Determination of the Crystal Structure of the A Form of D-Glucitol by Neutron and X-ray Diffraction

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The crystal structure of D-glucitol, $C_6H_{14}O_6$, A form, from ethanol solution, has been determined from three-dimensional X-ray and neutron diffractometer data. The structure was solved by direct methods using the Karle & Hauptman tangent formula, and refined anisotropically to an R value of 0.032 for the X-ray data and to R = 0.066 for the neutron data. The space group is $P2_12_12_1$, Z = 4, a = 8.677 (5) b = 9.311 (8), c = 9.727 (4) Å, $D_x = 1.541$, $D_m = 1.535$ g.cm⁻³. The molecule has the bent chain conformation, with C(1) 1.06 Å out of the plane of the other five carbon atoms, which are coplanar within \pm 0.01 Å. The C-C bond lengths are normal, with a mean value of 1.520 Å. The molecules stack with their chain axes approximately parallel, as is usual with the alditols. Each hydroxyl group is involved in two hydrogen bonds. These bonds form two infinite spirals, one linking the odd-numbered oxygen atoms in the c direction and the other linking the even-numbered oxygens in the a direction. There is an unexpected and unexplained systematic distinction between these chains in the OH...O hydrogen bond separations, the former ranging from 1.91 to 2.22 Å and the latter from 1.69 to 1.73 Å. The corresponding O-(H)...O separations are 2.88 to 3.17 Å and 2.65 to 2.68 Å. Because of this unusual feature of the intermolecular hydrogen bonding, which has not been observed in other alditol structures, the X-ray data collection was repeated, although the first data yielded an R = 0.04. The final parameters are all within 3σ of those from the first set of data. The neutron data confirmed the heavy atom positions and gave more precise parameters for the hydrogens.

Introduction

D-Glucitol (D-sorbitol) is a commercially important chemical. About 70,000 tons a year of 70% aqueous solution are used in the U.S.A., principally as an additive in the food, tobacco, confectionery and pharmaceutical industries. The solid is not well characterized and appears to exist in several polymorphic forms. The one melting at 110°C, as reported in some text books, does not now appear to exist. Pigman (1957) reports stable and labile forms melting at 97 and 92°C respectively, and a racemate melting at 136 to 138°C. The crystals studied in this work melted at 85°C. A hydrate is stable below 20°C.

This work is part of a series of structure determinations of the alditols which includes D,L-arabinitol (Hunter & Rosenstein, 1968); ribitol (Kim, Jeffrey & Rosenstein, 1969); xylitol (Kim & Jeffrey, 1969) Dmannitol (Berman, Jeffrey & Rosenstein, 1968; Kim, Jeffrey & Rosenstein, 1968); galactitol (Berman & Rosenstein, 1968); D-glucitol-pyridine (Kim, Jeffrey & Rosenstein, 1971); iditol and allitol (Jeffrey, Azarnia & Shen, 1970). Jeffrey & Kim (1970) have predicted that there should be two low-energy non-planar chain rotamers for D-glucitol in solution or the molten state. This compound would therefore seem to be a likely candidate for the interesting, but comparatively rare, phenomenon of conformational polymorphism; *cf.* DL-methionine (Mathieson, 1952). It is planned to examine the structures of all the polymorphic forms of D-glucitol, if suitable single crystals can be obtained.

Crystal data

Beautiful transparent crystals were provided in a variety of sizes by Dr L. F. Gleysteen of Atlas Chemical Industries. They were obtained by evaporation of a solution of the compound in 95% ethanol and gave the following data:

D-Glucitol, form A, $C_6H_{14}O_6$, M.W. 182.07, m.p.85°C. Space group $P2_12_12_1$, from systematic absences, h00 with h odd, 0k0 with k odd, 00l with l odd.

a = 8.677(5) Å	$D_x = 1.541 \text{ g.cm}^{-3}$
b = 9.311(8)	$D_m = 1.535$
c = 9.727(4)	$\mu_{Cu Ka} = 12.13 \text{ cm}^{-1}$
Z = 4	$\mu_{neutron} = 2.85 \text{ cm}^{-1}$
	$(\lambda_{C_{11}K_{2}} = 1.5418 \text{ Å})$.

Two powder samples were also examined. Form B, m.p. 93.5°, from Atlas Chemical Industries, and form Γ , m.p. 92°, from Fischer Scientific Company.* The

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^{*} As in the case of the polymorphs of D-mannitol (Kim, Jeffrey & Rosenstein, 1968) we have used upper case Greek letters to avoid confusion with α , β , which have other configurational connotations in carbohydrate chemistry.

powder data are given in Table 1, together with those of a sample of DL-glucitol, m.p. 127 °C. The crystal density was measured by the flotation method in a mixture of hexane and bromoform. Because of an unusual aspect of the hydrogen bonding, discussed later, the X-ray data were collected twice with different crystals. The second set of data is reported. The first set, from a slightly smaller crystal ($0.15 \times 0.15 \times 0.2$ mm) gave cell parameters which differed by less than 1σ from those above (where the σ 's are in parentheses), and included 691 reflections above background.

Table	1.	Powder	data	for	the	B and	dΓ.	forms
	of	D-glucit	ol and	d fo	r di	gluc	itol	-

B form Γ form					DL-G	ucitol
d In	tensity	d I	ntensity	/ - /	d	Intensity
8∙9 Å	16	9∙4 Å	16		9∙5 Å	3
6.7	34	7.8	14		8.8	70
5.95	80	7.45	70		7.6	5
5.15	10	6.30	18		6.35	. 4
4.98	50	5-89	28	-	5.88	66
4.66	74	5.25	20		5.15	9
4·38	18	4.95	26		4.69	27
4.24	42.	4.71	100		4·31	100
4·12	- 30	4.46	16	•	4.06	14
3.95	100	4.34	36		3.86	44
3.75	20	4.15	24		3.53	42
3.56	8	4·01	32		3.38	13
3.48	38 ·	3.90	36 a		3.24	13
3.37	20 ·	3.72	34		3.11	10
3.22	14	3.46	40		2·96	8
3.13	16	3.83	18		2.77	18
3.04	16	3.30	16		2.70	17
2.92	·4 · .	3.06	36	• ;	2.57	25
2.85	6	2.90	. 6		2.51	.3
2.79	34	2.8	30		2.43	15

X-ray determination

The unit-cell parameters and three-dimensional intensity data were measured with a Picker FACS I diffractometer using Cu $K\alpha$ radiation and a crystal of dimensions $0.2 \times 0.2 \times 0.2$ mm, which was mounted along the c^* axis. A 2θ scanning mode, with varying interval, gave 797 recorded reflections up to $2\theta = 130^\circ$, of which 742 were significantly above background. The data were reduced to structure amplitudes using an IBM 1130 program (Shiono, 1969) without absorption corrections.

The structure was solved by the application of the tangent formula to the first data set (Karle & Hauptman, 1956; Karle & Karle, 1966) using an IBM 7090 version of the Hall (1968) direct phasing method. Three origin-determining reflections and one defining the enantiomorph were selected as the starting set. Their indices, phases, and E_{hkl} values were as follows:

072,	$\pi/2$,	2.59;	1
601,	$\pi/2,$	2.56;	
170,	$\pi/2,$	2.42;	
180,	$\pi/2,$	2.28.	

The tangent-formula refinement was then applied to

148 reflections with E values > 1.30. The twelve highest peaks on the resulting E map corresponded to the six oxygen and six carbon atoms of the molecule. The first trial structure gave an R value of 0.22 for all reflections. Refinement was by several cycles of isotropic and of anisotropic structure-factor calculations



Fig. 1. Comparison of two sets of X-ray parameters (solid line) and one set each of X-ray and neutron parameters (dotted line). The distribution of Δ/σ values is shown in each case, where Δ/σ is the parameter difference divided by its standard error. (a) positional parameters, (b) thermal parameters.

using the block-diagonal least-squares program for the IBM 1130 (Shiono, 1968) and the full-matrix leastsquares program for the IBM 7090 (Shiono, 1966). The hydrogen atoms were located on difference maps and were assigned isotropic temperature factors of 2.0. The final refinement, which included all carbon and oxygen parameters and the positional parameters of hydrogen atoms and a scale factor, gave an R value of 0.04 for the first data set and 0.032 for the second set

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with the Hughes (1941) weighting scheme. The differences, Δ , between the two sets of parameters are indicated in Fig. 1, which shows the distribution of Δ/σ values. The atomic parameters from the second data set are given in Table 2, and the observed and calculated structure factors are listed in Table 3. The atomic scattering factors used were those of Cromer & Waber (1965) for carbon and oxygen and of Stewart, Davidson & Simpson (1965) for hydrogen.

Table 2. Fractional atomic coordinates $(\times 10^3)$ and anisotropic thermal parameters $(\times 10^4)$ for D-glucitol

The key to the atomic numbering is given in Fig. 3. The temperature factor expression used was

$$p \left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right].$$

The estimated standard deviations given in parentheses refer to the last decimal positions of the corresponding parameters. For each atom, the neutron result is given on the first line and the X-ray result on the second line.

	x	у	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	101.8 (3)	131.1 (3)	664.0 (3)	36 (3)	57 (3)	48 (3)	3 (3)	7 (3)	7 (3)
	101.8 (3)	131.1 (3)	663.3 (3)	76 (4)	58 (3)	63 (3)	9 (3)	6 (3)	-1(3)
C(2)	264.4 (3)	123.1 (3)	606.2 (3)	39 (3)	37 (3)	29 (3)	1 (2)	7 (2)	2 (2)
	264.7 (3)	122.9 (3)	606.1 (3)	72 (3)	54 (3)	40 (2)	-3 (3)	-3 (3)	-3 (2)
C(3)	311.7 (3)	-21·8 (3)	545.9 (3)	38 (3)	30 (2)	45 (3)	1 (2)	3 (2)	-4 (2)
	310.5 (3)	-22.0(3)	546.0 (3)	59 (3)	56 (3)	48 (3)	-1(3)	4 (3)	-1(2)
C(4)	282.5 (3)	-148.1 (3)	641.7 (3)	37 (3)	43 (3)	42(3)	-4 (2)	3 (2)	-4(2)
	283.8 (3)	-148.0(3)	641.4 (3)	59 (3)	57 (3)	48 (3)	-3(3)	2 (3)	-3(2)
C(5)	335.5 (3)	-291.8(3)	580.3 (3)	35 (2)	31 (2)	52 (3)	-5(2)	1(2)	-2(2)
	335.4 (3)	$-292\cdot2(3)$	581.0 (3)	64 (3)	56 (3)	52 (3)	-5(3)	4 (3)	9(2)
C(6)	303.6(3)	-413.7(3)	680.5(3)	69 (3) 87 (4)	30 (2) 52 (2)	$\frac{33}{72}$	-2(2)	-3(3)	-4(2) -1(3)
O(1)	504.8(3) 64.7(4)	-413.1(3) 273.0(4)	703.3(4)	67 (4) 55 (4)	52(5)	$\frac{72}{68}$	$2^{(3)}$	-4(3)	-10(3)
0(1)	64.9(3)	273.0(4) 274.2(2)	703.5 (2)	83 (3)	78 (3)	76(2)	25(4)	-1(2)	-17(2)
O(2)	281.6(4)	2742(2) 223.4(3)	494.4(4)	89 (4)	36(3)	46(3)	-15(3)	8 (3)	-1(3)
0(2)	$281 \cdot 7$ (2)	$223 \cdot 0$ (2)	495.4 (2)	114(3)	46 (2)	46 (2)	-13(2)	11 (2)	-1(2)
O(3)	471.0 (4)	-15.0(4)	509.4 (4)	46 (4)	49 (3)	69 (4)	2 (3)	26 (3)	6 (3)
	472.0 (2)	-16.8(2)	509.3 (2)	71 (3)	62 (2)	73 (2)	5 (2)	25 (2)	8 (2)
O(4)	358.9 (4)	-123.2(4)	769·0 (3)	80 (4)	55 (3)	33 (3)	-17(3)	-5(3)	-9(3)
	359.6 (3)	-122.0(2)	768.3 (2)	109 (3)	71 (2)	40 (2)	-26 (2)	-3(2)	-2(2)
O(5)	261.7 (5)	- 317.1 (4)	452.3 (4)	98 (5)	55 (3)	45 (4)	19 (3)	-6 (4)	-5(3)
	262.4 (3)	-316.8 (2)	451.3 (2)	115 (3)	75 (3)	52 (2)	19 (3)	-8(2)	-6(2)
O(6)	366.0 (4)	- 544.8 (4)	633.8 (5)	83 (5)	40 (3)	114 (5)	8 (4)	-36(4)	-15(4)
	365.6 (3)	- 544.4 (2)	632·6 (3)	111 (4)	49 (2)	111 (3)	17 (2)	-37(3)	-24(2)
H(C1)	18.7 (8)	103.0 (8)	585.3 (9)	76 (7)	98 (8)	129 (9)	-17(7)	-25 (8)	-25(7)
	21 (5)	95 (4)	592 (4)	105 (10)	107 (9)	01 (0)	31 (9)	40 (0)	60 (9)
$\mathbf{H}(\mathbf{C})$	89.7 (9)	59.2 (9)	749.3 (8)	125 (10)	107 (8)	91 (8)	21 (8)	40 (0)	00 (8)
H(C2)	/8 (5) 245 1 (7)	67 (4)	740 (5)	01 (7)	91 (6)	97 (6)	10 (6)	21 (6)	- 9 (6)
$\Pi(C2)$	343.1(7)	149.9 (7)	683(5)	01 (7)	01 (0)	82 (0)	- 10 (0)	-21(0)	-) (0)
H(C3)	243.8(8)	-40.1(7)	451.4(7)	96 (8)	80 (6)	71 (6)	-22(6)	- 19 (6)	-10(5)
11(05)	2450(0)	-41(4)	460 (4)	<i>J</i> U (0)	00 (0)	/1 (0)	22 (0)	17 (0)	10 (0)
H(C4)	168.6 (6)	-155.7(7)	659.0 (7)	48 (5)	98 (7)	95 (7)	-9(6)	16 (6)	-13 (6)
()	176 (5)	-152(4)	661 (4)	()				~ /	. ,
H(C5)	459.7 (7)	-286.5(8)	561.3 (8)	62 (7)	85 (7)	107 (8)	-5 (6)	15 (6)	-8 (6)
	490 (5)	-288(5)	561 (4)						
H(C6)	180.2 (9)	- 429.2 (7)	692.4 (10)	101 (9)	80 (7)	143 (10)	9 (7)	26 (9)	18 (8)
	189 (5)	- 429 (4)	689 (4)						
H′(C6)	353.6 (11)	-387.3(8)	781.9 (8)	179 (12)	90 (8)	87 (9)	28 (9)	- 52 (9)	-8(7)
	352 (5)	- 391 (5)	767 (5)				1 ((0)	a (0)	27 (7)
H(OI)	130.5 (8)	298.8 (9)	781.4 (9)	91 (8)	118 (9)	994(9)	14 (8)	-2(8)	-27(7)
	121 (5)	291 (5)	774 (5)	117 (0)	$(F(\mathbf{z}))$	70 (7)	0 (6)	4 (6)	0 (6)
H(O2)	295.0 (8)	318.0 (6)	538.3 (7)	117 (9)	65 (7)	. /0(/)	-9(0)	-4 (0)	-9(0)
U(02)	200 (5)	309 (4)	341 (3) 455-0 (8)	70 (8)	87 (7)	00 (8)	- 5 (6)	12 (7)	9 (7)
H(03)	409.3 (0)	10.3(1)	455.0 (8)	79 (0)	87 (7)	33 (0)	- 5 (0)	12(7))(1)
H(04)	306.2 (9)	-170.9(6)	843.6 (7)	153 (10)	53 (6)	73 (7)	-18(7)	12 (8)	-12(5)
	315 (5)	-158(4)	826 (5)		55 (5)		(/)	(9)	(•)
H(O5)	166.2 (9)	- 369.8 (8)	466.2 (9)	101 (9)	94 (7)	110 (8)	-12 (8)	-31 (7)	-18 (7)
	185 (5)	- 364 (4)	463 (5)		. /	. ,	. ,	. ,	
H(O6)	460-3 (8)	- 566-2 (7)	679.6 (8)	102 (9)	69 (7)	96 (8)	10 (6)	-31 (8)	-4 (6)
	447 (6)	-560(5)	674 (5)						

Neutron determination

The crystals used for the neutron data were from the same crystallization batch that provided the crystal for the X-ray measurements. The crystal was mounted along the c^* axis on a cadmium-plated brass rod. The data were collected automatically using the computercontrolled Multi-spectrometer Control System (Beaucage, Kelley, Ophir, Rankowitz, Spinrad & van Narton, 1966) with a monochromatic neutron beam ($\lambda = 0.974$ Å) from the Brookhaven National Laboratory High Flux Beam Reactor (flux 8×10^{6} n.cm⁻².sec⁻¹ at the specimen). A θ -2 θ step-scan method was applied with $\Delta(2\theta) = 0.6^{\circ}$ up to $\sin \theta / \lambda = 0.625$. Two crystals, with dimensions $1.21 \times 1.54 \times 3.79$ mm and $1.67 \times 1.61 \times 2.55$ mm, respectively, were used, because of gradual external deterioriation of the crystals in the Long Island environment. The data sets included the measurements of some symmetry-equivalent reflections. The data were reduced to structure amplitudes corrected for absorption, and the equivalent reflections were averaged using programs from the BNL CDC 6600 crystallographic program library. Of the 1032 recorded data, 164 reflections were too weak to be observed. In order to obtain independent confirmation of the positions

of hydrogen atoms deduced from the X-ray analysis, a difference Fourier synthesis was computed with the calculated structure factors of the heavy-atom X-ray positions. The refinement was then carried out in several full-matrix least-squares cycles on the IBM 7090 computer. The final R value was 0.066 for all reflections, including unobserved, with the Cruickshank (1961) weighting scheme, $w = (10.0 + 1.0 F_o + 0.025 F_o^2)^{-1}$. The positional and anisotropic thermal parameters for all atoms and a scale factor were varied. The atomic parameters are given in Table 2, and the observed and calculated structure factors are listed in Table 4. Neutron scattering lengths used were $\bar{b}_{\rm H} = -0.378$, $\bar{b}_{\rm C} = 0.661$, $\bar{b}_{\rm O} = 0.577 \times 10^{-12}$ cm (International Tables for X-ray Crystallography, 1968). The differences between the C and O parameters from the X-ray data (second set) and those from the neutron data are most noticeable for the diagonal elements of the anisotropic thermal parameter ellipsoids, which are larger for X-rays than for neutrons. These differences are shown in Fig. 1 in the same way as those between the two sets of X-ray parameters. The two sets of curves suggest that the discrepancies in the neutron and X-ray thermal parameters are a significant effect but that

Table 3. Observed and calculated structure factors for X-ray data

Columns are: Index, $10|F_{obs}|$, $10|F_{calc}|$. Asterisks indicate unobserved reflections.

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	 72 73 76 76 74 74 75 16 72 175 18 120 123 123 124 124 124 124 124 124 124 124 122 122 122 122 124 141 141			8 9 15 9 40 42 He 5 K 4 0 19 17 1 73 73 2 219 217 4 130 133 5 207 211 6 68 68 7 23 23 8 40 40 9 He 5 K 5 0 27 24 1 89 89 9 He 5 27 2 3 23 2 3 126 126	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2 89 8 3 91 8 4 38 3 5 96 9 6 80 1 0 70 4 1 91 9 1 91 9 1 3 128 12 4 60 5 5 55 5 6 70 K 0 105 10 1 85 8 2 95 9 3 3 5
$ 0 \ $	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} H= \begin{array}{c} 1 \ (\kappa = \ 5 \\ 1 \ (\delta + \ 176 \\ 1 \ 204 \ 200 \\ 2 \ 105 \ 108 \\ 3 \ 144 \ 145 \\ 4 \ 118 \\ 5 \ 245 \ 245 \\ 245 \ 245 \\ 245 \ 275 \\ 7 \ 110 \ 107 \\ 8 \ 72 \\ 7 \ 10 \ 107 \\ 8 \ 72 \\ 105 \ 176 \\ 105 \ 108 \\ 1 \ 45 \\ 22 \ 165 \ 174 \\ 3 \ 221 \ 223 \\ 4 \ 53 \ 56 \\ 5 \ 59 \ 59 \end{array}$	$ \begin{array}{c} 4 & 100 \\ 5 & 200 \\ 5 & 201 \\ 6 & 110 \\ 110 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ $	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
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these differences have only a small secondary effect on the atomic positional parameters from the two determinations.

Description of the structure

The molecular conformation and atomic numbering are shown in Fig. 2, in which the atoms are represented by the 50% probability ellipsoids (Johnson, 1965). As predicted from the configuration of glucitol (Jeffrey & Kim, 1970), no straight-chain conformation, Ia or Ib, with the parallel alignment of C(2)-OH and C(4)-OH, is observed in the crystal structure. Of the two bent chain conformations, IIa and IIb, which can be derived by the rotations shown in Ia and Ib so as to avoid this interaction, the simpler IIa is found. The same carbonchain conformation was found in the D-glucitol-pyridine complex (Kim, Jeffrey & Rosenstein, 1971). There is, however, a difference in the orientation of the terminal hydroxyl groups, which are both ap/ap and both Msc/Psc (Klyne & Prelog, 1960) with respect to the carbon chain, in this structure and in the complex, respectively. These results support the conclusion that the conformation of the carbon chain is a molecular property, whereas that of the terminal groups depends upon the intermolecular environment in the crystal (Jeffrey & Kim, 1970).



The equations of two least-squares best planes through carbon and oxygen atoms are given in Table 5. With the exception of C(1), the carbon atoms are coplanar within experimental error, and the coplanarity extends to the oxygens O(2) and O(6) to a close approximation.

The bond lengths and angles are given in Table 6. The differences between the X-ray and neutron results are within 3σ for the heavy atoms, except for C(3)– O(3), for which the difference is about 5σ , *i.e.* 0.018 Å.

Table 4. Observed and calculated structure factors for the neutron data

Columns are: Index, $100|F_{obs}|$, $100|F_{catc}|$. Asterisks indicate unobserved reflections.

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Table 5. Least-squares best planes in D-glucitol Equation for planes: AX+BY+CZ=D, where X, Y, Z and

		D are in A.			
	Distance fro	om best plane X-ray	N	Const	ants X-ray
C(2)*	0.011	0.010		0.011	0.017
$\mathcal{O}(2)^{*}$	-0.011	-0.012	A	0.911	0.91/
C(3)*	0.008	0.011	B	0.120	0.122
C(4)*	0.014	0.013	C ·	-0.393	-0.381
C(5)*	-0.007	-0.010	D	1.330	1.350
C(6)*	-0.003	-0.001			
C (1)	1.045	1.063			
O(2)*	0.059	0.053	A	0 ∙914	0.918
C(2)*	-0.079	-0.073	B	0.148	0.146
C(3)*	-0.032	-0.025	C -	-0.379	-0.369
C(4)*	0.020	0.018	D	1.386	1.398
C(5)*	0.025	0.020			
C(6)*	0.075	0.069			
O(6)*	-0.067	-0.062			
C(1)	0.986	1.008			· · ·

* Only these atoms were used to determine the best planes.





Fig. 2. Molecular conformation of D-glucitol. (a) thermal ellipsoids from neutron data, with key to atomic numbering. (b) thermal ellipsoids for carbon and oxygen atoms from X-ray data.

Since there is no reason to suspect that this bond is exceptional, the σ 's should probably be doubled to allow for systematic errors before applying significance tests. The mean C-C and C-O bond lengths are 1.525 and 1.422 Å from the neutron data and 1.520 and 1.427 Å from the X-ray data. The mean C-H and O-H bond lengths are 1.091 and 0.971 Å from the neutron data and 1.01 and 0.84 Å from the X-ray data, in agreement with the systematic differences observed in similar comparisons. The bond angles from the two determinations are in good agreement, with mean C-C-C and C-C-O angles of 113.1 and 109.7° from the neutron determination and 113.5 and 109.6° from the X-ray determination. These results are consistent with the mean C-C and C-O bond lengths of 1.521

Table 6. Bond lengths and angles in D-glucitol

The estimated standard deviations given in parentheses refer to the last decimal positions of the corresponding

parameters.

	Neutron	V-rov
C(1) $C(2)$		1.500 (4) \$
C(1) - C(2)	1.519 (4) A	1.520 (4) A
C(2) = C(3)	1.528 (4)	1.512 (4)
C(3) - C(4)	1521(4)	1.513 (4)
C(4) = C(5)	1.534 (4)	1.532(4)
C(J) = C(0)	1.321 (4)	1.311 (4)
C(1)-O(1)	1.412 (5)	1.425 (4)
C(2)-O(2)	1.441 (4)	1.431 (3)
C(3)-O(3)	1.428 (4)	1.446 (3)
C(4)–O(4)	1.423 (4)	1.419 (3)
C(5)-O(5)	1.419 (5)	1.429 (3)
C(6)–O(6)	1.410 (5)	1.412 (4)
C(1)-H(C1)	1.083 (8)	1.04 4)
C(1) - H'(C1)	1 071 (9)	0.97 (4)
C(2)-H(C2)	1.095 (7)	1.03 (4)
C(3)-H(C3)	1.105 (7)	1.02 (4)
C(4)–H(C4)	1.090 (7)	1.04 (4)
C(5)–H(C5)	1.095 (7)	1.02 (4)
C(6)–H(C6)	1.086 (9)	1.01 (4)
C(6)-H'(C6)	1.105 (9)	0.95 (4)
O(1)-H(O1)	0.979 (9)	0.85 (5)
O(2)-H(O2)	0.987 (8)	0.91 (4)
O(3)–H(O3)	0.969 (8)	0.88 (4)
O(4)–H(O4)	0.966 (8)	0.76 (4)
O(5)-H(O5)	0.972 (9)	0.81 (4)
O(6)–H(O6)	0.952 (8)	0.82 (5)
Mean values		t i s
C–C	1.525 (3)	1.520 (4)
C-0	1.422 (5)	1.427 (5)
C-H	1-091 (4)	1.01 (1)

0.971 (5)

0.84(2)



O-H

Fig. 3. Conformation angles in degrees around the C-C bonds in D-glucitol.

Table 6 (cont.)

Table 6 (cont.)

	Neutron	X-ray		Neutron	X-ray
C(1) - C(2) - C(3)	115·8 (2)°	115·3 (2)°	C(4) - C(3) - H(C3)	107.5 (4)	106 (2)
C(2) - C(3) - C(4)	113.7 (2)	114.3(2)	O(3) - C(3) - H(C3)	108·4 (4)	109 (2)
C(3) - C(4) - C(5)	112.7(2)	113.6 (2)	C(3) - C(4) - H(C4)	107.9 (4)	107 (2)
C(4) - C(5) - C(6)	110.3(2)	110.8 (2)	C(5) - C(4) - H(C4)	107.4 (4)	109 (2)
O(1) - C(1) - C(2)	111.0 (3)	110.8 (2)	O(4) - C(4) - H(C4)	109.6 (4)	108 (2)
C(1) - C(2) - O(2)	110.1 (2)	109.8 (2)	C(4) - C(5) - H(C5)	108.7 (4)	109 (2)
O(2) - C(2) - C(3)	109.7 (2)	109.1 (2)	C(6) - C(5) - H(C5)	108.6 (4)	109 (2)
C(2) - C(3) - O(3)	108.4 (2)	108.6 (2)	O(5) - C(5) - H(C5)	107.6 (4)	106 (2)
O(3)-C(3)-C(4)	110.4 (2)	109.0 (2)	C(5) - C(6) - H(C6)	110.2 (5)	109 (2)
C(3) - C(4) - O(4)	109.2 (2)	109.2 (2)	C(5)C(6)-H'(C6)	109.5 (5)	109 (3)
O(4) - C(4) - C(5)	110.0 (2)	110.3 (2)	O(6) - C(6) - H(C6)	107.4 (5)	106 (2)
C(4) - C(5) - O(5)	110.6 (3)	110.4 (2)	O(6) - C(6) - H'(C6)	109.2 (5)	109 (3)
O(5) - C(5) - C(6)	110.9 (3)	111.8 (2)	H(C6)-C(6)-H'(C6)	108.7 (7)	113 (4)
C(5) - C(6) - O(6)	111.7 (3)	111.3 (2)		107.9 (()	105 (2) 9
	110 0 (5)	112 (2)	C(1) - O(1) - H(O1)	107.8 (6)	$105(3)^{2}$
C(2) = C(1) = H(C1)	110.2 (5)	112(2)	C(2) = O(2) = H(O2)	105.3 (5)	102 (3)
C(2) - C(1) - H'(C1)	110.3 (5)	117(3)	C(3) = O(3) = H(O3)	109.3 (5)	107 (3)
O(1) - O(1) - H(C1)	105.4 (5)	109 (2)	C(4) = O(4) = H(O4)	111.0 (5)	109 (3)
U(1) - U(1) - H'(U1)	110.6 (5)	108 (3)	C(5) - O(5) - H(O5)	110.2 (6)	109 (3)
H(CI)-C(I)-H'(CI)	109.3 (6)	100 (3)	C(6) - O(6) - H(O6)	111.1 (6)	108 (3)
C(1) - C(2) - H(C2)	$108 \cdot / (4)$	110 (3)	Mean values		
C(3) = C(2) = H(C2)	107.8 (4)	106 (3)		112 1 (10)	112 5 (10)
U(2) - C(2) - H(C2)	109.5 (4)	111 (3)	0-0-0	$113 \cdot 1 (10)$	113.5(10)
C(2) - C(3) - H(C3)	108-2 (4)	109 (2)	0-0-0	109.7 (4)	109.6 (4)



Fig. 4. Molecular arrangement and hydrogen bonding in D-glucitol, viewed down the c axis. Solid lines are primary valence bonds; dotted lines are intermolecular hydrogen bonds (arrows represent directions in which hydrogens are donated). The a axis is vertical.

and 1.420 Å and with the mean C-C-C and C-C-O angles of 113 and 110° from the X-ray studies of other alditols. The principal conformational angles are shown in Fig. 3. They differ from the ideal value of 60° for staggered vicinal bonds up to $\pm 9^{\circ}$, as is commonly observed in other alditol structures.

The hydrogen bonding of the molecules is illustrated in Fig. 4. As is the general rule in the alditols, each hydroxyl is involved in two bonds, as donor in one and acceptor in the other. The bonding produces two separate infinite helical chains through the structure, *i.e.*,

 $O(1f) \rightarrow O(5) \rightarrow O(3b) \rightarrow O(1g) \rightarrow O(5h) \rightarrow O(3e) \rightarrow O(1a) \rightarrow$ in the direction of **c**, and $O(6b) \rightarrow O(4f) \rightarrow O(2) \rightarrow O(6d) \rightarrow O(4i) \rightarrow O(2c) \rightarrow O(6j) \rightarrow$ in the direction of **a**.

The hydrogen bond distances and angles are given in Table 7. There is a systematic distinction between those involving odd- and even-numbered oxygen atoms. The O-(H) \cdots O bonds, involving the odd-numbered oxygen atoms which form the chain extending in the c direction, are systematically longer than the bonds involving the even-numbered atoms. The even-atom bonds have $H \cdots O$ distances ranging from 1.691 to 1.729 Å, which is on the short side of the spectrum of observed $H \cdots O$ distances, while the odd-atom $H \cdots O$ distances range from 1.914 to 2.218. As shown in Fig. 5 and Table 7, there is no correlation of $H \cdots O$ distances with the linearity of the O-H···O bonds. In the even set the mean O-H...O angle is 166.4° , whereas in the odd set it is 167.1°. Similarly, there is no distinction between the O-H bonds. We have no detailed explanation for this interesting alternation of H bond lengths from one kind of chain to the other. It is not observed in the other ten alditol structures which we have studied. nor have we discovered a comparable case in the literature. We are led to the general conclusion that the van der Waals interactions, despite their nondirectional character, must play a significant rôle in determining molecular arrangement in this structure to the extent that they override the energy losses arising from a compression of the hydrogen bond in one direction and an extension in the other. In this connection it is interesting to note (see view down the b axis in Fig. 6) that each molecule is surrounded by six neighbours in an arrangement very close to the ideal hexagonal packing of cylinders, which would be the most stable arrangement in the absence of directional intermolecular forces.

0(6) + 0(4) + 0(2) + 0(6) +



 $O(1) \rightarrow O(5) \rightarrow O(3) \rightarrow O(1) \rightarrow$



Fig. 5. Stereochemical details of the intermolecular hydrogen bond chains in D-glucitol.

Table 7.	Hydrogen	bonding	distances	and	angles	in	D-glucitol
	2 .0						

<i>i</i> C(1) C(5) C(3) C(2) C(6) C(4)	<i>j</i> O(1) O(5) O(3) O(2) O(6) O(4)	k tom k H(O1) H(O5) H(O3) H(O2) H(O6) H(O4)	$l \\ O(5a) \\ O(3b) \\ O(1c) \\ O(6c) \\ O(4e) \\ O(2a)$	D(Neutron 2·881 Å 2·990 3·165 2·651 2·669 2·676	<i>jl</i>) X-ray 2·865 Å 2·983 3·167 2·646 2·671 2.695	D(jk) N 0.979 0.969 0.987 0.987 0.987 0.952) D(kl) eutron Å 1.914 Å 2.018 2.128 1.691 1.729 1.723	کر Neutron 104·0° 110·9 116·3 99·8 117·8	(<i>ijl</i>) X-ray 104·1° 110·1 115·6 100·5 116·5 116·3	∠(j. Neutron 168·3° 177·9 165·2 163·1 167·9 168·3	kl) X-ray 174° 178 160 159 167 169
				a – cd e f g h i j	Syn $0.5 - x$ $0.5 + x$ $0.5 + x$ $1 - x$ $0.5 - x$ $1 - x$ $0.5 - x$ $1 - x$ $0.5 - x$ $1 - x$ $0.5 + x$	$\begin{array}{c} -y \\ -0.5 - y \\ 0.5 - y \\ -1 + y \\ -0.5 + y \\ -1 + y \\ -1 - y \\ 0.5 + y \\ -0.5 - y \end{array}$	e 0.5-z 1-z 1-z z 1.5-z -0.5+z 1+z 1.5-z 1-z				



Fig. 6. The hydrogen bonding in D-glucitol, stereoscopic view approximately along the b axis, with the a axis vertical, the c axis horizontal. The heavy lines are primary bonds, the thin lines hydrogen bonds.

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