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*Acta Cryst.* (1995). **C51**, 1007–1012

### $\alpha,\alpha$ -allo-Trehalose Trihydrate†

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(Received 11 October 1994; accepted 26 October 1994)

#### Abstract

The low-temperature X-ray structure of  $\alpha,\alpha$ -allo-trehalose trihydrate ( $\alpha$ -D-allopyranosyl  $\alpha$ -D-allopyranoside trihydrate,  $C_{12}H_{22}O_{11} \cdot 3H_2O$ ) is reported. There are two conformationally similar, but symmetry-independent sugar molecules plus six water molecules in the asymmetric unit. The sugar molecules lack internal crystallographic symmetry because of the relative conformations of the hydroxymethyl substituents and the torsion angles about the glycosidic linkage. The pyranose rings have slightly distorted  ${}^4C_1$  conformations. The sugar and water molecules are linked by many hydrogen bonds to form a complex three-dimensional network. The intramolecular O...O contact distances are larger than those reported in a calcium complex of  $\alpha,\alpha$ -allo-trehalose.

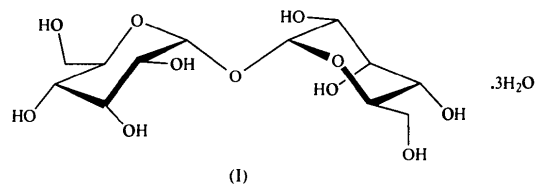
#### Comment

Studies (Birch, Cowell & Eyton, 1970; Lee & Birch, 1975) have shown that isomolar solutions of  $\alpha,\alpha$ -

† Crystal Structures of Trehalose Derivatives, Part 10. For Part 9, see Linden & Lee (1995).

trehalose, its derivatives and the corresponding methyl  $\alpha$ -D-glycopyranoside analogues are equisweet, suggesting that only one half of the disaccharide molecule is actually involved in the interaction with the taste-receptor site. In pyranose structures, the C(4) and C(3) hydroxy groups have been shown (Birch & Lee, 1974; Lindley & Birch, 1975) to be the Shallenberger AH,B glucophore (Shallenberger & Acree, 1967). However, the sweetness of D-galactose (Shallenberger & Acree, 1971),  $\alpha,\alpha$ -galacto-trehalose (Lee & Birch, 1975), D-allose and  $\alpha,\alpha$ -allo-trehalose (Lee, 1994) is only about half that of D-glucose, even though in each of these sugars the group C(4)—OH,C(3)—O acts as the AH,B glucophore. For this reason, we are interested in the three-dimensional molecular structure of these analogues of trehalose.

Furthermore, pyranose sugars and cyclohexitols are known to form strong complexes with cations if the six-membered ring contains an axial-equatorial-axial sequence of hydroxy groups (Angyal, 1974).  $\alpha,\alpha$ -allo-Trehalose has such an arrangement of hydroxy groups in each of its sugar rings. In fact, being a 1,1-linked disaccharide,  $\alpha,\alpha$ -allo-trehalose actually has an axial-equatorial-axial-equatorial-axial sequence of five O atoms and it has been found to complex with  $CaCl_2$  to form the pentadentate complex,  $\alpha,\alpha$ -allo-trehalose. $CaCl_2 \cdot 5H_2O$ , where the cation has an unusual ninefold coordination mode with five O atoms of the sugar and four water molecules (Ollis, James, Angyal & Pojer, 1978). It might be expected that the geometrical constraints induced by the coordination would cause conformational changes in the sugar molecule and it is of interest to compare the conformations of the free and coordinated sugars. Therefore, we now report the X-ray structure of  $\alpha,\alpha$ -allo-trehalose trihydrate, (I).



The asymmetric unit of (I) contains two independent molecules of  $\alpha,\alpha$ -allo-trehalose (molecules A and B) plus six independent water molecules. A comparison of the atomic coordinates of the eight residues in the asymmetric unit, by using the *MISSYM* routine (Le Page, 1987, 1988) of the program *PLATON* (Spek, 1990), confirmed that the molecules were unrelated by any crystallographic symmetry from a space group of higher symmetry. Molecules A and B, with their atomic numbering, are shown in Fig. 1. For comparison purposes, the atomic numbering for molecule B was obtained by adding 20 to the atom numbers of the corresponding atoms in molecule A. Fig. 1 also depicts the correct absolute configuration of the molecules as established by the synthesis of the compound. The two

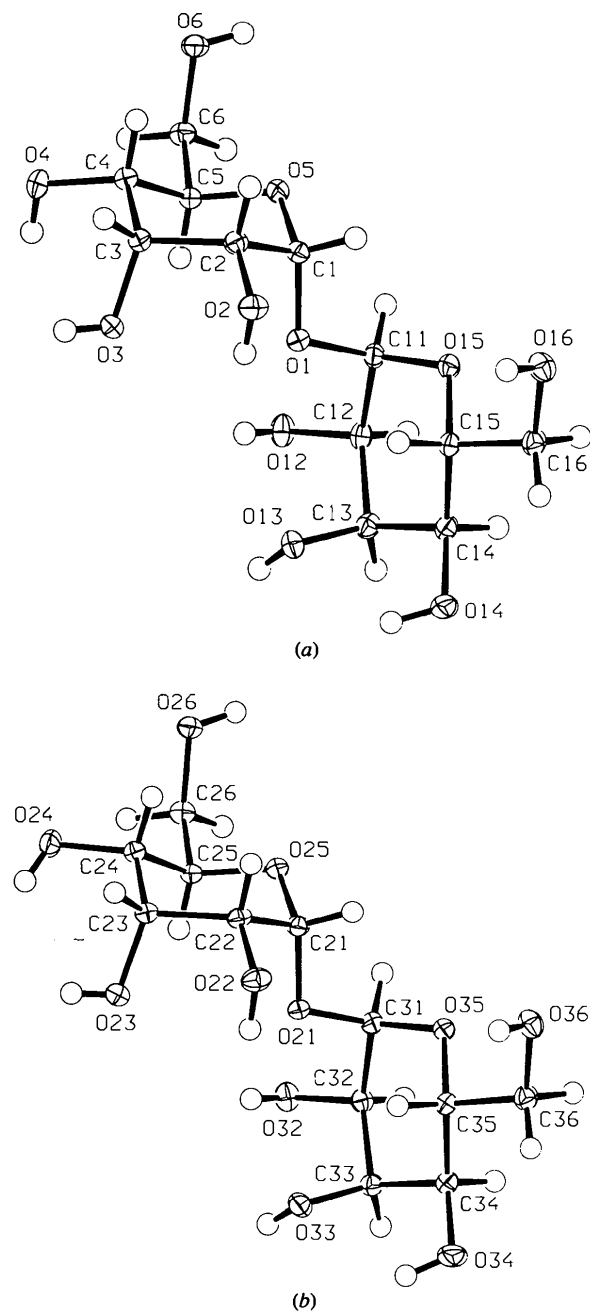


Fig. 1. Views of (a) molecule A and (b) molecule B of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

independent sugar molecules have very similar molecular dimensions and conformations. The maximum differences in bond lengths, bond angles and torsion angles are 0.013 (2) Å, 2.8 (1) and 7.9 (2)°, respectively. All bond lengths and angles (Table 2) are within expected ranges, and generally agree with the corresponding values in other  $\alpha,\alpha$ -trehalose compounds and other sugars.

The C—O bond lengths associated with the anomeric C atoms and the ring O atoms show systematic trends similar to those observed in other  $\alpha$ -pyranose sugars (Berman, Chu & Jeffrey, 1967).

Ollis, James, Angyal & Pojer (1978) reported that  $\alpha,\alpha$ -*allo*-trehalose complexes with CaCl<sub>2</sub> to form  $\alpha,\alpha$ -*allo*-trehalose·CaCl<sub>2</sub>·5H<sub>2</sub>O, where the sugar molecule acts as a pentadentate ligand and is chelated to the calcium ion *via* O(1), O(2), O(2'), O(3) and O(3') [for comparison purposes, O(2') and O(3') would correspond with O(12) and O(13), respectively, in molecule A of (I)]. The free and complexed sugars have no significant differences in bond lengths, not even for the C—OH bonds involving the O atoms that are coordinated to the Ca<sup>2+</sup> cation. The maximum difference of 0.022 Å is within the confidence limits of the structures. More notably, there are several small but significant differences in the bond angles (approximately 4–6°) involving the O atoms of the hydroxy groups that are chelated to the cation. In particular, the angle at the bridging O atom is approximately 5° wider in the complexed sugar and the O(1)—C(1)—C(2) angle has become approximately 6° smaller. There are also some substantial differences in some of the torsion angles. The largest differences involve the torsion angles about the O(1)—C(1) and O(1)—C(11) bonds of the glycosidic bridge, which vary between the free and complexed sugars by approximately 18 and 30°, respectively. Some of the torsion angles about ring C—C bonds also vary by up to 10°, which is an indication of small changes in the conformations of the pyranose rings. These changes in the torsion and bond angles are accompanied by smaller O...O spacings between the chelated O atoms (Table 4) and are attributed to the constraining effects of chelation of the O atoms to a cation, which require that the distances between coordinated O atoms are shorter than the usual distances between vicinal O atoms on a pyranoid ring. Thus, the O(1)...O(2) and O(2)...O(3) distances in both sugar rings of the CaCl<sub>2</sub> complex are shorter by 0.16–0.22 and 0.07–0.21 Å, respectively, compared with those of (I). The *syn*-axial O(1)...O(3) distances in the complexed sugar are also 0.20–0.33 Å shorter than those in (I). In addition, the large changes in the torsion angles about the glycosidic bridge may be partly due to the need for the sugar molecule to wrap itself around the Ca<sup>2+</sup> cation as it undergoes the pentadentate coordination. Such geometrical distortions of chelated sugars have been observed previously (Bugg & Cook, 1972; Cook & Bugg, 1973; Wood, James & Angyal, 1977; Ollis, James, Angyal & Pojer, 1978).

Excluding the hydroxymethyl groups, the two D-hexopyranosyl residues within each sugar molecule of (I) have approximate C<sub>2</sub> symmetry. As observed with anhydrous  $\alpha,\alpha$ -trehalose (Jeffrey & Nanni, 1985), its dihydrate (Brown *et al.*, 1972; Taga, Senma & Osaki, 1972) and many of its derivatives (Lee & Koh, 1994; Lee, Koh, Xu & Linden, 1994; Lee & Linden,

1994), the largest conformational difference between the two hexopyranosyl residues within each molecule occurs at the hydroxymethyl substituents. The torsion angles about the C(5)—C(6) and C(15)—C(16) bonds of molecule *A* differ by approximately  $124^\circ$ , while the corresponding torsion angles in molecule *B* differ by approximately  $128^\circ$ . The hydroxymethyl substituents at C(5) and C(25) adopt the *gauche-gauche* conformation and those at C(15) and C(35) possess the *gauche-trans* conformation. This same arrangement is found in both anhydrous and hydrated  $\alpha,\alpha$ -trehalose, and the chelated  $\alpha,\alpha$ -*allo*-trehalose. $\text{CaCl}_2\cdot 5\text{H}_2\text{O}$  complex (Ollis, James, Angyal & Pojer, 1978).

The two glycosidic torsion angles [O(ring)—C—O(bridge)—C] in each of the symmetry-independent molecules [ $74.7(2)$  and  $75.5(2)^\circ$  for molecule *A*;  $74.8(1)$  and  $73.2(1)^\circ$  for molecule *B*] indicate that the sugar rings are more symmetrically oriented about the central, glycosidic O atom than in  $\alpha,\alpha$ -trehalose dihydrate and  $\alpha,\alpha$ -*allo*-trehalose. $\text{CaCl}_2\cdot 5\text{H}_2\text{O}$ , in which the glycosidic torsion angles differ by  $13.1$  and  $12.0(3)^\circ$ , respectively. In anhydrous  $\alpha,\alpha$ -trehalose, the glycosidic torsion angles differ by less than  $1^\circ$ . This indicates the ease with which the glycosidic torsion angle may be influenced by the crystal-packing environment.

Each pyranose ring in (I) has the  ${}^4C_1$  conformation. The puckering parameters (Cremer & Pople, 1975) (Table 5) suggest slightly distorted chair conformations ( $\theta = 8$ – $11^\circ$ ). The distortion is in the direction of the  $E_5$  conformation ( $\varphi = 300^\circ$ ). The tendency towards coplanarity of O(5), C(1), C(2), C(3) and C(4) causes the C(1)—C(2)—C(3) angle to widen to  $114.2(1)^\circ$ . The corresponding angles in the other three pyranose rings are also in the range  $114$ – $115^\circ$ . Widening of the C(1)—C(2)—C(3) angle is not observed in the  $\alpha,\alpha$ -*allo*-trehalose. $\text{CaCl}_2\cdot 5\text{H}_2\text{O}$  complex (Ollis, James, Angyal & Pojer, 1978), presumably because of the effects of chelation on the ring geometry. The angles at the ring O atoms of (I) ( $114$ – $115^\circ$ ) are in the normal ranges for such angles in pyranose rings. This is in contrast to the corresponding angles in the complexed sugar, which are enlarged to  $117.1(2)$  and  $116.3(2)^\circ$ .

The two  $\alpha,\alpha$ -*allo*-trehalose and six water molecules in the asymmetric unit interact *via* a complex system of hydrogen bonds (Table 3) to form a three-dimensional hydrogen-bonding network through the crystal lattice (Fig. 2). Every hydroxy group of the sugar molecules and every H atom of the six water molecules act as hydrogen-bond donors for intermolecular hydrogen bonds. One of the hydroxy groups in each sugar molecule acts additionally as a donor for an intramolecular interaction [O(14)—H(14)···O(13) and O(34)—H(34)···O(33)]; these donors thereby form bifurcated hydrogen bonds. Two of the water molecules act as acceptors of two hydrogen bonds; the remaining four water molecules act as acceptors for only one interaction. Four of the water molecules hydrogen bond to each

other in a four-link chain, as well as to neighbouring sugar molecules; the other two water molecules interact only with sugar molecules. Each hydroxy group acts as an acceptor for at least one hydrogen bond; O(2), O(13), O(16), O(22), O(33) and O(36) accept two hydrogen bonds. The ring O atom, O(25), also acts as an acceptor; however, none of the other ring O atoms is involved in hydrogen-bonding interactions. This last feature destroys any potential crystallographic symmetry between the independent molecules and is presumably the main reason behind the presence of two molecules of the sugar in the asymmetric unit.

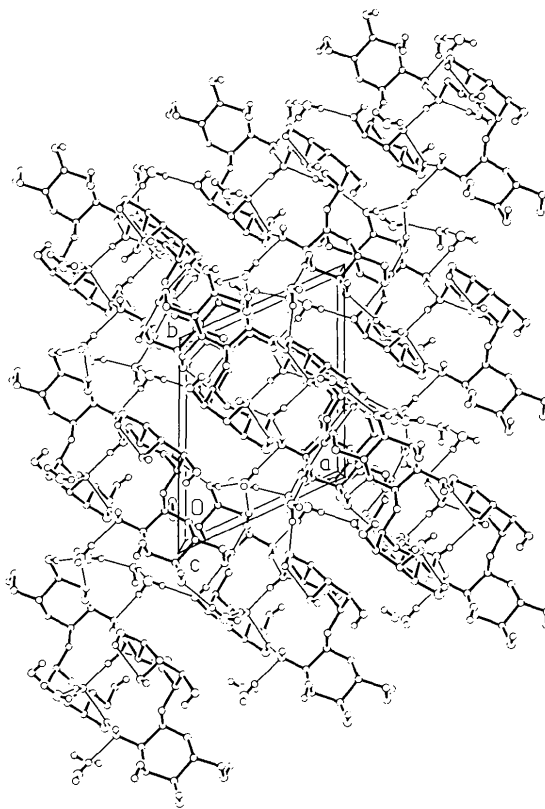


Fig. 2. The packing of (I) viewed down *c*. Thin lines indicate the hydrogen-bonding interactions.

The O···O distances between O(3) and O(4) and between the corresponding atoms in the other pyranose rings of molecules *A* and *B* (Table 4) are normal for *gauche* 1,2-hydroxy groups in pyranose sugars. The distances are within the limits which permit these groups to function as the Shallenberger AH,B glucophore (Shallenberger & Acree, 1967). However, the intensity of the sweetness of (I) is only half that of methyl  $\alpha$ -D-glucopyranoside (Lee, 1994). This has also been observed for  $\alpha,\alpha$ -*galacto*-trehalose (Lee & Birch, 1975).

In both of these trehalose analogues there is an axial hydroxy group, either at C(3), as in the *allo* analogue or at C(4), as in the *galacto* analogue, whereas in methyl  $\alpha$ -D-glucopyranoside these hydroxy groups occupy equatorial positions. Since the groups C(4)—OH, C(3)—O have been shown to be the sweet AH, B glucophore in pyranose structures (Birch & Lee, 1974), it appears that the stereo arrangement of the O(3) and O(4) substituents is an important factor in determining the glucophore's efficiency in eliciting the sweet taste. We are presently studying the taste properties of methyl  $\alpha$ -D-altropyranoside and  $\alpha$ , $\alpha$ -*altro*-trehalose.

## Experimental

Synthesis was performed according to the procedure of Birch, Lee, Richardson & Ali (1976). Suitable crystals were obtained from an aqueous acetone solution.

### Crystal data

C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>·3H<sub>2</sub>O

$M_r = 396.34$

Triclinic

$P1$

$a = 9.400(1) \text{ \AA}$

$b = 11.029(1) \text{ \AA}$

$c = 9.153(1) \text{ \AA}$

$\alpha = 96.144(9)^\circ$

$\beta = 96.84(1)^\circ$

$\gamma = 65.235(7)^\circ$

$V = 853.8(2) \text{ \AA}^3$

$Z = 2$

$D_x = 1.542 \text{ Mg m}^{-3}$

### Data collection

Rigaku AFC-5R diffractometer

$\omega/2\theta$  scans

Absorption correction:

none

5251 measured reflections

5251 independent reflections,  
(no averaging)

5106 observed reflections

$[I > 2\sigma(I)]$

Mo  $K\alpha$  radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 24  
reflections

$\theta = 19.5\text{--}20^\circ$

$\mu = 0.143 \text{ mm}^{-1}$

$T = 173(1) \text{ K}$

Prism

$0.48 \times 0.33 \times 0.30 \text{ mm}$

Colourless

$R_{\text{int}} = 0.009$  for 180 Friedel  
pairs

$\theta_{\text{max}} = 30^\circ$

$h = 0 \rightarrow 13$

$k = -14 \rightarrow 14$

$l = -12 \rightarrow 12$

3 standard reflections

monitored every 150

reflections

intensity decay: insignificant

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	$x$	$y$	$z$	$U_{\text{eq}}$
O(1)	0.90050	0.30360	0.85770	0.0142 (4)
O(2)	0.6239 (2)	0.2757 (2)	0.7444 (2)	0.0179 (4)
O(3)	0.7856 (2)	0.1179 (2)	0.9784 (2)	0.0158 (4)
O(4)	1.0179 (2)	-0.1416 (2)	0.9347 (2)	0.0186 (4)
O(5)	1.0510 (2)	0.1085 (2)	0.7192 (2)	0.0162 (4)
O(6)	1.2722 (2)	-0.1611 (2)	0.6762 (2)	0.0179 (4)
O(12)	1.1091 (2)	0.3372 (2)	1.0894 (2)	0.0185 (4)
O(13)	0.7916 (2)	0.5157 (2)	1.1165 (2)	0.0163 (4)
O(14)	0.6640 (2)	0.7576 (2)	1.0049 (2)	0.0201 (4)
O(15)	0.8958 (2)	0.4873 (2)	0.7442 (2)	0.0150 (4)
O(16)	0.6340 (2)	0.6330 (2)	0.5474 (2)	0.0186 (4)
C(1)	0.9027 (2)	0.2173 (2)	0.7296 (2)	0.0150 (5)
C(2)	0.7730 (2)	0.1669 (2)	0.7261 (2)	0.0145 (5)
C(3)	0.8088 (2)	0.0576 (2)	0.8323 (2)	0.0140 (5)
C(4)	0.9774 (2)	-0.0481 (2)	0.8227 (2)	0.0141 (5)
C(5)	1.0940 (2)	0.0163 (2)	0.8340 (2)	0.0136 (5)
C(6)	1.2609 (2)	-0.0849 (2)	0.8136 (2)	0.0158 (5)
C(11)	0.9839 (2)	0.3827 (2)	0.8384 (2)	0.0140 (5)
C(12)	1.0315 (2)	0.4383 (2)	0.9875 (2)	0.0145 (5)
C(13)	0.8965 (2)	0.5564 (2)	1.0565 (2)	0.0145 (5)
C(14)	0.8010 (2)	0.6577 (2)	0.9423 (2)	0.0147 (5)
C(15)	0.7552 (2)	0.5895 (2)	0.8013 (2)	0.0132 (5)
C(16)	0.6794 (3)	0.6897 (2)	0.6831 (2)	0.0168 (5)
O(21)	0.2902 (2)	0.7628 (2)	0.3468 (2)	0.0136 (4)
O(22)	0.5680 (2)	0.7863 (2)	0.3032 (2)	0.0182 (4)
O(23)	0.4072 (2)	0.9598 (2)	0.5320 (2)	0.0169 (4)
O(24)	0.1743 (2)	1.2281 (2)	0.4617 (2)	0.0200 (4)
O(25)	0.1400 (2)	0.9536 (2)	0.2162 (2)	0.0149 (4)
O(26)	-0.0769 (2)	1.2305 (2)	0.1838 (2)	0.0180 (4)
O(32)	0.0837 (2)	0.7313 (2)	0.5214 (2)	0.0178 (4)
O(33)	0.4039 (2)	0.5501 (2)	0.5813 (2)	0.0170 (4)
O(34)	0.5267 (2)	0.3048 (2)	0.4318 (2)	0.0250 (5)
O(35)	0.2931 (2)	0.5788 (2)	0.1895 (2)	0.0147 (4)
O(36)	0.5537 (2)	0.4363 (2)	0.0176 (2)	0.0189 (4)
C(21)	0.2889 (2)	0.8450 (2)	0.2369 (2)	0.0136 (5)
C(22)	0.4201 (2)	0.8946 (2)	0.2725 (2)	0.0142 (5)
C(23)	0.3860 (2)	1.0107 (2)	0.3902 (2)	0.0139 (5)
C(24)	0.2194 (2)	1.1159 (2)	0.3563 (2)	0.0137 (5)
C(25)	0.1006 (2)	1.0531 (2)	0.3398 (2)	0.0135 (5)
C(26)	-0.0657 (2)	1.1542 (2)	0.3045 (2)	0.0162 (5)
C(31)	0.2067 (2)	0.6828 (2)	0.2902 (2)	0.0138 (5)
C(32)	0.1620 (2)	0.6274 (2)	0.4154 (2)	0.0142 (5)
C(33)	0.2977 (2)	0.5095 (2)	0.4866 (2)	0.0147 (5)
C(34)	0.3909 (3)	0.4082 (2)	0.3680 (2)	0.0157 (5)
C(35)	0.4352 (2)	0.4774 (2)	0.2552 (2)	0.0138 (5)
C(36)	0.5127 (3)	0.3782 (2)	0.1298 (2)	0.0176 (5)
O(41)	0.9090 (2)	0.4776 (2)	0.3959 (2)	0.0242 (5)
O(42)	0.3747 (2)	0.1316 (2)	-0.0039 (2)	0.0264 (5)
O(43)	0.3932 (2)	0.1740 (2)	0.7135 (2)	0.0259 (5)
O(44)	0.6770 (2)	0.9892 (2)	0.1348 (2)	0.0221 (5)
O(45)	0.7872 (2)	0.9075 (2)	0.4170 (2)	0.0326 (6)
O(46)	0.2791 (3)	0.5927 (2)	0.8438 (2)	0.0304 (6)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Molecule A		Molecule B	
O(1)—C(1)	1.425 (2)	O(21)—C(21)	1.421 (2)
O(1)—C(11)	1.431 (2)	O(21)—C(31)	1.430 (2)
O(2)—C(2)	1.427 (2)	O(22)—C(22)	1.423 (2)
O(3)—C(3)	1.427 (2)	O(23)—C(23)	1.428 (2)
O(4)—C(4)	1.436 (2)	O(24)—C(24)	1.430 (2)
O(5)—C(1)	1.414 (2)	O(25)—C(21)	1.418 (2)
O(5)—C(5)	1.444 (2)	O(25)—C(25)	1.454 (2)
O(6)—C(6)	1.425 (2)	O(26)—C(26)	1.426 (2)
O(12)—C(12)	1.423 (2)	O(32)—C(32)	1.422 (2)
O(13)—C(13)	1.425 (2)	O(33)—C(33)	1.426 (2)
O(14)—C(14)	1.433 (2)	O(34)—C(34)	1.420 (2)
O(15)—C(11)	1.415 (2)	O(35)—C(31)	1.413 (2)
O(15)—C(15)	1.443 (2)	O(35)—C(35)	1.449 (2)
O(16)—C(16)	1.431 (2)	O(36)—C(36)	1.434 (2)
C(1)—C(2)	1.534 (2)	C(21)—C(22)	1.536 (2)
C(2)—C(3)	1.531 (2)	C(22)—C(23)	1.532 (2)

### Refinement

Refinement on  $F$

$R = 0.0270$

$wR = 0.0320$

$S = 1.817$

5106 reflections

690 parameters

All H-atom parameters  
refined

$w = 1/[\sigma^2(F_o) + (0.01F_o)^2]$

$(\Delta/\sigma)_{\text{max}} = 0.0004$

$\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors  
from *International Tables*  
for *Crystallography* (1992,  
Vol. C, Tables 4.2.6.8 and  
6.1.1.4)

Absolute configuration:  
assigned to agree with the  
known chirality at C(5)  
and C(25), as established  
by the synthesis of the  
compound

C(3)—C(4)	1.530 (2)	C(23)—C(24)	1.528 (2)	O(23)—C(23)—C(24)—O(24)	58.2 (2)
C(4)—C(5)	1.526 (2)	C(24)—C(25)	1.528 (2)	O(25)—C(21)—O(21)—C(31)	74.8 (1)
C(5)—C(6)	1.516 (2)	C(25)—C(26)	1.512 (2)	O(25)—C(21)—C(22)—C(23)	46.9 (2)
C(11)—C(12)	1.531 (2)	C(31)—C(32)	1.531 (2)	O(25)—C(25)—C(24)—C(23)	-61.7 (2)
C(12)—C(13)	1.528 (2)	C(32)—C(33)	1.529 (2)	O(25)—C(25)—C(26)—O(26)	-67.6 (2)
C(13)—C(14)	1.527 (2)	C(33)—C(34)	1.530 (2)	O(26)—C(26)—C(25)—C(24)	50.5 (2)
C(14)—C(15)	1.532 (2)	C(34)—C(35)	1.536 (2)	C(21)—O(25)—C(25)—C(24)	63.7 (1)
C(15)—C(16)	1.521 (2)	C(35)—C(36)	1.519 (2)	C(21)—C(22)—C(23)—C(24)	-46.3 (2)
C(1)—O(1)—C(11)	110.4 (1)	C(21)—O(21)—C(31)	110.2 (1)	C(22)—C(21)—O(21)—C(31)	-160.5 (1)
C(1)—O(5)—C(5)	114.4 (1)	C(21)—O(25)—C(25)	114.3 (1)	C(22)—C(21)—O(25)—C(25)	-55.8 (2)
C(11)—O(15)—C(15)	115.2 (1)	C(31)—O(35)—C(35)	114.3 (1)	C(22)—C(23)—C(24)—C(25)	53.6 (2)
O(1)—C(1)—O(5)	111.9 (1)	O(21)—C(21)—O(25)	111.4 (1)	O(21)—C(31)—C(32)—O(32)	51.6 (2)
O(1)—C(1)—C(2)	110.9 (1)	O(21)—C(21)—C(22)	111.4 (1)	O(21)—C(31)—C(32)—C(33)	-76.6 (2)
O(5)—C(1)—C(2)	110.5 (1)	O(25)—C(21)—C(22)	111.1 (1)	C(21)—O(21)—C(31)—C(32)	-162.3 (1)
O(2)—C(2)—C(1)	111.0 (1)	O(22)—C(22)—C(21)	111.0 (1)	O(32)—C(32)—C(33)—O(33)	-52.3 (2)
O(2)—C(2)—C(3)	112.2 (1)	O(22)—C(22)—C(23)	112.5 (1)	O(33)—C(33)—C(34)—O(34)	50.7 (2)
C(1)—C(2)—C(3)	114.2 (1)	C(21)—C(22)—C(23)	114.9 (1)	O(35)—C(31)—O(21)—C(21)	73.2 (1)
O(3)—C(3)—C(2)	108.8 (1)	O(23)—C(23)—C(22)	108.9 (1)	O(35)—C(31)—C(32)—C(33)	48.2 (2)
O(3)—C(3)—C(4)	110.7 (1)	O(23)—C(23)—C(24)	112.4 (1)	O(35)—C(35)—C(34)—C(33)	-57.8 (2)
C(2)—C(3)—C(4)	110.5 (1)	C(22)—C(23)—C(24)	108.8 (1)	O(35)—C(35)—C(36)—O(36)	60.3 (2)
O(4)—C(4)—C(3)	110.6 (1)	O(24)—C(24)—C(23)	113.4 (1)	O(36)—C(36)—C(35)—C(34)	178.4 (1)
O(4)—C(4)—C(5)	110.7 (1)	O(24)—C(24)—C(25)	110.7 (1)	C(31)—O(35)—C(35)—C(34)	62.7 (2)
C(3)—C(4)—C(5)	111.3 (1)	C(23)—C(24)—C(25)	110.8 (1)	C(31)—C(32)—C(33)—C(34)	-45.5 (2)
O(5)—C(5)—C(4)	109.3 (1)	O(25)—C(25)—C(24)	107.8 (1)	C(32)—C(31)—O(35)—C(35)	-57.3 (2)
O(5)—C(5)—C(6)	106.8 (1)	O(25)—C(25)—C(26)	107.1 (1)	C(32)—C(33)—C(34)—C(35)	50.1 (2)
C(4)—C(5)—C(6)	112.7 (1)	C(24)—C(25)—C(26)	112.3 (1)		
O(6)—C(6)—C(5)	112.0 (1)	O(26)—C(26)—C(25)	112.1 (1)		
O(1)—C(11)—O(15)	111.7 (1)	O(21)—C(31)—O(35)	111.6 (1)		
O(1)—C(11)—C(12)	110.7 (1)	O(21)—C(31)—C(32)	111.0 (1)		
O(15)—C(11)—C(12)	110.8 (1)	O(35)—C(31)—C(32)	111.1 (1)		
O(12)—C(12)—C(11)	112.3 (1)	O(32)—C(32)—C(31)	111.0 (1)		
O(12)—C(12)—C(13)	110.7 (1)	O(32)—C(32)—C(33)	112.1 (1)		
C(11)—C(12)—C(13)	114.0 (1)	C(31)—C(32)—C(33)	114.4 (1)		
O(13)—C(13)—C(12)	112.2 (1)	O(33)—C(33)—C(32)	112.4 (1)		
O(13)—C(13)—C(14)	107.7 (1)	O(33)—C(33)—C(34)	108.1 (1)		
C(12)—C(13)—C(14)	110.9 (1)	C(32)—C(33)—C(34)	110.3 (1)		
O(14)—C(14)—C(13)	109.4 (1)	O(34)—C(34)—C(33)	111.1 (1)		
O(14)—C(14)—C(15)	110.7 (1)	O(34)—C(34)—C(35)	110.9 (1)		
C(13)—C(14)—C(15)	111.5 (1)	C(33)—C(34)—C(35)	111.1 (1)		
O(15)—C(15)—C(14)	109.0 (1)	O(35)—C(35)—C(34)	109.0 (1)		
O(15)—C(15)—C(16)	106.3 (1)	O(35)—C(35)—C(36)	106.3 (1)		
C(14)—C(15)—C(16)	110.1 (1)	C(34)—C(35)—C(36)	110.4 (1)		
O(16)—C(16)—C(15)	113.2 (1)	O(36)—C(36)—C(35)	113.8 (1)		

## Molecule A

O(1)—C(1)—C(2)—O(2)	52.3 (2)
O(1)—C(1)—C(2)—C(3)	-75.8 (2)
O(2)—C(2)—C(3)—O(3)	-51.1 (2)
O(3)—C(3)—C(4)—O(4)	52.2 (2)
O(5)—C(1)—O(1)—C(11)	74.7 (2)
O(5)—C(1)—C(2)—C(3)	48.9 (2)
O(5)—C(5)—C(4)—C(3)	-57.1 (2)
O(5)—C(5)—C(6)—O(6)	-63.0 (2)
O(6)—C(6)—C(5)—C(4)	57.0 (2)
C(1)—O(5)—C(5)—C(4)	63.1 (2)
C(1)—C(2)—C(3)—C(4)	-45.5 (2)
C(2)—C(1)—O(1)—C(11)	-161.4 (1)
C(2)—C(1)—O(5)—C(5)	-58.2 (2)
C(2)—C(3)—C(4)—C(5)	49.4 (2)
O(1)—C(11)—C(12)—O(12)	50.5 (2)
O(1)—C(11)—C(12)—C(13)	-76.4 (2)
C(1)—O(1)—C(11)—C(12)	-160.5 (1)
O(12)—C(12)—C(13)—O(13)	-52.8 (2)
O(13)—C(13)—C(14)—O(14)	49.3 (2)
O(15)—C(11)—O(1)—C(1)	75.5 (2)
O(15)—C(11)—C(12)—C(13)	48.2 (2)
O(15)—C(15)—C(14)—C(13)	-56.3 (2)
O(15)—C(15)—C(16)—O(16)	61.8 (2)
O(16)—C(16)—C(15)—C(14)	179.8 (1)
C(11)—O(15)—C(15)—C(14)	61.8 (2)
C(11)—C(12)—C(13)—C(14)	-45.6 (2)
C(12)—C(11)—O(15)—C(15)	-57.3 (2)
C(12)—C(13)—C(14)—C(15)	49.5 (2)

## Molecule B

O(21)—C(21)—C(22)—O(22)	51.2 (2)
O(21)—C(21)—C(22)—C(23)	-77.9 (2)
O(22)—C(22)—C(23)—O(23)	-51.8 (2)

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O(2)—H(2)...O(36 <sup>i</sup> )	0.78 (3)	2.14 (3)	2.879 (2)	160 (3)
O(3)—H(3)...O(44 <sup>ii</sup> )	0.75 (3)	1.91 (3)	2.666 (2)	176 (3)
O(4)—H(4)...O(25 <sup>iii</sup> )	0.80 (3)	2.23 (3)	2.964 (2)	153 (2)
O(6)—H(6)...O(23 <sup>iv</sup> )	0.78 (3)	1.94 (3)	2.706 (2)	167 (3)
O(12)—H(12)...O(26 <sup>v</sup> )	0.74 (3)	2.00 (3)	2.737 (2)	173 (3)
O(13)—H(13)...O(41 <sup>vi</sup> )	0.79 (3)	1.89 (3)	2.665 (2)	172 (3)
O(14)—H(14)...O(13)	0.86 (3)	2.17 (3)	2.686 (2)	118 (2)
O(14)—H(14)...O(22 <sup>vii</sup> )	0.86 (3)	2.25 (3)	2.921 (2)	135 (2)
O(16)—H(16)...O(33)	0.85 (3)	1.89 (3)	2.736 (2)	173 (2)
O(22)—H(22)...O(16)	0.85 (3)	1.98 (3)	2.801 (2)	162 (3)
O(23)—H(23)...O(43 <sup>viii</sup> )	0.75 (3)	1.97 (3)	2.704 (2)	167 (3)
O(24)—H(24)...O(43 <sup>ix</sup> )	0.75 (3)	2.11 (3)	2.835 (2)	164 (3)
O(26)—H(26)...O(3 <sup>x</sup> )	0.80 (3)	1.85 (3)	2.648 (2)	169 (3)
O(32)—H(32)...O(6 <sup>xi</sup> )	0.77 (3)	1.95 (3)	2.712 (2)	169 (3)
O(33)—H(33)...O(46)	0.75 (3)	1.98 (3)	2.709 (2)	165 (3)
O(34)—H(34)...O(2)	0.81 (3)	2.23 (3)	2.907 (2)	142 (3)
O(34)—H(34)...O(33)	0.81 (3)	2.25 (3)	2.737 (2)	119 (2)
O(36)—H(36)...O(13 <sup>xii</sup> )	0.77 (3)	1.99 (3)	2.752 (2)	171 (3)
O(41)—H(41)...O(16)	0.77 (3)	2.12 (3)	2.859 (2)	163 (3)
O(41)—H(41)...O(24 <sup>xiii</sup> )	0.79 (3)	2.11 (3)	2.899 (2)	169 (3)
O(42)—H(42)...O(44 <sup>xiv</sup> )	0.79 (3)	2.08 (3)	2.825 (2)	156 (3)
O(42)—H(42)...O(12 <sup>xv</sup> )	0.81 (3)	1.93 (3)	2.730 (2)	167 (3)
O(43)—H(43)...O(42 <sup>xvi</sup> )	0.76 (3)	1.96 (3)	2.715 (2)	178 (3)
O(43)—H(43)...O(2)	0.81 (3)	1.99 (3)	2.804 (2)	176 (3)
O(44)—H(44)...O(14 <sup>xvii</sup> )	0.82 (4)	1.93 (4)	2.744 (2)	174 (3)
O(44)—H(44)...O(45)	0.76 (3)	2.01 (3)	2.763 (2)	171 (3)
O(45)—H(45)...O(22)	0.83 (3)	2.17 (3)	2.934 (2)	154 (3)
O(45)—H(45)...O(32 <sup>xviii</sup> )	0.81 (3)	1.96 (3)	2.772 (2)	177 (3)
O(46)—H(46)...O(4 <sup>xix</sup> )	0.88 (3)	2.17 (3)	3.040 (2)	170 (2)
O(46)—H(46)...O(36 <sup>xx</sup> )	0.80 (4)	2.09 (4)	2.837 (2)	155 (3)

Symmetry codes: (i)  $x, y, 1+z$ ; (ii)  $x, y-1, 1+z$ ; (iii)  $1+x, y-1, 1+z$ ; (iv)  $1+x, y-1, z$ ; (v)  $x, 1+y, z$ ; (vi)  $x-1, 1+y, z-1$ ; (vii)  $x-1, 1+y, z$ ; (viii)  $x, y, z-1$ ; (ix)  $x, y-1, z$ ; (x)  $x-1, y, z-1$ ; (xi)  $1+x, y, z$ .

Table 4. Intramolecular O...O contact distances less than 3.2 Å

Molecule A	Molecule B	CaCl <sub>2</sub> complex*		
O(1)...O(5)	2.352 (2)	O(21)...O(25)	2.345 (2)	2.364
O(1)...O(15)	2.356 (2)	O(21)...O(35)	2.352 (2)	2.354
O(1)...O(2)	2.809 (2)	O(21)...O(22)	2.808 (2)	2.638
O(1)...O(12)	2.816 (2)	O(21)...O(32)	2.804 (2)	2.602
O(1)...O(3)	3.033 (2)	O(21)...O(23)	3.094 (2)	2.780
O(1)...O(13)	3.084 (2)	O(21)...O(33)	3.111 (2)	2.830
O(2)...O(3)	2.780 (2)	O(22)...O(23)	2.793 (2)	2.642
O(3)...O(4)	2.802 (2)	O(23)...O(24)	2.934 (2)	2.888
O(5)...O(6)	2.843 (2)	O(25)...O(26)	2.899 (2)	2.806

O(12)···O(13)	2.828 (2)	O(32)···O(33)	2.856 (2)	2.711
O(13)···O(14)	2.686 (2)	O(33)···O(34)	2.737 (2)	2.838
O(15)···O(16)	2.852 (2)	O(35)···O(36)	2.847 (2)	2.868

\* Ollis, James, Angyal & Pojer (1978).

Table 5. Puckering parameters (Cremer & Pople, 1975) for the pyranose rings of the two symmetry-independent molecules of (I)

	Molecule A		Molecule B	
	Ring containing:		Ring containing:	
	O(5)	O(15)	O(25)	O(35)
Q (Å)	0.538	0.531	0.556	0.539
q <sub>2</sub> (Å)	0.080	0.074	0.106	0.085
q <sub>3</sub> (Å)	0.532	0.526	0.546	0.532
φ <sub>2</sub> (°)	314	309	289	306
θ (°)	8.53	8.04	11.0	9.10

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

CKL wishes to thank the National University of Singapore for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SH1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## α,α-galacto-Trehalose†

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(Received 9 November 1994; accepted 5 December 1994)

## Abstract

The low-temperature X-ray structure of α,α-galacto-trehalose (α-D-galactopyranosyl α-D-galactopyranoside, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>) is reported. Each galactopyranosyl residue in the molecule has the <sup>4</sup>C<sub>1</sub> conformation. The molecule does not possess any internal crystallographic symmetry, although the conformational differences between the two halves of the molecule are almost negligible. The molecules are linked by a large number of hydrogen bonds to form a complex three-dimensional network.

## Comment

Shallenberger (1963) attributed the low intensity of the sweetness of 'crystal' D-galactose, which is only approximately half as sweet as D-glucose, to an intramolecular hydrogen bond between its axial C(4) hydroxy group and its ring O atom. IR studies (Shallenberger, 1963) suggested this and it was also observed that as the temperature is raised, D-galactose increases in sweet-

† Crystal Structures of Trehalose Derivatives, Part 11. For Part 10, see Linden & Lee (1995).