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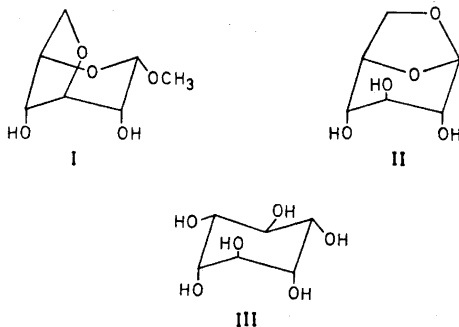
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## The Crystal and Molecular Structure of Methyl 3,6-Anhydro- $\alpha$ -D-glucopyranoside

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The pyranose rings in methyl 3,6-anhydro- $\alpha$ -D-glucopyranoside (I) and 1,6-anhydro- $\beta$ -D-glucopyranose (II) are forced into the <sup>1</sup>C<sub>4</sub> conformation and should be considerably distorted as a result of the strain caused by the *cis*-fused 5-membered ring. The distance between the axial oxygen atoms, O-2 and O-4, should therefore be longer in (II) and shorter in (I) than in a



corresponding unstrained system. A recent X-ray diffraction study of II<sup>1</sup> demonstrated, *inter alia*, that the distance between O-2 and O-4 was 3.30 Å. A similar study of methyl 3,6-anhydro- $\alpha$ -D-galactopyranoside<sup>2</sup> demonstrated the distortion of the pyranose ring.

That the distance between O-2 and O-4 in I is exceptionally short was indicated by two observations. Firstly the  $\beta$ -anomer of I, which should have a similar structure, showed unexpectedly high mobilities on paper electrophoresis in borate and sulfonated phenyl boronic acid buffers.<sup>3</sup> The complex formation with boron, which requires an O-O distance of approximately 2.4 Å,<sup>4</sup> can only take place between the axially disposed oxygen atoms O-2 and O-4.

Secondly Schwarz and Totty<sup>5,6</sup> observed that I was a considerably stronger acid ( $K_a$   $62.3 \times 10^{-14}$ ) than, e.g., the unstrained *muco*-inositol (III,  $K_a$   $7.10 \times 10^{-14}$ ). 1,6-Anhydro- $\beta$ -D-glucopyranose is even weaker ( $K_a$   $2.96 \times 10^{-14}$ ). These results were explained in terms of a hydrogen bridge between O-2 and O-4 in the corresponding anions. The distance between these atoms in III is about 2.89 Å and should consequently be considerably smaller in I.

We now report an X-ray diffraction study of I. The compound crystallized in space group  $P2_12_12_1$ ;  $a=8.210$  (1),  $b=17.764$  (3),  $c=5.555$  (1),  $Z=4$ . The crystals decomposed on X-ray irradiation. From equi-inclination Weissenberg photographs, taken using  $\text{CuK}\alpha$  radiation, 335 data were collected. The phase determinations were carried out by a computerized application

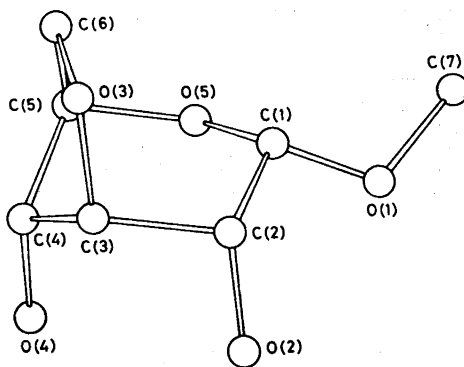


Fig. 1. The molecular structure of methyl 3,6-anhydro- $\alpha$ -D-glucopyranoside.

of direct methods using the weighted phase-sum formula.<sup>7</sup> Several cycles of full-matrix least-squares refinement (only isotropic non-hydrogen atoms included) gave an *R*-value of 0.136. The molecular structure is shown in Fig. 1. Intramolecular distances and angles are listed in Table I. Full details

Table I. Intramolecular distances and angles. Estimated standard deviations in parentheses.

C(1)–C(2) 1.50(3) Å	C(1)–C(2)–C(3) 108(2)°
C(2)–C(3) 1.57(3)	C(2)–C(3)–C(4) 118(2)
C(3)–C(4) 1.41(4)	C(3)–C(4)–C(5) 100(2)
C(4)–C(5) 1.56(3)	C(4)–C(5)–O(5) 109(2)
C(5)–C(6) 1.53(4)	C(5)–O(5)–C(1) 116(2)
C(1)–O(1) 1.38(2)	O(5)–C(1)–C(2) 116(2)
C(2)–O(2) 1.50(2)	C(1)–O(1)–C(7) 115(2)
C(3)–O(3) 1.50(3)	O(1)–C(1)–C(2) 108(2)
C(4)–O(4) 1.46(3)	O(1)–C(1)–O(5) 108(2)
C(5)–O(5) 1.49(2)	C(1)–C(2)–O(2) 108(2)
C(1)–O(5) 1.40(3)	O(2)–C(2)–C(3) 103(2)
C(6)–O(3) 1.44(3)	C(2)–C(3)–O(3) 104(2)
C(7)–O(1) 1.47(3)	C(3)–C(3)–C(4) 104(2)
	C(3)–C(4)–O(4) 120(2)
	O(4)–C(4)–C(5) 111(2)
	C(4)–C(5)–C(6) 97(2)
	C(6)–C(5)–O(5) 111(2)
	C(3)–O(3)–C(6) 105(2)
	O(3)–C(6)–C(5) 107(2)

of the X-ray diffraction investigation will be published elsewhere.

As expected, the distance between O-2 and O-4 is short, 2.76 Å, in accordance with the observed chemical properties. Furthermore, although the hydrogens have not been located, the packing of the molecules would suggest an intramolecular hydrogen bond between O-2 and O-4 in the crystalline state.

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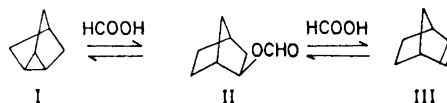
## Stereoselective Cyclopropane Ring Opening Reactions of Nortricyclene Hydrocarbons in Formic Acid I. Reactions of Nortricyclene, Norbornene and Tricyclene

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During the study of the stereochemistry of the nortricyclene compounds and their cyclopropane ring opening products in our laboratory, the course of the reactions of nortricyclene hydrocarbons in formic acid has been examined.<sup>1,2</sup> The protonation of the cyclopropane ring in this system apparently leads to the same cationic intermediates as are found in the *S<sub>N</sub>1* solvolyses and *E<sub>1</sub>* eliminations of 2-norbornyl derivatives.<sup>3,4</sup> The aim in the present series is to connect kinetic data with the intermediate and final product analysis.

The addition of formic acid to nortricyclene (I) or norbornene (III) has norbornyl-2-*exo*-formate (II) as the sole main product.<sup>5,6</sup> This was confirmed in the present study. The hydrocarbon III from I, or I from III, occurred as a minor side product of the reaction, leading to the following overall picture:



Only one ester product, isobornyl formate (V), was found from tricyclene (IV); the only hydrocarbon byproduct present