

dimensional hydrogen bond network. Some of the donor...acceptor distances are rather long, however, and some of the donor-H...acceptor angles deviate considerably from 180°, suggesting weak interactions. The angles at the hydrogen atoms are certainly not accurate, since the hydrogen atom positions were calculated on rather simplified assumptions (see above). The majority of hydrogen bonds are of the form N-H...Br, ranging from 3.31 to 3.68 Å. In several other structure determinations, distances for Br...N hydrogen bonds have been found to be around 3.3 Å. It is of interest that there also seem to be hydrogen bonds of the type N-H...O (sulfato) between neighboring cations, e.g. N(2)-H(4)...O(2d), 2.92 Å. This indicates that despite the +3 overall charge on the cations, the oxygen atoms are still negative enough to be hydrogen bond acceptors. The shortest intermolecular distances involving carbon atoms of the en groups (last two lines in Table 6) may be regarded as an accidental result of the molecular packing rather than hydrogen bonding.

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The Crystal Structure of 1,6:2,3-Dianhydro-β-D-gulopyranose

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The crystal structure of 1,6:2,3-dianhydro-β-D-gulopyranose, C₆O₄H₈, has been determined from X-ray diffraction data measured on an automatic diffractometer. The phase problem was solved by combining the minimum function and direct methods. $R=0.031$. The crystal data are: $P2_12_12_1$, $Z=8$, $D_m=1.55$ g.cm⁻³; the lattice parameters $a=6.825$ (15), $b=10.274$ (5), $c=17.618$ (20) Å changed during exposure. The twofold dehydration and formation of additional intramolecular five- and three-membered rings force changes in the conformation of the pyranose ring. Above all, the existence of the epoxy ring shortens the bond C(2)-C(3) from 1.53 to 1.46 Å. The crystal packing is determined by two independent hydrogen-bonding systems, which form infinite chains around the screw axes parallel to the a and b axes, respectively.

Introduction

Several anhydro sugars have been reported recently, since they are considered as possible intermediates in some metabolisms (Isaacs & Kennard, 1970) and since they can be used in the synthesis of derivatives (Carvalho & Schuerch, 1959).

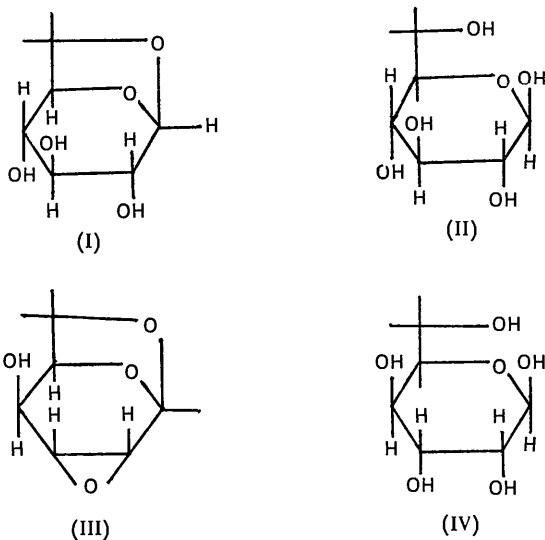
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The dehydration of pyranoses to form the anhydrides results in the formation of additional intramolecular rings. For example, the dicyclic ring system of 1,6-anhydro-β-D-glucopyranose (I) is the anhydride of D-glucopyranose (II), and the tricyclic ring system of 1,6:2,3-dianhydro-β-D-gulopyranose (III) is the dianhydride of β-D-gulopyranose (IV). The structure of (I) is known from an X-ray crystal structure analysis by Park, Kim & Jeffrey (1971). The structure of (III) was determined to investigate the conformation of the mol-

ecule, which is highly dependent upon the strain effects induced by the fusion of the three rings, especially the epoxy ring.



Experimental

Large, transparent single crystals of 1,6:2,3-dianhydro- β -D-gulopyranose, showing no characteristic faces, were provided by the Chemical Institute of the Slovak Academy of Sciences, Bratislava, Czechoslovakia.

The crystals were not stable in the X-ray beam; they turned brown and showed steady changes in cell parameters and a loss in intensity. The cell parameters and three-dimensional intensity data of two crystals were measured on a Picker FACS I diffractometer using Cu $K\alpha$ radiation and the θ - 2θ scanning mode. The initial average crystal data, (a , b , and c measured after some hours of exposure for photographic purposes), are:

$$a = 6.825 (2), b = 10.274 (3), c = 17.618 (4) \text{ \AA},$$

$$V = 1235 \text{ \AA}^3, \text{ Space group } P2_12_12_1, \text{ M.W. } 144.03,$$

$$Z = 8, D_m = 1.550 \text{ g.cm}^{-3}, D_x = 1.538 \text{ g.cm}^{-3},$$

$$\mu_{\text{Cu } K\alpha} = 11.4 \text{ cm}^{-1}.$$

The cell parameters were calculated from the angular settings of three reflections and, during data collection, they were remeasured about every eight hours. In the final stage, their values had changed to $a = 6.855$, $b = 10.267$, $c = 17.668 \text{ \AA}$ and $a = 6.844$, $b = 10.267$, $c = 17.655 \text{ \AA}$, respectively, indicating an increase of volume and a considerable shift in angular positions. The actual diffractometer positions were calculated according to the most recent cell parameter measurement.

Both crystals had the dimensions $0.3 \times 0.3 \times 0.3 \text{ mm}$, one was mounted along [100], the other along [130]. Data collection from crystal 1 was started with low-order reflections ($3^\circ \leq 2\theta \leq 80^\circ$) and that from crystal 2 with high-order reflections ($110^\circ \leq 2\theta \leq 130^\circ$). The additional overlap area ($80^\circ \leq 2\theta \leq 110^\circ$) served to scale and combine the two sets of data. The 2θ base width was chosen to be 2° . The loss of intensity of the three monitored reflections 060, 330 and 134 was nearly proportional and linear with exposure, the average rate being six per cent per day. All intensities were corrected for decay according to the intensity decrease of the three monitored reflections using a 4-point interpolation method (Shiono, 1969). The final data set contained 1233 reflections out of which 182 were considered as 'unobserved' because they did not exceed twice the standard deviation of the counting statistics. No absorption corrections were applied.

Structure determination

The structure was solved by combining Patterson superposition and direct methods at the stages at which they were each most reliable when used alone. Thus we obtained starting phases by means of the minimum func-

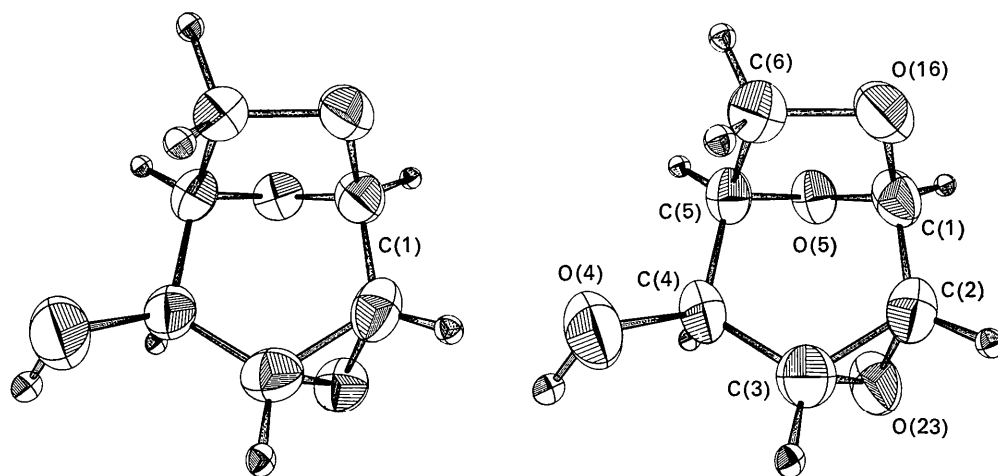


Fig. 1. The 50% probability ellipsoidal representation of atomic thermal parameters of the two independent molecules. The differences in corresponding ellipsoids are to be noted (Johnson, 1965).

atom rigid body was selected as the basis for the calculation of a three-atom symmetry minimum function (SMF), and its location was determined using the program system of Seeman (1970). The full minimum function with the imposed space group symmetry $P2_12_12_1$ was calculated by placing an origin of the Patterson map at each of the twelve so far atoms located (three located by the SMF in each of the four general positions of the space group). Instead of the absolute minimum of the superimposed twelve values, the average of the smallest three was used, as suggested by Nordman (1966), to avoid errors resulting from occasionally missing vectors.

Fourier transformations of the resulting function, above various peak height cutoffs, and analyses of structure factors, suggested a set of 15 phases ($|F_o| > 20$, $|F_c|/|F_o| > 0.5$) which were used as starting phases for tangent refinement. The solution was then found in a

straightforward manner by an E map, based on 182 reflections with $|E| \geq 1.4$.

Refinement and accuracy

For all subsequent calculations and discussions the set of cell parameters $a=6.831$, $b=10.273$, $c=17.630$ Å has been chosen. These are average values both over time and over both crystals.

The refinement of the atomic parameters was done by minimizing the function $\sum \omega \Delta F^2$ with $1/\omega = \sigma^2(F) = 2.0 + 0.02F^2$, and carried out by the block-diagonal least-squares program for the IBM 1130 computer (Shiono, 1968). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962) for the heavy atoms, and from Stewart, Davidson & Simpson (1965) for the hydrogen atoms. After three cycles of refinement with isotropic thermal

Table 2. Atomic parameters with e.s.d.'s for 1,6:2,3- β -D-gulopyranose

Positional parameters are given as fractions of the averaged lattice translations $a=6.831$, $b=10.273$, $c=17.630$ Å. Thermal parameters are given according to the expression: $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The e.s.d.'s given in parentheses refer to the least significant figures in the parameter values. They are taken from the least-squares refinement results. Because of the shifts in lattice parameters, they should be increased by a factor of 1.5.

Molecule 1				β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
	x	y	z	or B					
C(1)	0.6529(3)	0.6707(2)	-0.1389(1)	0.0207(5)	0.0087(2)	0.0033(1)	-0.0032(3)	0.0014(2)	-0.0006(1)
C(2)	0.4936(4)	0.7702(2)	-0.1471(1)	0.0282(6)	0.0062(2)	0.0027(1)	-0.0027(3)	-0.0003(2)	0.0001(1)
C(3)	0.3203(3)	0.7505(2)	-0.1003(1)	0.0187(5)	0.0066(2)	0.0037(1)	0.0012(3)	-0.0006(2)	-0.0008(1)
O(23)	0.4575(2)	0.8532(1)	-0.0829(1)	0.0244(4)	0.0058(1)	0.0037(1)	-0.0016(2)	-0.0005(1)	-0.0012(1)
C(4)	0.3137(3)	0.6368(2)	-0.0462(1)	0.0215(5)	0.0074(2)	0.0028(1)	-0.0009(3)	0.0012(2)	-0.0006(1)
O(4)	0.1359(3)	0.5671(2)	-0.0570(1)	0.0203(4)	0.0099(2)	0.0049(1)	-0.0032(3)	0.0037(1)	-0.0014(1)
C(5)	0.4825(4)	0.5447(2)	-0.0620(1)	0.0224(5)	0.0073(2)	0.0028(1)	0.0002(3)	0.0000(2)	0.0009(1)
O(5)	0.6571(2)	0.6218(2)	-0.0645(1)	0.0183(4)	0.0098(2)	0.0034(1)	0.0000(2)	-0.0017(1)	-0.0004(1)
C(6)	0.4760(4)	0.4842(2)	-0.1409(1)	0.0211(5)	0.0064(2)	0.0036(1)	-0.0004(3)	0.0016(2)	-0.0001(1)
O(16)	0.6058(3)	0.5634(2)	-0.1855(1)	0.0269(4)	0.0080(2)	0.0032(1)	-0.0031(2)	0.0036(1)	-0.0012(1)
H(1)	0.792(4)	0.704(3)	-0.149(2)	5.7(7)					
H(2)	0.488(4)	0.811(2)	-0.191(1)	3.9(5)					
H(3)	0.191(3)	0.785(2)	-0.116(1)	3.9(5)					
H(4)	0.319(3)	0.673(2)	0.007(1)	3.3(5)					
H(5)	0.498(4)	0.472(3)	-0.022(1)	4.2(5)					
H(61)	0.527(3)	0.392(2)	-0.143(1)	3.3(5)					
H(62)	0.325(3)	0.489(3)	-0.163(1)	4.2(5)					
H(O4)	0.071(4)	0.592(3)	-0.026(2)	5.5(7)					
Molecule 2				β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
	x	y	z	or B					
C(1)	0.5671(4)	-0.2908(2)	0.3819(1)	0.0282(6)	0.0064(2)	0.0035(1)	-0.0020(3)	-0.0016(2)	0.0011(1)
C(2)	0.3743(4)	-0.2213(3)	0.3864(1)	0.0237(6)	0.0099(2)	0.0031(1)	-0.0039(3)	0.0007(2)	0.0006(1)
C(3)	0.3545(4)	-0.1037(2)	0.3403(1)	0.0197(5)	0.0078(2)	0.0042(1)	-0.0008(3)	-0.0004(2)	0.0000(1)
O(23)	0.2595(3)	-0.2230(2)	0.3186(1)	0.0241(4)	0.0105(2)	0.0046(1)	-0.0059(3)	-0.0031(2)	0.0016(1)
C(4)	0.5241(4)	-0.0601(2)	0.2917(1)	0.0262(5)	0.0062(2)	0.0025(1)	-0.0019(3)	-0.0011(2)	0.0006(1)
O(4)	0.5681(3)	0.0724(2)	0.3072(1)	0.0300(5)	0.0058(1)	0.0039(1)	-0.0014(2)	-0.0018(1)	0.0007(1)
C(5)	0.7035(3)	-0.1401(2)	0.3097(1)	0.0224(5)	0.0065(2)	0.0027(1)	-0.0008(3)	0.0017(2)	-0.0004(1)
O(5)	0.6484(3)	-0.2753(1)	0.3090(1)	0.0279(4)	0.0056(1)	0.0034(1)	0.0009(2)	0.0011(1)	-0.0007(1)
C(6)	0.7792(3)	-0.1231(2)	0.3911(1)	0.0216(5)	0.0088(2)	0.0037(1)	-0.0011(3)	-0.0010(2)	0.0004(1)
O(16)	0.6984(3)	-0.2306(2)	0.4321(1)	0.0288(5)	0.0113(2)	0.0032(1)	-0.0034(3)	-0.0030(1)	0.0019(1)
H(1)	0.555(3)	-0.383(2)	0.388(1)	4.6(5)					
H(2)	0.294(4)	-0.228(3)	0.431(2)	5.9(7)					
H(3)	0.273(4)	-0.027(3)	0.356(1)	4.6(6)					
H(4)	0.487(4)	-0.074(2)	0.238(2)	4.2(6)					
H(5)	0.818(3)	-0.127(3)	0.272(2)	4.4(5)					
H(61)	0.917(5)	-0.124(4)	0.393(2)	6.9(8)					
H(62)	0.732(4)	-0.040(2)	0.410(1)	4.1(5)					
H(O4)	0.520(6)	0.114(3)	0.275(2)	7.2(8)					

parameters and all reflections and three more cycles with anisotropic thermal parameters and reflections with $\sin \theta \geq 0.4$ only, the hydrogen atoms could easily be located from a difference electron density map. Further refinement with anisotropic thermal motion for the heavy atoms and isotropic thermal motion for the hydrogen atoms converged at $R\left(\frac{\sum||F_o|-|F_c||}{\sum|F_o|}\right) = 0.039$ (0.045) for the observed (all) reflections. At this stage, the influence of extinction seemed to be obvious, so 14 reflections with $|F_o| > 55$ and $\sin \theta \leq 0.15$ or $|F_o| > 60$ and $\sin \theta \leq 0.35$ were removed from the data set: 004, 008, 013, 014, 020, 021, 031, 103, 112, 113,

115, 220, 221, 222. The final refinement converged with $R=0.031$ (0.039) and $R_w=0.050$ (0.050) with $[\sum(\Delta F_{\text{meas}}/\sigma_F)^2/(m-n)]^{1/2}=0.37$. The observed and calculated structure factors are listed in Table 1. The final atomic positional and thermal parameters with their standard deviations are given in Table 2. In Fig. 1, the two independent molecules are shown, their thermal parameters being represented as 50% probability ellipsoids. There are obvious differences in the ellipsoids of corresponding atoms in the two molecules.

The best least-squares fit of atomic anisotropic thermal parameters U_{ij} to a rigid body motion for each molecule (Schomaker & Trueblood, 1968) gave the

Table 3. Rigid body vibrational tensors

The tensors **L** for libration are referred to the crystal axes system a, b, c , the tensors **T** for translation and **S** for screw motion are referred to the directions of principal axes of **L**. The two origins are defined by symmetrizing **S** and have the coordinates 0.163, 0.055, 0.084 Å and 0.451, -0.041, 0.021 Å, respectively, referred to the center of mass and in the **L** system. Criteria for the rigid body fit and the tensors and their cosines are:

$[\sum\{U_{ij}(\text{meas})-U_{ij}(\text{calc})\}^2/(n-s)]^{1/2}$ E.s.d. of U_{ij}	Molecule 1			Molecule 2				
	0.0019 0.0023	(1)	(2)	(3)	0.0019 0.0024	(1)	(2)	(3)
L and direction cosines	6.36°	-0.368	-0.880	-0.302	6.81°	0.525	0.851	-0.003
	4.27	-0.794	0.128	0.594	4.71	0.459	-0.281	0.843
	2.86	-0.484	0.458	-0.745	3.27	0.716	-0.444	-0.538
T and direction cosines	0.203 Å	0.209	0.785	0.583	0.125 Å	0.353	0.602	0.716
	0.187	0.251	-0.620	0.744	0.180	0.241	-0.798	0.552
	0.176	0.945	-0.009	-0.326	0.173	0.904	-0.022	-0.427
S and direction cosines	0.003	0.660	-0.750	0.047	0.003	0.248	-0.605	-0.577
	0.000	0.165	0.084	-0.983	0.000	0.248	0.795	-0.554
	-0.003	0.733	0.656	0.179	-0.002	0.936	-0.050	0.347

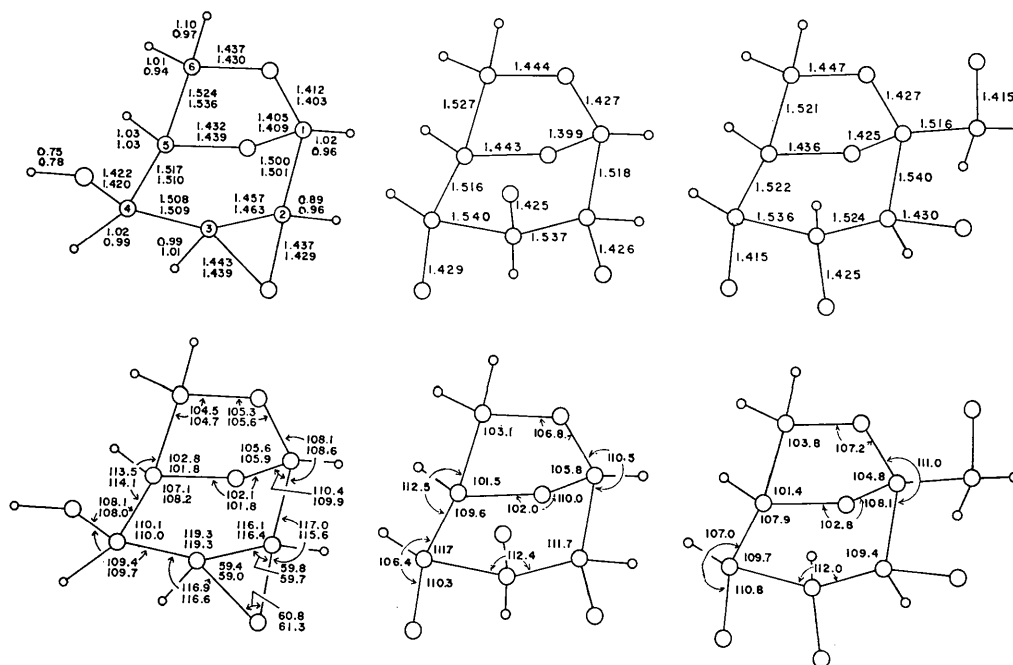


Fig. 2. Bond lengths (Å) and bond angles (°) are shown for, left: 1,6:2,3-dianhydro- β -D-gulopyranose (two molecules), center: 1,6-anhydro- β -D-glucopyranose (Park, Kim & Jeffrey, 1970), right: sedoheptulosan (Brown & Theissen, 1969).

parameters which are listed in Table 3. The rigid body fit seems to be satisfactory, since only one (out of 120) calculated rigid body U_{ij} value differs from the corresponding input U_{ij} value by more than three times the e.s.d. in the input U_{ij} . Both the lengths of the principal axes and the direction cosines of the translation tensors T are similar in both molecules when referred to the principal axes of the L systems. The bond lengths were corrected by the Busing-Levy method (Rutherford, 1968) on the assumption of rigid body motion (Table 4), the average increase being 0.010 Å.

Table 4. Distances and angles for 1,6:2,3-dianhydro- β -D-gulopyranose

The intramolecular bond lengths between heavy atoms are listed as uncorrected distances and as distances with corrections based on the rigid body mode of molecular thermal motion. Except for (i), the Table contains only distances and angles that are not shown in Fig. 2. In intermolecular distances or angles, the first molecule is assumed to be in (x, y, z) , the symmetry and translation relation of the second is given explicitly. The estimated standard deviations are as follows:

$$\begin{aligned} \text{C-C, C-O} & 0.004 \rightarrow 0.006 \text{ \AA} \\ \text{C-H, O-H} & 0.04 \text{ \AA} \rightarrow 0.06 \text{ \AA} \\ \text{Angles between heavy atoms} & 0.4^\circ \\ \text{Angles in which hydrogen atoms are involved} & 3^\circ \end{aligned}$$

(i) Uncorrected and corrected bond distances

	Molecule 1		Molecule 2	
	d_{uncorr} (Å)	d_{corr} (Å)	d_{uncorr} (Å)	d_{corr} (Å)
C(1)—C(2)	1.500	1.512	1.501	1.515
C(2)—C(3)	1.457	1.467	1.463	1.473
C(2)—O(23)	1.437	1.445	1.429	1.441
C(3)—O(23)	1.443	1.450	1.439	1.446
C(3)—C(4)	1.508	1.519	1.509	1.521
C(4)—O(4)	1.422	1.430	1.420	1.428
C(4)—C(5)	1.517	1.528	1.510	1.524
C(5)—O(5)	1.432	1.440	1.439	1.447
O(5)—C(1)	1.405	1.417	1.409	1.422
C(5)—C(6)	1.524	1.534	1.536	1.549
C(6)—O(16)	1.437	1.447	1.430	1.438
O(16)—C(1)	1.412	1.418	1.403	1.413

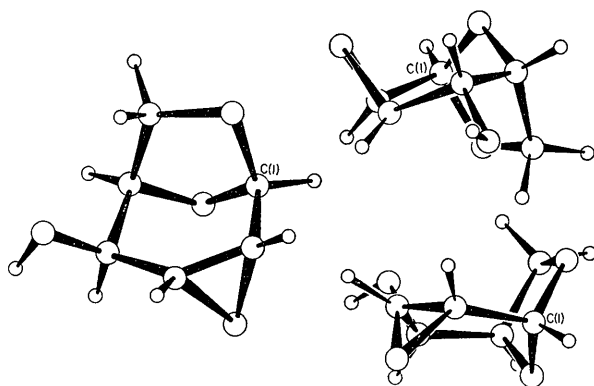


Fig. 3. The molecular conformation of 1,6:2,3-dianhydro- β -D-gulopyranose in three different projections (modified from ADAGE display).

Table 4 (cont.)

(ii) Bond angles in which hydrogen atoms are involved

	Molecule 1	Molecule 2
O(5)—C(1)—H(1)	105°	104°
O(16)—C(1)—H(1)	112	115
C(2)—C(1)—H(1)	115	113
C(1)—C(2)—H(2)	116	121
C(3)—C(2)—H(2)	122	117
O(23)—C(2)—H(2)	114	112
C(2)—C(3)—H(3)	121	123
C(4)—C(3)—H(3)	115	111
O(23)—C(3)—H(3)	112	119
C(3)—C(4)—H(4)	107	108
C(5)—C(4)—H(4)	112	109
O(4)—C(4)—H(4)	110	112
C(4)—C(5)—H(5)	114	114
C(6)—C(5)—H(5)	109	109
O(5)—C(5)—H(5)	110	108
C(5)—C(6)—H(61)	114	112
O(16)—C(6)—H(61)	108	111
H(62)—C(6)—H(61)	111	109
C(5)—C(6)—H(62)	109	108
O(16)—C(6)—H(62)	111	112
C(4)—O(4)—H(O4)	104	107

(iii) Hydrogen-bonding distances and angles

Molecule 1		
O(4)—O(23) in	$-\frac{1}{2}+x, \frac{1}{2}-y, -z$	2.87 Å
H(O4)—O(23) in	$-\frac{1}{2}+x, \frac{1}{2}-y, -z$	2.15
O(4)—O(5) in	$-1+x, y, z$	3.32
O(4)—H(O4)—O(23)		163°
Molecule 2		
O(4)—O(5) in	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	2.97
H(O4)—O(5) in	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	2.19
O(4)—O(23) in	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	3.27
O(4)—H(O4)—O(5)		173°

Because of the significant change in lattice parameters, the e.s.d.'s for bond lengths and bond angles should be larger than the results of the least-squares refinement suggest (0.003 \rightarrow 0.004 Å for C—O and C—C bonds). Considering the anisotropy of the change ($\frac{\Delta a}{a} > \frac{\Delta c}{c} > \frac{|\Delta b|}{b}$), it is obvious that bonds oriented along a are affected more severely. Within the following discussion, an average value of 0.005 Å seems to be appropriate, however.

The final difference Fourier synthesis does not show any evidence for disorder or the coming into existence of another structure, e.g. a decomposition of the epoxy ring as could be expected. The extreme peak heights are $\Delta\rho(\text{max}) = 0.14 \text{ e.}\text{\AA}^{-3}$ and $\Delta\rho(\text{min}) = -0.16 \text{ e.}\text{\AA}^{-3}$, respectively.

Discussion

(i) Geometry of the molecule

The geometry of the molecules is described in terms of the bond lengths and angles (Fig. 2 and Table 4), conformation angles, interplanar angles, and least-squares planes (Table 5). Corresponding values for the two molecules do not differ significantly so the average values may be used for discussion.

Table 5. *Least-squares planes and torsion angles and interplanar angles within 1,6:2,3-dianhydro- β -D-gulopyranose*

(i) Least-squares planes through atoms

Plane <i>P</i> 1:	C(1), C(2), C(3), C(4)
Plane <i>P</i> 2:	C(1), O(5), C(5), C(6), O(16)
Plane <i>P</i> 3:	C(1), C(5), C(6), O(16)
Plane <i>P</i> 4:	C(2), C(3), O(23)
Plane <i>P</i> 5:	C(2), C(3), H(2), H(3)

Equations of the planes, with x, y, z in Å

Molecule 1	
<i>P</i> 1	$0.418x + 0.558y + 0.717z = 3.955$
<i>P</i> 2	$0.770x - 0.627y + 0.116z = -0.932$
<i>P</i> 3	$0.818x - 0.513y + 0.262z = -0.491$
<i>P</i> 4	$0.515x - 0.627y + 0.585z = -4.738$
<i>P</i> 5	$0.185x + 0.865y + 0.466z = 6.259$

Molecule 2	
<i>P</i> 1	$0.346x + 0.551y + 0.759z = 4.803$
<i>P</i> 2	$0.839x - 0.537y - 0.089z = 4.491$
<i>P</i> 3	$0.750x - 0.615y - 0.244z = 3.129$
<i>P</i> 4	$0.808x - 0.264y - 0.527z = -0.921$
<i>P</i> 5	$0.757x + 0.396y + 0.519z = 4.547$

All C–C and C–O bonds and all angles in which the atoms C(2), C(3) and O(23) of the epoxy ring are not involved are in good agreement with those in 1,6-anhydro- β -D-glucopyranose (Park, Kim & Jeffrey, 1971) and sedoheptulosan monohydrate (Brown & Thiessen, 1969). These two compounds have the same five–six-membered ring combination (Fig. 2), the consequences of which have been discussed by these authors. However, in the vicinity of the epoxy ring, the bonds C(1)–C(2), C(2)–C(3) and C(3)–C(4) are reduced from around 1.53 Å to 1.500, 1.460 and 1.508 Å, respectively, with the angles at C(2) and C(3) increasing about 6° and thereby flattening the six-membered ring. In the epoxy ring, the average C–O bond is 1.437 Å, and all angles are close to 60°. All C–H bonds of the two molecules range between 0.89 and 1.10 Å with an average of 1.00 Å. The two O–H distances for the hydroxy groups are 0.75 and 0.78 Å.

The anhydride ring closures strain the pyranose ring and force changes in its conformation angles. Berman & Kim (1968) report values in unstrained pyranose

Table 5 (cont.)

(ii) Distances (Å) of some atoms from the least-squares planes. The values in italics belong to the atoms forming the planes. The standard deviations are 0.005 and 0.04 Å, depending on whether hydrogen atoms are involved.

	Molecule 1					Molecule 2				
	<i>P</i> 1	<i>P</i> 2	<i>P</i> 3	<i>P</i> 4	<i>P</i> 5	<i>P</i> 1	<i>P</i> 2	<i>P</i> 3	<i>P</i> 4	<i>P</i> 5
C(1)	<i>-0.004</i>	<i>-0.235</i>	<i>-0.035</i>	<i>+1.285</i>	<i>-0.611</i>	<i>-0.001</i>	<i>-0.235</i>	<i>-0.030</i>	<i>+1.294</i>	<i>-0.696</i>
C(2)	<i>+0.008</i>	<i>-1.731</i>	<i>-1.486</i>	<i>0.000</i>	<i>0.005</i>	<i>+0.002</i>	<i>-1.730</i>	<i>-1.476</i>	<i>0.000</i>	<i>-0.022</i>
C(3)	<i>-0.008</i>			<i>0.000</i>	<i>-0.005</i>	<i>-0.002</i>			<i>0.000</i>	<i>+0.022</i>
O(23)	<i>+1.191</i>			<i>0.000</i>		<i>+1.189</i>			<i>0.000</i>	
C(4)	<i>+0.004</i>	<i>-1.613</i>	<i>-1.323</i>	<i>+1.266</i>	<i>-0.581</i>	<i>+0.001</i>	<i>-1.613</i>	<i>-1.320</i>	<i>+1.270</i>	<i>-0.588</i>
O(4)	<i>-1.039</i>					<i>-1.061</i>				
C(5)	<i>-0.240</i>	<i>-0.163</i>	<i>+0.032</i>			<i>-0.211</i>	<i>-0.172</i>	<i>+0.027</i>		
O(5)	<i>+0.668</i>	<i>+0.254</i>	<i>+0.590</i>			<i>+0.694</i>	<i>+0.260</i>	<i>+0.602</i>		
C(6)	<i>-1.603</i>	<i>+0.031</i>	<i>+0.050</i>			<i>-1.576</i>	<i>+0.041</i>	<i>-0.043</i>		
O(16)	<i>-1.342</i>	<i>+0.113</i>	<i>+0.052</i>			<i>-1.324</i>	<i>+0.106</i>	<i>+0.046</i>		
H(1)	<i>+0.46</i>				<i>-0.22</i>	<i>+0.47</i>				<i>-0.31</i>
H(2)	<i>-0.33</i>			<i>-0.74</i>	<i>-0.003</i>	<i>-0.37</i>			<i>-0.84</i>	<i>+0.013</i>
H(3)	<i>-0.39</i>			<i>-0.84</i>	<i>0.003</i>	<i>-0.46</i>			<i>-0.81</i>	<i>-0.013</i>
H(4)	<i>+0.91</i>				<i>0.19</i>	<i>+0.88</i>				<i>0.15</i>
H(5)										
H(61)		<i>+0.89</i>	<i>+0.71</i>				<i>+0.83</i>	<i>+0.65</i>		
H(62)		<i>-0.84</i>	<i>-1.02</i>				<i>-0.72</i>	<i>-0.89</i>		
H(O4)										

(iii) Torsion angles within the six-membered ring

	C(1)–C(2)	C(2)–C(3)	C(3)–C(4)	C(4)–C(5)	C(5)–O(5)	O(5)–C(1)
Molecule 1	31.8°	-1.7°	11.0°	-50.2°	82.0°	-71.1°
Molecule 2	31.9	-0.4	8.8	-48.7	81.6	-71.0

(iv) Torsion angles within the five-membered ring

	C(1)–O(5)	O(5)–C(5)	C(5)–C(5)	C(6)–O(16)	O(16)–C(1)
Molecule 1	45.6	-37.9	17.8	+9.0	-33.9
Molecule 2	46.0	-38.6	19.1	7.9	-33.4

(v) Other torsion angles of interest

	H(2)–C(2)–C(3)–H(3)	H(1)–C(1)–C(2)–H(2)	H(3)–C(3)–C(4)–H(4)
Molecule 1	1.6°	-56.2°	92.5°
Molecule 2	-6.8	-59.0	98.6

(vi) Interplanar angles:

Planes	Molecule 1	Molecule 2
<i>P</i> 1, <i>P</i> 4	106.6°	105.4°
<i>P</i> 1, <i>P</i> 5	153.4	151.0
<i>P</i> 4, <i>P</i> 5	100.1	103.6
	360.1	360.0

rings, e.g. $56 \rightarrow 62^\circ$ in an 'ideal' pyranose ring and $54 \rightarrow 60^\circ$ for methyl α -D-glucopyranoside. In the dicyclic 1,6-anhydro- β -D-glucopyranose, the conformation angles vary from 35 to 76° , in this tricyclic dianhydro sugar the range has increased again: $0 \rightarrow 82^\circ$ (Table 5). Thus the molecules are no longer in the conventional $C1$ *trans* chair conformation of the unstrained pyranose ring, but rather can be described as a half-chair. The atoms C(1), C(2), C(3) and C(4) are

planar (Table 5) within 0.008 \AA , C(5) and O(5) being out of this plane by -0.23 and $+0.68 \text{ \AA}$, respectively.

The conformation of the five-membered anhydro ring approximates the envelope form. The atoms C(1), C(5), C(6) and O(16) are planar within 0.05 \AA . $P3$ is the best plane through four of the five atoms. The conformation of the molecules can be seen from Figs. 1 and 3.

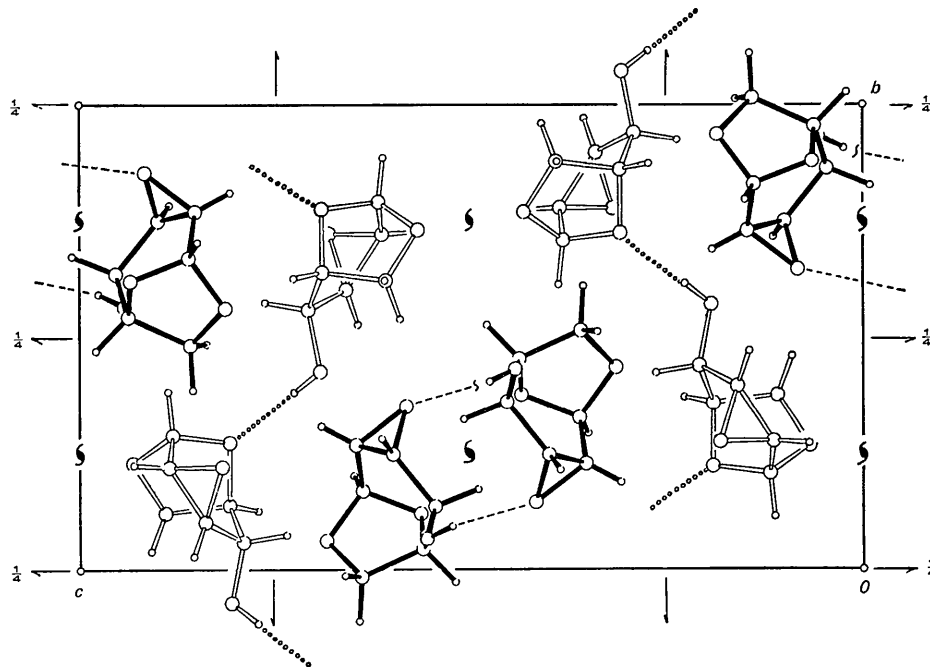


Fig. 4. The crystal structure of 1,6:2,3-dianhydro- β -D-gulopyranose as a projection down the a axis. The two different hydrogen-bonding systems are shown (Johnson, 1965).

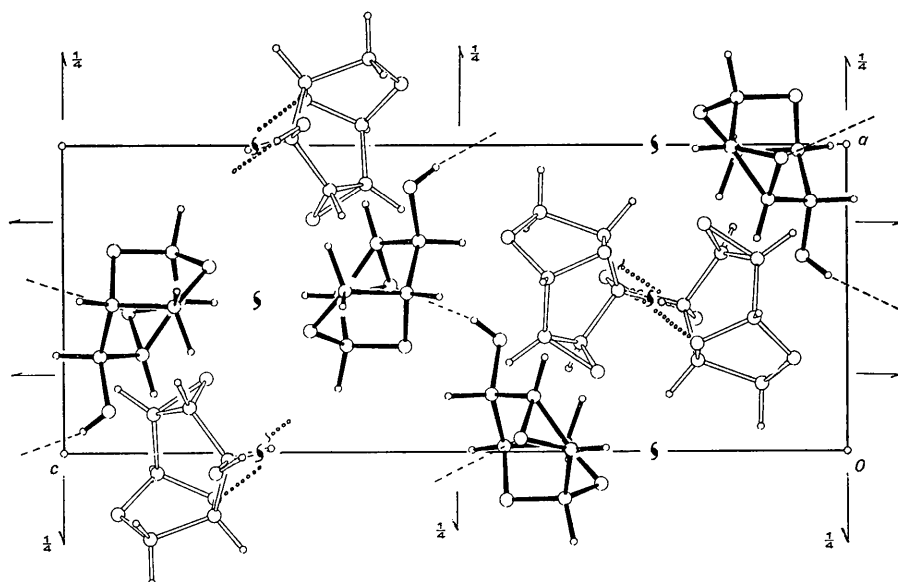


Fig. 5. The crystal structure of 1,6:2,3-dianhydro- β -D-gulopyranose as a projection along the b axis. The two different hydrogen-bonding schemes are shown (Johnson, 1965).

(ii) *The hydrogen-bonding system*

The molecules possess a possible donor in the hydroxyl group O(4)–H(O4) and possible acceptors in O(5) and the two anhydro oxygen atoms O(23) and O(16). The hydrogen-bonding scheme and its distances and angles are shown in Table 4 and Figs. 4 and 5. O(16) is not involved in hydrogen bonds at all, the closest intermolecular O(4)–O(16) distance being 3.85 Å.

The two independent molecules are not hydrogen-bonded to each other, but form two entirely separate bonding systems. In all molecules 1, atoms O(23) are the acceptors for hydrogen bonds of 2.87 Å length, by which the molecules are connected to infinite chains around the screw axis parallel to **a**. In all molecules 2, atoms O(5) play the roll of acceptors for hydrogen bonds of 2.97 Å length, by which the molecules are connected to infinite chains around the screw axes parallel to **b**. The next shortest O(4)–O distances are 3.27 and 3.32 Å. Even if they are considered as very weak hydrogen bonds, they do not form bonds between molecules 1 and molecules 2. Besides, there is no evidence for intramolecular hydrogen bonding.

The existence of 40 intermolecular distances smaller than 3.0 Å (not including those which are involved in hydrogen bonding) suggests strong van der Waals interactions between the molecules. The minimum values of 2.40 and 2.54 Å for H–H and O–H distances, respectively, are close to the sum of the van der Waals radii ($r_{\text{O}} = 1.4$, $r_{\text{H}} = 1.2$ Å).

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The Effect of Molecular Vibrations on Apparent Bond Lengths. II. Water Molecule

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The apparent contraction of the O–H bond in H₂O due to the nuclear vibrational motion has been studied using a convolution approximation with both Slater- and Gaussian-type wave functions. The bond length here is taken as the distance between the maxima in the charge density such as would be inferred from X-ray measurements. The predicted degree of contraction appears to be quite sensitive to the quality and type of wave function used. The Gaussian function did not adequately represent the charge density near the hydrogen nucleus. However, the best Slater-type wave function gave a bond contraction of 0.13 a₀. Difference densities were also investigated and an estimate was made of the contribution to the bond shortening from the bending motion alone.

Introduction

It is well known (Dawson, 1965) that bond lengths to terminal hydrogen atoms as determined by X-rays are generally smaller than those determined by spectroscopic or neutron- and electron-diffraction methods. In

a previous paper (Coulson & Thomas, 1971), which henceforth will be referred to as I, we have shown that some of this apparent shortening can be accounted for by considering the effect of the nuclear vibrational motion on the electronic charge density associated with the equilibrium molecular geometry. In general, the