

Conformational and Crystal Structure Studies of Septanosides.
I. Ethyl 2,3:4,5-di-*O*-isopropylidene-1-thio- β -D-glucoseptanoside, C₁₄O₅SH₂₄*

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The crystal structure of the compound ethyl 2,3:4,5-di-*O*-isopropylidene-1-thio- β -D-glucoseptanoside, C₁₄O₅SH₂₄, has been determined from visually estimated X-ray data. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 16.70$, $b = 11.70$, $c = 8.78$ Å, $Z = 4$. The central seven-membered septanose ring is found to be arranged in a twist-chair conformation and the two dioxolan rings are in twist conformations. The structure was solved using partial information derived from a Patterson synthesis and direct-phasing techniques involving the normalized structure factor magnitudes and the tangent formula.

Preliminary chemical data

Ethyl 2,3:4,5-di-*O*-isopropylidene-1-thio- β -D-glucoseptanoside (EITGS) was prepared by debenzoylation followed by demercaptalation of 6-*O*-benzoyl-2,3:4,5-di-*O*-isopropylidene-D-glucose diethyl dithioacetal. Chromatography over silicic acid of the mixture of products formed gave EITGS, which crystallized from aqueous ethanol in the form of rectangular prisms, m.p. 66–67°C [α]_D –156.0° (conc. 1.19 in CHCl₃) (Ng & Stevens, unpublished results).

The crystal used for the collection of intensity data was a rectangular prism with the (100), (010) and (001) faces most prominently developed, and with dimensions 0.042 × 0.020 × 0.05 cm.

Crystal data

C₁₄O₅SH₂₄; F.W. 304.41; $F_{000} = 656$

Orthorhombic: $a = 16.70 \pm 0.08$ Å
 $b = 11.70 \pm 0.06$
 $c = 8.78 \pm 0.04$
 $U = 1716$ Å³
 $Z = 4$

Space group $P2_12_12_1$ (No. 19, D_2^4 , from systematic absences)

$d_m = 1.20$ g.cm⁻³ (by flotation in a mixture of ethyl acetate and chloroform)

$d_c = 1.18$ g.cm⁻³, $\mu(\text{Cu } K\alpha) = 18.27$ cm⁻¹.

The intensities were recorded on multiple-film equi-inclination Weissenberg photographs taken around [001] ($l = 0, 1, 2 \dots 6$) with Cu $K\alpha$ radiation. 1322 independent intensities were estimated by visual comparison with a calibration strip. The unit-cell dimensions were obtained from zero-level precession photographs taken with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å).

* See Beale, J. P., Stephenson, N. C. & Stevens J. D. (1971). *Chem. Commun.* p. 484, for a preliminary communication.

Lorentz and polarization corrections were applied, and absorption corrections were made by the method of Coppens, Leiserowitz & Rabinovich (1965) with a grid of 256 (8 × 8 × 4) points. No extinction corrections were made.

For the calculation of structure factors the atomic scattering factors for sulphur, oxygen and carbon were computed from numerical Hartree–Fock wave functions by the method of Cromer & Mann (1968). The scattering factors for hydrogen were those given in *International Tables for X-ray Crystallography* (1968).

A correction for the real component of the anomalous dispersion of all atoms for Cu $K\alpha$ radiation was applied (Dauben & Templeton, 1955).

Observed and calculated structure factors are listed in Table 1.

Determination of the structure

The structure was elucidated by combining partial structural information derived from a Patterson synthesis with the tangent formula (Karle, 1968). The solution of the Patterson of synthesis was ambiguous in that four possible sulphur positions appeared plausible (Table 2). By considering each position separately, reliably phased data satisfying the criteria (i) $|F_{\text{calc}}| \geq 0.1|F_{\text{obs}}|$ and (ii) $|F_{\text{obs}}| \geq 1.50$ were selected and refined with the tangent formula. The refined phase angles of five intensity invariants were then compared with values derived from a \sum_1 summation (Table 3). From these comparisons in only one case [*i.e.* position S(4)] was complete agreement found between the \sum_1 phase values and the refined phase angles.

An E map, computed using the refined phase angles for this S(4) model, clearly revealed the locations of all atoms with the exception of the ethyl carbon atoms which were later located from Fourier difference syntheses.

The atomic positional and isotropic thermal parameters were refined by full-matrix least-squares methods in which values of $\sum w[|F_{\text{obs}}| - |F_{\text{calc}}|]^2$ were minimized

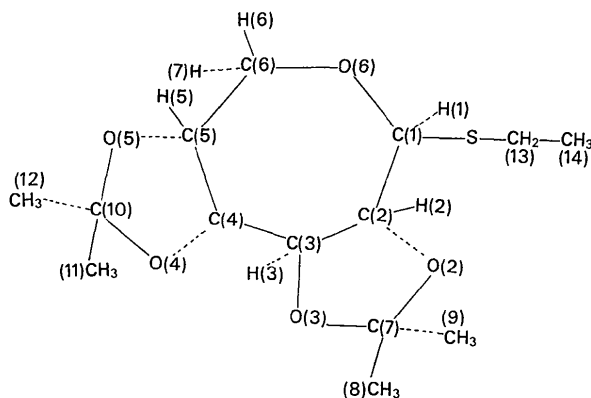


Fig. 1. Labelling of the molecule.

Table 2. Likely positions for the sulphur atoms as derived from the Patterson synthesis

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
S(1)	0.841	0.91	0.99
S(2)	0.742	0.91	0.99
S(3)	0.837	0.89	0.88
S(4)	0.842	0.78	0.88

and weights (*w*) were calculated from Cruickshank's (1965) weighting scheme. The isotropic refinement converged to a reliability index (*R*) of 0.161. Two further refinement cycles in which the interlayer scale factors were fixed and anisotropic temperature factors assigned to all atoms reduced the *R* value to 0.115. A difference Fourier synthesis calculated using the latest refined atomic and thermal parameters indicated the locations of the seven ring hydrogen atoms. However, difficulty was experienced in locating the remaining methyl hydrogen atoms, and it was only after repeating the above procedure several times and refining only on data with $\sin(\theta)/\lambda$ values greater than 0.3 that the seventeen remaining hydrogen atoms were located. These were the only significant peaks on the difference Fourier syntheses.

A final refinement cycle was computed in which the positional and thermal parameters of all non-hydrogen atoms were allowed to vary. The positional parameters of the seven ring hydrogen atoms were also permitted to vary, but modified by a damping factor. All hydrogen atoms were assigned isotropic temperature factors of 8 \AA^2 and the reliability index (*R*) converged to 0.103.

The final atomic and thermal parameters for the crystallographically independent atoms are listed in Tables 4 and 5.

Table 4. Final fractional coordinates

Standard deviations are given in brackets and refer to the least significant figures in the preceding coordinate.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
S	0.8414 (3)	0.7769 (4)	0.8857 (6)
O(2)	0.9138 (5)	0.6966 (8)	0.5549 (12)
O(3)	0.8470 (5)	0.6083 (8)	0.3565 (12)
O(4)	0.6778 (5)	0.5558 (9)	0.3394 (13)
O(5)	0.6044 (5)	0.6722 (8)	0.4935 (12)
O(6)	0.7177 (6)	0.7856 (7)	0.6874 (12)
C(1)	0.8034 (8)	0.7784 (12)	0.6956 (18)
C(2)	0.8340 (7)	0.6795 (10)	0.6050 (17)
C(3)	0.7873 (7)	0.6543 (9)	0.4569 (16)
C(4)	0.7203 (8)	0.5699 (11)	0.4780 (19)
C(5)	0.6545 (8)	0.6083 (13)	0.5943 (19)
C(6)	0.6779 (9)	0.6788 (13)	0.7289 (20)
C(7)	0.9195 (8)	0.6686 (12)	0.3917 (21)
C(8)	0.9869 (9)	0.5889 (16)	0.3683 (24)
C(9)	0.9271 (10)	0.7755 (18)	0.3015 (23)
C(10)	0.5998 (8)	0.6110 (12)	0.3485 (18)
C(11)	0.5364 (8)	0.5217 (17)	0.3556 (27)
C(12)	0.5943 (12)	0.6984 (17)	0.2222 (17)
C(13)	0.7996 (23)	0.9035 (30)	0.9588 (31)
C(14)	0.8106 (25)	1.0134 (33)	0.8864 (49)
H(1)	0.799 (14)	0.879 (23)	0.599 (31)
H(2)	0.843 (14)	0.643 (20)	0.755 (31)
H(3)	0.760 (13)	0.731 (23)	0.408 (27)
H(4)	0.740 (13)	0.450 (20)	0.511 (30)
H(5)	0.625 (14)	0.541 (22)	0.599 (29)
H(6)	0.714 (16)	0.660 (21)	0.859 (29)
H(7)	0.633 (15)	0.703 (22)	0.799 (29)
H(8)	0.740	0.950	0.960
H(9)	0.820	0.950	1.050
H(10)	0.760	1.080	0.987
H(11)	0.880	0.989	0.827
H(12)	0.860	1.020	0.751
H(13)	0.973	0.540	0.419
H(14)	0.993	0.542	0.256
H(15)	1.026	0.607	0.420
H(16)	0.870	0.810	0.299
H(17)	0.979	0.820	0.360
H(18)	0.950	0.780	0.200
H(19)	0.520	0.499	0.299
H(20)	0.530	0.459	0.512
H(21)	0.599	0.460	0.320
H(22)	0.540	0.720	0.222
H(23)	0.580	0.640	0.051
H(24)	0.680	0.740	0.187

Discussion of the structure

The labelling system used in this study is given in Fig. 1. A diagrammatic representation and a stereoview of the

Table 3. Σ_1 and refined phase values

Intensity	Σ_1 result			Refined phase values			
	E_{2h}	ϕ_{2h}	$P+(E_{2h})$	S(1)	S(2)	S(3)	S(4)
Invariant							
16 0 0	2.10	π	(0.16)	π	0	π	π
12 0 0	1.27	0	0.87	0	0	0	0
0 12 2	1.56	0	0.84	0	0	π	0
10 0 4	2.06	0	0.73	π	π	0	0
6 0 4	2.92	π	0.23	0	π	π	π

Table 5. The tensor components ($\text{\AA}^2 \times 10^3$) describing the anisotropic vibration of atoms

The tensor components are those occurring in the temperature factor $\exp[-2\pi^2(h^2a^{*2}U_{11} + 2hka^*b^*U_{12} + \dots)]$. All hydrogen atoms were assigned isotropic temperature factors of 8\AA^2 .

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	98.3	91.3	60.9	29.8	-25.2	-22.1
O(2)	50.9	65.9	56.6	-12.5	4.9	-7.7
O(3)	33.0	68.6	66.7	-11.6	-0.6	-26.5
O(4)	34.2	71.8	70.5	4.1	-0.9	-30.6
O(5)	52.1	53.2	57.3	21.9	-4.2	-3.9
O(6)	62.7	43.8	65.4	11.9	-7.8	-9.1
C(1)	64.6	49.1	56.5	13.0	-18.3	-6.8
C(2)	43.4	64.2	54.5	2.5	-5.2	3.7
C(3)	38.2	31.2	50.7	-1.2	-7.1	1.8
C(4)	43.3	46.7	60.3	1.4	2.7	-13.3
C(5)	43.1	65.5	62.8	13.5	11.5	-8.4
C(6)	60.3	66.5	51.8	6.0	2.0	-3.5
C(7)	44.0	55.8	76.3	-17.9	-6.7	-13.5
C(8)	49.4	95.2	99.1	3.8	-1.0	-17.9
C(9)	68.9	108.1	86.8	-32.8	-2.1	36.9
C(10)	49.5	63.9	52.9	3.9	-15.0	-13.4
C(11)	41.6	107.6	140.6	-8.9	-14.8	-72.0
C(12)	89.5	90.9	74.8	6.8	-11.3	6.6
C(13)	237.1	156.0	74.3	100.2	-70.2	-62.8
C(14)	252.4	140.0	182.8	63.1	-95.8	-91.6

structure of EITGS are given in Figs. 2 and 3 respectively. Intramolecular bond distances and angles are listed in Tables 6 and 7.

Table 6. Bond distances

O(6)—C(1)	1.435 (19) \AA	C(2)—H(2)	1.39 (30) \AA
C(1)—C(2)	1.493 (20)	C(3)—H(3)	1.09 (27)
C(2)—C(3)	1.543 (21)	C(4)—H(4)	1.47 (25)
C(3)—C(4)	1.504 (18)	C(5)—H(5)	0.93 (27)
C(4)—C(5)	1.566 (21)	C(6)—H(6)	1.31 (27)
C(5)—C(6)	1.493 (24)	C(6)—H(7)	1.02 (27)
C(6)—O(6)	1.462 (20)	C(13)—H(8)	1.13*
S—C(1)	1.785 (20)	C(13)—H(9)	1.03
S—C(13)	1.758 (29)	C(14)—H(10)	1.45
C(13)—C(14)	1.447 (6)	C(14)—H(11)	1.30
C(2)—O(2)	1.418 (17)	C(14)—H(12)	1.45
O(2)—C(7)	1.472 (22)	C(8)—H(13)	0.76
C(7)—C(8)	1.475 (23)	C(8)—H(14)	1.13
C(7)—C(9)	1.485 (25)	C(8)—H(15)	0.82
C(7)—O(3)	1.435 (16)	C(9)—H(16)	1.04
O(3)—C(3)	1.435 (17)	C(9)—H(17)	1.13
C(4)—O(4)	1.418 (21)	C(9)—H(18)	0.97
O(4)—C(10)	1.456 (17)	C(11)—H(19)	0.63
C(10)—C(11)	1.489 (24)	C(11)—H(20)	1.56
C(10)—C(12)	1.511 (26)	C(11)—H(21)	1.31
C(10)—O(5)	1.462 (20)	C(12)—H(22)	0.94
O(5)—C(5)	1.428 (19)	C(12)—H(23)	1.67
C(1)—H(1)	1.45 (29)	C(12)—H(24)	1.54

* Hydrogen atoms H(8)–H(24) were more difficult to locate than H(1)–H(7) and the positional parameters were not varied during refinement cycles. Standard deviations are expected to be greater than those listed for C–H bonds.

Previous studies (Brown & Levy, 1965; Parthasarathy & Davis, 1967; Kim, Jeffrey, Rosenstein & Corfield, 1967; Sundaralingam, 1965; Sundaralingam & Jensen, 1965; Harris & Macintyre, 1964; Kraut & Jensen, 1963; Trueblood, Horn & Luzzati, 1961; Jeffrey & Rosenstein, 1964) have shown that for pyranose and furanose

ring systems the carbon–oxygen ring bonds are significantly different in length, a feature which has been attributed to the particular (α or β) molecular configuration. In this study the C(6)–O(6) and C(1)–O(6) bond distances differ in length ($\Delta=0.027 \text{\AA}$) but this is not statistically significant due to larger standard deviations.

The conformation of this molecule is shown in Figs. 2 and 3 and can be expressed conveniently in terms of the torsional angles* which are listed in Table 8.

* In the four-atom system 1, 2, 3 and 4, torsional angle, τ , about the 2,3 bond is *positive* if it is necessary to rotate the nearest group through an angle less than 180° in a clockwise direction in order to produce eclipsing of atom 4 by atom 1, *i.e.*

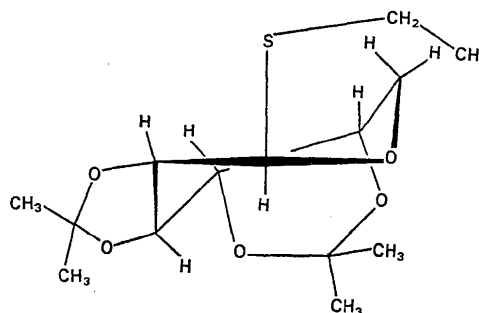
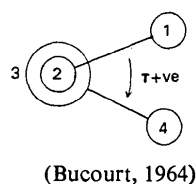


Fig. 2. Diagrammatic representation of the structure.

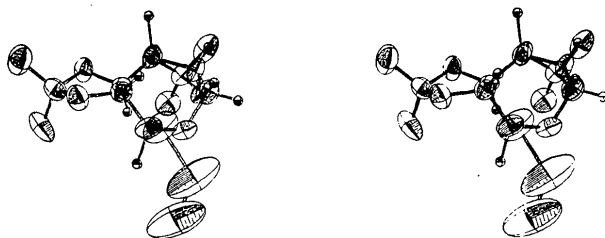


Fig. 3. Stereoscopic view of the molecule of EITGS.

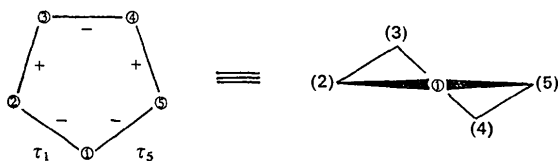


Fig. 4. Torsion angles in the five-membered rings.

The conformations of the five-membered rings can be easily deduced from the torsional angles about the ring bonds. An envelope or near-envelope conformation requires four of the five ring atoms to lie approximately in a plane, and consequently it is necessary for at least one torsional angle to be close to 0.0° . As all the relevant torsional angles are greater than 7.0° , it is evident that neither of the five-membered rings is in an envelope conformation.

Calculation of the displacements of each pair of adjacent atoms from the plane of the remaining three atoms showed that only for one pair were the displacements on opposite sides of the three-atom plane. This

is in accordance with the geometrical requirements for the twist form of a five-membered ring. An examination of the torsional angles alone is sufficient to allow a qualitative description of the ring conformation. For twist forms, the two torsional angles (τ_5 , τ_1 - see Fig. 4) involving the axis atom must have the same sign and the mode of twisting may be deduced from the sign (+ or -) of these two torsional angles. Viewing the ring with the axis atom closest and line of sight passing through the atom (3)-atom (4) bond, atom (3) is above the plane of (5), (1) and (2) if the atom (1)-atom (2) torsional angle (τ_1) is negative (see Fig. 4). In an ideal twist form, τ_1 and τ_5 are equal in magnitude as well as sign and the magnitude of the displacement of (4) and (5) from the three atom plane is the same. In EITGS, neither dioxolan ring has an ideal twist conformation. In the *trans*-fused dioxolan ring, atoms O(3) and C(3) are displaced -0.331 and $+0.193$ Å respectively from the plane of C(2), O(2) and C(9). The equation for this plane is

$$-0.219X + 0.948Y - 0.232Z - 3.250 = 0$$

where X , Y and Z are in Å and refer to the crystallographic axes.

Similarly, for the *cis*-fused *O*-isopropylidene group, atoms O(5) and C(5) are displaced $+0.195$ and -0.413 Å respectively from the plane of C(4), O(4), and C(12) of equation

$$0.399X + 0.848Y - 0.348Z - 8.99 = 0.$$

It is apparent from these results that both dioxolan rings have distorted twist conformations. Geometrical properties of such conformations require that the atom having greatest displacement from the three-atom plane

Table 7. Bond angles

C(6)—O(6)—C(1)	113 (1) ^o	O(3)—C(3)—H(3)	111 (13) ^o
O(6)—C(1)—C(2)	111 (1)	O(3)—C(3)—C(4)	110 (1)
C(1)—C(2)—C(3)	115 (1)	H(3)—C(3)—C(2)	113 (13)
C(2)—C(3)—C(4)	113 (1)	H(3)—C(3)—C(4)	106 (12)
C(3)—C(4)—C(5)	115 (1)	C(3)—C(4)—H(4)	119 (9)
C(4)—C(5)—C(6)	119 (1)	C(3)—C(4)—O(4)	110 (1)
C(5)—C(6)—O(6)	113 (1)	H(4)—C(4)—O(4)	100 (10)
O(6)—C(1)—S	114 (1)	H(4)—C(4)—C(5)	108 (10)
O(6)—C(1)—H(1)	83 (10)	C(4)—O(4)—C(10)	110 (1)
C(1)—S—C(7)	101 (1)	C(5)—C(4)—O(4)	104 (1)
S—C(1)—C(2)	112 (1)	O(4)—C(10)—C(11)	108 (1)
S—C(1)—H(1)	125 (11)	O(4)—C(10)—C(12)	109 (1)
S—C(13)—C(14)	123 (3)	O(4)—C(10)—O(5)	103 (1)
H(1)—C(1)—C(2)	110 (11)	C(11)—C(10)—C(12)	118 (1)
C(1)—C(2)—O(2)	112 (1)	C(12)—C(10)—O(5)	108 (1)
C(1)—C(2)—H(2)	77 (10)	C(11)—C(10)—O(5)	110 (1)
H(2)—C(2)—O(2)	104 (11)	C(10)—O(5)—C(5)	108 (1)
C(3)—C(2)—O(2)	104 (1)	O(5)—C(5)—C(4)	99 (1)
H(2)—C(2)—C(3)	142 (11)	O(5)—C(5)—H(5)	99 (17)
C(2)—O(2)—C(7)	109 (1)	O(5)—C(5)—C(6)	111 (1)
C(2)—C(3)—O(3)	104 (1)	H(5)—C(5)—C(4)	99 (16)
O(2)—C(7)—O(3)	105 (1)	H(5)—C(5)—C(6)	125 (17)
O(2)—C(7)—C(8)	109 (1)	C(5)—C(6)—H(6)	136 (11)
O(2)—C(7)—C(9)	110 (1)	C(5)—C(6)—H(7)	116 (15)
C(8)—C(7)—O(3)	108 (1)	H(6)—C(6)—H(7)	82 (18)
C(8)—C(7)—C(9)	113 (2)	H(6)—C(6)—O(6)	99 (12)
C(9)—C(7)—O(3)	112 (1)	H(7)—C(6)—O(6)	104 (16)
C(7)—O(3)—C(3)	106 (1)		

Table 8. *Torsional angles about the various groups*

O(6)-C(1):		C(3)-C(4):	
C(6)-C(2)	53.5°	C(2)-C(5)	60.4°
C(6)-H(1)	163.1	C(2)-O(4)	177.0
C(6)-S	-73.4	C(2)-H(4)	-68.9
C(1)-C(2):		O(3)-C(5)	176.3
O(6)-C(3)	35.7	O(3)-O(4)	-67.1
O(6)-O(2)	154.0	O(3)-H(4)	47.0
O(6)-H(2)	104.7	H(3)-C(5)	-63.3
S-C(3)	163.9	H(3)-O(4)	53.2
S-O(2)	-77.8	H(3)-H(4)	167.3
S-H(2)	23.6	C(4)-C(5):	
H(1)-C(3)	-57.0	C(3)-C(6)	-33.6
H(1)-O(2)	61.3	C(3)-O(5)	86.8
H(1)-H(2)	162.7	C(3)-H(5)	-176.6
C(2)-C(3):		O(4)-C(6)	-153.4
C(1)-C(4)	-91.2	O(4)-O(5)	-33.0
C(1)-O(3)	149.1	O(4)-H(5)	63.6
C(1)-H(3)	31.8	H(4)-C(6)	101.2
O(2)-C(4)	145.9	H(4)-O(5)	-138.4
O(2)-O(3)	26.2	H(4)-H(5)	-41.8
O(2)-H(3)	-91.1	C(5)-C(6):	
H(2)-C(4)	10.3	C(4)-O(6)	57.7
H(2)-O(3)	-109.4	C(4)-H(6)	-74.6
H(2)-H(3)	133.3	C(4)-H(7)	176.5
C(6)-O(6):		O(5)-O(6)	-56.8
C(5)-C(1)	-97.9	O(5)-H(6)	171.0
H(6)-C(1)	49.9	O(5)-H(7)	62.0
H(7)-C(1)	138.3	H(5)-O(6)	-169.2
S-C(13):		H(5)-H(6)	58.5
C(1)-C(14)	-54.6	H(5)-H(7)	-50.5
C(2)-O(2):		C(4)-O(4):	
C(1)-C(9)	-132.3	C(3)-C(10)	-107.4
H(2)-C(9)	145.0	C(5)-C(10)	15.6
C(3)-C(9)	-7.5	H(4)-C(10)	126.8
O(2)-C(7):		O(4)-C(10):	
C(2)-C(8)	-129.0	C(4)-C(11)	-109.0
C(2)-C(9)	106.8	C(4)-C(12)	122.3
C(2)-O(3)	-13.8	C(4)-O(5)	7.9
C(7)-O(3):		C(10)-O(5):	
O(2)-C(3)	30.9	O(4)-C(5)	-31.3
C(8)-C(3)	147.1	C(11)-C(5)	84.7
C(9)-C(3)	-88.1	C(12)-C(5)	-145.8
O(3)-C(3):		O(5)-C(5):	
C(7)-C(2)	-35.2	C(10)-C(4)	39.6
C(7)-C(4)	-156.8	C(10)-C(6)	166.1
C(7)-H(3)	83.0	C(10)-H(5)	-62.4
		S-C(1):	
		C(13)-O(6)	-56.3
		C(13)-C(2)	177.0
		C(13)-H(1)	43.9

is opposite the smaller of the two torsional angles of like sign. In the present cases, O(3) and C(3) are opposite torsional angles of -7.5 and -13.8° respectively and O(5) and C(5) are opposite torsional angles of 15.6 and 7.9° respectively.

The magnitudes of the largest torsional angles in the two dioxolan rings (-35.2 and 39.6° for the *trans* and *cis* fused rings) are of some interest. They are both

greater than the maximum torsion angle (30°) derived from an X-ray study on bis-1,3-dioxolan (Altona & van der Veeck, 1968).

There is a similarity between the torsion angles in the twist form of a five-membered ring and those in the twist form of a seven-membered ring. As with the five-membered ring, the two torsion angles involving the axis-of-symmetry atom in the twist-chair conformation of cycloheptane have the same sign and the mode of twisting follows as before. In the present case, the O(6)-C(1) and C(1)-C(2) torsion angles have the same sign and the signs of the other torsional angles are correct for a twist-chair conformation (Hendrickson, 1967). EITGS may therefore be described as having a twist-chair conformation corresponding to a cycloheptane twist-chair in which the axis of symmetry passes through C(1). As these two torsional angles are positive, C(3) lies below the plane of O(6), C(1), and C(2) viewed with O(6) to the right of C(1). Further qualitative information on the shape of the seven-membered ring follows from the magnitudes of the torsion angles - the atom, C(5), opposite the smaller of the two like-sign angles is displaced further from the three-atom plane O(6), C(1) and C(2) than is the other atom, C(4). The correctness of this qualitative description of the shape of the seven-membered ring is provided by calculations of atom displacements from planes - see Table 9. These calculations show that the seven-membered ring deviates slightly from a symmetrical twist-chair conformation, the plane of O(6), C(1), and C(2) passing through C(4) instead of through the midpoint of the C(4)-C(5) bond. It is instructive to compare the observed torsional angles with those computed (Hendrickson, 1967) for the twist-chair of cycloheptane (see Table 10). The similarity of these values is apparent.

Table 10. *Comparison of observed torsional angles and those computed for the twist-chair conformation of cycloheptane*

	Observed	Computed*
O(6)-C(1)	54	39
C(1)-C(2)	36	39
C(2)-C(3)	-91	-88
C(3)-C(4)	60	72
C(4)-C(5)	-34	-54
C(5)-C(6)	58	72
C(6)-O(6)	-98	-88

* Hendrickson (1967).

There are no major discrepancies between the bond lengths observed and those commonly accepted as

Table 9. *Displacements of atoms from planes in the seven-membered ring*

Planes	Distances (Å) of atoms from the plane			
	C(3)	C(4)	C(5)	C(6)
O(6), C(1), C(2)	-0.82	0.00	0.64	1.08
O(6), C(1), C(2), point midway between C(4) and C(5)	-0.99	-0.31	0.34	0.93

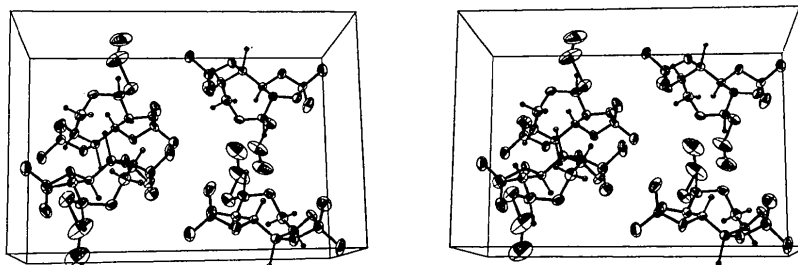


Fig. 5. Molecular packing in the unit cell.

'normal' bond lengths. The average C–O distance is 1.44 Å which is in good agreement with the C–O distances in ethers. The septanose ring C–O bond lengths of 1.462 (20) and 1.435 (19) Å are not significantly different although there is some indication that similar structures do have significant differences in bond lengths.

The C(1)–C(2), C(3)–C(4) and C(5)–C(6) bonds are 1.49 (2), 1.50 (2) and 1.49 (2) Å respectively and are shorter than the C(2)–C(3) and C(4)–C(5) bonds of length 1.54 (2) and 1.57 (2) Å respectively.

Both of these latter bonds form part of the dioxolan rings and we note that in a previously determined structure (Jakobs, Reno & Sundaralingam, 1972) the corresponding bond length in a *trans*-fused dioxolan ring is significantly longer than the other ring C–C bonds.

Bond angles within the seven-membered ring are all greater than the tetrahedral value, in particular, the 119° angle at C(5). Within the dioxolan rings all the angles are less than the tetrahedral value, angles at the oxygen atoms being larger (average 108°) than those involving carbon atoms (average 103°). These values

Table 11. Some intermolecular approach distances less the 4.0 Å in the crystal structure

The superscripts denote the various symmetry transformations.

	No superscript	<i>x</i>	<i>y</i>	<i>z</i>
		1.5 – <i>x</i>	1.0 – <i>y</i>	<i>z</i> – 0.5
	"	<i>z</i> – 0.5	1.5 – <i>y</i>	1.0 – <i>z</i>
C(4)–H(2')	3.34 (28) Å		O(4)–H(2')	2.46 (26) Å
C(4)–H(6')	3.09 (27)		O(4)–H(4')	3.19 (27)
C(7)–H(5')	3.63 (27)		O(4)–H(6')	3.11 (27)
O(3)–C(5')	3.42 (2)		C(10)–H(2')	3.23 (26)
O(3)–C(6')	3.56 (3)		C(11)–C(2')	3.88 (3)
O(3)–H(4')	3.43 (3)		C(11)–O(2')	3.76 (3)
O(3)–H(5')	2.90 (27)		C(11)–H(2')	2.93 (27)
O(3)–H(7')	3.69 (28)		C(10)–O(2'')	3.93 (2)
O(3)–H(6')	3.30 (26)		O(5)–O(2'')	3.56 (2)
C(8)–H(5')	3.37 (27)		O(5)–C(7'')	3.74 (2)
O(4)–S'	3.93 (2)		O(5)–C(8'')	3.62 (2)
O(4)–C(2')	3.44 (2)		O(5)–C(9'')	3.52 (3)
O(4)–C(4')	3.89 (2)		C(11)–O(2'')	3.96 (3)
O(4)–C(6')	3.78 (2)		C(12)–O(2'')	3.80 (3)

agree well with those reported for 5-*O*-chloroacetyl-1,2:3,4-di-*O*-isopropylidene- α -D-glucoseptanose (Jakobs, Reno & Sundaralingam, 1972).

Fig. 5 shows the molecular packing in the unit cell viewed along the *c* axis. Intermolecular approach distances less than 4.0 Å are given in Table 11.

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