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The Crystal Structure of 3-Amino-1,6-anhydro-3-deoxy-β-D-glucopyranose by Neutron Diffraction*

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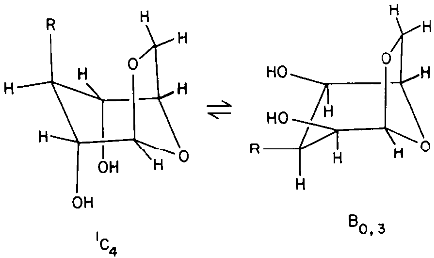
The crystal structure of 3-amino-1,6-anhydro-3-deoxy-β-D-glucopyranose, $C_6H_{11}NO_4$, has been determined from neutron diffraction data. The space group is $P2_12_12_1$, $Z = 4$, $a = 7{\cdot}804\,(8)$, $b = 14{\cdot}671\,(16)$, $c = 6{\cdot}236\,(8)$ Å. The structure was solved by direct methods with *MULTAN* and refined anisotropically against F_o^2 to an $R(F_o^2)$ value of 0·056. The molecular conformation has the amino group and the anhydro ring on the same side of a distorted $^1C_4$ pyranose ring. The distortion is in the direction of a sofa conformation with the ring O out of plane. There are significant differences in the ring C–O bond lengths, which are similar to those observed in the methyl pyranosides. There is only one strong hydrogen bond in the crystal structure, OH ··· NH_2 at 1·760 Å. The NH ··· O hydrogen bonds are weaker, at 2·212 and 2·258 Å, and the N–H bonds are shorter, at 1·000 and 1·019 Å, than generally found in the amino acid structures.

Introduction

The crystal structure of 3-amino-1,6-anhydro-3-deoxy-β-D-glucopyranose (I) was determined for comparison with that of 1,6-anhydro-β-D-glucopyranose (II) for which two independent X-ray determinations have been reported (Park, Kim & Jeffrey, 1971; Lindberg, 1974). It is of interest to ascertain how the substitution of an amino group for a hydroxyl affects the hydrogen bonding and the consequence, if any, on the conformation of the fused rings of the molecules. For both molecules, there are two possible conformations, a $^1C_4$ pyranose ring with axial substituents, or a $B_{0,3}$ pyranose ring with equatorial substituents, as shown below. In the crystal structure of (II) the conformation was that with the $^1C_4$ pyranose ring. However, (I) in dimethyl sulfoxide solution is reported to exist in an equilibrium between both forms (Trnka, Cerny, Budesinsky & Pacak, 1975), suggesting that the distortion of the pyranose ring might be greater with an amino group in place of the hydroxyl ion on C(3). This structure analysis also provides some precise data on the hydrogen bonding between $-NH_2$ and –OH groups in a carbohydrate, for comparison with the more extensive N–H ··· O data available from the neutron diffraction studies of the amino acids (Koetzle & Lehmann, 1975).



(I) R = NH_2
(II) R = OH

Crystal data

Transparent crystals of 3-amino-1,6-anhydro-3-deoxy-β-D-glucopyranose, $C_6H_{11}NO_4$, $M_r = 161{\cdot}16$, with well developed faces, were obtained from Professor M. Cerny, Charles University, Praha, Czechoslovakia. The crystal data are as follows: $a = 7{\cdot}804\,(8)$, $b = 14{\cdot}671\,(16)$, $c = 6{\cdot}236\,(8)$ Å, $V = 714{\cdot}0$ Å^3, $Z = 4$, $\mu(\text{neutron}) = 2{\cdot}47$ cm^{-1}, $D_n = 1{\cdot}50$, $D_m = 1{\cdot}49$ g cm^{-3}. The unit-cell dimensions were determined by least-squares refinement of the setting angles of 20 reflections, carefully centered on the neutron diffractometer. The crystal-monochromated neutron wavelength of 1·023 Å was calibrated with a KBr single crystal (f.c.c., $a = 6{\cdot}600$ Å). D_m was calculated from the weight of the crystal and the crystal dimensions measured for the absorption corrections.

Experimental

Crystal: weight 2·25 mg, volume 1·51 mm^3, bounded by 12 faces with forms {010}, {101}, {021}, and {120}, mounted about the *c* axis.

Data: 2695 *hkl* and $\bar{h}kl$ neutron diffraction intensities measured automatically to $2\theta_{\max} = 90°$ on a

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Brookhaven High Flux Beam Reactor single-crystal diffractometer operating under the control of *NEXDAS* (McMullan, 1976). A θ–2θ step scanning mode was used with scan widths of 3 ° for $2\theta < 60$ ° and 4·5° for $2\theta = 60$–90°. The corrections for background were interpolated from curves obtained by separate background intensity measurements with radial θ–2θ scans.

Absorption correction: analytical correction by *ABSOR* (Templeton & Templeton, 1973) with $\mu = 2{\cdot}47$ cm^{-1} (from the values of μ/ρ of 0·048 and 23·9 cm^2 g^{-1} for N and H respectively). The corrections applied to F_o^2 ranged from 1·15 to 1·25.

Agreement: symmetry-equivalent reflections gave a discrepancy index of 0·027. They were averaged to give 1170 unique F_o^2 of which 192 were $< 3\sigma$.

Structure determination: by *MULTAN* (Germain, Main & Woolfson, 1971) for the non-hydrogen atoms followed by Fourier synthesis for the H atoms.

Refinement: full-matrix least squares of $\Sigma w|F_o^2 - k^2|F_c|^2|^2$ with $w^{-1} = \sigma_c^2(F_o^2) + (0{\cdot}027F_o^2)^2$ where σ_c is from the counting statistics. The 200 variable parameters included atomic coordinates, anisotropic thermal parameters for all atoms, scale factor, and a Zachariasen isotropic extinction parameter, g. The extinction correction, applied to F_c^2, was $E = [1 + 2\bar{T}|F_c^2|g/V' \sin 2\theta]^{-1/2}$, where $\bar{T}$ is an effective mean path length given by $-\ln A/\mu$; A is the calculated absorption, and $V' = V^2\lambda^{-3}$ (Coppens & Hamilton, 1970). The refined value of $g = 1{\cdot}5\,(2) \times 10^4$. For 3% of the reflections the extinction corrections were severe, ranging between 0·57 to 0·90. The neutron scattering lengths used were $b_{\rm C} = 0{\cdot}6648$, $b_{\rm H} = -0{\cdot}374$, $b_{\rm O} = 0{\cdot}5803$, $b_{\rm N} = 0{\cdot}940 \times 10^{-12}$ cm.

Final agreement indices:

$$R = \Sigma|F_o^2 - k^2F_c^2|/\Sigma|F_o^2| = 0{\cdot}056,$$

$$R_w = (\Sigma\, w|F_o^2 - k^2F_c^2|^2/\Sigma\, w|F_o^2|^2)^{1/2} = 0{\cdot}080,$$

$$S = [\Sigma\, w|F_o^2 - k^2F_c^2|^2/(m-n)]^{1/2} = 1{\cdot}59.$$

The atomic coordinates and thermal parameters are given in Table 1.* The molecular conformation and atomic notation are shown in Fig. 1. The molecular dimensions are given in Table 2.

Thermal motion corrections

The thermal motion parameters β_{ij} were converted to thermal vibration tensor elements U_{ij}, referred to an orthogonal Cartesian axial system parallel to **a**, **b** and **c**. The tensor elements U_{ij} of the nonhydrogen atoms were fitted to rigid-body motions expressed in terms of **T**, **L** and **S** tensors with the method of Schomaker & Trueblood (1968). The average r.m.s. deviation of the experimental U_{ij} values from those calculated from the

Table 1. *Fractional atomic coordinates and anisotropic temperature parameters in 3-amino-1,6-anhydro-3-deoxy-β-D-glucopyranose*

The expression used for the anisotropic temperature factor was: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \times 10^{-4}]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N	0·5661 (2)	0·5230 (1)	0·0498 (3)	88 (2)	38 (1)	144 (4)	9 (1)	−6 (2)	−20 (1)
C(1)	0·3820 (2)	0·5992 (1)	0·4960 (3)	85 (3)	28 (1)	112 (4)	3 (1)	22 (3)	13 (2)
C(2)	0·5600 (2)	0·5660 (1)	0·4332 (3)	83 (3)	22 (1)	108 (4)	4 (1)	3 (3)	2 (2)
C(3)	0·6052 (2)	0·5964 (1)	0·2027 (3)	71 (3)	30 (1)	109 (4)	−3 (1)	0 (3)	−1 (2)
C(4)	0·5251 (3)	0·6897 (1)	0·1415 (3)	115 (3)	28 (1)	103 (5)	−10 (1)	−3 (3)	15 (2)
C(5)	0·3513 (3)	0·7050 (1)	0·2464 (4)	122 (3)	24 (1)	149 (5)	10 (1)	−7 (4)	7 (2)
C(6)	0·2177 (3)	0·6319 (1)	0·1994 (4)	92 (3)	33 (1)	181 (5)	6 (1)	−17 (4)	13 (2)
O(1)	0·2590 (3)	0·5619 (2)	0·3516 (4)	82 (3)	34 (1)	183 (6)	−5 (2)	−8 (4)	18 (2)
O(2)	0·6739 (3)	0·6011 (2)	0·5882 (4)	107 (4)	35 (1)	124 (5)	10 (2)	−24 (4)	−8 (2)
O(4)	0·6361 (4)	0·7624 (2)	0·1939 (5)	196 (5)	35 (1)	176 (1)	−40 (2)	−36 (6)	17 (2)
O(5)	0·3710 (3)	0·6944 (2)	0·4744 (4)	122 (4)	29 (1)	144 (1)	14 (2)	12 (4)	−3 (2)
H(N)	0·4453 (6)	0·5018 (4)	0·0604 (10)	121 (7)	55 (2)	347 (17)	−15 (4)	−18 (10)	−53 (6)
H′(N)	0·5832 (8)	0·5455 (4)	−0·1022 (8)	215 (11)	62 (3)	163 (12)	23 (5)	−11 (9)	−10 (5)
H(O2)	0·7813 (5)	0·5645 (3)	0·5782 (7)	114 (6)	50 (2)	176 (10)	5 (3)	−24 (7)	9 (4)
H(O4)	0·6803 (8)	0·7556 (4)	0·3377 (9)	241 (11)	50 (2)	219 (15)	−24 (4)	−45 (12)	2 (5)
H(1)	0·3489 (6)	0·5801 (3)	0·6621 (7)	165 (8)	60 (3)	140 (10)	3 (4)	35 (8)	24 (4)
H(2)	0·5591 (6)	0·4910 (3)	0·4363 (8)	170 (7)	26 (1)	240 (12)	5 (3)	−5 (9)	8 (4)
H(3)	0·7447 (5)	0·6074 (3)	0·1988 (8)	92 (6)	56 (2)	207 (11)	−11 (3)	−3 (7)	3 (5)
H(4)	0·5096 (7)	0·6918 (4)	−0·0336 (7)	201 (9)	52 (2)	128 (10)	−16 (4)	−18 (8)	14 (4)
H(5)	0·3051 (8)	0·7741 (3)	0·2164 (10)	232 (11)	29 (2)	244 (15)	23 (4)	−46 (11)	21 (4)
H(6)	0·2247 (7)	0·6047 (4)	0·0360 (8)	195 (9)	50 (2)	206 (12)	−18 (4)	−48 (9)	4 (5)
H′(6)	0·0897 (6)	0·6577 (4)	0·2301 (12)	115 (8)	65 (3)	458 (22)	19 (4)	−16 (11)	33 (7)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32044 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Molecular geometry of* 3-*amino*-1,6-*anhydro*-3-*deoxy*-β-D-*glucopyranose* (I) *and selected data from the related compounds discussed in the text*

(II) 1,6-Anhydro-β-D-glucopyranose; mean of two X-ray determinations; values differed by $1\cdot5\sigma = 0\cdot006$ Å, 0·3°, or less (Park, Kim & Jeffrey, 1971; Lindberg, 1974).

(III) 2,7-Anhydro-D-*altro*-heptulose monohydrate (Brown & Thiessen, 1969). (The data reported below for this compound are with reference to the atomic notation for a 1,6-anhydro ring system, to facilitate comparison with the other structures.)

(IV) 2,3-Di-*O*-acetyl-1,6-anhydro-β-D-galactopyranose (Foces-Foces, Cano & Garcia-Blanco, 1976).

(V) 2,3,4-Tri-*O*-acetyl-1,6-anhydro-β-D-glucopyranose (Leung & Marchessault, 1974).

Ring torsion angles (°)

	(I)	(II)	(III)	(IV)	(V)
Pyranose ring					
C(1)—C(2)—C(3)—C(4)	32·7	35·2	43·8	37·4	30·3
C(2)—C(3)—C(4)—C(5)	−33·4	−35·2	−44·6	−40·2	−32·0
C(4)—C(5)—O(5)—C(1)	−76·0	−75·3	−76·2	−76·0	−75·4
C(5)—O(5)—C(1)—C(2)	77·7	75·9	76·0	74·8	75·3
O(5)—C(1)—C(2)—C(3)	−56·4	−57·3	−60·7	−56·6	−53·7
C(3)—C(4)—C(5)—O(5)	55·1	55·8	60·7	60·5	55·7
Anhydro ring					
C(1)—O(1)—C(6)—C(5)	9·9	3·1	3·3	5·3	4·7
O(1)—C(6)—C(5)—O(5)	−33·7	−28·6	−28·5	−30·4	−30·4
C(6)—C(5)—O(5)—C(1)	45·1	43·8	43·2	44·8	44·6
C(5)—O(5)—C(1)—O(1)	−40·6	−43·4	−42·6	−42·9	−43·2
O(5)—C(1)—O(1)—C(6)	18·4	24·7	23·6	22·9	23·4

Torsion angles between vicinal C—H and N—H bonds in (I)

H(1)—C(1)—C(2)—H(2)	64·0°	H(5)—C(5)—C(6)—H(6)	92·6°
H(2)—C(2)—C(3)—H(3)	−94·1	H(5)—C(5)—C(6)—H′(6)	−31·3
H(3)—C(3)—C(4)—H(4)	90·0	H(N)—N—C(3)—H(3)	170·7
H(4)—C(4)—C(5)—H(5)	−66·7	H′(N)—N—C(3)—H(3)	−70·4

Bond lengths (Å). Distances in square brackets are corrected for thermal motion or minimum riding motion.

	(I)	(II)	(III)	(IV)	(V)
C(1)—C(2)	1·523 (3) [1·530]	1·521	1·540	1·526	1·516
C(2)—C(3)	1·546 (3) [1·551]	1·538	1·524	1·534	1·537
C(3)—C(4)	1·553 (3) [1·559]	1·538	1·536	1·522	1·531
C(4)—C(5)	1·523 (3) [1·529]	1·519	1·522	1·534	1·517
C(5)—C(6)	1·525 (3) [1·530]	1·525	1·521	1·517	1·526
C(1)—O(1)	1·426 (3) [1·429]	1·430	1·427	1·431	1·422
C(1)—O(5)	1·405 (3) [1·411]	1·402	1·425	1·404	1·415
C(2)—O(2)	1·410 (3) [1·414]	1·423	1·430	1·445	1·444
C(4)—O(4)	1·412 (4) [1·418]	1·430	1·425	1·417	1·443
C(5)—O(5)	1·438 (4) [1·442]	1·444	1·436	1·440	1·438
C(6)—O(1)	1·436 (3) [1·441]	1·445	1·447	1·454	1·448
C(3)—N	1·470 (3) [1·474]				

Bond lengths involving H atoms for (I)

C(1)—H(1)	1·103 (5) [1·108]	N—H	0·995 (5) [1·000]
C(2)—H(2)	1·101 (4) [1·106]	N—H′	1·013 (5) [1·019]
C(3)—H(3)	1·101 (4) [1·105]	O(2)—H	0·998 (5) [0·999]
C(4)—H(4)	1·099 (5) [1·103]	O(4)—H	0·966 (7) [0·967]
C(5)—H(5)	1·092 (5) [1·097]		
C(6)—H(6)	1·096 (6) [1·099]		
C(6)—H′(6)	1·085 (6) [1·093]		

Table 2 (*cont.*)

Valence angles (°) for (I)

C(1)—C(2)—C(3)	110·8 (2)	H(2)—C(2)—C(3)	107·8 (3)
C(2)—C(3)—C(4)	113·0 (2)	H(2)—C(2)—O(2)	110·9 (3)
C(3)—C(4)—C(5)	112·5 (2)	H(3)—C(3)—N	107·4 (3)
C(4)—C(5)—C(6)	115·0 (2)	H(3)—C(3)—C(2)	106·7 (3)
C(4)—C(5)—O(5)	108·3 (2)	H(3)—C(3)—C(4)	105·3 (3)
C(5)—O(5)—C(1)	102·1 (2)	H(4)—C(4)—C(3)	108·3 (3)
O(5)—C(1)—C(2)	110·4 (2)	H(4)—C(4)—O(4)	106·0 (3)
O(1)—C(1)—C(2)	109·2 (2)	H(4)—C(4)—C(5)	109·0 (3)
C(5)—C(6)—O(1)	102·9 (2)	H(5)—C(5)—C(4)	110·9 (4)
C(6)—O(1)—C(1)	107·1 (2)	H(5)—C(5)—C(6)	113·2 (4)
O(1)—C(1)—O(5)	106·3 (2)	H(5)—C(5)—O(5)	107·8 (4)
O(5)—C(5)—C(6)	100·8 (2)	H(6)—C(6)—O(1)	110·0 (4)
C(2)—C(3)—N	110·2 (2)	H(6)—C(6)—C(5)	113·6 (4)
C(4)—C(3)—N	113·8 (2)	H(6)—C(6)—H′(6)	109·7 (5)
C(1)—C(2)—O(2)	106·4 (2)	H′(6)—C(6)—O(1)	109·9 (4)
O(2)—C(2)—C(3)	112·9 (2)	H′(6)—C(6)—C(5)	110·5 (4)
C(3)—C(4)—O(4)	111·3 (2)	H(N)—N—H′(N)	106·8 (5)
O(4)—C(4)—C(5)	109·6 (2)	H(N)—N—C(3)	112·5 (4)
H(1)—C(1)—C(2)	112·0 (3)	H′(N)—N—C(3)	110·0 (4)
H(1)—C(1)—O(1)	109·7 (3)	H(O2)—O(2)—C(2)	106·9 (4)
H(1)—C(1)—O(5)	109·2 (3)	H(O4)—O(4)—C(4)	110·8 (4)
H(2)—C(2)—C(1)	108·0 (3)		

values of **T**, **L** and **S** is 0·0014 Å^2. The r.m.s. amplitudes of translation along the principal axes are 0·15, 0·15 and 0·14 Å. The principal libration axes had r.m.s. amplitudes of 4·6, 3·0 and 2·6°. The effective screw translations are −0·022, 0·024 and 0·012 Å, referred to the principal libration axes. Corrections to bond lengths between atoms in the rigid body were obtained from the rigid-body librations and the corrected distances are included in Table 2. Corrections to bond lengths involving H atoms were calculated according to the minimum correction (Busing & Levy, 1964) and these corrected distances are also given in Table 2.

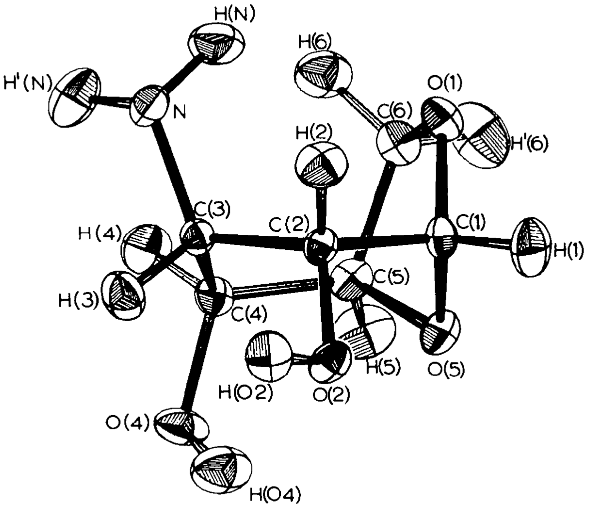


Fig. 1. Atomic notation and thermal ellipsoids (50% probability) for 3-amino-1,6-anhydro-3-deoxy-β-D-glucopyranose (Johnson, 1965).

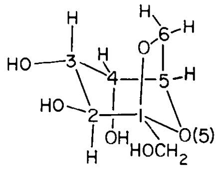
Results and discussion

Molecular conformation and structure

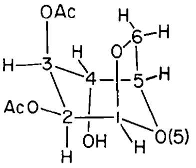
As shown in Fig. 1 and by the torsion angles given in Table 2, the molecular conformation of (I) is very close to that observed in the 3-hydroxy compound (II) with the pyranose ring in a distorted $^1C_4$ chair form. In the absence of the anhydro ring, as in β-D-glucose, this ring conformation is unstable relative to the $^4C_1$, since all the substituent groups are axial and would incur steric repulsions. The pyranose ring conformation is almost midway between that of the ideal $^1C_4$ chair and the sofa in which the ring oxygen O(5) is out of the plane of the other five atoms. The ring-puckering parameters calculated by the method of Cremer & Pople (1975) are $\theta = 152\cdot6$, $\varphi = 179\cdot6°$, $q_2 = 0\cdot283$, $q_3 = 0\cdot546$ Å and $Q = 0\cdot615$ Å. These parameters indicate that the distortion from the ideal $^1C_4$ chair, for which $\theta = 180°$, is in the direction of the $B_{0,3}$ boat ($\theta = 90°$) and midway to the sofa conformation, for which $\theta = 126°$.

This distortion is also shown by the ring torsion angles, which have mean values of 76 and 33° at the ring oxygen O(5) and across the ring at C(3). In unfused pyranose rings, these angles commonly vary by less than ±3° from the average values of 61·5 and 53° respectively (*cf.* Arnott & Scott, 1972). The sharpening of the ring at O(5) is also accompanied by a closure of the C—O—C valence angle from the usual value of about 114° to 105°. The widening of the ring valence angle now occurs at C(2)—C(3)—C(4) which is 113°, rather than the more usual 110°. These distortions are such as to bring O(1) and C(6) closer together, as required for the geometry of the anhydro ring. The flattening of the ring at C(3) also reduces the intramolecular steric interactions between the *syn*-diaxial pairs of substituents, *i.e.* O(2) with O(4) and N with C(6) and O(1). With an undistorted ring these atoms would be about 2·5 Å apart, whereas, due to the ring distortion at C(3), they are separated by distances greater than 3·0 Å. The intramolecular distances O(2)···O(4), N···C(6) and N···O(1) are 3·426, 3·289 and 3·100 Å respectively.

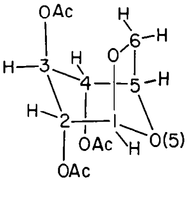
In addition to (I) and (II), three other sugars with 1,6-anhydropyranose ring systems have been studied and selected data concerning the molecular geometry of these structures, (III), (IV) and (V), are included in Table 2 for comparison.



(III)



(IV)



(V)

In all five structures, the ring torsion angles of the bonds common to both rings, *i.e.* C(1)—O(5) and C(5)—O(5), are nearly constant, having a spread of less than 3°. This shows that the fused-ring component of the structures is very rigid and little affected by either configurational changes elsewhere in the molecule or by the intermolecular forces in the crystal.

Similar values of 75–77° have been observed in other carbohydrate fused-ring compounds, such as 1,6-anhydro-β-D-mannofuranose (Lechat & Jeffrey, 1972), methyl 3,6-anhydro-α-D-glucopyranoside (Lindberg, Lindberg & Svensson, 1973), methyl 3,6-anhydro-α-D-galactopyranoside (Campbell & Harding, 1972).

In contrast, there are small, but systematic, differences in the ring torsion angles at the opposite side of the pyranose ring, *i.e.* at C(3), where there is more flexibility. These differences can be qualitatively related to the steric interactions between the substituents at C(2), C(3) and C(4), and do not appear to be sensitive to differences in intermolecular packing. As would be expected, the least flattening at C(3) is observed in (III), where only one of the three hydroxyls is axial and consequently there are no axial nonbonding interactions. The torsion angles about C(3) are 44°. The introduction of the axial acetyl group on C(3) in (IV) results in a reduction of these angles by about 6°, so as to reduce the steric interaction of the acetyl group with C(6) and O(1) of the anhydro ring. In (I) and (II), where the axial substituents on C(3) are NH_2 and OH groups, the flattening is further increased and the ring torsion angles at C(3) become 33 and 35° respectively. This difference is presumably caused by the addition of a *syn*-diaxial repulsion between the hydroxyl groups on C(2) and C(4) which was not present in (II) and (IV). Finally, the largest distortion occurs in (V), where there are axial acetyl groups in all three positions.

The major difference in the anhydro ring conformations is between (I) and (II). The former approaches the symmetrical twist conformation, whereas the latter is nearer to the envelope. This difference is such that in the amino compound O(1) is closer to, and C(6) further away from, the amino hydrogen H(N) which points inwards towards the center of the ring. It could be the result of a weak intramolecular attraction between H(N) and O(1) at 2·488 Å and a repulsion between H(N) and H(6) at 2·295 Å.

There is a close correspondence between the bond lengths which are common to all five structures, as shown in Table 2. Of particular interest is the variation of the C—O bonds in the anhydro ring, in which the two external bonds of the C—O—C—O—C sequence are longer than the internal bonds, as shown in Table 3. These differences are of the same order of magnitude as observed in the gas electron diffraction study of dimethoxymethane CH_3—O—CH_2—O—CH_3 (Astrup, 1973) and in methyl pyranosides and the glycosidic linkages in di- and trisaccharides, where they have been associated with the 'anomeric effect' by Jeffrey, Pople & Radom (1974). This is therefore another example of differences in bond character due to the back donation of oxygen π-type lone-pair electrons, originally pointed out by Romers, Altona, Buys & Havinga (1969). These differences should be dependent on orbital overlap and therefore on the central-bond torsion angles; these results provide data for the conformations where the angles are around −40 and +20°.

With the exception of the differences in the C–O bond lengths, the pyranose ring is close to having a mirror plane of symmetry through C(3) and O(5). The differences in the bond angles and torsion angles related by this pseudomirror are no more than 2°. The C(2)–C(3) and C(3)–C(4) bonds are longer than the other two by ~ 0·025 Å. This was not affected by the thermal motion corrections and may be a real characteristic of the geometry of this ring system. The six-membered chain with mirror symmetry through opposite atoms is not a flexible conformation (*cf.* Dunitz & Waser, 1972) and therefore the distortions in ring torsion angles from those of a strain-free chair will be accompanied by energetically comparable distortions of the bond lengths and angles. A stretch of 0·025 Å in a C–C bond is approximately equivalent to a C–C torsion angle distortion of 10°, and could therefore be a real characteristic of the molecule. A similar lengthening is observed in (II) and (V), but not in (III) and (IV).

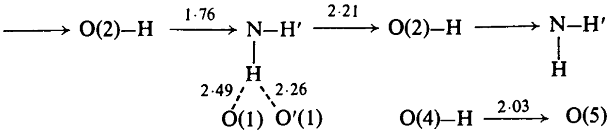
Table 3. C–O *bond-length variations in the anhydro rings*

Compound*	Mean C–O distance	Δ from mean value (Å ×10³)			
		C(5)–O(5)–	C(1)–	O(1)–	C(6)
(I)	1·431	+11	−20	−2	+10
(II)	1·430	+14	−28	0	+15
(III)	1·432	+4	−7	−5	+15
(IV)	1·432	+8	−28	−1	+22
(V)	1·431	+7	−16	−9	+17

* For key to compounds, see Table 2.

Hydrogen bonding

The hydrogen bonding is shown schematically below and is illustrated in Figs. 2 and 3.



The principal intermolecular bonding consists of an infinite chain linking the O(2)H and NH_2 groups, which extends through the crystal structure in the **c** direction. The chain forms a loop which includes the O(2)H and NH' of the same molecule, as shown on the right of Fig. 2. The O(2)H···N bonds are the only strong hydrogen bonds in the crystal structure. The O(2)–H···N angle is 165° and the H(O2)···N distance is

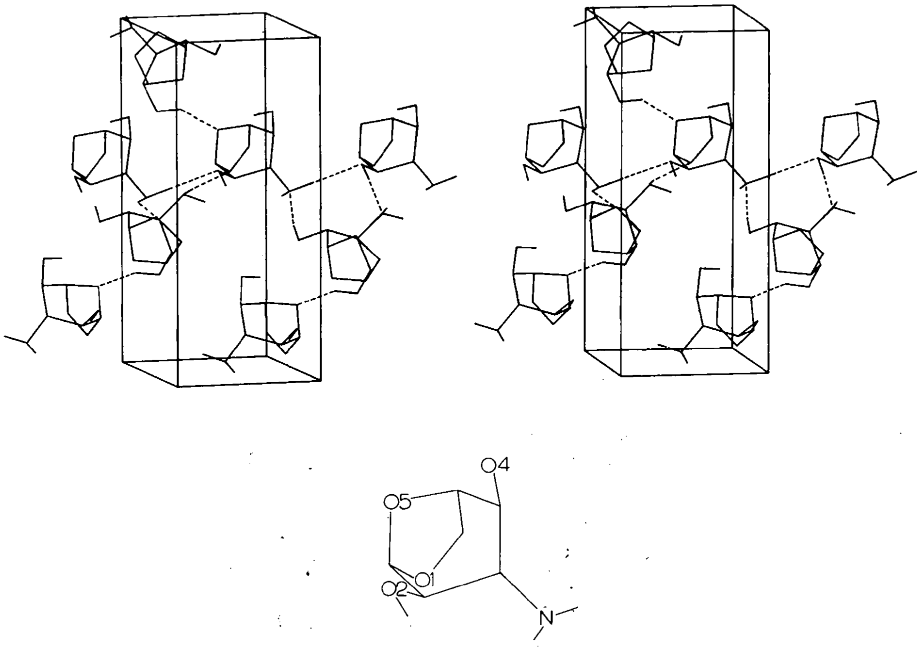


Fig. 2. Stereo view of molecular packing of 3-amino-1,6-anhydro-3-deoxy-β-D-glucopyranose along **a**. Dotted lines represent the hydrogen bonds.

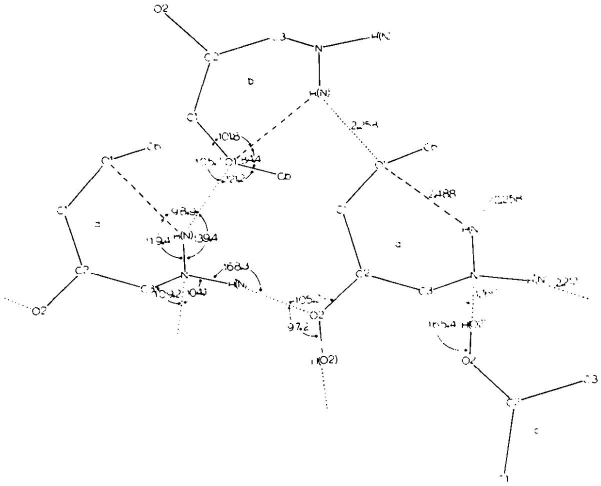


Fig. 3. Details of the hydrogen-bond geometry in 3-amino-1,6-anhydro-3-deoxy-β-D-glucopyranose. Dotted lines represent hydrogen bonds. The dashed line is a possible weak interaction. Symmetry and translation relations: (*a*) *x*, *y*, *z*; (*b*) $\frac{1}{2} - x$, $1 - y$, $\frac{1}{2} + z$; (*c*) $\frac{3}{2} - x$, $1 - y$, $z - \frac{1}{2}$; (*d*) *x*, *y*, $1 + z$.

1·760 Å. The O(2)···H′(N) bond is weaker, having a length of 2·212 Å and a O(2)···H′(N)–N angle of 168°. The second amino H points towards two anhydro-ring O atoms, O(1), O′(1), in the same and in adjacent molecules. The (N)H···O distances are both long, 2·488 and 2·258 Å, for the intra- and intermolecular distances respectively, and only the latter may be considered to be a weak hydrogen bond. The position of H(N) is determined therefore more by that of the other amino H atom, which is strongly bonded, than by its own nearest neighboring atoms, which also include a methylene H on C(6) of the same molecule at 2·295 Å. These weak interactions do, however, appear to influence the shape of the anhydro ring as described above. The remaining hydrogen bond linking the molecules is a comparatively weak bond from H(O4) to a ring O(5) of an adjacent molecule, with an O(5)···H(O4) distance of 2·032 Å and an O(4)–H···O(5) angle of 140°. Ether O atoms are normally weak hydrogen-bond acceptors and this is true for both ring O atoms in this structure.

As might be anticipated, the introduction of the amino group in place of a hydroxyl considerably weakened the intermolecular hydrogen bonding, as shown by comparison with the 1,6-anhydro-β-D-glucopyranose structure, where the molecules are linked by three strong O–H···O bonds with O···O distances between 2·75 and 2·77 Å. There is an inverse correlation between the covalent O–H or N–H bond lengths and the hydrogen-bond lengths, as has been observed in the neutron diffraction study of the amino acids (Koetzle & Lehmann, 1975). The shorter, and presumably stronger, hydrogen bond corresponds to the longer covalent bond. O(2)–H is 0·032 Å longer than O(4)–H, and the hydrogen bond is 0·26 Å shorter. For the N–H···O hydrogen bonds observed in this structure, the N–H bonds are shorter and the H···O bonds longer than the mean of those observed between quaternary NH_3^+ and carboxyl or hydroxy O atoms in the amino acids, *i.e.* 1·04 and 1·85 Å respectively. The N–H distances of 1·000 and 1·019 Å, observed in the present structure, correspond within experimental error to the 1·007 and 1·019 Å values for the unprotonated amino group which forms no hydrogen bonds in L-arginine.$2H_2O$ (Lehmann, Verbist, Hamilton & Koetzle, 1973).

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