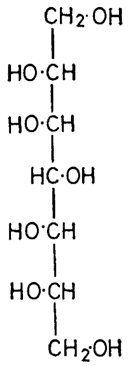
Crystal Structure of *meso*-L-*glycero*-L-*gulo*-Heptitol

By **Kloy Nimgirawath** and **Veronica J. James,*** School of Physics, The University of New South Wales, P.O. Box 1, Kensington 2033, Australia
John A. Mills,* Division of Chemical Technology, C.S.I.R.O., P.O. Box 310, South Melbourne 3205, Australia

The crystal structure of the title compound (I) has been determined from three-dimensional diffractometer data. Crystals are monoclinic, space group $P2_1/c$, with unit cell parameters: $a = 4.920(1)$, $b = 17.186(3)$, $c = 10.993(2)$ Å, $\beta = 97.25(2)°$, $Z = 4$. The structure was solved by direct methods and refined by full-matrix least-squares to R 0.044 for 1 373 independent reflections. The heptitol has a non-planar conformation with gauche arrangements round the bonds C(4)–C(5) and C(5)–C(6), a type not previously observed in alditols. All hydroxy-hydrogens except H(O7) are disordered over two positions. There are two alternative, centrosymmetrically-related hydrogen-bonding schemes, each having a finite main chain extended in the direction of the b axis and a branched chain, combined at O(1).

PROTON magnetic resonance measurements [1] showed that *meso*-L-*glycero*-L-*gulo*-heptitol (I) probably exists as a mixture of conformers in aqueous solution, one of which contains the planar, zig-zag carbon chain. Current theories of conformational analysis do not permit a firm prediction of the preferred conformation, because both the planar conformation and the most probable non-planar conformation contain elements of conformational instability.[2] An X-ray structure determination was therefore carried out.



$$\begin{array}{c} CH_2\cdot OH \\ | \\ HO\cdot CH \\ | \\ HO\cdot CH \\ | \\ HC\cdot OH \\ | \\ HO\cdot CH \\ | \\ HO\cdot CH \\ | \\ CH_2OH \end{array}$$

(I)

EXPERIMENTAL

The compound normally crystallises in very slender, fibrous needles, but a suitable crystal was obtained fortuitously during its recrystallisation from 90% ethanol. The recovered solid was washed in turn with absolute ethanol, acetone, and light petroleum. The very dilute solution in the combined washings deposited some rectangular prisms of suitable size.

Space-group and unit-cell data were obtained from Weissenberg photographs. Final unit-cell dimensions and X-ray intensity data were measured on a Siemens automatic single-crystal diffractometer by use of Cu-K_α radiation ($\lambda = 1.5418$ Å) and Ni attenuators.

Crystal Data.—$C_7H_{16}O_7$, $M = 212.20$. Monoclinic, $a = 4.920(1)$, $b = 17.186(3)$, $c = 10.993(2)$ Å, $\beta = 97.25(2)°$, $U = 923$ Å^3, $D_c = 1.54$, $Z = 4$, $D_m = 1.53$ g cm^{-3} (by flotation). Space group $P2_1/c$ from systematic absences: $0k0$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$. μ(Cu-K_α) = 12.126 cm^{-1}.

The integrated intensities of 1 455 independent reflections, $\theta < 70°$, were recorded on the diffractometer by the method of Hoppe.[3] The scanning procedure utilised the moving-crystal–moving-detector method (θ—2θ scan).[4] Lorentz, polarisation, and absorption corrections were applied. Towards the end of the refinement an isotropic correction was also made for extinction.[5]

Solution and Refinement of the Structure.—The structure was solved by direct methods with the program MULTAN [6] and $E > 1.5$ reflections. The E map computed from the solution with the best figure-of-merit revealed all non-hydrogen atom positions, and the structure was refined isotropically to R 0.13. Refinement was by full-matrix, least-squares,[7] the individual weights used being equal to the reciprocal of the square of the standard deviation determined from counting statistics, and the function minimised being $\Sigma w(|F_o| - |F_c|)^2$. Anisotropic temperature factors reduced R to 0.086. Two cycles of refinement using only high-angle data [$(\sin\theta)/\lambda > 0.35$] were then carried out to aid in locating hydrogen atoms. These ' high-angle ' parameters were used to calculate structure factors for all data, from which a difference synthesis revealed the position of all hydrogen atoms attached to carbon atoms.

It became evident from subsequent Fourier difference syntheses that there were three possible positions for H(O4) and two possible positions for each of the remaining hydrogen atoms except H(O7). Refinement of alternative positions H(O6)A and H(O6)B led to the assumption that there was some disorder over these two positions, with each appearing equally favoured within the limits of an X-ray refinement; these positions were not refined later. The other hydroxy-hydrogen atom positions were obtained by taking into account possible hydrogen bonding O · · · O, generating from O(6) and O(6) at $2 - x$, $-y$, $1 - z$; it was found that all hydroxy-hydrogen atoms except H(O7) were disordered over two positions, A and B. The remaining position for H(O4), [H(O4)C], was not included as it did not

---

† *Present address:* School of Chemistry, The University of New South Wales.

[1] S. J. Angyal, D. Greeves, and J. A. Mills, *Austral. J. Chem.*, 1974, **27**, 1447.

[2] J. A. Mills, *Austral. J. Chem.*, 1974, **27**, 1433.

[3] W. Hoppe, *Angew. Chem. Internat. Edn.*, 1965, **4**, 508.

[4] U. W. Arndt and B. T. M. Willis, ' Single Crystal Diffractometry,' Cambridge University Press, Cambridge, 1966.

[5] A. C. Larson, in ' Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970, p. 291.

[6] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

[7] W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS, a FORTRAN Crystallographic Least-Squares Program, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1962, Report ORNL-TM-305.

form part of either hydrogen-bonding scheme. The structure was then refined anisotropically to R 0.044.

In the refinement the isotropic extinction parameter[5] was applied, the temperature parameters of the hydrogen atoms were kept equal to those of the atoms with which they were most closely associated, and the occupancy of the disordered hydrogen atoms was fixed at $\frac{1}{2}$. The anomalous scattering factors for oxygen were taken from ref. 8.

A final electron-density difference map showed two prominent peaks with heights 0.40 and 0.41 e$Å^{-3}$. One of these was close to the position of H′(C7), the other was H(O4)C. Apart from these two peaks, the fluctuations in this map did not exceed ±0.25 e$Å^{-3}$.

One has a planar, zig-zag carbon chain and therefore a non-bonded interaction between the parallel bonds C(3)–O(3) and C(5)–O(5) of the type known to be highly unfavourable in acyclic carbohydrates and related compounds.[9-11] There seems to be a substantial amount of this conformer in aqueous solutions of the heptitol.[1] If present in the crystal this conformation would offer the possibility of an intramolecular hydrogen bond between the hydroxy-groups in 1,3-parallel orientation. There is no clear picture of the factors which promote the formation of such intramolecular bonds in the solid state.[11]

TABLE 1

Atomic co-ordinates and thermal parameters * (all $\times 10^4$)

(*a*) Non-hydrogen atoms

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	8 715(3)	4 352(1)	2 928(2)	283(6)	24(1)	57(2)	−2(1)	25(3)	5(1)
O(2)	3 598(3)	3 461(1)	3 144(2)	240(6)	28(1)	61(2)	9(1)	−6(2)	−2(1)
O(3)	9 766(3)	3 228(1)	5 326(2)	190(6)	23(0)	83(2)	2(1)	−7(2)	−2(1)
O(4)	4 965(4)	2 530(1)	6 065(2)	610(10)	28(1)	78(2)	38(2)	138(4)	10(1)
O(5)	6 131(3)	982(1)	5 675(2)	296(7)	20(0)	69(2)	−17(1)	27(3)	6(1)
O(6)	10 984(3)	674(1)	4 533(2)	265(6)	23(1)	101(2)	29(1)	0(3)	2(1)
O(7)	8 385(4)	773(1)	2 076(2)	515(9)	26(1)	63(2)	27(2)	56(3)	2(1)
C(1)	7 030(4)	4 431(1)	3 888(2)	318(9)	18(1)	55(3)	7(2)	28(3)	1(1)
C(2)	5 549(4)	3 690(1)	4 156(2)	219(7)	18(1)	48(3)	8(2)	23(3)	−2(1)
C(3)	7 486(3)	3 000(1)	4 484(2)	186(7)	17(1)	49(3)	3(1)	15(3)	−2(1)
C(4)	5 964(4)	2 313(1)	4 971(2)	234(7)	19(1)	51(3)	0(2)	38(3)	−0(1)
C(5)	7 744(4)	1 589(1)	5 225(2)	214(7)	17(1)	52(3)	−11(1)	−4(3)	4(1)
C(6)	9 096(3)	1 283(1)	4 154(2)	193(7)	13(1)	67(3)	4(1)	16(3)	2(1)
C(7)	7 081(4)	976(1)	3 103(2)	297(9)	26(1)	56(3)	3(2)	24(3)	−3(1)

(*b*) Hydrogen atoms [thermal parameters assigned equal to those of atom to which bonded (all $\times 10^3$)]

	x/a	y/b	z/c		x/a	y/b	z/c
H(O1)	787(17)	436(4)	217(9)	H(O6)B	1 050	23	476
H(O1)B	998(14)	394(4)	299(6)	H(O7)	950(7)	32(2)	221(3)
H(O2)	223(14)	378(4)	301(6)	H(C1)	820(6)	458(2)	462(3)
H(O2)B	401(12)	291(4)	304(6)	H′(C1)	564(6)	484(2)	363(3)
H(O3)	920(13)	347(4)	598(7)	H(C2)	457(6)	382(2)	481(3)
H(O3)B	1 110(14)	295(4)	569(6)	H(C3)	824(6)	283(2)	370(3)
H(O4)	325(18)	280(4)	585(7)	H(C4)	440(6)	216(2)	428(3)
H(O4)B	494(15)	220(5)	663(7)	H(C5)	910(6)	172(2)	590(3)
H(O5)	442(15)	91(4)	532(7)	H(C6)	1 018(6)	169(2)	385(3)
H(O5)B	692(14)	75(4)	660(9)	H(C7)	616(6)	52(2)	343(3)
H(O6)	1 250	79	490	H′(C7)	560(6)	137(2)	271(3)

* Estimated standard deviations are in parentheses. Where none appears for a hydrogen atom, its positional parameters were not refined towards the end of refinement.

Final positional and thermal parameters are listed in Table 1. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21567 (11 pp., 1 microfiche).*

DISCUSSION

Crystal structures of heptitols have not been reported previously. It has been deduced[2] that heptitols and higher alditols generally will show more interesting conformational features than pentitols and hexitols. *meso*-L-*glycero*-L-*gulo*-Heptitol (I) was chosen for study because it was impossible to decide[2] between two possible conformations, each possessing features of special interest.

The other possibility is a non-planar conformation in which there are gauche segments of carbon chain round two consecutive C–C bonds, C(4)–C(5) and C(5)–C(6). Although free of parallel 1,3-interactions, it has a substantial number of unfavourable gauche interactions.[2] A related non-planar conformation was predicted as a possibility for D-glucitol, but was not observed.[9] This non-planar conformation of the heptitol is chiral: equal numbers of the enantiomorphous conformers will therefore be present.

The structure determination showed that the second possibility is correct, and that the crystal shows an unusual pattern of intermolecular hydrogen bonding. The molecular structure and atom-numbering system are

---

* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1974, Index issue.

[8] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[9] G. A. Jeffrey and H. S. Kim, *Carbohydrate Res.*, 1970, **14**, 207.

[10] P. L. Durette and D. Horton, *Adv. Carbohydrate Chem. Biochem.*, 1971, **26**, 49.

[11] G. A. Jeffrey, in 'Carbohydrates in Solution,' *Adv. in Chem. Ser.*, No. 117, ed. R. F. Gould, Amer. Chem. Soc., Washington, 1973, ch. 10.

shown in Figure 1, bond lengths and bond angles involving non-hydrogen atoms and torsional angles involving carbon atoms in Table 2, and dihedral angles about C–C bonds in Figure 2.

Carbon atoms C(1)—(5) all lie within 0.072 Å of the best plane through them, and they and O(5) are all coplanar to within 0.090 Å. Atoms C(5)—(7), and O(7) are coplanar to within 0.038 Å. The equations of the best least-squares planes through these sets of atoms and the deviations of the atoms from the planes are listed in Table 3. The terminal hydroxy-group at C(7) is in an extended conformation, which is probably a position of minimum energy, but the hydroxy-group at C(1) is gauche to O(2) and C(3), as in D-mannitol. This orientation is almost certainly determined by the crystal-field forces of the intermolecular hydrogen bonding.[9]

TABLE 2

Molecular geometry

(*a*) Interatomic distances (Å), with standard deviations in parentheses

O(1)–C(1)	1.429(3)	C(4)–C(5)	1.527(2)
C(1)–C(2)	1.515(3)	O(5)–C(5)	1.435(2)
O(2)–C(2)	1.430(3)	C(5)–C(6)	1.517(3)
C(2)–C(3)	1.534(2)	O(6)–C(6)	1.425(2)
O(3)–C(3)	1.417(2)	C(6)–C(7)	1.518(3)
C(3)–C(4)	1.531(2)	O(7)–C(7)	1.412(3)
O(4)–C(4)	1.406(3)		

(*b*) Interatomic angles (°) with standard deviations in parentheses

O(1)–C(1)–C(2)	113.7(2)	O(4)–C(4)–C(5)	108.3(2)
C(1)–C(2)–O(2)	111.8(2)	C(4)–C(5)–O(5)	109.0(1)
C(1)–C(2)–C(3)	113.3(1)	C(4)–C(5)–C(6)	116.0(2)
O(2)–C(2)–C(3)	107.9(2)	O(5)–C(5)–C(6)	109.4(1)
C(2)–C(3)–O(3)	110.9(1)	C(5)–C(6)–O(6)	111.1(2)
C(2)–C(3)–C(4)	111.2(1)	C(5)–C(6)–C(7)	113.7(2)
O(3)–C(3)–C(4)	111.5(2)	O(6)–C(6)–C(7)	107.9(2)
C(3)–C(4)–O(4)	109.4(2)	C(6)–C(7)–O(7)	112.0(2)
C(3)–C(4)–C(5)	113.5(1)		

(*c*) Torsion angles (°) involving carbon atoms, with standard deviations in parentheses

C(1)–C(2)–C(3)–C(4)	169.6(2)
C(2)–C(3)–C(4)–C(5)	175.8(2)
C(3)–C(4)–C(5)–C(6)	−56.1(2)
C(4)–C(5)–C(6)–C(7)	−65.8(2)

TABLE 3

Equations of least-squares planes in the form $AX + BY + CZ = D$, where X, Y, Z are in Å. Distances (Å) of atoms for the plane are given in square brackets

Plane (1): C(1)—(5)

$$0.0397X + 0.2999Y + 0.9405Z = 6.3791$$

[C(1) 0.062, C(2) −0.072, C(3) −0.051, C(4) 0.068, C(5) −0.007]

Plane (2): C(1)–(5), O(5)

$$0.0737X + 0.3103Y + 0.9309Z = 6.5073$$

[C(1) 0.90, C(2) −0.085, C(3) −0.047, C(4) 0.029, C(5) −0.033, O(5) 0.046]

Plane (3): C(5)—(7), O(7)

$$-0.0491X + 0.9207Y - 0.3779Z = 0.1206$$

[C(5) 0.035, C(6) −0.037, C(7) −0.036, O(7) 0.038]

There is no significant systematic shortening of the C–C bonds at the ends of the molecule, or of the C–O bonds of the terminal hydroxy-groups. The mean C–C and C–O bond lengths are 1.524(3) and 1.422(3) Å, respectively. The C–C–C angles are consistently greater than the normal tetrahedral value, mean 113.5(2)°. The mean value of the C–C–O angles is 110.2(2)°. These mean bond lengths and angles are in good agreement with those of other crystal structures in the alditol series.[9,12] Widening of C–C–C angles has been observed in paraffins and other long-chain carbon compounds, and has been attributed to repulsions between substituent groups.[13]

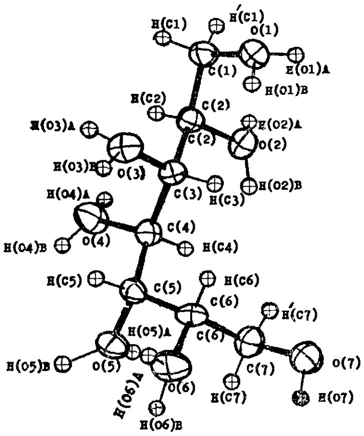


FIGURE 1 ORTEP plot of the thermal ellipsoids, showing the atom numbering system

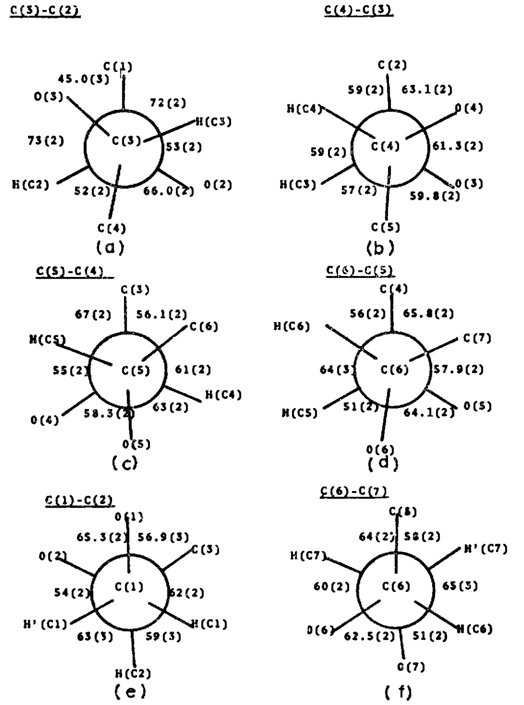


FIGURE 2 Dihedral angles (°) about C–C bonds: (a) C(3)–C(2), (b) C(4)–C(3), (c) C(5)–C(4), (d) C(6)–C(5), (e) C(1)–C(2), (f) C(6)–C(7)

---

[12] N. Azarnia, G. A. Jeffrey, and M. S. Shen, *Acta Cryst.*, 1972, **B28**, 1007.

[13] J. B. Pedley, *Trans. Faraday Soc.*, 1961, **57**, 1492.

meso-L-*glycero*-L-*gulo*-Heptitol is the fourth *meso*-alditol found to crystallise in a chiral conformation. Of the other three,[9] ribitol resembles the heptitol in crystallising as an assembly of equal numbers of enantiomorphous non-planar conformers in space group $P2_1/c$. Xylitol also crystallises in a non-planar conformation, but a crystal (space group $P2_12_12_1$) contains conformers of only one kind, and segregation of enantiomorphs must therefore occur on crystallisation. Galactitol crystallises in the extended form, with a planar carbon chain, but the conformers acquire chirality in the crystal by being somewhat distorted from the true centrosymmetric conformation.

Hydrogen Bonding.—Each oxygen atom, except O(7), has two partial hydrogen atoms, A and B, attached to it. The heptitol molecules are associated in the crystal by intermolecular hydrogen bonding between the hydroxy-groups. In this structure, as in the majority of crystalline alditols,[11] each hydroxy-group acts as hydrogen bond donor and acceptor. There are two alternative, centrosymmetrically-related hydrogen bonding schemes, having $(1,0,\frac{1}{2})$ as a centre of inversion. Each of these has a finite main chain extending in the b axis direction and a branched chain, combined at O(1), shown schematically as:

$$\begin{tikzcd}
{} \arrow[r] & O(6)B \arrow[r] & O(6)A \arrow[r] & O(5)B \arrow[r] & O(1)B \arrow[r] & O(2)B \arrow[d] \\
{} & O(5)A \arrow[l] & O(1)A \arrow[l] & O(7) \arrow[l] & O(3)A \arrow[l] & O(4)A \arrow[l] \\
& & O(2)A \arrow[u] & O(4)B \arrow[l] & O(3)B \arrow[l] &
\end{tikzcd}$$

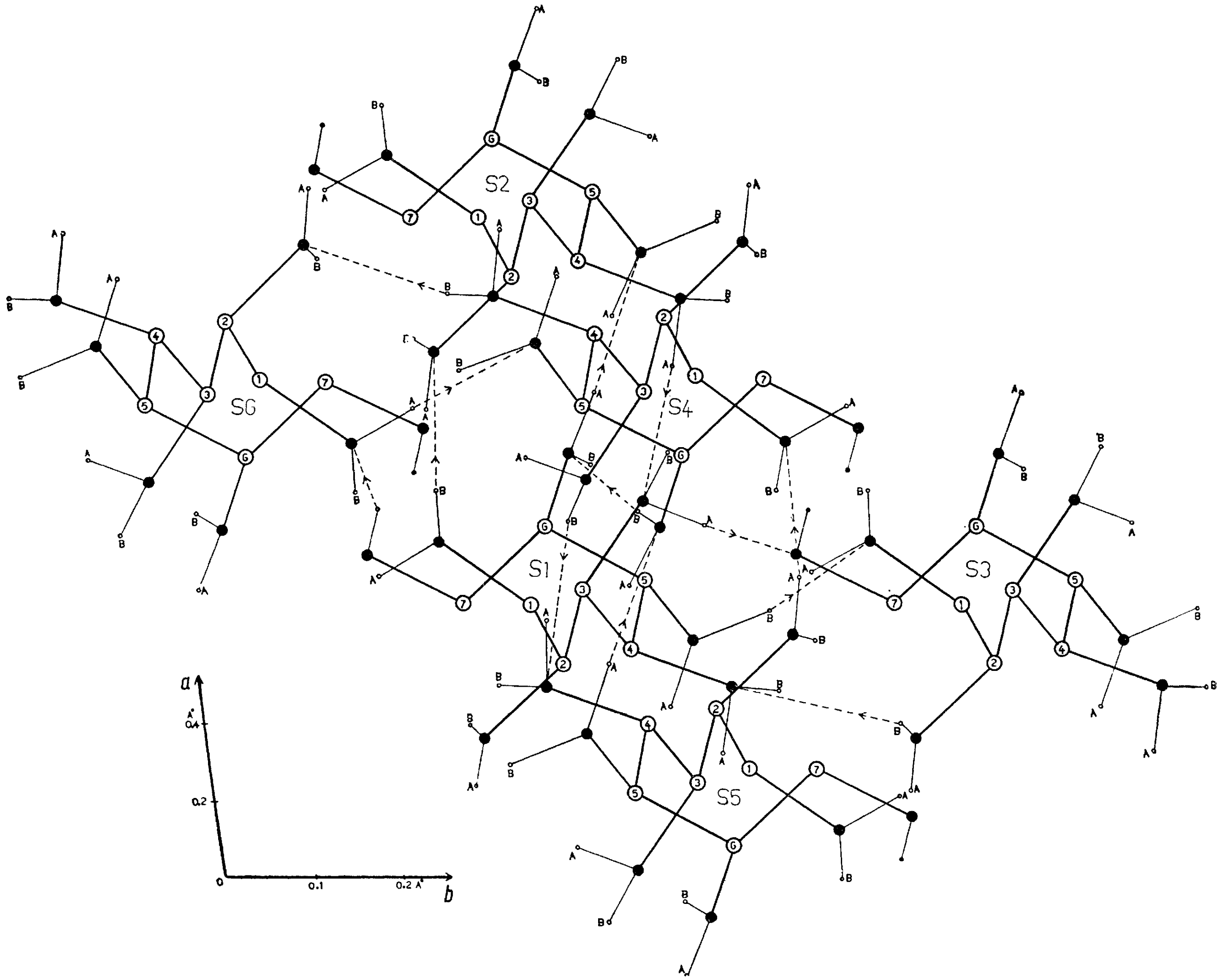


FIGURE 3 Projection of the structure along [101], showing one of the hydrogen-bonding schemes. Large open circles represent C atoms, large closed circles O, small closed circles H, small open circles $\frac{1}{2}$H. S1 is at x,y,z; S2 at $1+x,y,z$; S3 at $x,\frac{1}{2}-y,\frac{1}{2}+z$; S4 at $2-x,-y,1-z$; S5 at $1-x,-y,1-z$; S6 at $2-x,-\frac{1}{2}+y,\frac{1}{2}-z$

TABLE 4

Intermolecular hydrogen-bond distances (Å), angles (deg.), with standard deviations in parentheses

D–H · · · A *	D–H	H · · · A	D · · · A	D–H–A
	Dij	Djl	Dil	<ijl
O(6$^{\mathrm{III}}$)–H(B) · · · O(6)	0.848(2)	1.921(2)	2.759(3)	169.5(1)
O(6)–H(A) · · · O(5$^{\mathrm{I}}$)	0.826(2)	1.908(2)	2.732(2)	175.0(2)
O(5$^{\mathrm{I}}$)–H(B) · · · O(1$^{\mathrm{IX}}$)	1.1(1)	1.6(1)	2.699(2)	161(5)
O(1$^{\mathrm{IX}}$)–H(B) · · · O(2$^{\mathrm{X}}$)	0.93(7)	1.95(7)	2.833(2)	157(6)
O(2$^{\mathrm{X}}$)–H(B) · · · O(4$^{\mathrm{II}}$)	0.99(7)	2.40(7)	2.995(2)	118(5)
O(4$^{\mathrm{II}}$)–H(A) · · · O(3$^{\mathrm{I}}$)	0.97(9)	1.89(9)	2.849(2)	174(7)
O(3$^{\mathrm{I}}$)–H(A) · · · O(7$^{\mathrm{IX}}$)	0.90(8)	1.86(8)	2.727(2)	162(7)
O(7$^{\mathrm{IX}}$)–H · · · O(1$^{\mathrm{V}}$)	0.96(4)	1.89(4)	2.828(2)	165(3)
O(1$^{\mathrm{V}}$)–H(A) · · · O(5$^{\mathrm{VI}}$)	0.9(1)	1.8(1)	2.699(2)	161(7)
O(5$^{\mathrm{VI}}$)–H(A) · · · O(6$^{\mathrm{VII}}$)	0.89(8)	1.84(8)	2.732(2)	175(7)
O(3$^{\mathrm{VI}}$)–H(B) · · · O(4$^{\mathrm{VIII}}$)	0.87(7)	2.03(7)	2.849(2)	157(6)
O(4$^{\mathrm{VIII}}$)–H(B) · · · O(2$^{\mathrm{IV}}$)	0.84 (8)	2.19(8)	2.995(2)	161(6)
O(2$^{\mathrm{IV}}$)–H(A) · · · O(1$^{\mathrm{V}}$)	0.86(7)	1.99(7)	2.833(2)	168(7)

* D = donor, A = acceptor. Roman numeral superscripts refer to the following equivalent positions, relative to the reference molecule at x,y,z:

I	$1 + x,y,z$	VI	$3 - x,\frac{1}{2} + y,\frac{3}{2} - z$
II	$2 + x,y,z$	VII	$4 - x,\frac{1}{2} + y,\frac{3}{2} - z$
III	$2 - x,-y,1 - z$	VIII	$2 - x,\frac{1}{2} + y,\frac{3}{2} - z$
IV	$2 - x,1 - y,1 - z$	IX	$1 + x,\frac{1}{2} - y,\frac{1}{2} + z$
V	$3 - x,1 - y,1 - z$	X	$2 + x,\frac{1}{2} - y,\frac{1}{2} + z$

Figure 3 shows a projection of the structure along [101], and represents one of the hydrogen-bonding schemes. Hydrogen bond distances and angles in the sequence of bonds are listed in Table 4. The mean O · · · O distance is 2.810(3) Å, with a spread from 2.699(2) to 2.995(2) Å. The hydrogen bonding O(2)→O(4) seems to be rather weak, with O(2) · · · O(4) and H(O2)B · · · O(4) 2.995(2) and 2.398(66) Å, and O(2)–H(O2)B · · · O(4) 118(5)°. Every hydroxy-oxygen atom is involved in hydrogen bonding with two other hydroxy-oxygens, except for O(1), which is bonded to three other hydroxy-oxygens.

Since the location of the hydrogen atoms was not well defined by use of X-ray intensity data, we hope to confirm the suggested hydrogen-bonding schemes by a neutron diffraction study.

We thank Dr. A. D. Rae for his interest in this work and suggestions about hydrogen-bonding schemes, and D. C. Craig for collecting the intensity data.

[5/1305 *Received, July 2nd,* 1975]