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The Structure of 1,6-Anhydro- β -D-allopyranose: Allosan

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Abstract

The crystal structure of allosan, 1,6-anhydro- β -D-allopyranose, $C_6H_{10}O_5$, is monoclinic, space group $P2_1$ with $a = 10.974$ (2), $b = 6.850$ (2), $c = 14.213$ (2) Å and $\beta = 109.30$ (2)° ($Z = 6$, $V = 1008.4$ Å³ and $D_{\text{calc}} = 1.60$ Mg m⁻³). The structural parameters, describing the three crystallographically independent allosan molecules, were refined with the 1744 most significant reflections, $d \geq 0.71$ Å, to a conventional linear R value of 0.029. The three molecules have different types of intra- and intermolecular hydrogen-bonding schemes, which are obviously of relevance for the deviations observed between the three molecular conformations. Assuming a similar coexistence of different conformers also in solution offers a plausible structural explanation for the anomalous NMR T_1 values observed for allosan. The conformations of the pyranose and anhydro rings of all three allosan molecules are partially flattened 3C_0 chair and E_0 envelope, respectively. Two of the hydroxyl groups are axial relative to the pyranose ring at C(2) and C(4), and the third is equatorial at C(3).

Introduction

Allosan, 1,6-anhydro- β -D-allopyranose, shows NMR parameters which differ significantly from those observed for other 1,6-anhydro sugars (Bock, Hall & Pedersen, 1981) assuming a rigid chair conformation. In the 1,6-anhydro sugars whose structures have been determined so far (for references see e.g. Noordik & Jeffrey, 1977), the conformations of the pyranose rings

have always been flattened chairs (3C_0). In view of the pattern of the three hydroxyl substituents in allosan, such a conformation would yield several short intramolecular contacts between the hydroxyl groups, indicating different possibilities for intramolecular hydrogen bonds. The present investigation was undertaken in order to elucidate whether the anomalous NMR relaxation data of allosan can be ascribed to structural effects.

Experimental

A single crystal of dimensions 0.08 × 0.12 × 0.50 mm was selected from a crystalline specimen obtained by slow evaporation of an aqueous solution. Investigations of the single crystal by X-ray photographic and diffractometer techniques suggested $P2_1$ as the most probable noncentrosymmetric space group. Preliminary unit-cell parameters, $a = 10.974$ (2), $b = 6.850$ (2), $c = 14.213$ (2) Å and $\beta = 109.30$ (2)°, were determined from observed θ values of 17 high-order reflections. The preliminary unit-cell volume of 1008.4 Å³ indicates that the number (Z) of allosan molecules per unit cell is six, since a volume of 167.3 Å³ per molecule was observed in the structure of the closely related substance levoglucosan (Park, Kim & Jeffrey, 1971).

The intensities of all the 3158 unique reflections with $\theta \leq 30^\circ$ were collected on a computer-controlled diffractometer (CAD-4), using graphite-monochromatized Mo $K\alpha$ radiation and a scintillation detector with a pulse-height discriminator set to accept 95% of the incident radiation. The intensities, collected with the ω - 2θ scan techniques, using a scan interval of 0.7° +

Table 2 (cont.)

Molecule C	x	y	z	U(Å ²)
C(1)	0.1415 (3)	-0.1418 (5)	0.2908 (2)	0.035
C(2)	0.0987 (3)	-0.1904 (5)	0.3792 (2)	0.033
C(3)	0.0322 (2)	-0.0130 (4)	0.4070 (2)	0.030
C(4)	-0.0540 (3)	0.0974 (4)	0.3159 (2)	0.030
C(5)	0.0125 (3)	0.1123 (5)	0.2382 (2)	0.037
C(6)	0.1486 (3)	0.1935 (6)	0.2786 (3)	0.054
O(1)	0.2271 (2)	0.0223 (4)	0.3136 (2)	0.052
O(2)	0.0169 (2)	-0.3568 (3)	0.3527 (1)	0.038
O(3)	-0.0358 (2)	-0.0672 (4)	0.4725 (1)	0.039
O(4)	-0.1737 (2)	0.0003 (3)	0.2746 (1)	0.033
O(5)	0.0354 (2)	-0.0821 (3)	0.2094 (1)	0.031
H(1)	0.185 (3)	-0.257 (5)	0.274 (2)	0.041 (8)
H(2)	0.177 (2)	-0.211 (4)	0.431 (2)	0.028 (7)
H(3)	0.104 (2)	0.069 (4)	0.445 (2)	0.011 (5)
H(4)	-0.063 (3)	0.218 (5)	0.341 (2)	0.031 (7)
H(5)	-0.043 (2)	0.177 (5)	0.180 (2)	0.039 (8)
H(6a)	0.161 (3)	0.269 (7)	0.339 (3)	0.079 (13)
H(6b)	0.177 (4)	0.250 (8)	0.222 (3)	0.081 (15)
H(O2)	0.021 (3)	-0.406 (5)	0.407 (2)	0.044 (10)
H(O3)	-0.095 (3)	-0.098 (7)	0.443 (3)	0.055 (15)
H(O4)	0.765 (3)	0.057 (6)	0.266 (2)	0.052 (12)

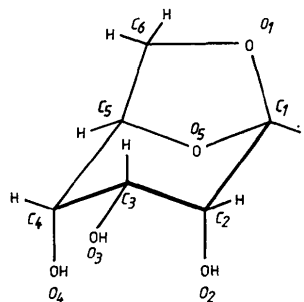
The 418 structural parameters, describing anisotropically vibrating nonhydrogen atoms and isotropic H atoms, were refined by conventional least-squares techniques (Sheldrick, 1976) with the 1744 most significant [$\sigma(I_o)/I_o < 0.33$] reflections and minimizing $\sum w ||F_o| - |F_c||^2$. The individual weights w used were calculated as $w = 1/[\sigma^2(I_o) + (kI_o)^2]/4I_o$, where $\sigma(I_o)$ are the e.s.d.'s of the net intensities based on counter statistics and where k was estimated from measurements of symmetry-related reflections to be 0.028. In

Table 3. Intramolecular bond distances (Å) with e.s.d.'s for the three independent allosan molecules (A, B, and C)

	A	B	C
C(1)—C(2)	1.533 (4)	1.515 (4)	1.517 (5)
C(2)—C(3)	1.532 (4)	1.547 (5)	1.535 (4)
C(3)—C(4)	1.522 (5)	1.524 (4)	1.528 (3)
C(4)—C(5)	1.522 (4)	1.512 (4)	1.515 (5)
C(5)—C(6)	1.511 (6)	1.524 (4)	1.518 (4)
C(1)—O(5)	1.397 (4)	1.411 (3)	1.404 (3)
C(5)—O(5)	1.443 (4)	1.445 (4)	1.439 (4)
C(1)—O(1)	1.419 (4)	1.435 (3)	1.432 (4)
C(6)—O(1)	1.441 (4)	1.444 (4)	1.443 (4)
C(2)—O(2)	1.413 (4)	1.424 (3)	1.423 (4)
C(3)—O(3)	1.429 (4)	1.428 (4)	1.421 (4)
C(4)—O(4)	1.427 (4)	1.424 (3)	1.415 (3)
C(1)—H(1)	0.99 (2)	0.98 (3)	0.99 (4)
C(2)—H(2)	0.98 (4)	0.94 (2)	0.94 (2)
C(3)—H(3)	0.98 (3)	0.98 (3)	0.97 (2)
C(4)—H(4)	1.03 (3)	1.02 (3)	0.91 (3)
C(5)—H(5)	0.87 (4)	1.08 (3)	0.96 (3)
C(6)—H(6a)	1.00 (3)	1.03 (4)	0.98 (4)
C(6)—H(6b)	0.93 (4)	0.95 (4)	1.03 (5)
O(2)—H(O2)	0.83 (3)	0.81 (3)	0.83 (3)
O(3)—H(O3)	0.71 (4)	0.78 (4)	0.68 (3)
O(4)—H(O4)	0.75 (4)	0.80 (3)	0.75 (4)

Table 4. Intramolecular bond angles (°) with e.s.d.'s for the three independent allosan molecules (A, B, and C)

	A	B	C
C(2)—C(1)—O(1)	109.5 (3)	107.8 (2)	110.2 (2)
C(2)—C(1)—O(5)	110.3 (2)	110.1 (2)	110.3 (2)
O(1)—C(1)—O(5)	106.5 (3)	106.2 (2)	105.1 (2)
C(1)—O(1)—C(6)	106.0 (3)	107.2 (2)	106.7 (2)
C(1)—C(2)—C(3)	108.8 (2)	109.0 (2)	110.1 (2)
C(1)—C(2)—O(2)	111.4 (3)	111.4 (2)	107.3 (2)
C(3)—C(2)—O(2)	105.4 (2)	114.4 (2)	113.0 (2)
C(2)—C(3)—C(4)	110.1 (2)	113.4 (2)	112.8 (2)
C(2)—C(3)—O(3)	111.3 (2)	111.8 (3)	111.0 (2)
C(4)—C(3)—O(3)	112.2 (2)	111.6 (2)	111.9 (2)
C(3)—C(4)—C(5)	109.0 (2)	110.2 (2)	109.8 (2)
C(3)—C(4)—O(4)	110.8 (2)	112.7 (2)	110.4 (2)
C(5)—C(4)—O(4)	110.5 (3)	111.2 (2)	109.5 (2)
C(4)—C(5)—C(6)	114.1 (3)	113.3 (2)	113.6 (3)
C(4)—C(5)—O(5)	107.5 (3)	108.1 (2)	108.4 (2)
C(6)—C(5)—O(5)	101.7 (2)	101.8 (2)	101.8 (2)
C(1)—O(5)—C(5)	101.1 (2)	102.2 (2)	102.1 (2)
C(5)—C(6)—O(1)	103.7 (3)	103.0 (3)	103.5 (3)

Fig. 1. Schematic structural formula of allosan, 1,6-anhydro- β -D-allopyranose, together with atomic labels used in the present study.

the final refinement cycle the linear unweighted R value became 0.029, while the weighted R_w [$= (\sum w ||F_o| - |F_c||^2 / \sum w |F_o|^2)^{1/2}$] was 0.031. The atomic form factors used were those of *International Tables for X-ray Crystallography* (1974).

In Tables 2, 3 and 4* the atomic coordinates and the intramolecular bond distances and angles obtained are listed. The atomic labelling used is shown in Fig. 1.

Discussion

The molecular packing and hydrogen bonds are shown in Fig. 2. The three independent molecules (designated *A*, *B* and *C* in Fig. 2) have rather different surroundings in the crystal structure which obviously

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35852 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

influence the observed molecular conformations to a certain extent. The crystal structure can be considered as composed of layers (with a thickness of two molecules) stacked along the $\langle 20\bar{1} \rangle$ direction and held together by mainly van der Waals forces. No hydrogen bonds appear to be formed between these layers; the intermolecular hydrogen bonds form a three-dimensional network within each layer. Thus, the *A* molecules form an infinite hydrogen-bonded array along the twofold screw axis through $(\frac{1}{2}, 0, 0)$, through the hydrogen bond numbered 1 in Fig. 2 and Table 5. The *C* molecules form a similar array (hydrogen-bond number 2) along the 2_1 axis through $(0, 0, \frac{1}{2})$. These arrays of *A* and *C* molecules are hydrogen bonded to each other by the bond numbered 3. The layer is further stabilized by the four hydrogen bonds (numbers 4–7) formed between the *B* molecules and the two molecular arrays. The hydrogen bonds are formed mainly between the hydroxyl groups of the allosan molecules; the only endocyclic O atom involved in hydrogen bonding is the O(1) atom in the anhydro ring of molecule *B*. This bond is probably of relevance with regard to the larger deformation observed for this ring (*cf.* Table 6).

The only hydroxyl groups which do not act as hydrogen donors in any intermolecular hydrogen bonds are those at O(4) and O(3) in the *A* and *B* molecules, respectively. These atoms are instead involved in short intramolecular contacts (numbers 8 and 9), indicating that intramolecular hydrogen bonds are formed in the *A* and *B* molecules from O(4) to O(2) and from O(3) to O(4), respectively. The H atom attached to the O(3) atom of molecule *C* shows a short intramolecular contact (number 10) with the O(4) atom. Since O(3) is also involved as a donor to a rather strong intermolecular hydrogen bond (number 6), the observations indicate that O(3)–H possibly participates in a bifurcated bond composed of one strong intermolecular bond and one weaker intramolecular bond. As discussed below the difference in the intramolecular hydrogen-bonding schemes for the three molecules is in accordance with the observed larger puckering of the pyranose ring in molecule *A*. In a recent structural

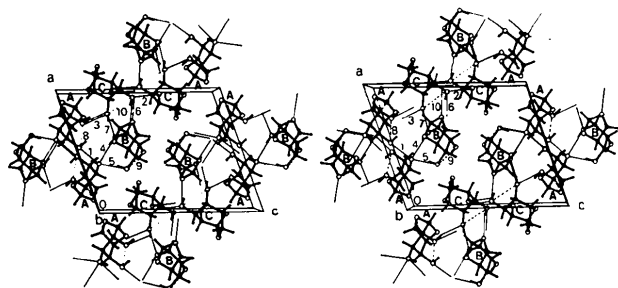


Fig. 2. Stereoscopic packing diagram of the allosan structure viewed along the *b* axis. Intermolecular hydrogen bonds are indicated by thin lines, and intramolecular hydrogen bonds by dashed lines.

study of 1,6-anhydro- β -D-galactopyranose (Ceccarelli, Ruble & Jeffrey, 1979), the observed differences among the three crystallographically independent molecules are possibly also due to differences in the hydrogen-bond schemes.

The conformations obtained for the three allosan molecules agree in general (see Table 6) with those found earlier in other anhydro sugars, such as 1,6-anhydro- β -D-glucopyranose (levoglucosan, Park, Kim & Jeffrey, 1971) and 1,6-anhydro-3,4-*O*-isopropylidene- β -D-talopyranose (AIT, Panagiotopoulos, 1974).

Table 5. Short interatomic contacts indicating possible hydrogen bonds

The atoms involved are identified by the atomic label followed by the molecular label (*A*, *B* or *C*, *cf.* Fig. 2). The H...O distances given in parentheses correspond to O–H bond distances of 1.0 Å. The e.s.d.'s are about 0.004 and 0.04 Å for O...O and H...O contacts respectively.

Number		Symmetry code for acceptor atom	O...O	H...O
1	O(3A)–H...O(4A)	$1 - x, -\frac{1}{2} + y, -z$	2.718 Å	2.08 (1.83) Å
2	O(2C)–H...O(3C)	$-x, \frac{1}{2} + y, 1 - z$	2.820	2.00 (1.83)
3	O(2A)–H...O(4C)	$-1 + x, -1 + y, z$	2.716	1.92 (1.77)
4	O(2B)–H...O(3A)	$1 - x, \frac{1}{2} + y, -z$	2.787	1.99 (1.83)
5	O(4B)–H...O(3A)	$1 - x, \frac{1}{2} + y, -z$	2.763	2.02 (1.85)
6	O(3C)–H...O(1B)	$1 + x, 1 + y, z$	2.821	2.20 (1.90)
7	O(4C)–H...O(2B)	$-1 + x, y, z$	2.819	2.08 (1.83)
8	O(4A)–H...O(2A)	None	2.779	2.29 (2.14)
9	O(3B)–H...O(4B)	None	2.781	2.34 (2.26)
10	O(3C)–H...O(4C)	None	2.756	2.36 (2.28)

Table 6. Some relevant torsion angles within the three independent allosan molecules (*A*, *B*, and *C*) compared to those observed for levoglucosan and for 1,6-anhydro-3,4-*O*-isopropylidene- β -D-talopyranose (AIT)

The e.s.d.'s of the torsion angles involving nonhydrogen atoms are 0.3°.

	<i>A</i>	<i>B</i>	<i>C</i>	Levo-glucosan	AIT
Pyranose ring					
C(1)–C(2)–C(3)–C(4)	45.9°	39.6°	39.4°	35.2°	25.2°
C(2)–C(3)–C(4)–C(5)	–49.0	–41.3	–41.4	–39.5	–27.9
C(3)–C(4)–C(5)–O(5)	65.2	59.6	60.4	55.8	55.0
C(4)–C(5)–O(5)–C(1)	–76.4	–76.2	–76.4	–75.3	–79.7
C(5)–O(5)–C(1)–C(2)	75.0	76.3	75.0	75.1	77.8
O(5)–C(1)–C(2)–C(3)	–61.4	–58.2	–57.5	–57.3	–50.7
Anhydride ring					
O(1)–C(1)–O(5)–C(5)	–43.7	–40.2	–43.7	–40.6	–43.2
C(1)–O(5)–C(5)–C(6)	43.8	43.5	43.6	45.1	42.3
O(5)–C(5)–C(6)–O(1)	–28.9	–31.1	–27.8	–33.7	–27.6
C(5)–C(6)–O(1)–C(1)	3.1	7.3	2.0	9.9	2.0
C(6)–O(1)–C(1)–O(5)	25.2	20.0	25.5	18.4	25.4
Hydroxyl groups					
O(5)–C(1)–C(2)–O(2)	54.3	68.9	65.8		
C(1)–C(2)–C(3)–O(3)	171.0	166.9	165.8		
C(2)–C(3)–C(4)–O(4)	72.8	83.4	79.4		
Hydroxyl hydrogens					
C(1)–C(2)–O(2)–H	63	–56	157		
C(2)–C(3)–O(3)–H	–57	–90	–86		
C(3)–C(4)–O(4)–H	–69	–77	127		

Thus, the pyranose rings adopt flattened 3C_0 chair conformations (Schwarz, 1973) and the five-membered anhydro rings distorted E_0 envelope conformations. The differences between the anhydro sugar molecules as regards the pyranose and anhydro ring conformations are consistent with the different hydrogen-bonding schemes in the structures. Thus, the strain introduced by the intramolecular hydrogen bond between O(4) and O(2) of the allosan molecule *A* is expected to give rise to increased torsion angles in the pyranose ring, except for those about the C(5)–O(5) and O(5)–C(1) bonds. Furthermore, the torsion angles involving the hydroxyl groups at C(2) and C(4), *viz* O(5)–C(1)–C(2)–O(2) and C(2)–C(3)–C(4)–O(4), would decrease, while C(1)–C(2)–C(3)–O(3) would increase. These effects are evident from Table 6. The effect of a strong intramolecular hydrogen bond between O(3) and O(4), on the other hand, would give decreased torsion angles over the C(1)–C(2), C(2)–C(3), C(3)–C(4) and C(4)–C(5) bonds, similar to (but smaller than) the effect of the 3,4-*O*-isopropyl substituent in AIT (Table 6). However, in the present study the hydrogen bonds between O(3) and O(4) in the *B* and *C* molecules are rather weak and do not seem to influence the pyranose conformation to any great extent. As regards the conformations of the anhydro rings, the endocyclic O(1) atom in the *B* molecule participates in an intermolecular hydrogen bond (number 6 in Table 5), yielding a small distortion of the ring. A similar hydrogen bond occurs in the levoglucosan structure but not in the AIT structure, which explains the similarities between the anhydro ring conformations of levoglucosan and allosan molecule *B*, and the similarities between AIT and molecules *A* and *C*.

Fig. 3 shows the conformations of the three allosan molecules, as seen perpendicular and parallel to the least-squares plane through the atoms C(1), C(2), C(4)

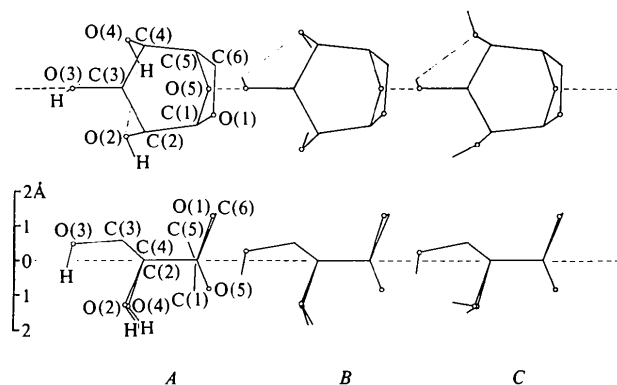


Fig. 3. Conformations of the three crystallographically independent allosan molecules viewed perpendicular and parallel to the least-squares planes through the atoms C(1), C(2), C(3), and C(5).

and C(5) of the pyranose rings. The root-mean-square deviations (r.m.s.d.'s) of these four atoms from the planes are 0.018, 0.008 and 0.014 Å for the *A*, *B* and *C* molecules, respectively. Least-squares planes through the atoms O(1), C(1), C(5) and C(6) of the anhydro rings give r.m.s.d.'s of 0.015, 0.035 and 0.010 Å, and angles to the pyranose ring planes above of 111.2, 109.5 and 111.0°, respectively.

The intramolecular non-hydrogen-bond distances and angles in the pyranose and anhydro rings agree well with those found in other anhydro sugars (Noordik & Jeffrey, 1977), except for the bond angle C(2)–C(3)–C(4) which is considerably smaller (110.1 compared to 113.4 and 112.8°) in allosan molecule *A*. This is obviously another effect of the rather strong intramolecular hydrogen bond between the hydroxyl groups at C(2) and C(4) in this molecule. Hydrogen-bond effects are evidently also responsible for the observed differences in some of the exocyclic non-hydrogen-bond angles involving the three hydroxyl O atoms [O(2), O(3) and O(4)]. It is likely that at least some of the observed intramolecular hydrogen bonds also occur in solution, yielding different conformers. The coexistence of several allosan conformers in solution offers a plausible structural explanation for the anomalous NMR T_1 values of allosan as compared to other anhydro sugars.

As in other anhydro sugars there is a disproportionation of the C–O bond lengths in the anhydro rings, due to the so-called anomeric effect (*cf.* Berman, Chu & Jeffrey, 1967). Thus the outer bonds of the C(5)–O(5)–C(1)–O(1)–C(6) fragment are somewhat longer than the inner bonds, as is evident from the average values in the allosan molecules of 1.442, 1.404, 1.428 and 1.443 Å, respectively.

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