CRYSTAL STRUCTURE OF 1,6-ANHYDRO-1(6)-THIO-β-D-GLUCOPYRANOSE S-OXIDE

Jiří NOVOTNÝ[a], Jaroslav PODLAHA[b] and Miloslav ČERNÝ[b]

[a] *Department of Solid State Chemistry,*
Prague Institute of Chemical Technology, 166 28 Prague 6
[b] *Department of Chemistry, Charles University, 128 40 Prague 2*

Received February 15, 1991
Accepted March 11, 1991

The crystals of the title compound are orthorhombic, space group $P2_12_12_1$, $a = 6{\cdot}193(1)$, $b = 6{\cdot}3734(7)$, $c = 38{\cdot}553(6)$ Å, $Z = 8$. The structure was solved by direct methods and refined to $R = 0{\cdot}035$ for 1 460 independent reflections. It is composed of two crystallographically independent but chemically almost identical molecules. The structure is stabilized by hydrogen bonding characterized by strong participation of the sulfoxide groups. A comparison with the structure of the thio derivative demonstrates that the exo-sulfoxide oxygen influences very little the overall conformation of the bicyclic skeleton.

In connection with our previous studies of the reactivity of 1,6-anhydro-β-D-glucopyranose[1] we were interested in the behaviour of the corresponding 1(6)-thio-analogue, namely 1,6-anhydro-thio-β-D-glucopyranose. In the latter compound, the hydroxyl group at C3 might hinder sterically the access to the sulfur atom from the endo-position and thus enable a stereoselective formation of only one conformer of the S-oxide having the (*S*)-configuration. According to the expectation, the title compound was obtained[2] in high yield by oxidation of 1,6-anhydro-1(6)-thio-β-D-glucopyranose with hydrogen peroxide in acetic acid solution.

EXPERIMENTAL

Attempts to obtain X-ray quality crystals using standard methods suffered from a pronounced tendency of needle-like crystals to aggregate along the needle axis. Single crystals were eventually obtained from a solution in aqueous acetone by slow absorption of water vapours into a 4A molecular sieve in a closed system at room temperature. The density was determined by flotation in chloroform-benzene mixture. Crystal data, measurement and refinement details are summarized in Table I. The structure was solved by direct methods (SHELXS 86, see ref.[3]) and refined anisotropically by full-matrix least squares as implemented in the SDP program package[4]. The C-bonded hydrogen atoms were fixed in theoretical positions, the O-bonded ones either as found from a difference map or in the positions calculated from average parameters of hydrogen bonding[5] (where appropriate); the thermal displacement parameters of all hydrogen atoms were included in the refinement. No peaks of chemical significance appeared in the final difference map.

RESULTS AND DISCUSSION

Fractional coordinates are given in Table II, bond distances and angles in Table III.*

The structure is composed of two crystallographically independent but chemically almost identical molecules labeled *A* and *B*. Figure 1 depicts the perspective view of molecule *A* with atom numbering; for molecule *B*, the first digit of the atom labels

TABLE I

Crystal data, measurement and refinement details

Formula	$C_6H_{10}O_5S$
M.w.	194·2
Space group	$P2_12_12_1$, No. 19
Cell dimensions (Å)	$a = 6{\cdot}193(1)$, $b = 6{\cdot}3734(7)$, $c = 38{\cdot}553(6)$
V(Å^3)	1 517(1)
Z	8
D_m, D_c (g cm^{-3})	1·68, 1·70
Radiation	MoK$_\alpha$, $\lambda = 0{\cdot}71073$ Å
Absorption correction	None, $\mu = 0{\cdot}383$ mm^{-1}
F(000)	816
Temperature (K)	293(1)
Crystal dimensions (mm)	0·21 × 0·07 × 0·07
No. of reflections for lattice parameter determination	18 ($10° < \Theta < 15°$)
Diffractometer	CAD4
Scan mode	$\omega/(4/3\Theta)$
sin Θ/λ_{max}(Å^{-1})	0·595
Standard reflections (variation)	014, 0–14 (0·4%)
Interval h, k, l	$\langle -7, 7\rangle$, $\langle -7, 7\rangle$, $\langle -45, 45\rangle$
No. of reflections measured	10 748
No. of symetrically independent reflections used [$I > 3\sigma(I)$]	1 460
Residual electron density (e Å^{-3})	0·46, −0·40
Function minimized	$\sum w(\|F_o\| - \|F_c\|)^2$
Weight	$4F_o^2/[\sigma(F_o^2)]^2$
Maximal shift-to-error ratio in final refinement cycle	0·03
R, wR, R_{int}, S	0·035, 0·040, 0·031, 0·886
Source of scattering factors	ref.[4]

---

* Supplementary material comprising hydrogen atom coordinates, anisotropic thermal displacement factors and structure factors is available from the authors upon request.

TABLE II

Fractional coordinates (.10^4) of non-hydrogen atoms with estimated standard deviations in parentheses. $B_{eq} = 4/3(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33})$

Atom	x/a	y/b	z/c	B_{eq}, Å^2
S11	2770(2)	−476(2)	2872·7(3)	2·39(3)
O11	475(5)	−1278(5)	2864(1)	3·0(1)
O12	5698(6)	775(6)	3781·5(9)	3·2(1)
O13	7064(5)	1339(6)	2868·5(9)	3·1(1)
O14	5475(6)	5215(5)	3494(1)	3·1(1)
O15	2212(5)	2174(4)	3374·5(8)	2·0(1)
C11	3239(6)	186(5)	3330(1)	1·8(1)
C12	5628(6)	364(6)	3420(1)	2·1(1)
C13	6742(5)	2091(5)	3209(1)	2·0(1)
C14	5342(6)	4077(6)	3188(1)	2·4(2)
C15	2979(6)	3506(6)	3108(1)	2·3(2)
C16	2660(6)	2319(5)	2768(1)	2·8(2)
S21	2641(2)	4910(2)	4823·2(3)	2·21(2)
O21	4947(4)	4362(5)	4922·2(9)	2·8(1)
O22	−170(5)	1962(6)	4003·4(9)	2·4(1)
O23	−1596(6)	6035(6)	4623·8(9)	2·9(1)
O24	12(6)	6357(6)	3726·2(9)	3·1(1)
O25	3273(5)	4733(6)	4154·8(8)	1·9(1)
C21	2278(6)	3471(6)	4405(1)	2·1(1)
C22	−113(5)	3104(6)	4315(1)	2·0(1)
C23	−1255(5)	5201(6)	4285(1)	2·2(1)
C24	30(6)	6841(6)	4089(1)	2·5(2)
C25	2413(5)	6802(6)	4197(1)	2·1(1)
C26	2769(6)	7343(6)	4576(1)	2·1(1)

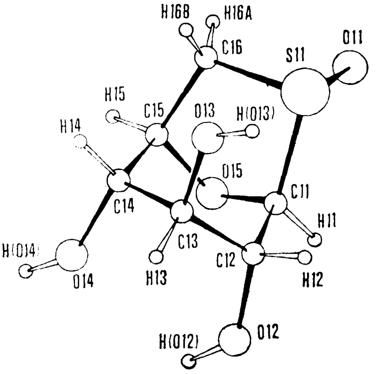

FIG. 1

Perspective view of molecule *A* with atom numbering

TABLE III

Bond distances (Å) and angles for molecules *A* and *B* (°) with estimated standard deviations in parentheses for molecules *A* and *B*. For molecule *B*, the first digit of the atom labels is 2

Atoms	Distance		Atoms	Angle	
	A	*B*		*A*	*B*
S11—O11	1·511(3)	1·519(3)	O11—S11—C11	104·4(2)	102·5(2)
S11—C11	1·835(4)	1·868(4)	O11—S11—C16	106·8(2)	106·6(2)
S11—C16	1·828(3)	1·821(4)	C11—S11—C16	89·7(2)	88·4(2)
O12—C12	1·421(5)	1·406(5)	C11—O15—C15	107·1(2)	106·7(3)
O13—C13	1·410(5)	1·427(5)	S11—C11—O15	104·5(2)	105·0(3)
O14—C14	1·387(5)	1·433(5)	S11—C11—C12	112·9(2)	112·6(2)
O15—C11	1·428(4)	1·398(5)	O15—C11—C12	109·8(3)	110·9(3)
O15—C15	1·416(5)	1·431(5)	O12—C12—C11	105·5(3)	107·2(3)
C11—C12	1·524(5)	1·539(5)	O12—C12—C13	112·0(3)	112·3(3)
C12—C13	1·532(5)	1·517(5)	C11—C12—C13	111·7(3)	109·4(3)
C13—C14	1·536(5)	1·516(5)	O13—C13—C12	108·2(3)	109·1(3)
C14—C15	1·539(5)	1·534(5)	O13—C13—C14	108·1(3)	106·1(3)
C15—C16	1·526(5)	1·517(5)	C12—C13—C14	111·4(3)	113·6(3)
O14··O25	2·906(5)		O14—C14—C13	110·6(3)	109·5(3)
O15··O22	2·841(5)		O14—C14—C15	110·5(3)	105·6(3)
O13··O11′	2·692(5)		C13—C14—C15	110·6(3)	111·0(3)
O23··O21″	2·654(5)		O15—C15—C14	108·4(3)	111·0(3)
			O15—C15—C16	106·5(3)	105·3(3)
			C14—C15—C16	114·4(3)	113·4(3)
			S11—C15—C16	106·7(2)	107·7(2)

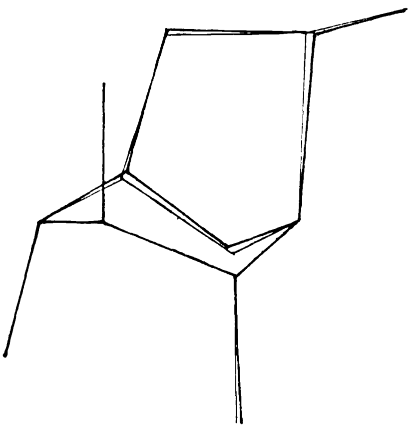

FIG. 2

Superposition of molecules *A* (bold lines) and *B* is 2. As can be seen from Fig. 2, molecules *A* and *B* are very nearly superimposable. The largest differences between the corresponding parameters is 0·046 Å, 4·9° and 5·9° for bond distances, bond and torsion angles respectively.

The bond distances and angles are all unexceptional. As usual in the 1,6-anhydropyranoses series, the pyranose ring adopts a slightly distorted $^1C_4(D)$ chair conformation. Approximate mirror planes passing through C13 and O15 atoms (C23 and O25 for molecule *B*) bisect the pyranose rings, resulting in ring-puckering parameters[6] ΔC_s = 1·9° and 3·9° for molecules *A* and *B*, respectively. Analogous parameters[7] of the five-membered 1,3-oxathiolane ring (ΔC_s, φ_m = 35·6°, 48·9° and 34·2°, 49·6° for molecules *A* and *B*, respectively) demonstrate that the ring has a nearly ideal envelope conformation with O15 (O25) as the out-of plane atom. The oxygen atom of the sulfoxide group is located in exo-position relative to the pyranose ring and, somewhat surprisingly, it has little if any effect on the geometry of the bicyclic skeleton. Comparison with the parent structure of thiolevoglucosan[8] yields 6·0° as the largest difference between the corresponding endocyclic torsion angles.

Molecular packing is depicted in Fig. 3. Hydrogen bonds O14···O25 and O15···O22 join the symmetrically independent molecules *A* and *B* and these pairs are linked along the *a*-axis through further two hydrogen bonds involving sulfoxide oxygens, O13···O11($x + 1, y, z$) and O23···O21($x - 1, y, z$). The resulting infinite chains are stacked at van der Waals or longer distances along the *c*-axis. Taking into account that the largest differences in geometry between molecules *A* and *B* are located near

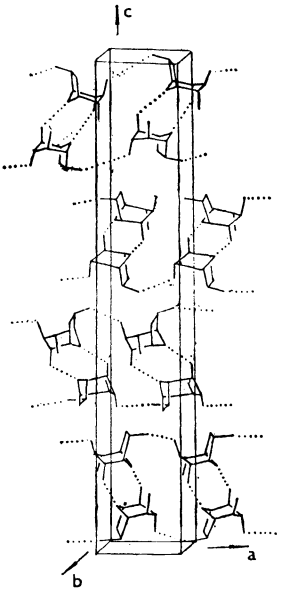

FIG. 3
Unit cell content

O14 and O24, it seems likely that hydrogen bonding requirements are the main reason for nonequivalence of the two molecules.

REFERENCES

1. Černý M., Staněk J. jr.: Adv. Carbohydr. Chem. Biochem. *34*, 23 (1977).
2. Černý M.: Unpublished results.
3. Sheldrick G. M.: *SHELXS 86. Program for Crystal Structure Solution from Diffraction Data.* University of Goettingen, Goettingen 1986.
4. Frenz B. A. and Associates Inc.: *SDP. Structure Determination Package.* College Station, Texas and Enraf-Nonius, Delft, Delft 1985.
5. Taylor R., Kennard O.: Acc. Chem. Res. *17*, 320 (1984).
6. Duax W. L., Weeks C. M., Rohrer D. C.: Top. Stereochem. *9*, 271 (1976).
7. Altona C., Geise H. J., Romers C.: Tetrahedron *24*, 13 (1968).
8. Takagi S., Jeffrey G. A.: Acta Crystallogr., B *34*, 816 (1978).

Translated by the author (J.P.).