

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including torsion angles and N...O contact distances, have been deposited with the IUCr (Reference: PA1149). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 747–751

3-O-Benzoyl-4,6;4',6'-di-O-benzylidene-2,2'-dideoxy- α,α -ribo-trehalose†

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(Received 16 November 1994; accepted 12 December 1994)

Abstract

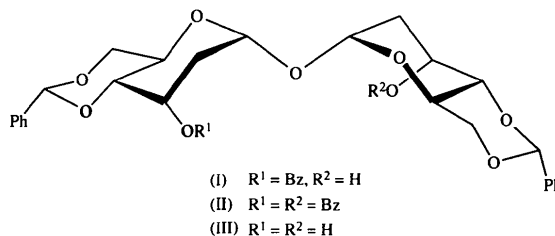
The low-temperature X-ray structure of an asymmetrically substituted derivative of α,α -trehalose, 3-O-benzoyl-4,6;4',6'-di-O-benzylidene-2,2'-dideoxy- α,α -ribo-trehalose (3-O-benzoyl-4,6-O-benzylidene-2-deoxy- α -D-ribo-hexopyranosyl 4,6-O-benzylidene-2-deoxy- α -D-ribo-hexopyranoside, $C_{33}H_{34}O_{10}$), is reported. The hexopyranosyl rings and the 1,3-dioxane rings have normal 4C_1 chair conformations, so that each half of the molecule has a double-chair conformation, resem-

† Crystal Structures of Trehalose Derivatives, Part 8. For Part 7, see Lee & Linden (1994).

bling a *trans*-decalin ring system. Each benzylidene acetal group takes the form of the thermodynamically more stable (*R*)-diastereomer with its phenyl group attached to the 1,3-dioxane ring in an equatorial orientation. The conformations about the glycosidic linkages are stabilized by the anomeric effect and by an intramolecular hydrogen bond between the lone hydroxy group and the glycosidic O atom.

Comment

α,α -Trehalose (α -D-glucopyranosyl α -D-glucopyranoside) is widely distributed in nature (Birch, 1963; El-bein, 1974; Lee, 1980). Chemical modification of the disaccharide is relatively facile and generally results in symmetrical modification of both glycosyl moieties, because of the twofold symmetry about the bridging O atom. However, most symmetrical derivatives show no trehalase activity, suggesting that one intact α -D-glucopyranosyl ring, or a close modification thereof, is a prerequisite for enzymatic recognition (Labat-Robert, 1982). Significantly, a number of such asymmetrically substituted derivatives, particularly monoaminated ones, occur naturally as antibiotically active metabolites (Arcamone & Bizioli, 1957; Umezawa, Tasuta & Muto, 1967; Uramoto, Otaka & Yonehara, 1967; Naganawa, Usui, Hamada, Maeda & Umezawa, 1974), but the selective synthetic modification of only one of the two glucosyl rings to give non-symmetrical analogues is generally difficult (Guilloux, Percheron & Defaye, 1969; Richardson & Tarelli, 1971; Hanessian & Lavallée, 1973; Defaye, Driguez, Henrissat, Gelas & Bar-Guilloux, 1978; Defaye & Horton, 1978; Dolak, Castle & Laborde, 1980). Here we report the synthesis and X-ray structure of an asymmetrically substituted derivative of α,α -trehalose: 3-O-benzoyl-4,6;4',6'-di-O-benzylidene-2,2'-dideoxy- α,α -ribo-trehalose (I).



It has been observed that several years storage of 3,3'-di-O-benzoyl-4,6;4',6'-di-O-benzylidene-2,2'-dideoxy- α,α -ribo-trehalose, (II) (Hough, Richardson & Tarelli, 1971), resulted in the loss of one of the C-3,3' benzoate substituents to yield (I). The synthesis of (I) can also be achieved by selective benzoylation of 4,6;4',6'-di-O-benzylidene-2,2'-dideoxy- α,α -ribo-trehalose, (III), using *N*-benzylimidazole in chloroform. The structure of (I) is consistent with the ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR data.

A view of (I), showing the displacement ellipsoids and the atomic numbering, is given in Fig. 1. The figure

depicts the correct absolute configuration of the molecule, which was assigned to agree with that of its known precursor. All bond lengths and angles (Table 2), except C(1)—C(2)—C(3) and C(21)—C(22)—C(23), are within expected ranges and generally agree with the corresponding values in other α,α -trehalose analogues and other sugars. The two exceptional ring angles are larger than normal, probably due to distortion arising from the formation of the cyclic benzylidene acetal (1,3-dioxane) ring and the presence of an axial substituent at C(3). 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 α -pyranose sugars (Berman, Chu & Jeffrey, 1967).

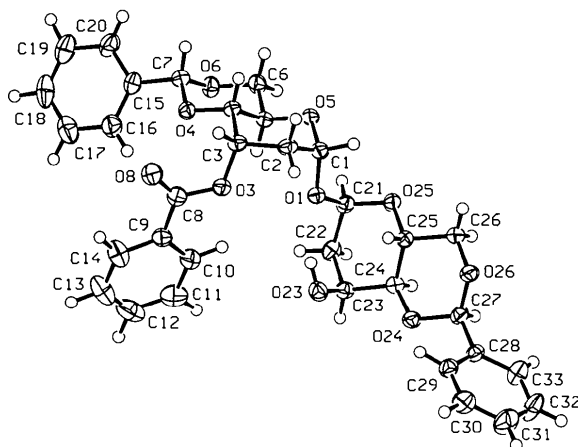


Fig. 1. View of the molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

The torsion angles about the glycosidic linkage [O(5)—C(1)—O(1)—C(21) = 57.3(3), C(1)—O(1)—C(21)—O(25) = 64.9(3) $^\circ$ and C(1)—O(1)—C(21)—C(22) = -170.9(2), C(2)—C(1)—O(1)—C(21) = -179.4(2) $^\circ$] define for each of the hexopyranosyl-O(1) groups the A1 conformer (de Hoog, Buys, Altona & Havinga, 1969), which is usually found for crystalline α -pyranosides. These angles deviate only very slightly from the most stable +synclinal and antiperiplanar conformations. In this conformation, there is no interaction between the lone-pair electrons of the glycosidic O atom and those of the ring O atoms ('rabbit-ear' interaction) (Lemieux, 1971; Pérez & Marchessault, 1979).

Each of the pyranosyl and 1,3-dioxane rings has the 4C_1 conformation. Each half of the molecule adopts a double-chair conformation, resembling a *trans*-decalin ring system, with the phenyl group attached to the 1,3-dioxane ring in an equatorial orientation so that both C(7) and C(27) have an *R* configuration. The puckering parameters (Cremer & Pople, 1975) indicate that the 4C_1 conformations of both pyranosyl rings are slightly distorted [for the pyranosyl rings containing

O(5) (ring A) and O(25) (ring B), $\theta = 10.4(3)$ and $7.0(3)^\circ$, respectively] (Table 3). The distortion of ring A is towards the E_5 conformation [$\varphi = 301(2)^\circ$] and is probably caused by the presence of the 1,3-dioxane ring and an axial benzoyl group at C(3). 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 $114.6(2)^\circ$. Ring B is distorted towards the E_4 conformation [$\varphi = 230(3)^\circ$]. A smaller widening of the C(21)—C(22)—C(23) angle [$112.8(2)^\circ$] is observed, probably because of the absence of a bulky axial substituent at C(23).

The $^{\alpha}C_{\alpha 1}$ and $^{\alpha}C_{\alpha 1'}$ conformations (Schwarz, 1973) of the two 1,3-dioxane rings are closer to ideal chair conformations [$\theta = 4.0(3)$ and $0.9(3)^\circ$] (Table 3). The ring torsion angles differ only slightly from ideal values, lying in the range 59 – 60° for the ring containing O(4) (ring C) and 56 – 61° for the ring containing O(24) (ring D).

The plane of each 1,3-dioxane ring is nearly perpendicular to the plane of its phenyl substituent. The values of the torsion angles O(6)—C(7)—C(15)—C(16) [$84.6(3)^\circ$] and O(26)—C(27)—C(28)—C(29) [$82.7(3)^\circ$] are about 24° from the value for the most stable *gauche* conformation (60°). In this slightly twisted conformation, the *ortho* H atoms of the phenyl rings will have minimum steric interactions with the H atoms bonded to C(7) and C(27), as well as with the O atoms of the respective 1,3-dioxane rings. In the less stable (*S*)-benzylidene acetal of α -D-glucopyranoside and galactopyranoside, the plane of the phenyl ring is roughly parallel to the plane containing the C(4)—H(4) and C(6)—H(6)_{ax} bonds, since this minimizes the non-bonded interactions between the *ortho* H atoms of the aromatic ring and H(4) and H(6)_{ax} (Barnes, Brimacombe, Nichols & Weakley, 1979). The plane of the phenyl ring of the benzoate group at C(3) in (I) is also roughly perpendicular to the plane of its parent sugar ring.

The lone hydroxy group at C(23) forms an intramolecular hydrogen bond with the glycosidic O atom, thereby forming a six-membered ring [O(23)—H = 0.88(3), O(23)···O(1) = 2.837(3), H(23)···O(1) = 2.06(4) Å, O(23)—H···O(1) = $147(3)^\circ$]. This interaction, together with the anomeric effect, helps to stabilize the conformations about the bridging C—O bonds.

Experimental

A cold solution of *N*-benzoylimidazole (Carey & Hodgson, 1970) (0.12 g, 1.1 equiv.) in purified chloroform (5 ml) was added to a solution of 4,6,4',6'-di-*O*-benzylidene-2,2'-dideoxy- α,α -D-ribo-trehalose (III) (Hough, Richardson & Tarelli, 1971) (0.32 g) in purified chloroform (7.5 ml). The mixture was stirred at 323–333 K for about 6–8 h, when TLC (1:2 ethyl acetate–hexane) showed the presence of a major and a minor compound and some unreacted material. The mixture was concentrated and

the resultant syrup was eluted from a short column of silica gel, using the same solvent system, to afford, in order of elution, 3,3'-di-*O*-benzoyl-4,6;4',6'-di-*O*-benzylidene-2,2'-dideoxy- α,α -D-*ribo*-trehalose, (II) {0.17 g, 38%; m.p. 514–515 K (ether); $[\alpha]_D +82^\circ$ (*c* 1, dichloromethane); [literature (Hough, Richardson & Tarelli, 1971) m.p. 514–516 K; $[\alpha]_D +81^\circ$ (chloroform)]; ^{13}C NMR (500 MHz, CDCl_3) δ 33.5 [*s*, C(2,2')], 59.3 [*s*, C(5,5')], 65.3 [*s*, C(3,3')], 69.3 [*s*, C(6,6')], 77.4 [*s*, C(4,4')], 89.8 [*s*, C(1,1')], 101.1 [*s*, PhCH]}, 3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy- α -D-*ribo*-hexopyranosyl 4,6-*O*-benzylidene-2-deoxy- α -D-*ribo*-hexopyranoside, (I) {0.13 g, 32%; m.p. 425 K (ether), $[\alpha]_D +82^\circ$ (*c* 1, chloroform); ^1H NMR (500 MHz, CDCl_3) δ 7.2–8.2 (*m*, 15 H, 3 Ph), 5.65 (*m*, 1 H, H-3), 5.62, 5.58 (2*s*, 2 H, 2 PhCH), 5.26 (*t*, 1 H, $J_{1,2ax}$ 4.1, $J_{1,2eq}$ <1 Hz, H-1), 5.26 (*d*, 1 H, $J_{1',2'ax}$ 3.6, $J_{1',2'eq}$ 0 Hz, H-1'), 4.44 (*sx*, 1 H, $J_{4,5}$ 9.6, $J_{5,6ax}$ 10.2, $J_{5,6eq}$ 5.1 Hz, H-5), 4.32 (*q*, 1 H, $J_{6ax,6eq}$ 10.2 Hz, H-6_{eq}), 4.28 (*q*, 1 H, $J_{5',6'eq}$ 5.1, $J_{6'ax,6'eq}$ 10.2 Hz, H-6'_{eq}), 4.18 (*sx*, 1 H, $J_{4',5'}$ 9.7, $J_{5',6'ax}$ 10.2 Hz, H-5'), 4.11 (*m*, 1 H, H-3'), 3.87 (*dd*, 1 H, $J_{3,4}$ 3.0 Hz, H-4), 3.78 (*t*, 1 H, H-6_{ax}), 3.60 (*t*, 1 H, H-6'_{ax}), 3.60 (*dd*, 1 H, $J_{3',4'}$ 2.8 Hz, H-4'), 2.43 (*dd*, 1 H, $J_{2'ax,2'eq}$ 15.5, $J_{2'eq,3'}$ 2.7 Hz, H-2'_{eq}), 2.30 (*dt*, 1 H, $J_{2'ax,3'}$ 3.8 Hz, H-2'_{ax}), 2.15 (*dd*, 1 H, $J_{2ax,2eq}$ 15.0, $J_{2eq,3}$ 1.9 Hz, H-2_{eq}), 2.10 (*dt*, 1 H, $J_{2ax,3}$ 4.4 Hz, H-2_{ax}); ^{13}C NMR (500 MHz, CDCl_3) δ 33.6 [*s*, C(2')], 35.5 [*s*, C(2)], 58.7 [*s*, C(5')], 59.5 [*s*, C(5)], 64.5 [*s*, C(3)], 65.8 [*s*, C(3')], 69.2, 69.3 [2*s*, C(6,6')], 77.5 [*s*, C(4)], 79.6 [*s*, C(4')], 91.2, 92.3 [2*s*, C(1,1')], 101.9, 102.1 [2*s*, 2 PhCH]; e.i. m.s. (70 eV) *m/z* 590 (M^+), 339 ($M^+ - 16 - 235$), 235 ($M^+ - 16 - 339$), 217, 105 (100%); analysis calculated for $\text{C}_{33}\text{H}_{34}\text{O}_{10}$ C 67.1, H 5.8%; found C 67.0, H 5.9% and the starting material (III) {77 mg; ^{13}C NMR (500 MHz, CDCl_3) δ 35.6 [*s*, C(2,2')], 59.2 [*s*, C(5,5')], 64.8 [*s*, C(3,3')], 69.3 [*s*, C(6,6')], 79.8 [*s*, C(4,4')], 93.9 [*s*, C(1,1')], 102.8 [*s*, PhCH]}.

Crystals of (I) were grown from an aqueous acetone solution at room temperature.

Crystal data

$\text{C}_{33}\text{H}_{34}\text{O}_{10}$
 $M_r = 590.63$
 Monoclinic
 $P2_1$
 $a = 9.604$ (6) Å
 $b = 9.994$ (4) Å
 $c = 16.072$ (5) Å
 $\beta = 103.68$ (3)°
 $V = 1498.9$ (9) Å³
 $Z = 2$
 $D_x = 1.309$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71069$ Å
 Cell parameters from 24 reflections
 $\theta = 18.5$ – 20.0°
 $\mu = 0.0905$ mm⁻¹
 $T = 173$ (1) K
 Prism
 $0.43 \times 0.33 \times 0.25$ mm
 Colourless

Data collection

Rigaku AFC-5R diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 4849 measured reflections
 4601 independent reflections
 3393 observed reflections [$I > 2\sigma(I)$]
 $R_{int} = 0.019$

$\theta_{max} = 30^\circ$
 $h = 0 \rightarrow 13$
 $k = 0 \rightarrow 14$
 $l = -21 \rightarrow 21$
 3 standard reflections monitored every 150 reflections
 intensity decay: insignificant

Refinement

Refinement on F
 $R = 0.0416$
 $wR = 0.0317$
 $S = 1.577$
 3393 reflections
 523 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o) + (0.005F_o)^2]$

$(\Delta/\sigma)_{max} = 0.01$
 $\Delta\rho_{max} = 0.20$ e Å⁻³
 $\Delta\rho_{min} = -0.17$ e Å⁻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)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^*$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O(1)	0.1509 (2)	0.25760	-0.0363 (1)	0.0284 (6)
O(3)	-0.1009 (2)	0.1380 (3)	-0.1512 (1)	0.0308 (6)
O(4)	-0.2426 (2)	0.3405 (3)	-0.2511 (1)	0.0278 (6)
O(5)	0.0241 (2)	0.4597 (3)	-0.0650 (1)	0.0306 (6)
O(6)	-0.1187 (2)	0.5225 (3)	-0.2920 (1)	0.0318 (6)
O(8)	-0.3136 (2)	0.0549 (3)	-0.2265 (1)	0.0428 (7)
O(23)	0.3047 (2)	0.0127 (3)	-0.0148 (1)	0.0354 (7)
O(24)	0.5453 (2)	0.0425 (3)	0.1289 (1)	0.0302 (6)
O(25)	0.3549 (2)	0.3540 (3)	0.0543 (1)	0.0309 (6)
O(26)	0.5290 (2)	0.1724 (3)	0.2470 (1)	0.0362 (7)
C(1)	0.0467 (3)	0.3426 (3)	-0.0128 (2)	0.0304 (9)
C(2)	-0.0897 (3)	0.2620 (4)	-0.0200 (2)	0.0298 (9)
C(3)	-0.1748 (3)	0.2372 (3)	-0.1115 (2)	0.0287 (8)
C(4)	-0.1837 (3)	0.3666 (3)	-0.1624 (2)	0.0263 (8)
C(5)	-0.0367 (3)	0.4291 (3)	-0.1532 (2)	0.0267 (8)
C(6)	-0.0544 (3)	0.5571 (3)	-0.2050 (2)	0.0312 (9)
C(7)	-0.2540 (3)	0.4601 (3)	-0.3001 (2)	0.0291 (9)
C(8)	-0.1847 (3)	0.0610 (3)	-0.2130 (2)	0.0337 (9)
C(9)	-0.0971 (3)	-0.0146 (3)	-0.2619 (2)	0.0337 (9)
C(10)	0.0492 (3)	0.0072 (4)	-0.2513 (2)	0.053 (1)
C(11)	0.1245 (4)	-0.0617 (5)	-0.3018 (3)	0.066 (2)
C(12)	0.0537 (5)	-0.1516 (5)	-0.3622 (2)	0.063 (2)
C(13)	-0.0894 (5)	-0.1752 (4)	-0.3721 (2)	0.064 (2)
C(14)	-0.1647 (4)	-0.1066 (4)	-0.3228 (2)	0.050 (1)
C(15)	-0.3117 (3)	0.4243 (3)	-0.3929 (2)	0.0318 (9)
C(16)	-0.2721 (3)	0.3062 (4)	-0.4259 (2)	0.042 (1)
C(17)	-0.3246 (4)	0.2757 (5)	-0.5119 (2)	0.054 (1)
C(18)	-0.4153 (4)	0.3629 (5)	-0.5639 (2)	0.058 (1)
C(19)	-0.4556 (4)	0.4811 (5)	-0.5316 (2)	0.058 (1)
C(20)	-0.4036 (3)	0.5111 (4)	-0.4453 (2)	0.045 (1)
C(21)	0.2871 (3)	0.3197 (3)	-0.0316 (2)	0.0295 (9)
C(22)	0.3744 (3)	0.2243 (4)	-0.0720 (2)	0.033 (1)
C(23)	0.4218 (3)	0.1000 (4)	-0.0176 (2)	0.0303 (9)
C(24)	0.4964 (3)	0.1504 (4)	0.0709 (2)	0.0266 (8)
C(25)	0.3987 (3)	0.2389 (3)	0.1074 (2)	0.0267 (8)
C(26)	0.4788 (4)	0.2877 (4)	0.1951 (2)	0.038 (1)
C(27)	0.6201 (3)	0.0910 (3)	0.2110 (2)	0.0302 (9)
C(28)	0.6700 (3)	-0.0253 (4)	0.2692 (2)	0.0307 (9)
C(29)	0.5860 (3)	-0.1377 (4)	0.2667 (2)	0.0331 (9)
C(30)	0.6302 (4)	-0.2433 (4)	0.3222 (2)	0.045 (1)
C(31)	0.7609 (4)	-0.2362 (4)	0.3808 (2)	0.057 (1)
C(32)	0.8464 (4)	-0.1242 (5)	0.3836 (2)	0.058 (1)
C(33)	0.8009 (3)	-0.0190 (4)	0.3285 (2)	0.044 (1)

Table 2. Selected geometric parameters (Å, °)

O(1)—C(1)	1.430 (3)	O(1)—C(21)	1.434 (3)
O(3)—C(3)	1.452 (3)	O(23)—C(23)	1.433 (3)
O(4)—C(4)	1.429 (3)	O(24)—C(24)	1.431 (3)
O(4)—C(7)	1.421 (3)	O(24)—C(27)	1.428 (3)
O(5)—C(1)	1.427 (3)	O(25)—C(21)	1.422 (3)
O(5)—C(5)	1.433 (3)	O(25)—C(25)	1.436 (3)
O(6)—C(6)	1.432 (3)	O(26)—C(26)	1.438 (4)
O(6)—C(7)	1.419 (3)	O(26)—C(27)	1.415 (3)
C(1)—C(2)	1.519 (4)	C(21)—C(22)	1.513 (4)
C(2)—C(3)	1.524 (4)	C(22)—C(23)	1.526 (4)
C(3)—C(4)	1.521 (4)	C(23)—C(24)	1.519 (4)
C(4)—C(5)	1.519 (4)	C(24)—C(25)	1.506 (3)

C(5)—C(6)	1.514 (4)	C(25)—C(26)	1.518 (4)
C(7)—C(15)	1.506 (4)	C(27)—C(28)	1.499 (4)
O(3)—C(8)	1.360 (3)	C(8)—C(9)	1.487 (4)
O(8)—C(8)	1.207 (3)		

C(4)—O(4)—C(7)	111.1 (2)	C(24)—O(24)—C(27)	111.2 (2)
C(1)—O(5)—C(5)	112.1 (2)	C(21)—O(25)—C(25)	112.8 (2)
C(6)—O(6)—C(7)	111.7 (2)	C(26)—O(26)—C(27)	112.3 (2)
O(1)—C(1)—O(5)	110.5 (2)	O(1)—C(21)—O(25)	111.0 (2)
O(1)—C(1)—C(2)	108.0 (2)	O(1)—C(21)—C(22)	107.2 (2)
O(5)—C(1)—C(2)	112.4 (2)	O(25)—C(21)—C(22)	113.3 (2)
C(1)—C(2)—C(3)	114.6 (2)	C(21)—C(22)—C(23)	112.8 (2)
O(3)—C(3)—C(2)	109.2 (2)	O(23)—C(23)—C(22)	112.5 (2)
O(3)—C(3)—C(4)	108.4 (2)	O(23)—C(23)—C(24)	112.0 (2)
C(2)—C(3)—C(4)	109.2 (2)	C(22)—C(23)—C(24)	106.1 (2)
O(4)—C(4)—C(3)	109.9 (2)	O(24)—C(24)—C(23)	111.7 (2)
O(4)—C(4)—C(5)	108.1 (2)	O(24)—C(24)—C(25)	109.1 (2)
C(3)—C(4)—C(5)	111.4 (2)	C(23)—C(24)—C(25)	111.2 (2)
O(5)—C(5)—C(4)	109.6 (2)	O(25)—C(25)—C(24)	111.1 (2)
O(5)—C(5)—C(6)	109.2 (2)	O(25)—C(25)—C(26)	107.9 (2)
C(4)—C(5)—C(6)	108.2 (2)	C(24)—C(25)—C(26)	109.0 (2)
O(6)—C(6)—C(5)	107.4 (2)	O(26)—C(26)—C(25)	107.9 (2)
O(4)—C(7)—O(6)	111.8 (2)	O(24)—C(27)—O(26)	110.4 (2)
O(4)—C(7)—C(15)	108.1 (2)	O(24)—C(27)—C(28)	109.3 (2)
O(6)—C(7)—C(15)	108.0 (2)	O(26)—C(27)—C(28)	109.1 (2)
C(1)—O(1)—C(21)	114.6 (2)	O(3)—C(8)—C(9)	111.3 (2)
C(3)—O(3)—C(8)	116.2 (2)	O(8)—C(8)—C(9)	124.3 (3)
O(3)—C(8)—O(8)	124.4 (3)		

O(1)—C(1)—O(5)—C(5)	64.5 (3)
O(1)—C(1)—C(2)—C(3)	-74.5 (3)
O(3)—C(3)—C(2)—C(1)	73.5 (3)
O(3)—C(3)—C(4)—O(4)	51.9 (3)
O(3)—C(3)—C(4)—C(5)	-67.9 (3)
O(4)—C(4)—C(3)—C(2)	170.7 (2)
O(4)—C(4)—C(5)—O(5)	178.6 (2)
O(4)—C(4)—C(5)—C(6)	59.5 (3)
O(4)—C(7)—O(6)—C(6)	-59.9 (3)
O(4)—C(7)—C(15)—C(16)	-36.5 (3)
O(5)—C(1)—O(1)—C(21)	57.3 (3)
O(5)—C(1)—C(2)—C(3)	47.7 (3)
O(5)—C(5)—C(4)—C(3)	-60.6 (3)
O(6)—C(6)—C(5)—C(4)	-59.2 (3)
O(6)—C(7)—O(4)—C(4)	59.3 (3)
O(6)—C(7)—C(15)—C(16)	84.6 (3)
C(1)—O(5)—C(5)—C(4)	62.9 (3)
C(1)—C(2)—C(3)—C(4)	-44.8 (3)
C(2)—C(1)—O(1)—C(21)	-179.4 (2)
C(2)—C(1)—O(5)—C(5)	-56.3 (3)
C(2)—C(3)—C(4)—C(5)	50.9 (3)
C(3)—C(4)—C(5)—C(6)	-179.7 (2)
C(4)—O(4)—C(7)—C(15)	178.0 (2)
C(5)—C(4)—O(4)—C(7)	-59.1 (3)
C(5)—C(6)—O(6)—C(7)	59.5 (3)
C(2)—C(3)—O(3)—C(8)	151.0 (2)
C(4)—C(3)—O(3)—C(8)	-90.1 (2)
O(1)—C(21)—O(25)—C(25)	68.3 (3)
O(1)—C(21)—C(22)—C(23)	-70.6 (3)
O(23)—C(23)—C(22)—C(21)	69.6 (3)
O(23)—C(23)—C(24)—O(24)	56.3 (3)
O(23)—C(23)—C(24)—C(25)	-65.8 (3)
O(24)—C(24)—C(23)—C(22)	179.5 (2)
O(24)—C(24)—C(25)—O(25)	175.9 (2)
O(24)—C(24)—C(25)—C(26)	57.0 (3)
O(24)—C(27)—O(26)—C(26)	-60.9 (3)
O(24)—C(27)—C(28)—C(29)	-38.1 (3)
O(25)—C(21)—O(1)—C(1)	64.9 (3)
O(25)—C(21)—C(22)—C(23)	52.2 (3)
O(25)—C(25)—C(24)—C(23)	-60.5 (3)
O(26)—C(26)—C(25)—C(24)	-56.3 (3)
O(26)—C(27)—O(24)—C(24)	60.4 (3)
O(26)—C(27)—C(28)—C(29)	82.7 (3)
C(21)—O(25)—C(25)—C(24)	56.4 (3)
C(21)—C(22)—C(23)—C(24)	-53.1 (3)
C(22)—C(21)—O(1)—C(1)	-170.9 (2)
C(22)—C(21)—O(25)—C(25)	-52.4 (3)
C(22)—C(23)—C(24)—C(25)	57.4 (3)
C(23)—C(24)—C(25)—C(26)	-179.4 (2)
C(24)—O(24)—C(27)—C(28)	-179.6 (2)

C(25)—C(24)—O(24)—C(27)	-59.0 (3)
C(25)—C(26)—O(26)—C(27)	58.9 (3)
O(3)—C(8)—C(9)—C(10)	-7.8 (4)
C(3)—O(3)—C(8)—C(9)	167.4 (2)

Table 3. Puckering parameters (Cremer & Pople, 1975) for the pyranose and 1,3-dioxane rings of (I)

Q (Å)	Sugar rings containing atoms:		1,3-Dioxane rings containing atoms:	
	O(5)	O(25)	O(4)	O(24)
q ₂ (Å)	0.543 (3)	0.556 (3)	0.589 (3)	0.579 (3)
q ₃ (Å)	0.098 (3)	0.068 (3)	0.042 (3)	0.010 (3)
φ ₂ (°)	0.534 (3)	0.552 (3)	0.588 (3)	0.579 (3)
θ (°)	301 (2)	230 (3)	57 (4)	61 (17)
θ (°)	10.4 (3)	7.0 (3)	4.0 (3)	0.9 (3)

The absolute configuration was assigned to agree with the known chirality, as established by the synthesis of the compound.

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* direct methods (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: AB1243). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 751–754

2,2',3,3'-Tetra-*O*-benzoyl-6,6'-dideoxy-4,4'-di-*O*-mesyl-6,6'-dithiocyanato- α,α -trehalose †

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(Received 12 August 1994; accepted 13 October 1994)

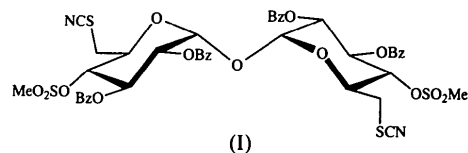
Abstract

The low-temperature X-ray crystal structure of 2,3-di-*O*-benzoyl-6-deoxy-4-*O*-mesyl-6-thiocyanato- α -D-glucopyranosyl 2,3-di-*O*-benzoyl-6-deoxy-4-*O*-mesyl-6-thiocyanato- α -D-glucopyranoside (the title compound), $C_{44}H_{40}N_2O_{17}S_4$, is reported. The absolute configuration has been determined. The molecule has only approximate C_2 symmetry but the differences in the orientation of the C(5) substituents and the torsion angles about the glycosidic linkage are very much less than in α,α -trehalose and its derivatives. Each of the hexopyranosyl residues has a nearly perfect 4C_1 conformation. The planes of the phenyl rings of the benzoyl groups are oriented such that they are approximately perpendicular to the plane of the parent pyranose ring.

† Crystal Structures of Trehalose Derivatives, Part 9. For Part 8, see Linden & Lee (1995).

Comment

α,α -Trehalose is widespread in nature, where it is found in bacteria, insect blood, fungi, algae lichens and some higher plants (Birch, 1963; Elbein, 1974; Lee, 1980). It is a non-reducing disaccharide, consisting of two α -D-glucopyranosyl residues, linked by a glycosidic O-atom bridge between their anomeric C atoms. We are interested in this disaccharide for two reasons. Firstly, the similarity of its structure to many food sugars and its unique molecular symmetry and conformational stability under relatively severe reaction conditions make it an ideal model in studies of the relationship between molecular structure and the organoleptic effect (Lee, 1987). Secondly, trehalases, which are distributed far wider in nature than their substrate, are highly specific glucosidases whose specificities, as well as those of related enzymes, for trehalose, and its analogues, are of interest (Elbein, 1974; Labat-Robert, 1982). Modified analogues of trehalose are important for such studies. The synthesis of the title compound, (I), has been described by Birch, Lee & Richardson (1974). We now report its X-ray crystal structure.



A view of (I) showing the displacement ellipsoids and the atomic numbering is given in Fig. 1. The figure depicts the correct absolute configuration of the molecule, which was assigned to agree with that of its known precursor (Birch, Lee & Richardson, 1974) and was further confirmed by the X-ray analysis.

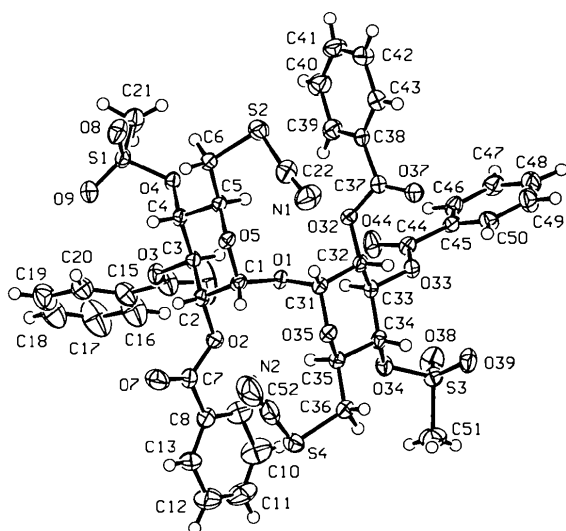


Fig. 1. View of the molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.