

case of BDP, where C(1)···C(6) is 2.30 Å, these values prove the minimal nature of the corresponding C—C overlap.

All F atoms are involved in H···F distances <2.50 Å, an approximate value of the sum of the van der Waals radii. Two of these rather short contacts concern both H atoms at C(16), while no H···F distances below 2.80 Å are observed for the H atoms of the other bridgehead C atom.

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α -L-Sorbopyranose: A Neutron Diffraction Refinement*

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Abstract. C₆H₁₂O₅, $M_r = 180.16$, $P2_12_12_1$, $a = 6.545(2)$, $b = 18.062(7)$, $c = 6.310(2)$ Å, $D_x = 1.604$, $D_m = 1.607$ Mg m⁻³, $V = 745.94$ Å³. More accurate dimensions were obtained and the disorder in the orientation of the primary alcohol group, observed in the previous X-ray study [Kim & Rosenstein (1967). *Acta Cryst.* **22**, 648–656], is confirmed and better defined. The *gauche/trans* orientation of the primary alcohol hydroxyl group has 0.625 occupancy and the *gauche/gauche* 0.375. The major component forms a

normal hydrogen bond with an H···O distance of 1.867 Å; the minor component forms a bifurcated hydrogen bond having two interactions with H···O distances of 2.151 and 2.209 Å at an angle of 81°.

Introduction. The X-ray crystal structure of α -L-sorbose (Kim & Rosenstein, 1967) revealed disorder in the orientation of the primary alcohol group between two of the three possible 'staggered' positions for the hydroxyl group. This implies two possible hydrogen-bonding arrangements of comparable energy. The purpose of this neutron diffraction study was to determine the precise hydrogen-bond geometry associated with these two arrangements. Suitable transparent crystals of good optical quality were obtained by slow evaporation from an ethanol–water solution. One *hkl* octant and part of an *h $\bar{k}l$* octant of neutron diffraction

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data were collected using an octagonal crystal of volume 8.5965 mm³ at room temperature on the Brookhaven High Flux Beam Reactor single-crystal diffractometer by the procedure described by Takagi & Jeffrey (1977a). The unit-cell parameters were determined by a least-squares procedure from 29 high 2θ reflections. The values agree with those from the X-ray determination within 2σ . The structure refinement data are given in Table 1.

Table 1. Structure refinement data for α -L-sorbopyranose

Morphology: octahedron with faces {011}, {110}.
 μ (neutron) = 0.2574 mm⁻¹; maximum and minimum corrections 1.615, 1.499.
 Intensities: 2003 hkl and $h\bar{k}l$ measured with $\theta/2\theta$ step-scan and width $\Delta 2\theta = 2.4^\circ$ for $2\theta < 60^\circ$; $2.0 + 1.4 \tan \theta$ for $60 < 2\theta < 105^\circ$. Agreement between absorption-corrected symmetry-equivalent F_{hkl} and $F_{\bar{h}\bar{k}l}$ was $R_F = 0.030$. Intensities were averaged to give 1611 symmetry-unique data of which 1437 had $F^2 > \sigma(F^2)$.
 The parameter refinement was on $R_{wF} = (\sum w F_o - k F_c)^2 / w F_o^2)^{1/2}$, with $w^{-1} = [\sigma_c^2(F_o^2) + (0.02 F_o^2)^2] / 4 F_o^2$.
 Refined extinction parameter, $g = 2.4(3) \times 10^{-4}$ (Coppens & Hamilton, 1970).
 Final agreement was $R_F = 0.044$, $R_{wF} = 0.037$ for 1437 data, $R_F = 0.064$, $R_{wF} = 0.044$ for all 1611 reflections.

Table 2. Fractional atomic coordinates ($\times 10^4$) for α -L-sorbopyranose

The standard deviations are given in parentheses.

	x	y	z
C(1A)	5293 (21)	1691 (5)	5127 (19)
C(1B)	5397 (30)	1521 (9)	5350 (31)
C(2)	3942 (3)	1197 (1)	3716 (2)
C(3)	3363 (2)	1665 (1)	1770 (2)
C(4)	1762 (2)	1274 (1)	416 (2)
C(5)	-63 (2)	1047 (1)	1763 (2)
C(6)	648 (3)	619 (1)	3699 (3)
O(1A)	6310 (17)	1243 (9)	6642 (16)
O(1B)	4722 (37)	2185 (11)	6087 (34)
O(2)	4897 (3)	556 (1)	2976 (3)
O(3)	5110 (3)	1808 (1)	526 (3)
O(4)	1135 (4)	1755 (1)	-1239 (3)
O(5)	-1376 (3)	592 (1)	534 (4)
O(6)	2144 (3)	1023 (1)	4881 (3)
H(C1A)1	6390 (20)	1991 (6)	4200 (23)
H(C1A)2	4458 (47)	2102 (14)	6079 (46)
H(C1B)1	5763 (40)	1170 (24)	6735 (61)
H(C1B)2	6827 (26)	1674 (12)	4405 (31)
H(C3)	2688 (6)	2188 (2)	2361 (6)
H(C4)	2451 (6)	773 (2)	-279 (6)
H(C5)	-865 (6)	1557 (2)	2254 (7)
H(C6)1	1279 (8)	87 (2)	3158 (9)
H(C6)2	-614 (7)	514 (3)	4789 (8)
H(O1A)	6029 (15)	1372 (6)	8017 (12)
H(O1B)	4098 (36)	2089 (8)	7385 (25)
H(O2)	5403 (6)	260 (3)	4143 (7)
H(O3)	5545 (6)	2317 (2)	762 (6)
H(O4)	1281 (9)	1526 (3)	-2570 (6)
H(O5)	-2737 (6)	626 (3)	1100 (9)

The non-hydrogen atom coordinates and the occupancy factors for the O(1) disorder from the X-ray analysis were used to calculate the phases and a difference Fourier synthesis, which showed all the H atoms except those attached to O(1). Fourier refinement, followed by isotropic and anisotropic least-squares refinement, with an isotropic extinction parameter, gave the final atomic parameters given in Table 2. The resolution of the disorder was unconvincing until it was realized, from a difference synthesis, that the C(1) atoms were also disordered. A stereoview of the molecule is shown in Fig. 1; the molecular dimensions are given in Fig. 2.*

Discussion. The molecule has the ²C₅-(L) conformation, which is very close to an ideal chair as shown by the puckering parameters (Cremer & Pople, 1975); $\theta = 178.3^\circ$, $\varphi = 138.7^\circ$, $Q = 0.553$, $q_2 = 0.017$, $q_3 = -0.553$ Å. The C-C bond lengths, excluding C(1)-C(2), vary by 0.020 Å (10 σ) with a mean of

* Lists of structure factors, bond angles not included in Fig. 2, and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34149 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

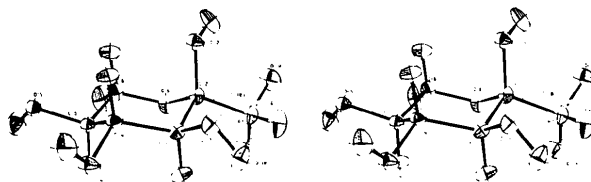


Fig. 1. Stereoview of α -L-sorbopyranose. The minor component of the disorder is shown by the open lines.

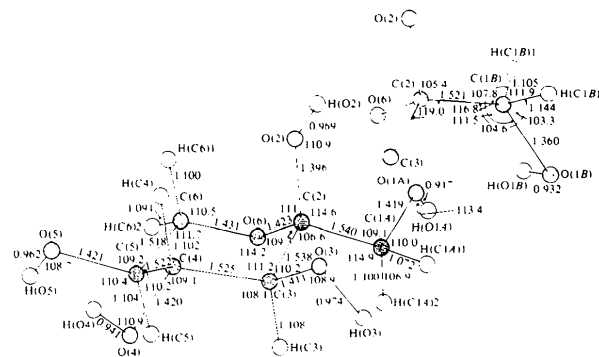


Fig. 2. Bond lengths (Å) and angles ($^\circ$) of α -L-sorbopyranose. Those of the minor component of the disordered primary alcohol group are shown in the top right-hand corner. The bond length σ 's are C-C, 0.002; C-O, 0.003; C-H, 0.004; O-H, 0.005 Å. The bond angle σ 's are C-C-C, 0.1; C-C-O, 0.2; C-O-H, C-C-H, and O-C-H, 0.3; H-C-H, 0.4 $^\circ$. Bond angles not included in the figure have been deposited.

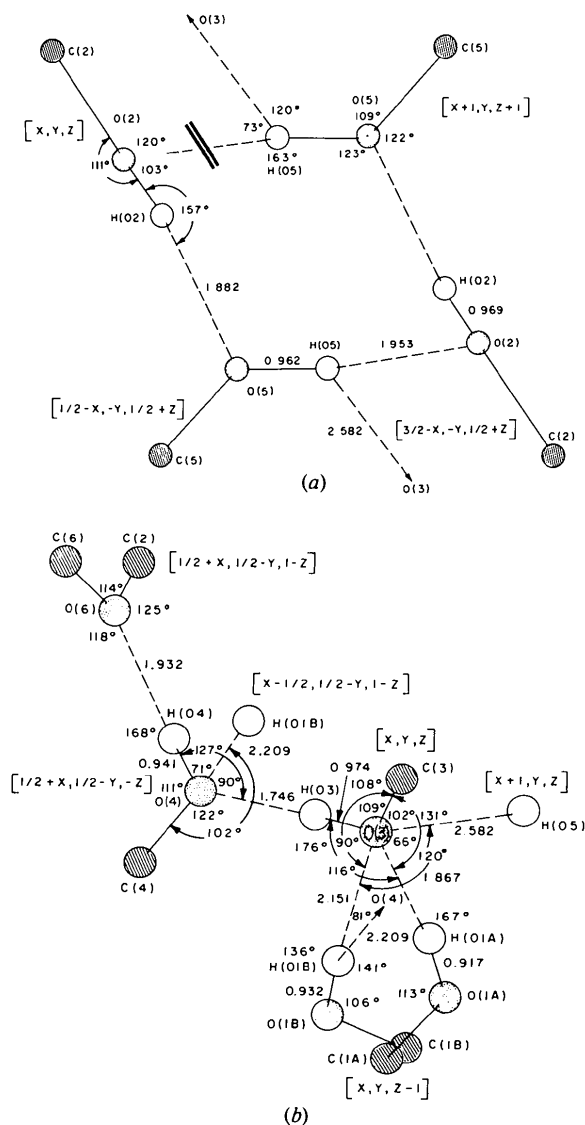


Fig. 3. Hydrogen bonding in α -L-sorbopyranose. (a) The infinite chain, (b) the finite chain.

1.5258 Å (0.01 Å longer than the mean X-ray values); the C—O bond lengths, with the exception of the hemiacetal group, vary by 0.010 Å (3σ) with a mean of 1.4178 Å. The C—O bond lengths in the hemiacetal moiety have C(6)—O(6) > O(6)—C(2) > C(2)—O(2), in agreement with the prediction from *ab initio* quantum-mechanical calculations of the model compound, H₃C—O—CH₂—OH, in which the optimized values were 1.444, 1.421 and 1.417 Å (Jeffrey, Pople & Radom, 1974). The C—H bond lengths vary by 0.040 Å (10σ) with a mean of 1.1030 Å; the O—H bond lengths vary

by 0.031 Å (6σ) with a mean of 0.9615 Å. Those of the disordered hydroxyls are foreshortened due to increased thermal motion.

The disorder of the primary alcohol group is 0.625 *gauche/trans* and 0.375 *gauche/gauche*, these being the two preferred staggered orientations which avoid the syndiaxial interaction with O(3)H.

The hydrogen bonding is shown in Fig. 3. It consists of infinite and finite chains. The infinite chains, which link the O(2)H and O(5)H hydroxyls in a spiral arrangement, have longer than average H...O distances; 1.882 and 1.953 Å *versus* 1.815 Å for the mean of 25 neutron diffraction observations for bonds of this type (Jeffrey & Takagi, 1978). However, O(5)H is also involved in a weak interaction with O(3) at 2.582 Å, forming an asymmetrical bifurcated hydrogen bond (see Jeffrey & Takagi, 1978; Newton, Jeffrey & Takagi, 1979), similar to that observed in the neutron diffraction study of β -D-fructopyranose (Takagi & Jeffrey, 1977*b*). The finite chains, which originate at O(1A) or O(1B) and terminate at the ring oxygens, have a short central H...O bond of 1.746 Å. The bond to the ring O(6) atom agrees well with the mean value of 1.954 Å for 11 neutron and X-ray data (Jeffrey & Takagi, 1978). When O(1B)—H substitutes for O(1A)—H, the normal hydrogen bond of length 1.867 Å is replaced by a bifurcated interaction with two H...O bonds of 2.151 and 2.209 Å at an angle of 81°. This is similar to the bifurcated hydrogen bonds observed in methyl α -D-altropyranoside (Poppleton, Jeffrey & Williams, 1975). It can be inferred that the bifurcated interaction is comparable in energy to the normal linear hydrogen bond. *Ab initio* calculations on model systems give theoretical support for that view (Newton, Jeffrey & Takagi, 1979).

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