

THE MOLECULAR STRUCTURE OF
5-NORBORNENE - 2,3 ENDO-DICARBOXYLIC ANHYDRIDE

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The conformation of the derivatives of norbornane and related hydrocarbons is a subject of considerable interest, which is evident in an extensive series of experimental physico-chemical studies (1,2,3,4,5,6,7,8) and many semi-empirical calculations (9,10,11,12,13,14). This interest has prompted a determination of the crystal structure of 5-norbornene-2,3 endo-dicarboxylic anhydride $C_9H_8O_3$ by X-ray diffraction.

The crystals of the substance are orthorhombic, space group $P 2_1^2 2_1^2 2_1$, with $a = 13.5394 (\pm 0.0008)$, $b = 9.5648 (\pm 0.0016)$, $c = 5.9721 (\pm 0.0003)$ Å and four molecules per unit cell. These data were obtained by Cohen's back reflection method, as described by Buerger (15), using $Cu K\alpha$ radiation ($\lambda_1 = 1.54051$, $\lambda_2 = 1.54433$ 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 (16). The measured density is 1.417 g cm^{-3} and the corresponding calculated value is 1.409.

The structure was solved by three-dimensional Patterson synthesis and refined by least-squares. At the end of the refinement, the R index is 0.072 on 802 observed independent reflexions.

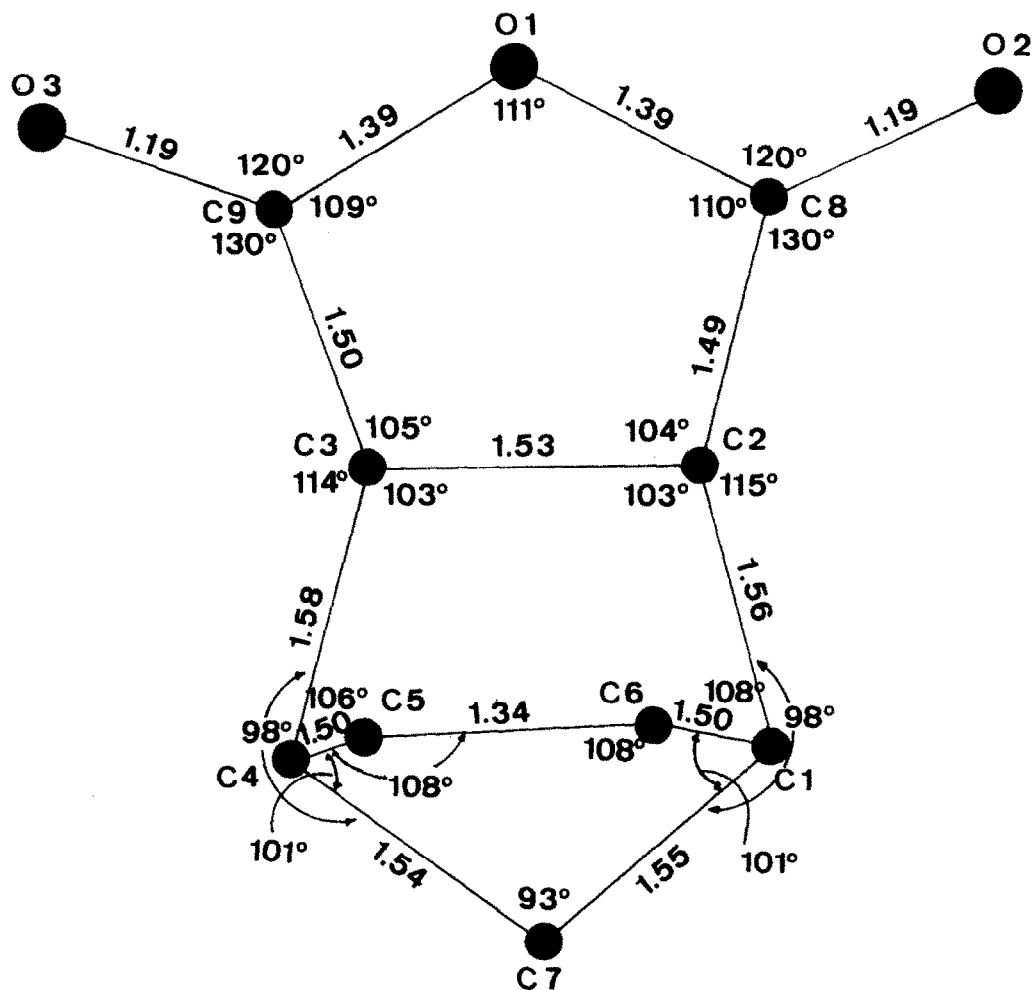


Figure 1 - Bond distances and angles in 5-norbornene-2,3 endo-dicarboxylic anhydride. The molecule is seen along the direction corresponding to the maximum moment of inertia.

The most salient details of the molecular geometry are reported in Figure 1. The bridgehead angle C(1)-C(7)-C(4) can be compared with a value of 92.7° , 97° and 96° , as found in the nucleus of cyclopentadiene dimer (6), tricyclo [3,2,1,0^{2,4}] octane (4) and norbornene (5), respectively, by X-ray diffraction, or with 93.2° or 92° , as obtained for norbornane and norbornadiene, respectively, by electron diffraction in gas phase (7).

The length of the double bond C(5)-C(6) is normal; the single bonds C(1)-C(2) and C(3)-C(4) are significantly longer than C(1)-C(6) and C(4)-C(5). A similar effect occurs in the nucleus of cyclopentadiene dimer (6).

In the norbornene nucleus, the atoms C(1), C(2), C(3) and C(4) are coplanar within 0.02 \AA ; the atoms C(1), C(4), C(5) and C(6) are coplanar within 0.01 \AA . The dihedral angle between these two planes is 113° ; the angles between them and the plane defined by C(1), C(4) and C(7) are 117° and 130° , respectively.

The bond distances and angles in the anhydride group are similar to the ones of succinic anhydride, as found by Ehrenberg (17) and Biagini and Cannas (18); all the carbon and oxygen atoms in this group are coplanar within 0.04 \AA .

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