

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 ± 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) D-mannitol (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.

$$\begin{array}{ll} a = 8.677(5) \text{ \AA} & D_x = 1.541 \text{ g.cm}^{-3} \\ b = 9.311(8) & D_m = 1.535 \\ c = 9.727(4) & \mu_{Cu \text{ K}\alpha} = 12.13 \text{ cm}^{-1} \\ Z = 4 & \mu_{neutron} = 2.85 \text{ cm}^{-1} \\ & (\lambda_{Cu \text{ K}\alpha} = 1.5418 \text{ \AA}). \end{array}$$

Two powder samples were also examined. Form *B*, m.p. 93.5°, from Atlas Chemical Industries, and form *\Gamma*, 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 × 0.15 × 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 Γ forms of D-glucitol and for DL-glucitol

B form		Γ form		DL-Glucitol	
d	Intensity	d	Intensity	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	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 Kα radiation and a crystal of dimensions 0.2 × 0.2 × 0.2 mm, which was mounted along the *c** axis. A 2θ scanning mode, with varying interval, gave 797 recorded reflections up to 2θ = 130°, 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:

- 0 7 2, π/2, 2.59;
- 6 0 1, π/2, 2.56;
- 1 7 0, π/2, 2.42;
- 1 8 0, π/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

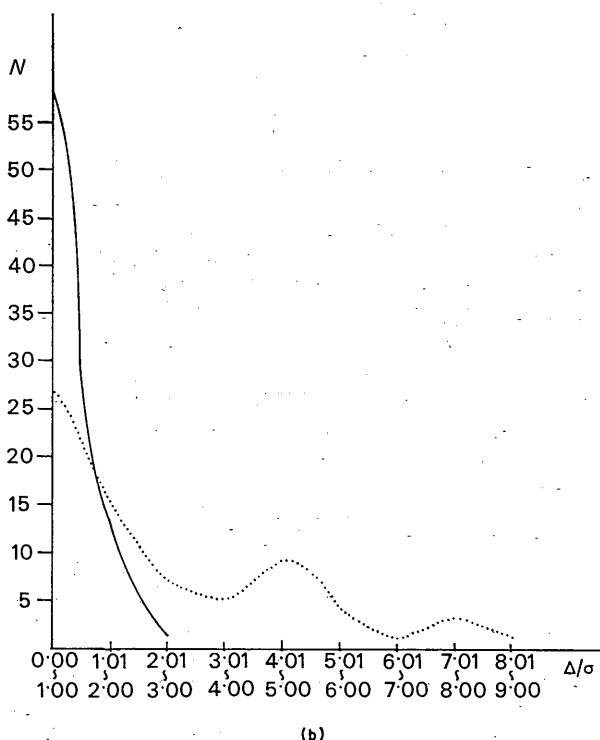
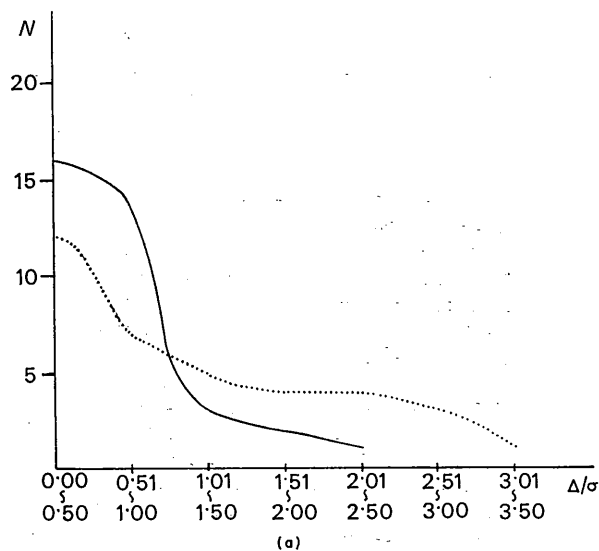


Fig. 1. Comparison of two sets of X-ray parameters (solid line) and one set each of X-ray and neutron parameters (dotted line). The distribution of Δ/σ values is shown in each case, where Δ/σ is the parameter difference divided by its standard error. (a) positional parameters, (b) thermal parameters.

using the block-diagonal least-squares program for the IBM 1130 (Shiono, 1968) and the full-matrix least-squares 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

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

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

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	y	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)	-292.2 (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)	36 (2)	55 (3)	-2 (2)	-5 (3)	-4 (2)
	304.8 (3)	-413.1 (3)	681.0 (3)	87 (4)	52 (3)	72 (3)	2 (3)	-4 (3)	-1 (3)
O(1)	64.7 (4)	273.0 (4)	703.3 (4)	55 (4)	67 (4)	68 (4)	29 (4)	6 (4)	-10 (3)
	64.9 (3)	274.2 (2)	703.5 (2)	83 (3)	78 (3)	76 (2)	25 (2)	-1 (2)	-17 (2)
O(2)	281.6 (4)	223.4 (3)	494.4 (4)	89 (4)	36 (3)	46 (3)	-15 (3)	8 (3)	-1 (3)
	281.7 (2)	223.0 (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)						
H'(C1)	89.7 (9)	59.2 (9)	749.3 (8)	125 (10)	107 (8)	91 (8)	21 (8)	48 (8)	60 (8)
	78 (5)	67 (4)	740 (5)						
H(C2)	345.1 (7)	149.9 (7)	688.1 (7)	81 (7)	81 (6)	82 (6)	-10 (6)	-21 (6)	-9 (6)
	343 (5)	143 (5)	683 (5)						
H(C3)	243.8 (8)	-40.1 (7)	451.4 (7)	96 (8)	80 (6)	71 (6)	-22 (6)	-19 (6)	-10 (5)
	246 (5)	-41 (4)	460 (4)						
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)						
H(O1)	130.5 (8)	298.8 (9)	781.4 (9)	91 (8)	118 (9)	99.4(9)	14 (8)	-2 (8)	-27 (7)
	121 (5)	291 (5)	774 (5)						
H(O2)	295.0 (8)	318.0 (6)	538.3 (7)	117 (9)	65 (7)	70 (7)	-9 (6)	-4 (6)	-9 (6)
	286 (5)	309 (4)	541 (5)						
H(O3)	489.3 (8)	70.5 (7)	455.0 (8)	79 (8)	87 (7)	99 (8)	-5 (6)	12 (7)	9 (7)
	487 (5)	65 (5)	466 (4)						
H(O4)	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)						
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)						

Table 5. *Least-squares best planes in D-glucitol*

Equation for planes: $AX+BY+CZ=D$, where X, Y, Z and D are in Å.

	Distance from best plane		Constants	
	Neutron	X-ray	Neutron	X-ray
C(2)*	-0.011	-0.012	A 0.911	0.917
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.

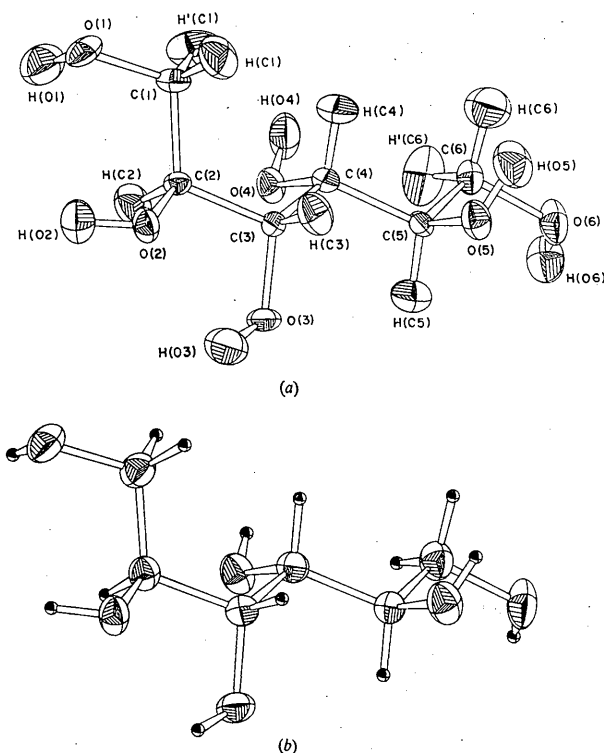


Fig. 2. Molecular conformation of D-glucitol. (a) thermal ellipsoids from neutron data, with key to atomic numbering. (b) thermal ellipsoids for carbon and oxygen atoms from X-ray data.

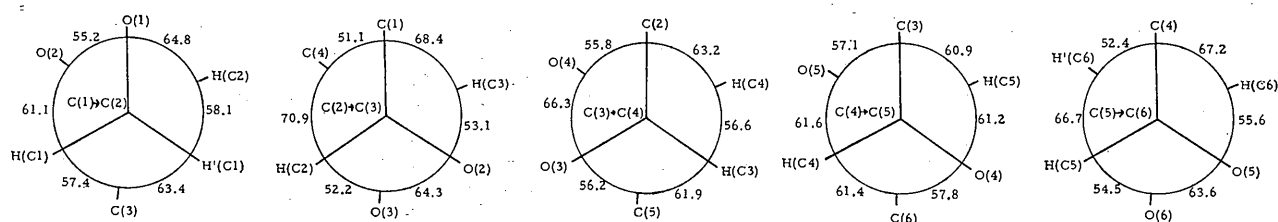


Fig. 3. Conformation angles in degrees around the C-C bonds in D-glucitol.

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	X-ray
C(1)-C(2)	1.519 (4) Å	1.520 (4) Å
C(2)-C(3)	1.528 (4)	1.523 (4)
C(3)-C(4)	1.521 (4)	1.513 (4)
C(4)-C(5)	1.534 (4)	1.532 (4)
C(5)-C(6)	1.521 (4)	1.511 (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		
C-C	1.525 (3)	1.520 (4)
C-O	1.422 (5)	1.427 (5)
C-H	1.091 (4)	1.01 (1)
O-H	0.971 (5)	0.84 (2)

Table 6 (cont.)

	Neutron	X-ray
C(1)—C(2)—C(3)	115.8 (2) ^o	115.3 (2) ^o
C(2)—C(3)—C(4)	113.7 (2)	114.3 (2)
C(3)—C(4)—C(5)	112.7 (2)	113.6 (2)
C(4)—C(5)—C(6)	110.3 (2)	110.8 (2)
O(1)—C(1)—C(2)	111.0 (3)	110.8 (2)
C(1)—C(2)—O(2)	110.1 (2)	109.8 (2)
O(2)—C(2)—C(3)	109.7 (2)	109.1 (2)
C(2)—C(3)—O(3)	108.4 (2)	108.6 (2)
O(3)—C(3)—C(4)	110.4 (2)	109.0 (2)
C(3)—C(4)—O(4)	109.2 (2)	109.2 (2)
O(4)—C(4)—C(5)	110.0 (2)	110.3 (2)
C(4)—C(5)—O(5)	110.6 (3)	110.4 (2)
O(5)—C(5)—C(6)	110.9 (3)	111.8 (2)
C(5)—C(6)—O(6)	111.7 (3)	111.3 (2)
C(2)—C(1)—H(C1)	110.2 (5)	112 (2)
C(2)—C(1)—H'(C1)	110.3 (5)	117 (3)
O(1)—C(1)—H(C1)	105.4 (5)	109 (2)
O(1)—C(1)—H'(C1)	110.6 (5)	108 (3)
H(C1)—C(1)—H'(C1)	109.3 (6)	100 (3)
C(1)—C(2)—H(C2)	108.7 (4)	110 (3)
C(3)—C(2)—H(C2)	107.8 (4)	106 (3)
O(2)—C(2)—H(C2)	109.5 (4)	111 (3)
C(2)—C(3)—H(C3)	108.2 (4)	109 (2)

Table 6 (cont.)

	Neutron	X-ray
C(4)—C(3)—H(C3)	107.5 (4)	106 (2)
O(3)—C(3)—H(C3)	108.4 (4)	109 (2)
C(3)—C(4)—H(C4)	107.9 (4)	107 (2)
C(5)—C(4)—H(C4)	107.4 (4)	109 (2)
O(4)—C(4)—H(C4)	109.6 (4)	108 (2)
C(4)—C(5)—H(C5)	108.7 (4)	109 (2)
C(6)—C(5)—H(C5)	108.6 (4)	109 (2)
O(5)—C(5)—H(C5)	107.6 (4)	106 (2)
C(5)—C(6)—H(C6)	110.2 (5)	109 (2)
C(5)—C(6)—H'(C6)	109.5 (5)	109 (3)
O(6)—C(6)—H(C6)	107.4 (5)	106 (2)
O(6)—C(6)—H'(C6)	109.2 (5)	109 (3)
H(C6)—C(6)—H'(C6)	108.7 (7)	113 (4)
C(1)—O(1)—H(O1)	107.8 (6)	105 (3) ^o
C(2)—O(2)—H(O2)	105.3 (5)	102 (3)
C(3)—O(3)—H(O3)	109.3 (5)	107 (3)
C(4)—O(4)—H(O4)	111.0 (5)	109 (3)
C(5)—O(5)—H(O5)	110.2 (6)	109 (3)
C(6)—O(6)—H(O6)	111.1 (6)	108 (3)
Mean values		
C—C—C	113.1 (10)	113.5 (10)
C—C—O	109.7 (4)	109.6 (4)

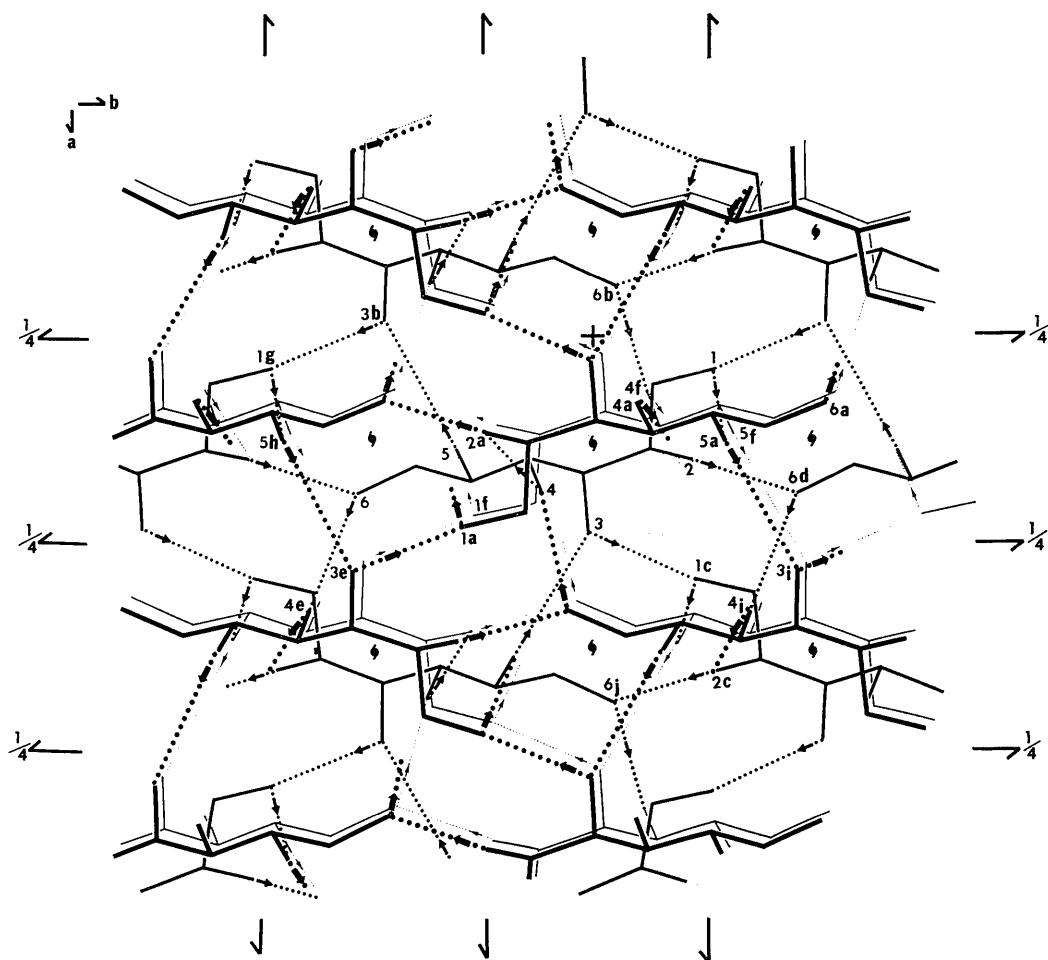


Fig. 4. Molecular arrangement and hydrogen bonding in D-glucitol, viewed down the c axis. Solid lines are primary valence bonds; dotted lines are intermolecular hydrogen bonds (arrows represent directions in which hydrogens are donated). The a axis is vertical.

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(1*f*)→O(5)→O(3*b*)→O(1*g*)→O(5*h*)→O(3*e*)→O(1*a*)→
in the direction of **c**, and

O(6*b*)→O(4*f*)→O(2)→O(6*d*)→O(4*i*)→O(2*c*)→O(6*j*)→
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)···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···O distances ranging from 1.691 to 1.729 Å, which is on the short side of the spectrum of observed H···O distances, while the odd-atom H···O distances range from 1.914 to 2.218. As shown in Fig. 5 and Table 7, there is no correlation of H···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 non-directional 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.

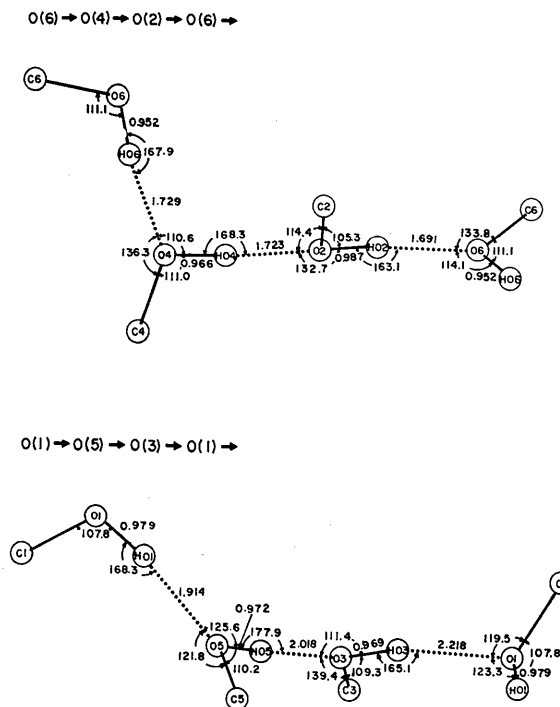


Fig. 5. Stereochemical details of the intermolecular hydrogen bond chains in D-glucitol.

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

<i>i</i>	<i>j</i>	Atom		<i>D</i> (<i>jl</i>)		<i>D</i> (<i>jk</i>)		<i>D</i> (<i>kl</i>)		\angle (<i>ijl</i>)		\angle (<i>jkl</i>)	
		<i>k</i>	<i>l</i>	Neutron	X-ray	Neutron	Neutron	Neutron	X-ray	Neutron	X-ray		
C(1)	O(1)	H(O1)	O(5 <i>a</i>)	2.881 Å	2.865 Å	0.979 Å	1.914 Å	104.0°	104.1°	168.3°	174°		
C(5)	O(5)	H(O5)	O(3 <i>b</i>)	2.990	2.983	0.972	2.018	110.9	110.1	177.9	178		
C(3)	O(3)	H(O3)	O(1 <i>c</i>)	3.165	3.167	0.969	2.128	116.3	115.6	165.2	160		
C(2)	O(2)	H(O2)	O(6 <i>c</i>)	2.651	2.646	0.987	1.691	99.8	100.5	163.1	159		
C(6)	O(6)	H(O6)	O(4 <i>e</i>)	2.669	2.671	0.952	1.729	117.8	116.5	167.9	167		
C(4)	O(4)	H(O4)	O(2 <i>a</i>)	2.676	2.695	0.966	1.723	116.3	116.3	168.3	169		

Symmetry code

<i>a</i>	0.5 - <i>x</i>	- <i>y</i>	0.5 - <i>z</i>
<i>b</i>	-0.5 + <i>x</i>	-0.5 - <i>y</i>	1 - <i>z</i>
<i>c</i>	0.5 + <i>x</i>	0.5 - <i>y</i>	1 - <i>z</i>
<i>d</i>	<i>x</i>	1 + <i>y</i>	<i>z</i>
<i>e</i>	1 - <i>x</i>	-0.5 + <i>y</i>	1.5 - <i>z</i>
<i>f</i>	0.5 - <i>x</i>	- <i>y</i>	-0.5 + <i>z</i>
<i>g</i>	<i>x</i>	-1 + <i>y</i>	<i>z</i>
<i>h</i>	0.5 - <i>x</i>	-1 - <i>y</i>	1 + <i>z</i>
<i>i</i>	1 - <i>x</i>	0.5 + <i>y</i>	1.5 - <i>z</i>
<i>j</i>	0.5 + <i>x</i>	-0.5 - <i>y</i>	1 - <i>z</i>

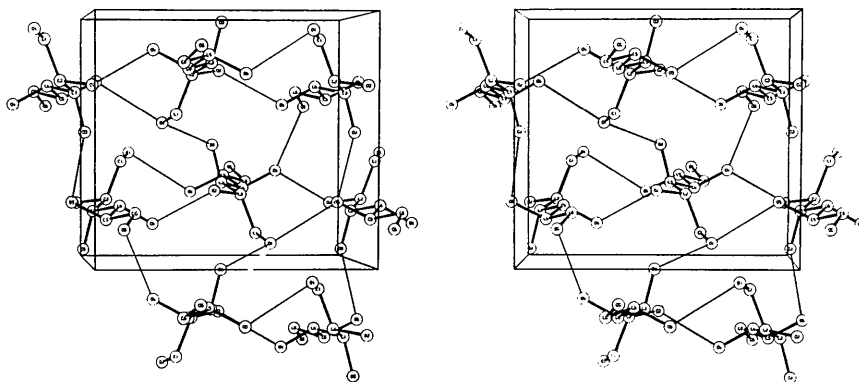


Fig. 6. The hydrogen bonding in D-glucitol, stereoscopic view approximately along the b axis, with the a axis vertical, the c axis horizontal. The heavy lines are primary bonds, the thin lines hydrogen bonds.

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References

- BEAUCAGE, D. R., KELLEY, M. A., OPHIR, D., RANKOWITZ, S., SPINRAD, R. J. & VAN NARTON, R. (1966). *Nucl. Instrum. Meth.* **40**, 26.
- BERMAN, H. M., JEFFREY, G. A. & ROSENSTEIN, R. D. (1968). *Acta Cryst.* **B24**, 442.
- BERMAN, H. M. & ROSENSTEIN, R. D. (1968). *Acta Cryst.* **B24**, 435.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
- CRUICKSHANK, D. W. J. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 45. New York: Pergamon Press.
- HALL, S. R. (1968). *Direct Phasing Methods Program*. UWAC-17. Univ. of Western Australia, revised for the IBM 7090 by H. BERMAN, Univ. of Pittsburgh.
- HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
- HUNTER, F. D. & ROSENSTEIN, R. D. (1968). *Acta Cryst.* **B24**, 1652.
- International Tables for X-ray Crystallography* (1968). Vol. III. Birmingham: Kynoch Press.
- JEFFREY, G. A., AZARNIA, N. & SHEN, M. S. (1970). Unpublished work.
- JEFFREY, G. A. & KIM, H. S. (1970). *Carbohydrate Res.* **14(2)** 207.
- JOHNSON, C. K. (1965). *ORTEP*. ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635.
- KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.
- KIM, H. S. & JEFFREY, G. A. (1969). *Acta Cryst.* **B25**, 2607.
- KIM, H. S., JEFFREY, G. A. & ROSENSTEIN, R. D. (1968). *Acta Cryst.* **B24**, 1449.
- KIM, H. S., JEFFREY, G. A. & ROSENSTEIN, R. D. (1969). *Acta Cryst.* **B25**, 2223.
- KIM, H. S., JEFFREY, G. A. & ROSENSTEIN, R. D. (1971). *Acta Cryst.* **B27**, 307.
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521.
- MATHIESON, A. MCL. (1952). *Acta Cryst.* **5**, 332.
- PIGMAN, W. (1957). *The Carbohydrates*. New York: Academic Press.
- SHIONO, R. (1966). Modification of the Oak Ridge Least-Squares Program, ORNL-TM-305 (1962) of Busing, Martin & Levy.
- SHIONO, R. (1968). Unpublished work.
- SHIONO, R. (1969). Unpublished work.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.