° for bond angles.

considering the maximum overlap with vectors relative to an assumed molecular model.

An unique set of three rotational angles was found: the position of the molecule in the unit cell was then chosen according to the best fit of calculated and observed structure factors.The correct solution of the structure was confirmed in the subsequent refinement by least-squares.At the end of the refinement the R index is 0.098 for 596 observed independent reflexions collected about the c axis. Anisotropic temperature factors for carbon and oxygen atoms were used in the final least-squares.

The molecular geometry is reported in Fig.1 . It is quite similar to the one of the endo compound, as it can be expected, and agrees with those of similar compounds already studied by X-ray diffraction (5, 6, 7) or by electron diffraction in gas phase (8).

In the norbornene nucleus the atoms C(1), C(4), C(5), C(6) are coplanar within less than 0.01 Å; the atoms C(1),C(2),C(3),C(4) are coplanar within 0.01 Å. The dihedral angle between these two planes is 110° ,the angles between them and the plane defined by the atoms C(1), C(4), C(7) are 128° and 121°,respectively. The bridgehead angle C(1)-C(7)-C(4) is 93° a value consistently found in all norbornane or norbornene derivatives unsubstituted at C(7) (1,7,8).

The anhydride group is planar within 0.016 Å and the bond distances and angles are similar to the ones found in the endo compound (1), in bicyclo (2,2,2) octene 2,3 endo-dicarboxylic anhydride (9) and in the succinic anhydride (10, 11).

The dihedral angle between the anhydride group and the plane defined by the atoms C(1), C(2), C(3), C(4) is 117° .

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