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The Crystal and Molecular Structure of Trehalose Dihydrate*

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The crystal structure of trehalose dihydrate has been solved by direct methods and refined to an R index of 0·057 using anisotropic refinement. The space group is $P2_12_12_1$ and four formula units of $C_{12}H_{22}O_{11}.2H_2O$ are contained in the unit cell of dimensions $a=17{\cdot}90$, $b=12{\cdot}21$ and $c=7{\cdot}586$ Å. The two glucopyranose residues in the trehalose molecule have the chair $^4C_1$ form, and are bonded by the $\alpha\ 1 \rightarrow 1$ glycosidic link in approximate twofold symmetry. Departures from symmetry are found in torsion angles about the $\alpha\ 1 \rightarrow 1$ link and in conformations of the primary alcohol groups O(6)H and O(6′)H. The C–O bond lengths show systematic trends similar to those in other α-pyranose sugars and at the same time show some characteristic features related to the $\alpha\ 1 \rightarrow 1$ link of the two glucose residues. There are two indirect intramolecular hydrogen bonds incorporating water molecules. Neither the ring oxygens nor the glycosidic linkage oxygen accept hydrogen bonds. The molecular packing in the crystal is mainly determined by the hydrogen bonds.

Introduction

Trehalose is a naturally occurring disaccharide found in trehalamanna, the cocoons of a parasitic beetle (*Laurinus* species). It also occurs in a variety of fungi, *e.g. Amanita muscaria*, and is isolated from bakers' yeast Another name of trehalose is mycose; trehalose-6,6′-dimycolate was confirmed as a 'code factor' in the mycobacterium *Tuberculosis* (Bloch *et al.*, 1957). Trehalose consists of two D-glucopyranoses connected between carbons 1 and 1′ by an α-glycosidic link (Hudson, 1916), and it is more completely described as *O*-α-D-glucopyranosyl-(1 → 1)-α-D-glucopyranoside. Two other diastereoisomers of trehalose, α,β and β,β forms, were obtained as synthetic products (Fischer & Delbrück, 1909; Schlubach & Maurer, 1925; Haworth & Hickinbottom, 1931).

The present X-ray work on trehalose dihydrate crystal was performed in order to establish the conformation of the molecule, which is expected to have twofold symmetry. The C–O–C–O–C–O–C conjugated system in this molecule is interesting in connexion with the nature of the C(1)–O(1) bond which has been the subject of some discussion (Berman, Chu & Jeffrey, 1967; Sundaralingam, 1968).

Experimental

Transparent plate-like crystals of trehalose dihydrate were obtained from ethanol solution by evaporation.

Crystal data are as follows.

Trehalose dihydrate, $C_{12}H_{22}O_{11}.2H_2O$, M.W. 378·35, space group $P2_12_12_1$ (No. 19) from systematic absences $h00$ with h odd, $0k0$ with k odd, $00l$ with l odd.
$a=17{\cdot}90\pm0{\cdot}02$ Å, $b=12{\cdot}21\pm0{\cdot}01$, $c=7{\cdot}586\pm0{\cdot}008$, $Z=4$
$D_x=1{\cdot}517$ g.cm^{-3}, $D_m=1{\cdot}515$ g.cm^{-3} (at 25°C)
$\mu_{\text{Cu }K\alpha}=12{\cdot}28$ cm^{-1}, $\lambda_{\text{Cu }K\alpha}=1{\cdot}5418$ Å.

Unit-cell parameters were determined from the $hk0$ and $h0l$ Weissenberg photographs calibrated with NaCl ($a_0=5{\cdot}6396$ Å). The crystal density was measured by the flotation method in a mixture of carbon tetrachloride and chloroform.

Three-dimensional intensity data were collected by visual estimation of a series of Weissenberg photographs recorded with crystals of dimensions 0·37 × 0·38 × 1·23 mm mounted along the c axis, and dimensions 0·37 × 0·40 × 0·40 mm mounted along the b axis, using Ni-filtered Cu $K\alpha$ radiation. The data were correlated and reduced to structure amplitudes without absorption correction, and converted to $|E|$ data with the scale and temperature factors given by Wilson's method. The number of observed independent reflexions is 1892.

Determination and refinement of the structure

The structure was solved by the application of the symbolic-addition procedure and tangent formula refinement (Karle & Karle, 1966), using the FACOM 230–60 program for the direct phasing methods (Taga, 1971; Taga & Osaki, 1971).

The following six reflexions were selected as starting phases:

h	k	l	φ	$\|E\|$	h	k	l	φ	$\|E\|$
0	5	2	$\pi/2$	3·31	5	9	0	p	3·37
4	0	3	$\pi/2$	2·74	8	1	1	q	2·19
9	4	0	$\pi/2$	2·42	4	5	5	r	2·25

The phases of 117 reflexions with $|E|>1{\cdot}6$ were determined by application of formula (3·18) of Karle & Karle (1966). The tangent formula refinement was applied to 324 reflexions with $|E|>1{\cdot}3$ for the 32 cases given by assuming the systematic phase values for the

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* An article describing three independent determinations of this crystal structure appears on pp. 3145-3158.

symbols. The resulting E map for the case $p=\pi/2$, $q=\pi$, $r=\pi/2$, which gave the small R value of Drew *et al.* (1969), revealed the 23 highest peaks, which corresponded to 12 carbon and 11 oxygen atoms of a reasonable model for the trehalose molecule. The two water molecules were found in the Fourier map phased on these 23 atoms of trehalose molecule. Four cycles of isotropic diagonal least-squares refinement involving these water molecules by the *SDLF* program (T.T.) reduced the R index to 0·108. Successive difference Fourier map revealed all the hydrogen atoms at reasonable positions.

Refinement of the carbon and oxygen parameters and hydrogen positional parameters was finished by the block-diagonal least-squares program *HBLS* by Ashida in UNICS (1967). Five cycles of anisotropic refinement with the weighting scheme of Cruickshank (1961) resulted in all the parameter shifts being less than their estimated standard deviations. The final R index was 0·057 for all the observed reflexions. The final atomic parameters of the carbon and oxygen atoms are given in Table 1 and the positional parameters of the hydrogen atoms in Table 2. The structure factors calculated at the final cycle, using the atomic scattering factors given in the *International Tables for X-ray Crystallography* (1962), are listed in Table 3.

Molecular conformation

The molecular conformation of trehalose with the identification of each atom is shown in Figs. 1 and 2. Both pyranose rings have the chair $^4C_1$ form. The conformation angles of the rings (Table 4) are in the same range as those observed in other pyranose sugars

Table 2. *Fractional atomic coordinates* ($\times 10^3$) *of the hydrogen atoms in trehalose dihydrate*

Standard deviations given in parentheses refer to the last decimal places of the respective values.

	x	y	z
H(C1)	916 (4)	221 (5)	428 (9)
H(C2)	995 (4)	355 (6)	560 (10)
H(C3)	880 (4)	511 (6)	420 (9)
H(C4)	1030 (4)	495 (5)	310 (9)
H(C5)	913 (4)	407 (6)	86 (9)
H(C6)	1010 (4)	453 (6)	− 78 (9)
H′(C6)	1002 (4)	319 (6)	− 74 (10)
H(O2)	902 (4)	323 (6)	730 (9)
H(O3)	931 (4)	591 (6)	647 (10)
H(O4)	949 (4)	615 (5)	237 (10)
H(O6)	1102 (4)	352 (6)	134 (9)
H(C1′)	823 (4)	217 (5)	157 (10)
H(C2′)	698 (4)	242 (6)	156 (10)
H(C3′)	710 (4)	363 (5)	459 (10)
H(C4′)	645 (4)	157 (6)	464 (10)
H(C5′)	791 (4)	213 (5)	598 (9)
H(C6′)	733 (4)	8 (6)	543 (9)
H(C6′)	728 (4)	57 (5)	735 (9)
H(O2′)	747 (4)	431 (6)	185 (10)
H(O3′)	592 (4)	364 (5)	452 (10)
H(O4′)	667 (4)	297 (5)	724 (10)
H(O6′)	847 (4)	− 27 (6)	568 (9)
H(*W*1)	745 (4)	397 (6)	883 (9)
H′(*W*1)	793 (4)	399 (6)	731 (9)
H(*W*2)	887 (4)	127 (5)	773 (9)
H′(*W*2)	940 (4)	151 (6)	893 (10)

Table 1. *Fractional atomic coordinates and thermal parameters in trehalose dihydrate*

Temperature factor expression: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$. Standard deviations given in parentheses refer to the last decimal place of the respective values. All the parameters are $\times 10^4$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	9162 (2)	2950 (4)	3975 (6)	13 (1)	27 (3)	79 (7)	1 (3)	4 (5)	4 (8)
C(2)	9410 (2)	3810 (4)	5288 (6)	13 (1)	32 (3)	74 (7)	5 (3)	0 (5)	8 (8)
C(3)	9337 (2)	4942 (4)	4462 (6)	12 (1)	27 (3)	88 (7)	−1 (3)	2 (5)	−5 (8)
C(4)	9796 (2)	4969 (4)	2768 (6)	12 (1)	28 (3)	83 (7)	−1 (3)	−3 (5)	6 (8)
C(5)	9632 (2)	4000 (3)	1541 (6)	13 (1)	28 (3)	63 (6)	−2 (3)	−3 (5)	1 (8)
C(6)	10204 (3)	3901 (4)	53 (6)	13 (1)	40 (3)	69 (7)	−2 (3)	3 (5)	−1 (8)
O(1)	8414 (2)	3205 (2)	3523 (4)	11 (1)	25 (2)	86 (5)	−1 (2)	4 (4)	−6 (6)
O(2)	8972 (2)	3770 (3)	6862 (5)	19 (1)	47 (3)	85 (5)	2 (3)	6 (4)	5 (7)
O(3)	9611 (2)	5791 (3)	5544 (5)	19 (1)	44 (2)	129 (6)	−7 (3)	11 (4)	−19 (7)
O(4)	9656 (2)	5917 (3)	1756 (5)	28 (1)	27 (2)	98 (6)	−2 (3)	1 (5)	6 (6)
O(5)	9642 (2)	2977 (3)	2479 (4)	13 (1)	24 (2)	85 (5)	1 (2)	8 (4)	5 (6)
O(6)	10951 (2)	3981 (3)	658 (5)	12 (1)	49 (2)	110 (6)	−1 (3)	5 (4)	22 (7)
C(1′)	8013 (3)	2366 (4)	2638 (6)	15 (2)	31 (3)	73 (7)	0 (3)	3 (5)	−8 (8)
C(2′)	7242 (3)	2847 (4)	2235 (6)	16 (2)	32 (3)	66 (7)	−4 (3)	−4 (5)	1 (8)
C(3′)	6822 (2)	3072 (4)	3929 (6)	12 (1)	32 (3)	73 (7)	3 (3)	−4 (5)	4 (8)
C(4′)	6806 (2)	2084 (4)	5133 (6)	12 (1)	35 (3)	87 (7)	−1 (3)	5 (5)	4 (8)
C(5′)	7588 (2)	1599 (3)	5340 (6)	12 (1)	24 (2)	73 (6)	−2 (3)	2 (5)	0 (7)
C(6′)	7553 (3)	489 (4)	6242 (7)	15 (2)	35 (3)	112 (8)	1 (3)	7 (5)	1 (9)
O(2′)	7307 (2)	3810 (3)	1183 (4)	24 (1)	39 (2)	57 (5)	−1 (3)	−3 (4)	14 (6)
O(3′)	6078 (2)	3417 (3)	3502 (5)	16 (1)	64 (3)	94 (6)	12 (3)	0 (4)	17 (8)
O(4′)	6513 (2)	2374 (3)	6795 (5)	18 (1)	45 (2)	101 (6)	4 (3)	15 (4)	18 (7)
O(5′)	7948 (2)	1422 (3)	3691 (4)	14 (1)	20 (2)	98 (5)	−1 (2)	8 (4)	−1 (6)
O(6′)	8274 (2)	119 (3)	6787 (5)	18 (1)	40 (2)	98 (6)	9 (3)	−1 (4)	2 (7)
O(W1)	7493 (2)	4156 (3)	7710 (5)	23 (1)	47 (2)	79 (5)	3 (3)	5 (4)	−2 (7)
O(W2)	9040 (2)	1780 (3)	8487 (6)	26 (2)	52 (3)	191 (8)	4 (3)	−31 (6)	4 (9)

(*cf.* Kim & Jeffrey, 1967). The two glucose residues are not exactly related by a twofold axis through the O(1) atom. The torsion angles about the C(1)–O(1) bond significantly differ from those about the C(1′)–O(1) bond (Table 4). The planes O(1)C(1)C(2) and O(1)C(1′)C(2′) make angles 14·4 and 2·1° respectively with the plane C(1)O(1)C(1′). The C(2) atom deviates about 0·36 Å from the least-squares plane through C(1), O(1), C(1′) and C(2′), which is expressed (in Å) by the following equation:

$$0{\cdot}3265x+0{\cdot}3427y-0{\cdot}8809z=3{\cdot}9202\,.$$

Discrepancy in the two glucose residues is also found in the conformations of the primary alcohol groups O(6)H and O(6′)H. The C(6)–O(6) bond has the '$-sc$' conformation as was found in α-D-glucose (Brown & Levy, 1965), while the C(6′)–O(6′) bond has the '$+sc$' conformation as was found in the β-D-glucose (Ferrier, 1963).

Table 3. *Observed and calculated structure factors in trehalose dihydrate*

Columns are: index, $5\times|F_{\rm obs}|$, $5\times|F_{\rm calc}|$.

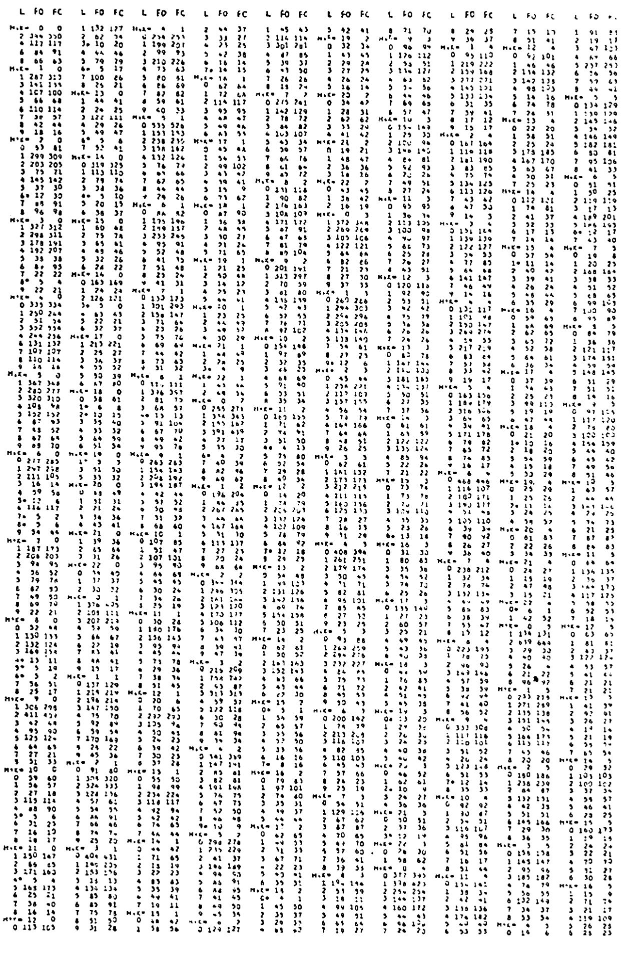

Table 3 (*cont.*)

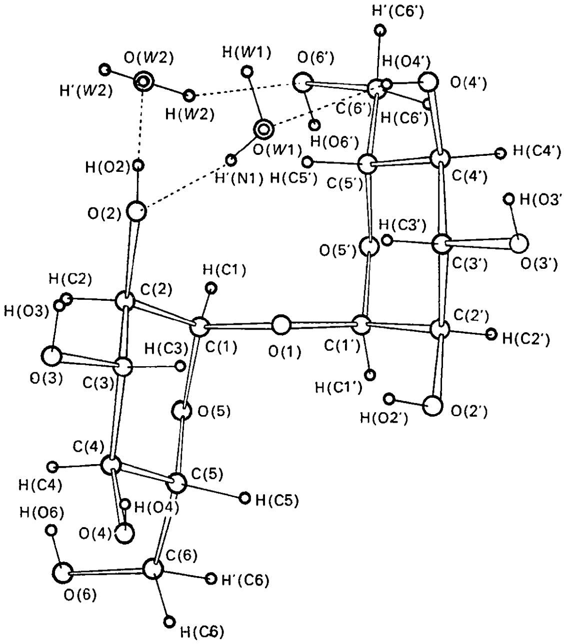

Fig. 1. Molecular conformation of trehalose dihydrate viewed along the approximate twofold axis.

Bond lengths and angles with their estimated standard deviations are given in Table 5. The C–C bond lengths range from 1·513 to 1·535 Å and none differs significantly from the mean value of 1·523 Å. The C–OH bond lengths range from 1·410 to 1·435 Å with the mean value of 1·422 Å. The C–O bond lengths associated with the anomeric carbon atoms and the ring oxygen atoms show systematic trends similar to those observed in other α-pyranose sugars (Berman *et al.*, 1967; Sundaralingam, 1968), and at the same time show some characteristic features related to the α 1 → 1 link of the two pyranose rings. Variations of the C–O bond lengths from the mean value are +0·015, +0·001, −0·005, −0·001, −0·015 and +0·002 Å for C(5)–O(5), O(5)–C(1), C(1)–O(1), O(1)–C(1′), C(1′)–O(5′) and O(5′)–C(5′), respectively. In each pyranose ring, the glycosidic C(1)–O(1) bond length is close to the normal value and the two ring C–O bond lengths are apparently different, which is the same as in other pyranose sugars having the axial C(1)–O(1)R bonds, *cf.* sucrose (Brown & Levy, 1963), methyl β-maltoside (Chu & Jeffrey, 1967) or α-methyl-D-galactoside-6-bromohydrin (Robertson & Sheldrick, 1965). The C(1)–O(1) and C(1′)–O(1) bond lengths, especially, correspond most closely to that in sucrose, where there is a C–O–C–O–C–O–C conjugated system in the α link. Comparing the C–O bonds in the different pyranose rings, the bonds in one ring are longer than the corresponding bonds in the other, consisting of primed atoms; the difference in the bond lengths between C(1)–O(5) and C(1′)–O(5′) is just over 3·0σ and that between C(5)–O(5) and C(5′)–O(5′) is 2·6σ. As a consequence, the C(1′)–O(5′) bond is shortened and the

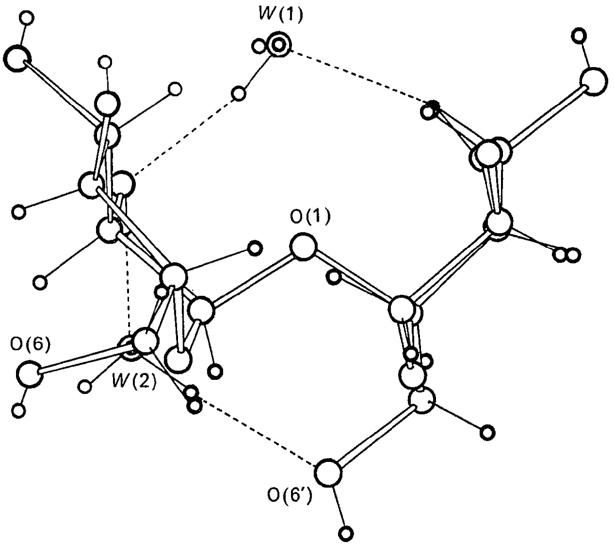

Fig. 2. Molecular conformation of trehalose dihydrate viewed perpendicular to the approximate twofold axis.

Table 5. *Bond lengths and bond angles with estimated standard deviations in parentheses refered to the last decimal places of the respective values*

C(1) –C(2)	1·514 (6) Å	O(5) –C(1) –O(1)	111·9 (4)°
C(2) –C(3)	1·523 (6)	C(2) –C(1) –O(1)	106·4 (3)
C(3) –C(4)	1·526 (6)	C(2) –C(1) –O(5)	109·4 (3)
C(4) –C(5)	1·533 (6)	C(1) –C(2) –O(2)	111·5 (4)
C(5) –C(6)	1·528 (6)	C(3) –C(2) –O(2)	109·1 (4)
C(1) –O(1)	1·417 (5)	C(1) –C(2) –C(3)	109·5 (4)
C(2) –O(2)	1·429 (6)	C(2) –C(3) –O(3)	113·5 (4)
C(3) –O(3)	1·410 (6)	C(4) –C(3) –O(3)	106·7 (3)
C(4) –O(4)	1·412 (5)	C(2) –C(3) –C(4)	108·6 (4)
C(5) –O(5)	1·437 (5)	C(3) –C(4) –O(4)	112·3 (4)
C(6) –O(6)	1·425 (5)	C(5) –C(4) –O(4)	105·6 (4)
C(1) –O(5)	1·423 (5)	C(3) –C(4) –C(5)	113·1 (4)
C(1′)–C(2′)	1·531 (6)	C(4) –C(5) –O(5)	111·6 (4)
C(2′)–C(3′)	1·513 (6)	C(6) –C(5) –O(5)	106·8 (3)
C(3′)–C(4′)	1·514 (6)	C(4) –C(5) –C(6)	112·4 (4)
C(4′)–C(5′)	1·526 (6)	C(5) –C(6) –O(6)	112·9 (4)
C(5′)–C(6′)	1·519 (6)	O(5′)–C(1′)–O(1)	111·3 (4)
C(1′)–O(1)	1·421 (5)	C(2′)–C(1′)–O(1)	105·9 (4)
C(2′)–O(2′)	1·425 (5)	C(2′)–C(1′)–O(5′)	110·7 (4)
C(3′)–O(3′)	1·435 (5)	C(1′)–C(2′)–O(2′)	110·7 (4)
C(4′)–O(4′)	1·411 (6)	C(3′)–C(2′)–O(2′)	111·5 (4)
C(5′)–O(5′)	1·424 (6)	C(1′)–C(2′)–C(3′)	110·3 (4)
C(6′)–O(6′)	1·429 (6)	C(2′)–C(3′)–O(3′)	108·8 (4)
C(1′)–O(5′)	1·407 (5)	C(4′)–C(3′)–O(3′)	110·7 (4)
		C(2′)–C(3′)–C(4′)	112·2 (4)
		C(3′)–C(4′)–O(4′)	110·2 (4)
		C(5′)–C(4′)–O(4′)	110·3 (4)
		C(3′)–C(4′)–O(5′)	110·7 (4)
		C(4′)–C(5′)–O(5′)	112·6 (4)
		C(6′)–C(5′)–O(5′)	106·2 (3)
		C(4′)–C(5′)–C(6′)	110·8 (3)
		C(5′)–C(6′)–O(6′)	112·1 (4)
		C(1) –O(1) –C(1′)	115·7 (3)
		C(1) –O(5) –C(5)	114·1 (3)
		C(1′)–O(5′)–C(5′)	114·3 (3)

Table 4. *Conformation angles*

Within the pyranose rings			
O(5)–C(1)–C(2)–C(3)	62·7°	O(5′)–C(1′)–C(2′)–C(3′)	55·5°
C(1)–C(2)–C(3)–C(4)	−56·8	C(1′)–C(2′)–C(3′)–C(4′)	−51·6
C(2)–C(3)–C(4)–C(5)	50·0	C(2′)–C(3′)–C(4′)–C(5′)	48·8
C(3)–C(4)–C(5)–O(5)	−47·9	C(3′)–C(4′)–C(5′)–O(5′)	−50·2
C(4)–C(5)–O(5)–C(1)	53·9	C(4′)–C(5′)–O(5′)–C(1′)	60·0
C(5)–O(5)–C(1)–C(2)	−61·7	C(5′)–O(5′)–C(1′)–C(2′)	−59·1
Outside the pyranose rings			
C(2)–C(1)–O(1)–C(1′)	−165·6°	C(2′)–C(1′)–O(1) –C(1)	−177·9°
O(5)–C(1)–O(1)–C(1′)	75·0	O(5′)–C(1′)–O(1) –C(1)	61·7
C(4)–C(1)–O(1)–C(1′)	134·1	C(4′)–C(1′)–O(1) –C(1)	120·7
C(4)–C(5)–C(6)–O(6)	47·4	C(4′)–C(5′)–C(6′)–O(6′)	−167·7
O(5)–C(5)–C(6)–O(6)	−75·3	O(5′)–C(5′)–C(6′)–O(6′)	69·8

C(5)–O(5) bond is lengthened in the C–O bonds involved in the C–O–C–O–C–O–C conjugated system. The C(1′)–O(5′) bond length of 1·407 Å corresponds to the short C(1)–O(5) bond lengths found in sucrose or methyl β-maltoside. Such a feature might be related to the asymmetry of the molecular conformation and to the difference in the packings of the two glucose residues in the crystal.

The carbon valence angles inside the rings range from 108·6 to 113·1° with a mean value of 110·9° and those outside the rings range from 105·6 to 113·5° with a mean value of 109·6°. The valence angles of the anomeric carbon atoms C(1) and C(1′) show similar trends pointed out by Sundaralingam (1968). The smallest angle C(5)–C(4)–O(4) of 105·6° may be related to the asymmetric configuration of the hydrogen bonds at the O(4) atom. The valence angles 114·1 and 114·3° of the ring oxygen atoms are close to the corresponding angle of 114·0° in methyl α-D-glucopyranoside (Berman & Kim, 1968). The C(1)–O(1)–C(1′) glycosidic bridge angle of 115·7° is comparable with those found in other oligosaccharides: 116·1° in cellobiose (Chu & Jeffrey, 1968), 117·6° in methyl β-maltoside, 114·4° in sucrose, 122·1° in raffinose (Berman, 1970), 119·4° in 1-kestose (Jeffrey & Park, 1972) or 116·9° in planteose (Rohrer,1972).

Hydrogen bonding

The arrangement of the molecules in the crystal is shown in Fig. 3. The molecules are linked by an extensive network of hydrogen bonds, whose distances and angles are given in Table 6. All the hydroxyl groups act as a donor and an acceptor except O(4′)H, which is a donor and accepts two hydrogen bonds. None of the ring oxygen atoms accepts hydrogen bonds. The glycosidic linkage oxygen atom does not have a short intermolecular contact less than 3·5 Å. The water molecule *W*(1) has four hydrogen bonds in a distorted tetrahedral configuration, while the water molecule *W*(2) has three hydrogen bonds in an approximately planar trigonal arrangement. The hydrogen bond system in the crystal consists of these hydroxyl groups and the water molecules, as is shown in the following donor–acceptor sequence:

Table 6. *Hydrogen bond distances and angles*

i	*j*	*k*	*D*(*ij*)	*D*(*jk*)	Angle *ijk*
C(2)	O(2)	O(*W*1)		2·756 Å	135·5°
C(2)	O(2)	O(*W*2)		2·727	112·6
C(3)	O(3)	O(3′) (*b*)		2·737	125·5
C(3)	O(3)	O(*W*2) (*d*)		2·799	140·4
C(4)	O(4)	O(3′) (*b*′)		2·911	140·3
C(4)	O(4)	O(4′) (*b*′)		2·955	134·4
C(6)	O(6)	O(4′) (*e*)		2·733	122·1
C(6)	O(6)	O(6′) (*d*′)		2·697	107·3
C(2′)	O(2′)	O(*W*1) (*b*′)		2·764	121·2
C(2′)	O(2′)	O(*W*1) (*a*′)		2·689	133·4
C(3′)	O(3′)	O(3) (*b*′)		2·737	135·0
C(3′)	O(3′)	O(4) (*b*)		2·911	108·1
C(4′)	O(4′)	O(4) (*b*)		2·955	115·6
C(4′)	O(4′)	O(6) (*c*)		2·733	128·0
C(4′)	O(4′)	O(*W*1)		2·880	100·3
C(6′)	O(6′)	O(6) (*f*′)		2·679	115·2
C(6′)	O(6′)	O(*W*2)		2·766	110·5
O(2)	O(*W*1)	O(2′) (*b*)	2·765 Å	2·764	86·1
O(2′) (*b*)	O(*W*1)	O(2′) (*a*)	2·764	2·690	124·6
O(2′) (*a*)	O(*W*1)	O(4′)	2·690	2·880	92·4
O(4′)	O(*W*1)	O(2)	2·880	2·765	113·5
O(2)	O(*W*1)	O(2′) (*a*)	2·765	2·690	108·6
O(2′) (*b*)	O(*W*1)	O(4′)	2·764	2·880	131·1
O(2)	O(*W*2)	O(3) (*f*)	2·727	2·799	122·8
O(3) (*f*)	O(*W*2)	O(6′)	2·799	2·766	103·5
O(6′)	O(*W*2)	O(2)	2·766	2·727	114·9

Intermolecular non-bonding distances less than 3·5 Å

i	*j*	*D*(*ij*)
O(2)	C(6) (*a*)	3·277 Å
O(5)	O(4′) (*e*)	3·421

Symmetry code

–	*x*	*y*	*z*				
a	*x*	*y*	1·0+*z*	*a*′	*x*	*y*	−1·0+*z*
b	1·5−*x*	1·0−*y*	0·5+*z*	*b*′	1·5−*x*	1·0−*y*	−0·5+*z*
c	−0·5+*x*	0·5−*y*	1·0−*z*	*c*′	−0·5+*x*	0·5−*y*	−*z*
d	2·0−*x*	0·5+*y*	1·5−*z*	*d*′	2·0−*x*	0·5+*y*	0·5−*z*
e	0·5+*x*	0·5−*y*	1·0−*z*	*e*′	0·5+*x*	0·5−*y*	−*z*
f	2·0−*x*	−0·5+*y*	1·5−*z*	*f*′	2·0−*x*	−0·5+*y*	0·5−*z*

$$\begin{tikzcd}
 & & & & & {} \arrow[d] & & & & \\
 & & & {} \arrow[r] & \mathrm{O(6)}(c) \arrow[d] & \mathrm{O(2')}(b) \arrow[d] & & & & \\
{} \arrow[r] & \mathrm{O(3)}\,(b') \arrow[r] & \mathrm{O(3')} \arrow[r] & \mathrm{O(4)}(b) \arrow[r] & \mathrm{O(4')} \arrow[r] & \mathrm{O}(W1) \arrow[r] \arrow[d] & \mathrm{O(2)} \arrow[r] & \mathrm{O}(W2) \arrow[r] \arrow[d] & \mathrm{O(3)}(f) \arrow[r] & {} \\
 & & & & & \mathrm{O(2')}(a) \arrow[d] & & \mathrm{O(6')} \arrow[r] & \mathrm{O(6)}(f) \arrow[r] & {} \\
 & & & & & {} & & & &
\end{tikzcd}$$

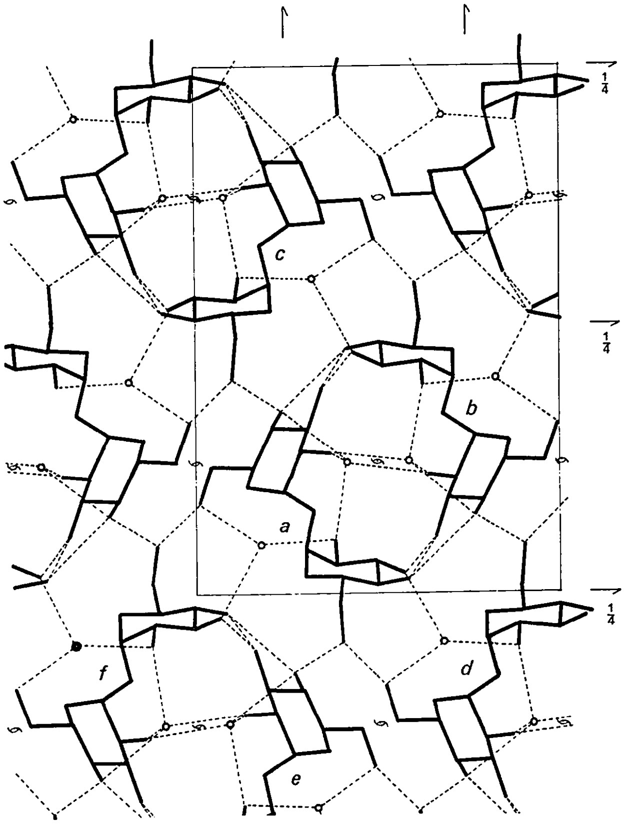

Fig. 3. The projection of the structure along the c axis. The broken lines are hydrogen bonds.

The hydrogen bonds O(2')···O(W1) form the infinite spiral chain about the twofold screw axis in the c direction. The water molecule W(2) links together the molecules related by another screw axis in the b direction.

There is no intramolecular hydrogen bonding as in other disaccharides, sucrose, cellobiose (Brown, 1966) or methyl β-maltoside. However, the water molecule W(1) acts as a bridge between O(2) and O(4') in the same molecule and the water W(2) also acts as another bridge between O(2) and O(6') (Figs. 1 and 2). These hydrogen bonds O(2)···W(1)···O(4') and O(2)···W(2)···O(6') may be looked upon as indirect intramolecular hydrogen bonds and the asymmetric torsion angles about the 1 → 1 link, which were already mentioned, may be under the influence of these hydrogen bondings.

All the computations in this work were performed on the FACOM 230–60 at the Data Processing Center, Kyoto University.

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