with the first one being responsible for the stability of the complex.

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Structure of 2,3:4,5-Di-O-isopropylidene-β-D-fructopyranose

BY T. LIS AND A. WEICHSEL

Institute of Chemistry, The University, 50–383 Wrocław, Poland

Abstract. $C_{12}H_{20}O_6$, $M_r = 260.3$, tetragonal, $P4$, $a = 21.51$ (1), $c = 5.940$ (3) Å, $V = 2748$ Å^3, $Z = 8$, $D_m = 1.23$, $D_x = 1.26$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0.71069$ Å, $\mu = 0.11$ mm^{-1}, $F(000) = 1120$, $T = 300$ (2) K, final $R = 0.044$ for 2932 observed reflexions. The six-membered β-fructopyranose ring in the two crystallographically independent molecules (A and B) is in an $^2S_0$ twist-boat conformation. The hydroxyl groups of four A molecules and, independently, four B molecules form square donor–acceptor hydrogen-bond systems about the fourfold axes at $00z$ and $\frac{1}{2}\frac{1}{2}z$, respectively. There are no hydrogen bonds between A and B molecules.

Introduction. It is known that carbohydrates and acetone form isopropylidene acetals in the presence of acids. From the condensation of D-fructose with acetone it is easy to obtain two crystalline di-isopropylidene derivatives: 1,2:4,5-di-O-isopropylidene-β-D-fructopyranose and 2,3:4,5-di-O-isopropylidene-β-D-fructopyranose (Ohle & Koller, 1924). The structure of the first of these has been published (Takagi, Shiono & Rosenstein, 1973). Here we report the crystal structure of the second compound, which occurs in the unusual space group $P4$, in order to compare the molecular structures of both isomers.

Experimental. The title compound was prepared according to the procedure of Ohle & Koller (1924). Colorless, long needle crystals were obtained by slow evaporation at room temperature of the 2-propanol solution. D_m by flotation in an aqueous solution of $Ca(NO_3)_2$. Preliminary examination by rotation and Weissenberg photographs. A specimen $0.6 \times 0.8 \times 0.08$ mm was cut from a large crystal. Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation for lattice parameters (15 reflexions in range $20 < 2\theta < 26°$) and intensity measurements; ω–2θ scan technique; 4393 reflexions measured in the range $2 \le \theta \le 30°$; $h\ 0\rightarrow30$, $k\ 1\rightarrow30$, $l\ 0\rightarrow8$; two standards measured after every 50 reflexions, variation 5%. Absorption ignored. Structure solved by direct methods with *MULTAN80* (Main et al., 1980). 31 atoms located in the E map with highest combined figure of merit. The remaining heavy atoms, and finally all the H atoms, were located from subsequent difference Fourier maps. Full-matrix least-squares refinement using *XTL/XTLE* programs (Syntex, 1976) based on F values (O, C anisotropic, H isotropic) for 2932 reflexions with $I \ge 2\sigma(I)$, $w = 1/\sigma^2(F_o)$ gave $R = 0.044$ and $wR = 0.036$; max. $\Delta/\sigma = 0.4$. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974), real and imaginary components of anomalous dis-

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Table 1. *Positional parameters and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{1}{3}(B_{11} + B_{22} + B_{33}).$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Molecule A				
O(1)	0·0845 (2)	0·0314 (2)	0·3041 (9)	4·27 (25)
O(2)	0·1074 (2)	0·1580 (2)	0·3934 (6)	3·31 (20)
O(3)	0·1837 (2)	0·1761 (2)	0·1369 (7)	3·44 (19)
O(4)	0·2768 (2)	0·0501 (2)	0·3507 (8)	3·98 (22)
O(5)	0·3246 (2)	0·1152 (2)	0·5982 (9)	5·75 (29)
O(6)	0·1859 (2)	0·1259 (2)	0·6333 (7)	3·79 (21)
C(1)	0·1237 (2)	0·0499 (2)	0·4813 (10)	3·87 (33)
C(2)	0·1543 (2)	0·1124 (2)	0·4353 (9)	3·04 (25)
C(3)	0·1948 (2)	0·1154 (2)	0·2244 (9)	3·10 (28)
C(4)	0·2643 (2)	0·1116 (2)	0·2726 (10)	3·29 (28)
C(5)	0·2844 (2)	0·1530 (2)	0·4672 (10)	3·65 (29)
C(6)	0·2306 (2)	0·1749 (2)	0·6096 (10)	3·91 (33)
C(7)	0·1140 (3)	0·2590 (3)	0·2138 (13)	5·39 (48)
C(8)	0·0769 (2)	0·1654 (3)	0·0000 (11)	4·63 (42)
C(9)	0·1194 (2)	0·1895 (2)	0·1834 (10)	3·81 (32)
C(10)	0·3255 (2)	0·0539 (2)	0·5138 (10)	4·39 (34)
C(11)	0·3106 (4)	0·0107 (3)	0·7030 (13)	7·00 (65)
C(12)	0·3880 (3)	0·0418 (5)	0·4039 (17)	7·60 (80)
H(O1)	0·059 (2)	0·046 (2)	0·306 (8)	2·3 (10)
Molecule B				
O(1)	0·4962 (2)	0·4088 (2)	1·1042 (9)	4·35 (26)
O(2)	0·3822 (2)	0·3516 (2)	1·0 (fixed)	3·48 (20)
O(3)	0·3826 (2)	0·2724 (2)	1·2513 (8)	3·90 (21)
O(4)	0·5299 (2)	0·2150 (2)	1·0504 (8)	4·48 (24)
O(5)	0·4818 (2)	0·1533 (2)	0·7945 (9)	6·66 (33)
O(6)	0·4367 (2)	0·2862 (2)	0·7598 (8)	3·89 (21)
C(1)	0·4914 (2)	0·3662 (2)	0·9245 (10)	3·92 (33)
C(2)	0·4390 (2)	0·3194 (2)	0·9620 (9)	3·31 (28)
C(3)	0·4448 (2)	0·2780 (2)	1·1715 (9)	3·27 (29)
C(4)	0·4668 (2)	0·2118 (2)	1·1201 (10)	3·80 (30)
C(5)	0·4335 (2)	0·1826 (2)	0·9166 (11)	4·30 (35)
C(6)	0·4014 (2)	0·2299 (2)	0·7721 (11)	4·13 (34)
C(7)	0·2850 (3)	0·3182 (3)	1·1597 (15)	6·12 (57)
C(8)	0·3641 (3)	0·3766 (3)	1·3927 (11)	5·19 (46)
C(9)	0·3532 (2)	0·3311 (2)	1·2042 (10)	4·19 (35)
C(10)	0·5398 (3)	0·1647 (3)	0·8976 (12)	5·81 (46)
C(11)	0·5863 (5)	0·1856 (5)	0·7227 (17)	9·9 (11)
C(12)	0·5608 (5)	0·1083 (4)	1·0227 (20)	8·16 (86)
H(O1)	0·477 (2)	0·428 (2)	1·101 (9)	2·6 (11)

persion included for O and C atoms. Residual electron density in final difference Fourier map within -0.20 and 0.15 e Å^{-3}.

The final atomic parameters are given in Table 1.*

Discussion. The molecular structure and atom-numbering scheme for one of the two symmetry-independent molecules are illustrated in Fig. 1. Bond distances and angles (with the exceptions of those at $-CH_3$ groups) in both molecules (denoted A and B) are comparable within 3σ (Table 2). Selected torsion angles and puckering parameters (Cremer & Pople, 1975) are summarized in Table 2(c). The conformation of molecules A and B is essentially the same. The pyranosyl rings adopt the $^2S_0$ twist-boat form. This conformation is the result of distortion introduced by the fusion of one six- and two five-membered rings, and is significantly different from the $^5C_2$ pyranose ring

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44035 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

geometry in 1,2:4,5-di-O-isopropylidene-β-D-fructopyranose (Takagi et al., 1973), in which one five-membered ring is spiro fused at C(2). The $^2S_0$ twist-boat conformation corresponds to the skew form suggested earlier on the basis of ^{1}H NMR studies (Maeda, Tori, Satoh & Tokuyama, 1969). This conformation is different from that observed in other crystal structures containing the fructopyranose ring, but was predicted from an inspection of molecular models. The two five-membered rings in both A and B have different conformations (Table 2c). The 2,3-isopropylidene ring in A and B is close to an envelope (^3E). The 4,5-isopropylidene ring is close to ^5_4T in A and to $_1E$ in B. The orientation of the hydroxyl group (in A and B) is *trans* to O(6) and *gauche* to C(3).

The C—C and C—O bond lengths and valence angles are normal. In contrast to 1,2:4,5-di-O-isopropylidene-β-D-fructopyranose, the endocyclic-pyranose bonding lengths C—O, i.e. C(2)—O(6) and C(6)—O(6), are somewhat different; their mean values are 1·396 (5) and 1·438 (5) Å, respectively.

The hydrogen-bonding scheme (Table 3) is unusual. The hydroxyl group (in A and B) is utilized in hydrogen bonds as an acceptor and donor simultaneously. The hydroxyl groups, O(1), of four A molecules form a donor–acceptor hydrogen-bond system about the fourfold axis at (00z). The edge length of the square is equal to the O···O hydrogen-bond length of 2·751 (4) Å. In a similar way four B molecules form a square donor–acceptor hydrogen-bond system around the fourfold axis at ($\tfrac{1}{2}\tfrac{1}{2}z$) with an O···O distance of 2·784 (4) Å. The hydrogen-bond system and the packing of the crystal are shown in Fig. 2. There are no hydrogen bonds between molecules of type A and B. There is no intramolecular hydrogen bond between O(1) and O(4), although this hydrogen bond exists in a dilute solution of the compound in CCl_4 examined by IR spectroscopy (Maeda et al., 1969).
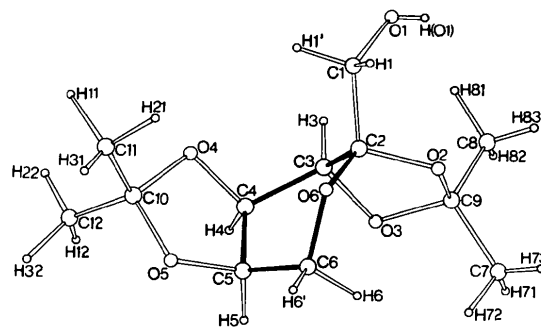
Fig. 1. Molecular geometry and numbering scheme of molecule B.

Table 2. *Geometric parameters for 2,3:4,5-di-O-isopropylidene-β-D-fructopyranose*

	Molecule A	Molecule B		Molecule A	Molecule B		Molecule A	Molecule B
(a) Bond lengths (Å)								
O(1)—C(1)	1·410 (7)	1·414 (7)	O(2)—C(9)	1·446 (6)	1·437 (5)	C(4)—C(5)	1·525 (7)	1·543 (7)
O(2)—C(2)	1·433 (4)	1·426 (4)	O(3)—C(9)	1·443 (4)	1·443 (4)	C(5)—C(6)	1·513 (6)	1·503 (7)
O(3)—C(3)	1·429 (5)	1·429 (5)	O(4)—C(10)	1·433 (6)	1·431 (7)	C(7)—C(9)	1·514 (6)	1·521 (6)
O(4)—C(4)	1·431 (5)	1·425 (5)	O(5)—C(10)	1·414 (5)	1·416 (6)	C(8)—C(9)	1·517 (7)	1·509 (7)
O(5)—C(5)	1·422 (6)	1·418 (6)	C(1)—C(2)	1·525 (5)	1·531 (5)	C(11)—C(10)	1·497 (9)	1·514 (12)
O(6)—C(6)	1·439 (5)	1·437 (5)	C(2)—C(3)	1·531 (6)	1·539 (7)	C(12)—C(10)	1·521 (9)	1·498 (11)
O(6)—C(2)	1·392 (6)	1·401 (6)	C(3)—C(4)	1·528 (5)	1·535 (5)	O(1)—H(O1)	0·63 (4)	0·59 (4)
(b) Valence angles (°)								
C(1)—C(2)—C(3)	115·6 (4)	116·2 (4)	C(2)—C(3)—O(3)	104·0 (4)	104·0 (4)	O(2)—C(9)—C(7)	110·3 (4)	109·3 (4)
C(2)—C(3)—C(4)	113·8 (4)	113·8 (4)	C(4)—C(3)—O(3)	106·4 (4)	106·1 (4)	O(2)—C(9)—C(8)	110·7 (4)	111·2 (4)
C(3)—C(4)—C(5)	113·0 (4)	113·1 (4)	C(3)—C(4)—O(4)	107·1 (4)	108·0 (4)	O(3)—C(9)—C(7)	107·2 (4)	107·4 (4)
C(4)—C(5)—C(6)	113·0 (4)	112·8 (4)	C(5)—C(4)—O(4)	104·0 (4)	103·7 (4)	O(3)—C(9)—C(8)	112·0 (4)	111·0 (4)
C(7)—C(9)—C(8)	112·2 (5)	113·5 (5)	C(4)—C(5)—O(5)	104·7 (4)	104·0 (4)	O(4)—C(10)—C(11)	108·5 (5)	108·1 (6)
C(11)—C(10)—C(12)	114·0 (6)	112·5 (7)	C(6)—C(5)—O(5)	109·8 (4)	110·3 (4)	O(4)—C(10)—C(12)	110·4 (5)	110·2 (6)
O(1)—C(1)—C(2)	112·0 (4)	111·9 (4)	C(5)—C(6)—O(6)	109·9 (4)	111·0 (4)	O(5)—C(10)—C(11)	108·2 (5)	109·9 (6)
C(1)—C(2)—O(2)	109·5 (4)	109·6 (4)	C(6)—O(6)—C(2)	113·5 (4)	114·0 (4)	O(5)—C(10)—C(12)	109·0 (5)	109·9 (6)
C(1)—C(2)—O(6)	104·2 (4)	103·7 (4)	C(2)—O(2)—C(9)	110·3 (3)	111·0 (3)	O(2)—C(9)—O(3)	104·1 (4)	104·1 (4)
C(3)—C(2)—O(2)	103·4 (4)	103·0 (4)	C(3)—O(3)—C(9)	106·0 (4)	105·9 (4)	O(4)—C(10)—O(5)	106·5 (4)	106·0 (5)
C(3)—C(2)—O(6)	114·0 (4)	113·8 (4)	C(4)—O(4)—C(10)	107·8 (4)	106·9 (4)	C(1)—O(1)—H(O1)	112 (4)	112 (5)
O(2)—C(2)—O(6)	110·4 (4)	110·8 (4)	C(5)—O(5)—C(10)	110·5 (4)	110·5 (4)			

(c) Selected torsion angles (°), puckering parameters and conformations

	A	B		A	B		A	B
H(O1)—O(1)—C(1)—C(2)	−77 (4)	−76 (4)	C(3)—C(4)—C(5)—C(6)	15·7 (6)	17·0 (9)	O(6)—C(2)—C(3)—C(4)	18·8 (5)	17·8 (10)
O(1)—C(1)—C(2)—C(3)	−59·8 (6)	−60·8 (10)	C(4)—C(5)—C(6)—O(6)	38·4 (7)	36·6 (9)	O(2)—C(2)—C(3)—O(3)	23·3 (5)	22·7 (8)
O(1)—C(1)—C(2)—O(6)	174·4 (5)	173·6 (10)	C(5)—C(6)—O(6)—C(2)	−69·6 (6)	−68·9 (9)	O(4)—C(4)—C(5)—O(5)	19·3 (6)	19·9 (7)
C(2)—C(3)—C(4)—C(5)	−45·2 (7)	−45·0 (9)	C(6)—O(6)—C(2)—C(3)	38·4 (6)	38·6 (9)			

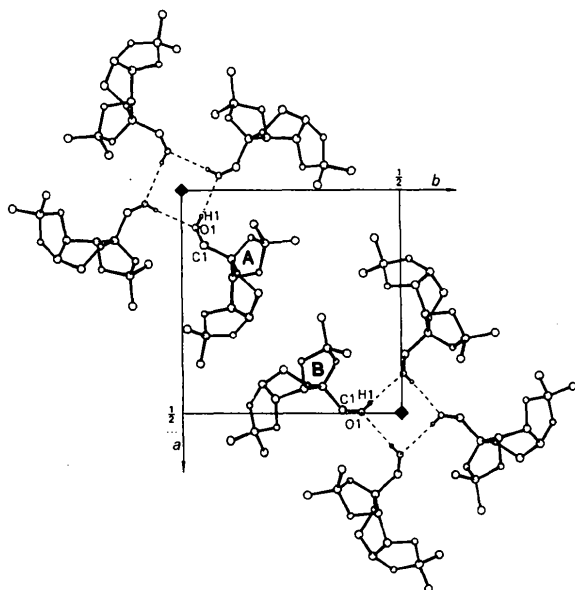|	Molecule	Q (Å)	θ (°)	φ (°)	Conformation
Pyranose ring					
O(6)—C(2)—C(3)—C(4)—C(5)—C(6)	A	0·664 (5)	97·0 (4)	147·5 (4)	$^{2}S_{0}$
O(6)—C(2)—C(3)—C(4)—C(5)—C(6)	B	0·653 (5)	96·5 (5)	149·1 (5)	$^{2}S_{0}$
2,3-Isopropylidene ring					
O(2)—C(9)—O(3)—C(3)—C(2)	A	0·326 (5)		78·9 (7)	^{3}E
O(2)—C(9)—O(3)—C(3)—C(2)	B	0·323 (5)		77·9 (7)	^{3}E
4,5-Isopropylidene ring					
O(4)—C(10)—O(5)—C(5)—C(4)	A	0·239 (5)		165·7 (11)	$^{4}_{5}T \rightarrow {}_{1}E$
O(4)—C(10)—O(5)—C(5)—C(4)	B	0·278 (5)		172·8 (11)	$_{1}E$

Fig. 2. A view down the *c* axis of the hydrogen bonding and packing. The hydrogen bonds are shown as dotted lines. (Carbon-bonded H atoms are omitted for clarity.)

Table 3. *Hydrogen-bond lengths (Å) and angles (°)*

Values in square brackets are O···H bond distances and O—H···O bond angles normalized to a standard covalent-bond-length value of 0·96 Å by moving the H atom along the direction of the O—H bond.

O—H···O	O···O	H···O	∠O—H···O
O(1A)—H(O1A)···O(1A^{i})	2·751 (4)	2·13 (4) [1·79]	174 (5) [171]
O(1B)—H(O1B)···O(1B^{ii})	2·784 (4)	2·20 (4) [1·83]	176 (6) [175]

Symmetry code: (i) −y, x, z; (ii) y, 1−x, z.

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