A Neutron Diffraction Refinement of the Crystal Structure of β-Maltose Monohydrate

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Single-crystal neutron diffraction data on β-maltose monohydrate have provided an accurate description of the hydrogen bonding, which consists of a finite chain intersecting two infinite chains. With the exception of an intramolecular hydrogen bond (H$\cdots$O = 1·835 Å), the hydroxyl interactions are all of the donor/acceptor type ($\cdots$O–H$\cdots$O). The shortest bonds are those to the water molecules (1·762 and 1·798 Å). The remainder range from 1·812 to 1·927 Å, the shortest being that from the β-anomeric hydroxyl. The α- and β-glucopyranose residues have small dimensional differences in their ring torsion angles, C–O bond lengths and ring-oxygen valence angles, which are analogous to those observed in the α- and β-pyranose monosaccharides.

Introduction

The crystal structure of 4-O-(α-D-glucopyranosyl)-β-D-glucopyranose (β-maltose) monohydrate, $C_{12}H_{22}O_{11}.H_2O$, was determined by Quigley, Sarko & Marchessault (1970) using X-ray diffraction. The principal purpose of this neutron diffraction refinement is to provide a more accurate description of the hydrogen-bond structure for comparison with the results available from the neutron diffraction studies of other mono- and disaccharides, *i.e.* α-D-glucose (Brown & Levy, 1965), methyl α-D-altropyranoside (Poppleton, Jeffrey & Williams, 1975), methyl α-D-glucopyranoside and methyl α-D-mannopyranoside (Jeffrey, McMullan & Takagi, 1977), and sucrose (Brown & Levy, 1973). In particular, we wished to observe whether there were any systematic correlations between bond lengths and type of O–H$\cdots$O interaction, such as had been noted in the methyl pyranosides (Jeffrey, Gress & Takagi, 1977).

It is also of interest to provide a more precise comparison of the dimensions of the α- and β-glucopyranose residues in the disaccharide because of the small, but significant, differences in certain bond lengths and valence angles, which have been noted between α- and β-pyranose monosaccharides (*cf.* Arnott & Scott, 1972; Jeffrey & Takagi, 1977).

Data collection and parameter refinement

Large crystals of β-maltose monohydrate were provided by W. E. Dick and J. A. Rendleman, Northern Regional Research Laboratory, US Department of Agriculture (Hodge, Rendleman & Nelson, 1972). The crystal data are given in Table 1. The lattice constants

were determined by least-squares fit to 27 independent reflection angles centered on a single-crystal neutron diffractometer at the Brookhaven High Flux Beam Reactor with a Ge (220) monochromator. The neutron wavelength of 1·1059 Å was determined by least squares from 24 reflections of a standard KBr crystal ($a = 6·600$ Å).

For data collection, a crystal 2·7 mm³ in volume was mounted on a cadmium-coated brass pin along **b***. The intensity data were collected at room temperature on the neutron diffractometer operating under control of the program *NEXDAS* (McMullan, 1976) with a θ–2θ step-scan procedure. The background was interpolated from smooth curves constructed from separate background intensity measurements along radial θ–2θ scans. A summary of the data-collection method and the absorption corrections is given in Table 2.

The H atom positions were located by a difference Fourier calculation phased by the heavy-atom positions from the X-ray structure determination. The anisotropic refinement was by full-matrix least squares with *FLINUS*, a local version of *ORFLS* (Busing, Martin & Levy, 1962), with the 432 variable parameters in two blocks. The neutron scattering lengths used were $b_C = 0·665 \times 10^{-12}$, $b_O = 0·577 \times 10^{-12}$ and $b_H = -0·372 \times 10^{-12}$ cm (Neutron Diffraction Commission, 1969).

Table 1. *Crystal data*

The cell parameters from the X-ray determination (Quigley, Sarko & Marchessault, 1970) are given in square brackets.

$C_{12}H_{22}O_{11}.H_2O, M_r = 360·32$
$a = 4·866$ (2) Å [4·92 (3)]
$b = 15·077$ (6) [15·23 (8)]
$c = 10·702$ (5) [10·68 (4)]
$\beta = 97·07$ (2)° [97·5 (1)]
$V = 779·2$ Å³
Space group $P2_1, Z = 2$
$D_c = 1·536, D_m = 1·538$ g cm⁻³

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Table 2. *Experimental and structure-refinement data*

Crystal weight 4·2 mg
Number of faces 10
Crystal habit {001} {100} {023} {012} {230} {231} {201}
Mounted along **b***
Number of reflections
  Total measured 3507 ($2\theta_{max} = 90°$)
  $\pm hkl$ and $\pm hk\bar{l}$ quadrants
  Averaged 1843 with $F_o^2 > 0$
Data collection mode
  θ–2θ step scan
  Fixed width 1·50°, 6° < 2θ < 50°, $\Delta 2\theta = 0·02°$
  Fixed width 1·80°, 50° < 2θ < 70°, $\Delta 2\theta = 0·02°$
  Fixed width 4·98°, 70° < 2θ < 90°, $\Delta 2\theta = 0·06°$
Absorption correction
  DeMeulenaer–Tompa–Alcock method (Templeton &
    Templeton, 1973)
  $\mu = 2·274$ cm^{-1}
  Maximum correction to F_o^2 1·451
  Minimum correction to F_o^2 1·154
Refinement
  Full-matrix anisotropic least-squares refinement of
  $\Sigma w(|F_o| - k|F_c|)^2$, where $w^{-1} = [\sigma_C^2(F_o^2) + (aF_o^2)^2]/4F_o^2$,
    where σ_C is from counting statistics and $a = 0·02$
  Number of observations 1843
  Number of variables 432 (refined in two blocks of 235 each)
  Zachariasen isotropic extinction parameter, $g = 4·6$ (6) × 10^5
    applied to F_c^2 (Coppens & Hamilton, 1970).
  $R = \Sigma|F_o - kF_c|/\Sigma|F_o|, R = 0·044$ (all reflections)
  $R_w = [\Sigma w(F_o - kF_c)^2/\Sigma wF_o^2]^{1/2}, R = 0·047$ (all reflections)
  $S = [\Sigma w(F_o - kF_c)^2/(N_o - N_v)]^{1/2}, S = 2·84$

The details of the final refinement cycle are given in Table 2. The final positional parameters are given in Table 3.† Fig. 1 gives an *ORTEP* stereoview of the conformation and thermal parameters of the β-maltose and water molecules. Fig. 2 shows a lateral view of the conformation of the pyranose rings and reports the bond lengths in the molecule. The standard carbohydrate atomic notation used is the same as in the previous X-ray study. A rigid-body thermal-motion analysis was made with the procedure of Schomaker & Trueblood (1968). The results are shown in Table 4, with the corresponding rigid-body and riding-motion corrections for the bond lengths.

Discussion

The hydrogen bonding

The hydrogen bonding consists of a finite chain intersecting two infinite chains, as shown in Fig. 3. The finite chain originates with an intramolecular hydrogen bond

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† Lists of structure factors, anisotropic thermal parameters and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32499 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Fractional atomic coordinates* ($\times 10^4$) *for β-maltose monohydrate*

Estimated standard deviations are given in parentheses for the least significant figures. The y coordinate of O(W) was fixed to specify the origin.

	x	y	z
C(1)	5301 (4)	3010 (2)	1764 (2)
C(2)	5627 (4)	3261 (2)	400 (2)
C(3)	3030 (4)	2993 (2)	−461 (2)
C(4)	2463 (4)	2011 (2)	−278 (2)
C(5)	2302 (4)	1809 (2)	1109 (2)
C(6)	2099 (6)	822 (2)	1355 (2)
C(1')	1874 (4)	5228 (2)	5082 (2)
C(2')	2737 (4)	5649 (2)	3888 (2)
C(3')	2345 (4)	4999 (2)	2785 (2)
C(4')	3745 (4)	4117 (2)	3166 (2)
C(5')	2671 (4)	3777 (2)	4367 (2)
C(6')	3919 (5)	2900 (2)	4845 (2)
O(1)	3106 (5)	3511 (2)	2157 (2)
O(2)	6303 (6)	4163 (2)	312 (3)
O(3)	3415 (5)	3155 (2)	−1732 (3)
O(4)	−88 (6)	1755 (2)	−985 (3)
O(5)	4785 (5)	2098 (2)	1859 (2)
O(6)	1996 (6)	647 (2)	2653 (3)
O(1')	2618 (6)	5801 (2)	6084 (3)
O(2')	1110 (6)	6412 (2)	3573 (3)
O(3')	3516 (6)	5336 (2)	1731 (3)
O(5')	3290 (5)	4414 (2)	5342 (2)
O(6')	6842 (6)	2928 (2)	5117 (3)
O(W)	8207 (6)	3770	7368 (3)
H(W1)	8039 (12)	4407 (4)	7304 (6)
H(W2)	6652 (12)	3580 (5)	7782 (5)
H(C1)	7218 (9)	3133 (4)	2377 (5)
H(C2)	7357 (9)	2889 (4)	112 (5)
H(C3)	1242 (9)	3382 (4)	−217 (5)
H(C4)	4200 (11)	1637 (4)	−583 (5)
H(C5)	517 (10)	2138 (4)	1430 (5)
H(C6A)	3858 (19)	480 (5)	1045 (7)
H(C6B)	254 (17)	559 (6)	829 (6)
H(C1')	−385 (10)	5109 (4)	4949 (5)
H(C2')	4958 (10)	5836 (4)	4082 (5)
H(C3')	115 (9)	4874 (3)	2514 (4)
H(C4')	5991 (8)	4219 (3)	3357 (4)
H(C5')	409 (9)	3670 (4)	4171 (5)
H(C6A')	3429 (14)	2387 (4)	4108 (6)
H(C6B')	2974 (12)	2693 (4)	5666 (6)
H(O2)	5056 (11)	4519 (4)	751 (5)
H(O3)	1695 (11)	3404 (4)	−2150 (5)
H(O4)	18 (12)	1806 (5)	−1874 (5)
H(O6)	3797 (11)	769 (4)	3118 (5)
H(O1')	1151 (12)	5813 (4)	6628 (5)
H(O2')	1767 (12)	6887 (4)	4140 (5)
H(O3')	2303 (13)	5789 (5)	1346 (6)
H(O6')	7296 (11)	3299 (4)	5867 (6)

[O(2)–H···O(3')] between the two glucopyranose residues and terminates at a primary alcohol hydroxyl O(6)H. It links the maltose and water molecules in the **b** direction [as shown in Fig. 4 of the X-ray structure analysis (Quigley, Sarko & Marchessault, 1970)]. This chain intersects two infinite chains of hydrogen bonds, one involving the water molecules and the O(3)H hydroxyls and the other the primary alcohol of the α residue and the reducing hydroxyl O(1')H on the β

Table 4. *Least-squares fit to rigid-body motion for β-maltose monohydrate*

Model A comprises the six atoms of the pyranose ring, which is calculated for both α- and β-glucopyranose residues. In model B, O(1), O(2), O(3), O(4), C(6) and O(1'), O(2'), O(3'), O(4') and O(6') are included.

	α-Residue		β-Residue		β-Maltose molecule
	A	B	A	B	B
$\langle$R.m.s. $\|U_{ij} - U_{ijRBM}\|\rangle$	0·0010 Å²	0·0020 Å²	0·0010 Å²	0·0020 Å²	0·0034 Å²
Max$\|U_{ij} - U_{ijRBM}\|$	0·0024	0·0051	0·0020	0·0054	0·0108
$\langle\sigma(U_{ij})\rangle$	0·0015	0·0024	0·0016	0·0024	0·0037

Rigid-body **T** and ω elements and r.m.s. values for principal axes of the **T** and ω tensors referred to the axes a, b and c^* of model B

		α-Residue					β-Residue	
T	179 (13)	5 (9)	−22 (9) (Å × 10⁴)		**T**	194 (13)	0 (9)	−32 (9) (Å × 10⁴)
		164 (9)	−4 (8)				169 (8)	−8 (7)
			169 (9)					177 (9)
ω	7·0 (9)	−0·9 (9)	−1·8 (7) (deg²)		ω	4·7 (7)	−3·8 (8)	−0·4 (7) (deg²)
		2·9 (1·4)	−0·8 (8)					8·7 (1·3)	4·5 (7)
			10·5 (1·0)					5·5 (1·0)

	α-Residue					β-Residue			
	R.m.s. value	Directions relative to axes				R.m.s. value	Directions relative to axes		
		a	b	c^*			a	b	c^*
T	0·14 Å	39·9°	79·5°	127·9°	**T**	0·15 Å	38·6°	84·0°	127·9°
	0·13	98·2	10·5	83·4		0·13	106·5	20·4	101·7
	0·12	51·3	90·1	38·7		0·12	56·3	70·6	40·3
ω	3·4°	111·9	92·7	22·1	ω	3·6°	112·0	37·6	61·3
	2·6	26·6	106·6	69·8		2·2	43·4	94·0	46·9
	1·6	75·7	16·8	81·4		1·0	54·9	52·7	123·3

Thermal-motion corrections (Å) to bond lengths in β-maltose monohydrate

	Rigid-body thermal motion†		Minimum riding motion	
	α-Residue	β-Residue	α-Residue	β-Residue
C—C	0·003 (0·004)	0·003 (0·003)		
C—O	0·003 (0·004)	0·002 (0·002)		
C—H(ring)	0·002 (0·004)	0·003 (0·004)	0·004	0·004
C—H(methylene)			0·013	0·007
O—H			0·002	0·002

† With model B. The values in parentheses also included the hydrogen atoms attached to the pyranose ring.

Fig. 1. *ORTEP* stereoview (Johnson, 1976) of β-maltose monohydrate. The thermal ellipsoids are at 50% probability.

residue. These chains extend in the **a** direction, as shown in Fig. 3, and complete the three-dimensional hydrogen-bonding network. Fig. 4 shows the coordination of the oxygen atoms O(W) and O(6), which are at the intersections of the chains. Both are very distorted tetrahedra. Neither the ring oxygens nor the glycosidic linkage oxygen are involved in hydrogen-

bonding. The nearest-intermolecular-neighbor atoms to O(5), O(5') and O(1) are H(5) at 2·883, H(O6) at 2·886, and H(1) at 2·959 Å respectively, all of which are well beyond bonding distances.

With the exception of the intramolecular bond, O(2)—H···O(3'), all the hydroxyl groups are involved in both donor and acceptor hydrogen-bond interac-
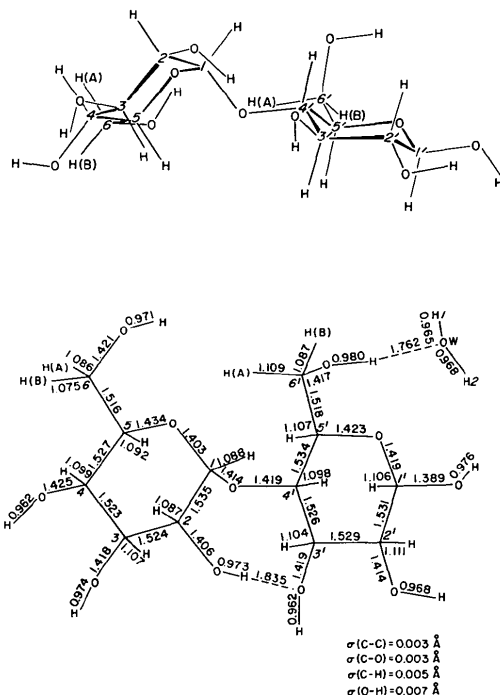
Fig. 2. Views of the glucopyranose rings in β-maltose monohydrate, with the bond lengths (uncorrected for thermal motion) and atomic notation.
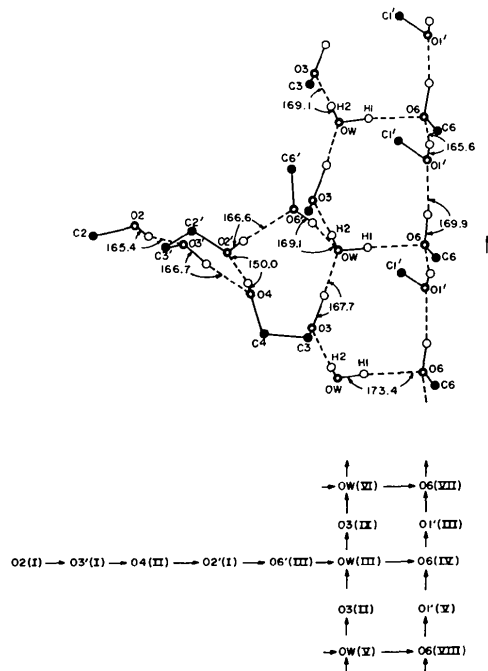
σ(C-C)=0.003 Å
σ(C-O)=0.003 Å
σ(C-H)=0.005 Å
σ(O-H)=0.007 Å

Fig. 3. The hydrogen-bond structure in β-maltose monohydrate: actual and schematic. The symmetry transformations are as follows: (I) x,y,z; (II) −x, ½ + y, −z; (III) 1 − x, ½ + y, 1 − z; (IV) x, 1 + y, z; (V) −x, ½ + y, 1 − z; (VI) 2 − x, ½ + y, 1 − z; (VII) 1 + x, 1 + y, z; (VIII) −1 + x, 1 + y, z; (IX) 1 − x, ½ + y, −z.

tions. As shown in Table 5, the shortest hydrogen bonds are those from hydroxyls to the water oxygens. Hydrogen bonding in which the acceptor bonds to water molecules are shorter than the donor bonds has also been observed in 2-keto-L-gulonic acid hydrate (Hvoslef & Bergen, 1975), and isomaltulose hydrate (Dreissig & Luger, 1973), but this does not appear to be a general rule in carbohydrate hydrate crystals.

With one exception, the other hydrogen-bond lengths span an unusually narrow range from 1·812 to 1·849 Å. The exception is the O(4)—H···O(2') bond of 1·927 Å which has the largest deviation from linearity, i.e. 30°. These bond lengths are longer than those for the same donor–acceptor type of interaction in the methyl α-D-pyranosides reported by Jeffrey, McMullan & Takagi (1977), where the range was 1·763 to 1·810 Å. The same is true for the donor/acceptor bonds in sucrose (1·760–1·908 Å) (Brown & Levy, 1973) and we believe this may be a general consequence of the more complex packing requirements for the large disaccharide molecules (cf. Jeffrey, Gress & Takagi, 1977). The shortest of the hydrogen bonds between the hydroxyl groups is that from the anomeric O(1')H. This is in agreement with the prediction of Tse & Newton (1977) that anomeric hydroxyls are capable of forming stronger hydrogen bonds by reason of the electronic structure of the hemiacetal group of which they are a part.
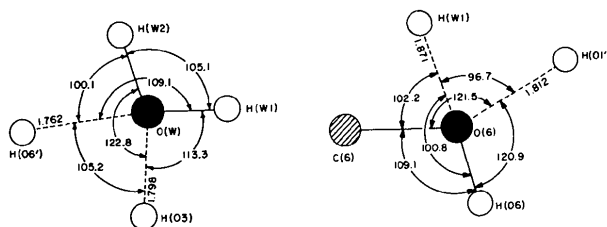

Fig. 4. Nearest-neighbor coordination around O(W) and O(6) in β-maltose monohydrate.

The molecular dimensions

The bond lengths and selected torsion angles of the β-maltose molecule are shown in Fig. 2 and Table 6 respectively. The greatest difference in the two glucopyranose residues is in the conformation of the primary alcohol group, which is +sc (gauche–trans) in the α residue and −sc (gauche–gauche) in the β residue. The conformation is similar to that observed in the methyl β-maltopyranoside monohydrate structure (Chu & Jeffrey, 1967), as shown by the comparison of the torsion angles in Table 6. The greatest difference is in the conformation about the glycosidic C(1)—O(1) bonds, resulting from a difference in the hydrogen-bond linkages between the two glucose residues. In β-maltose

Table 5. *Hydroxyl and hydrogen-bond distances* (Å) *and angles* (°) *in the crystal structure of β-maltose monohydrate*

These distances are uncorrected for thermal motion, which will increase the O—H and decrease the H···O distances by 0·002 Å or more (see Table 4).

Type of interaction	O—H	H···O	O···O	O—H···O
···O—H···O(W)(H)				
O(6')—H···O(W)	0·980 (7)	1·762 (6)	2·730 (4)	169·1 (5)
O(3)—H···O(W^a)	0·973 (6)	1·798 (6)	2·757 (4)	167·7 (5)
···O(W)—H···O(H)				
O(W)—H(2)···O(3^b)	0·968 (7)	1·834 (7)	2·791 (4)	169·1 (6)
O(W)—H(1)···O(6^c)	0·965 (6)	1·871 (7)	2·832 (3)	173·4 (5)
···O—H···O(H)				
O(1')—H···O(6^d)	0·976 (6)	1·812 (6)	2·768 (4)	165·6 (5)
O(3')—H···O(4^e)	0·962 (7)	1·824 (7)	2·769 (4)	166·7 (6)
O(6)—H···O(1'^{f})	0·971 (6)	1·846 (6)	2·807 (4)	169·9 (6)
O(2')—H···O(6'^{c})	0·968 (7)	1·849 (6)	2·800 (4)	166·6 (6)
O(4)—H···O(2'^{g})	0·961 (7)	1·927 (6)	2·801 (4)	150·0 (6)
O—H···O(H)*				
O(2)—H···O(3')	0·975 (7)	1·835 (6)	2·789 (4)	165·4 (5)

Symmetry code: (a) $-1 + x$, y, $-1 + z$; (b) x, y, $1 + z$; (c) $1 - x$, $\frac{1}{2} + y$, $1 - z$; (d) $-x$, $\frac{1}{2} + y$, $1 - z$; (e) $-x$, $\frac{1}{2} + y$, $-z$; (f) $1 - x$, $-\frac{1}{2} + y$, $1 - z$; (g) $-x$, $-\frac{1}{2} + y$, $-z$.

* Intramolecular bond.

monohydrate, there is only one intramolecular hydrogen bond, whereas in the methyl maltoside, the primary alcohol groups on the other side of the rings are also linked through hydrogen bonds to the water molecule.

Small, but significant, differences in the dimensions of the α and β residues are observed which correspond with those reported in a detailed comparison between the methyl α- and methyl β-glucopyranosides (Jeffrey & Takagi, 1977). The α-pyranose ring is the more regular, as shown by the smaller range of the ring torsion angles given in Table 6 and by the puckering parameters given in Table 7. It is interesting to note that the differences in these parameters between the α and β residues are in the same direction as in the methyl glucopyranosides, although the magnitudes are somewhat different. This suggests that these small variations in ring conformation are not entirely determined by the intermolecular forces, but may also be a function of the difference between the α and β configurations.

The ring C—C bonds vary by 2σ, or less, from the mean value of 1·529 Å. Only the C—C bonds of the primary alcohol may differ significantly, being shorter by 0·012 Å. The C—O bonds in the acetal and hemiacetal sequences of the α- and β-pyranose residues show the same differences as were observed in the methyl β-maltoside molecule. In the α residue, the two inner bonds of the C(5)—O(5)—C(1)—O(1)—C(4') sequence are shorter than the two outer bonds. In the β-glucose unit, the C(1')—O(1') bond has the usual

Table 6. *Selected torsion angles* (°) *for β-maltose monohydrate*

Corresponding values for methyl β-maltoside monohydrate are given in parentheses.

Ring torsion angles	α Residue	β Residue
C(1)—C(2)—C(3)—C(4)	−54·7 (−58·5)	−51·4 (−50·0)
C(2)—C(3)—C(4)—C(5)	+54·6 (+60·5)	+53·9 (+52·0)
C(3)—C(4)—C(5)—O(5)	−55·5 (−60·0)	−59·6 (−58·3)
C(4)—C(5)—O(5)—C(1)	+59·6 (+58·2)	+64·8 (+65·1)
C(5)—O(5)—C(1)—C(2)	−60·6 (−56·1)	−61·7 (−64·9)
O(5)—C(1)—C(2)—C(3)	+57·4 (+56·3)	+53·9 (+55·7)

Exocyclic torsion angles		
O(5)—C(1)—O(1)—C(4')	+121·7 (+109·3)	
C(5)—O(5)—C(1)—O(1)	+59·9 (+64·0)	−179·9 (+176·7)
C(1)—O(1)—C(4')—C(3')		+132·8 (+129·2)
O(5)—C(5)—C(6)—O(6)	+59·1 (+60·4)	−62·4 (−67·9)
C(1)—C(2)—O(2)—H(O2)	−48·3	+75·7
C(2)—C(3)—O(3)—H(O3)	−138·8	−75·3
C(3)—C(4)—O(4)—H(O4)	+65·5	
C(5)—C(6)—O(6)—H(O6)	−70·8	+70·0
O(5)—C(1)—O(1)—H(O1)		−100·9

Vicinal C—H torsion angles		
H(C1)—C(1)—C(2)—H(C2)	56·7	173·1
H(C2)—C(2)—C(3)—H(C3)	−177·6	−173·2
H(C3)—C(3)—C(4)—H(C4)	176·4	175·0
H(C4)—C(4)—C(5)—H(C5)	−176·5	−179·6
H(C6A)—C(6)—C(5)—H(C5)	−179·9	60·2
H(C6B)—C(6)—C(5)—H(C5)	61·8	−57·0

Table 7. *Puckering parameters* (*Cremer & Pople, 1975*) *for the α- and β-glucopyranose rings in β-maltose*

The values in parentheses are those from the crystal structures of methyl α-D-glucopyranoside (Berman & Kim, 1968) and methyl β-D-glucopyranoside hemihydrate (Jeffrey & Takagi, 1977).

	α Residue	β Residue
q_2	0·010 (0·023) Å	0·050 (0·072) Å
q_3	0·572 (0·567) Å	0·577 (0·593) Å
$θ$	1·0 (2·4)°	5·0 (7·0)°
$φ_2$	119·6 (116)°	50·7 (38·8)°
Q	0·572 (0·568) Å	0·577 (0·598) Å

value for a β-anomeric bond of close to 1·38 Å. This is in agreement with the predictions from theoretical calculations on model compounds (Jeffrey, Pople & Radom, 1972, 1974), and with the results from the more recent comparison of a series of methyl α- and methyl β-pyranosides (Jeffrey & Takagi, 1977).

The mean O—H bond length is 0·970 Å. The trend for the longer bonds to be associated with the shorter hydrogen bonds is not significant in terms of the standard deviations and riding-motion corrections (Table 4). The mean C—H bond length is 1·095 Å. With one exception, each C—H bond on the β residue is

longer than its α counterpart; their mean values differ by 0·015 Å (3σ). This cannot be accounted for by any difference in the thermal motion of the two residues, as shown by the rigid-body analysis of the thermal motion given in Table 4, with the possible exception of the C—H bonds on the primary alcohol groups. We assume, therefore, that this discrepancy is due to some systematic error, not included in the σ's. The torsion angles between the vicinal C—H bonds are all within $\pm 7°$ of the ideal 180 or 60°, as shown in Table 6.

The majority of the bond valence angles* are within 1° of 109·5°. Notable exceptions are those at the linkage oxygen C(1)—O(1)—C(4′), 117·8°, and at the ring oxygens, 113·8 and 112·7°. Similar values of 117·6, 114·7 and 111·5° were observed in methyl β-maltopyranoside. That of the α residue is the larger, but the difference is not as great as was observed with the methyl pyranosides (Jeffrey & Takagi, 1977). In both residues, the C(4)—C(5)—C(6) angle is increased (112·2 and 114·2°) at the expense of C(6)—C(5)—O(5) (105·7 and 107·5°). There is a tendency for angles involving C—H bonds to be less than tetrahedral and there are eight examples of C—C—H or O—C—H angles of 106–108°. The H—O(W)—H angle is 105·1°.

The other dimensions of interest are the torsion angles of the linkage bonds C(1)—O(1) and O(1)—C(4′) given in Table 6. These are strongly influenced by the geometrical requirements for the formation of an intramolecular hydrogen bond between the two residues. The preferred angle for an α-glycosidic bond, C(1)—O(1), of close to +60°, as found in the methyl α-pyranosides, is not observed. The linkage conformation is such that C(1)—H and C(4′)—H are partially eclipsed, making an angle of 26·3°, with a H···H nonbonding distance of 2·071 Å.

The O(1)···O(4) and O(1)···O(1′) distances in the α- and β-glucopyranose residues are 4·41 and 5·47 Å, in good agreement with the values of 4·39 and 5·44 Å in the methyl α- and methyl β-glucosides. Other dimensions, which are useful in constructing polymer models, are the conformational angles H(C1)—C(1)—O(1)—C(4′) +4·8°, C(1)—O(1)—C(4′)—H(C4′) +13·3°, and the 'ring-twist' angles (Rees & Scott, 1971) C(4′)—O(1)—C(1)···O(4) 180°, C(1)—O(1)—C(4′)···O(1′) −163°. The latter two are in good agreement with the values of 181 and −167° reported from the X-ray study. The angle between the virtual bonds O(4)···O(1) and O(1)···O(1′) is 157·0°.

This research has been performed under the auspices

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* See deposition footnote.

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