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Octa-*O*-acetyl-β,β-thiotrehalose

Magnus Färnbäck,[a]* Lars Eriksson[b] and Göran Widmalm[c]

[a]Department of Organic Chemistry and Division of Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden, [b]Division of Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden, and [c]Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden
Correspondence e-mail: magnusf@struc.su.se

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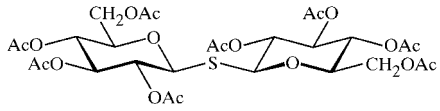
The structure of the title compound, $C_{28}H_{38}O_{18}S$, has been determined. The torsion angles of the glycosidic linkage in the non-reducing disaccharide, φ_H and $\varphi_{H'}$, have values of 3 and 53°, respectively. The latter torsion angle is in agreement with the *exo*-anomeric effect, whereas the former shows an eclipsed conformation. Both glycopyranosyl residues adopt a slightly distorted chair conformation.

Comment

We have previously determined crystal structures of mono- and disaccharides where hydroxyl groups of the saccharides form intermolecular hydrogen bonds (Eriksson *et al.*, 1996, 1997). Both infinite chains and short terminated chains of hydrogen bonds were located in those crystal structures. The molecular conformation and crystal structure of saccharides are also dependent on weak interactions between non-hydroxyl substituents as has been shown recently from a study of a partially protected monosaccharide (Eriksson *et al.*, 1999), where both a plausible hydrogen bond as well as intermolecular interactions between phenyl substituents of the monosaccharide contribute to the molecular packing.

In the present investigation we have determined the crystal structure of octa-*O*-acetyl-β,β-thiotrehalose, (I), which is fully substituted by *O*-acetyl groups and thus is devoid of hydrogen bonding *via* O—H···O interactions. The title compound is a synthetic intermediate in the preparation of other acyl-substituted analogues prepared in our laboratory and studied by NMR spectroscopy. Hence, the conformation of the molecule is of basic interest. The most pronounced intermolecular interactions in the present crystal structure are the lipophilic close contacts between the methyl groups of the acetyl substituents. The molecules pack in the *a* and *c* directions of the unit cell with only lipophilic contacts and the molecular packing in the *b* direction can be modelled by C—H···O interactions (Steiner, 1996). There are three close C···O ($\leq$ 3.4 Å) intermolecular distances and two of these can describe very well the observed packing along the *b* axis. The third of these close intermolecular C—H···O contacts contribute to the packing along the *c* axis.



(I)

For the title compound, the torsion angles of the glycosidic linkage, φ_H and $\varphi_{H'}$, have values of 3 (1) and 53 (1)°, respectively. The former shows an eclipsed conformer, whereas the latter is staggered, in the region where the *exo*-anomeric effect prevails. Recent *ab initio* calculations on *S*-glycosyl compounds have shown that an *exo*-anomeric effect is also present for thio-analogues (Tvaroška & Carver, 1996).

Both glycopyranosyl residues adopt a slightly distorted chair conformation as defined by the Cremer & Pople (1975) puckering parameters, Q = 0.599 Å, q_2 = 0.119 Å, q_3 = 0.587 Å, θ = 11.5° and φ_2 = 32.8° for the O5 → C5 ring and Q = 0.578 Å, q_2 = 0.067 Å, q_3 = 0.574 Å, θ = 6.6° and φ_2 = 316.2° for the O5′ → C5′ ring. Some years ago, the crystal structure of β,β-trehalose was determined (Lee & Koh, 1993). That molecule showed exact twofold symmetry with the glycosidic O atom lying on the twofold axis.

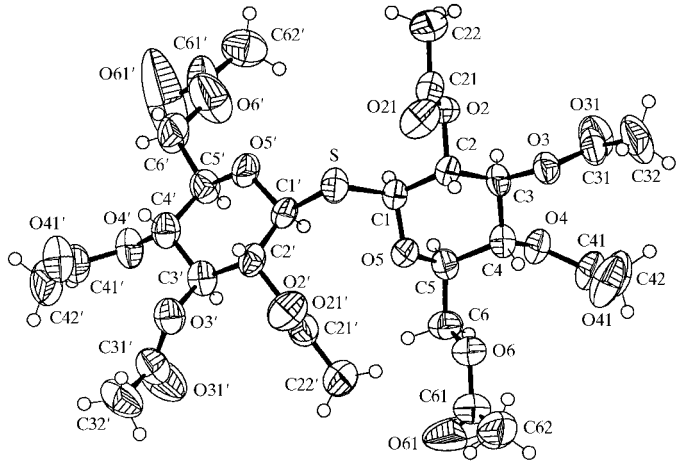


Figure 1
Molecular structure of (I) showing 50% probability displacement ellipsoids.

Experimental

Octa-*O*-acetyl-β,β-thiotrehalose was prepared (Schneider & Wrede, 1917) from 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide and H_2S. The disaccharide was crystallized from ethanol at ambient temperature.

Crystal data

$C_{28}H_{38}O_{18}S$
M_r = 694.64
Monoclinic, $P2_1$
a = 14.463 (4) Å
b = 5.805 (2) Å
c = 20.927 (7) Å
β = 101.27 (4)°
V = 1723.0 (10) Å^3
Z = 2
D_x = 1.339 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1068 reflections
θ = 1.98–25.86°
μ = 0.170 mm^{-1}
T = 293 (2) K
Prism, colourless
0.20 × 0.05 × 0.05 mm

Data collection

Stoe IPDS diffractometer	$R_{int} = 0.103$
Area detector scans	$\theta_{max} = 25.86°$
13406 measured reflections	$h = -17 \rightarrow 17$
6524 independent reflections	$k = -7 \rightarrow 6$
2091 reflections with $I > 2\sigma(I)$	$l = -25 \rightarrow 25$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.055$	$\Delta\rho_{max} = 0.81$ e Å^{-3}
$wR(F^2) = 0.124$	$\Delta\rho_{min} = -1.34$ e Å^{-3}
$S = 1.321$	Extinction correction: *SHELXL*97 (Sheldrick, 1997)
6524 reflections	Extinction coefficient: 0.0095 (8)
425 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = −0.02 (18)
$w = 1/[\sigma^2(F_o^2)]$	

Table 1
Selected geometric parameters (Å, °).

S—C1	1.780 (7)	C1···C1′	2.694 (8)
S—C1′	1.784 (7)		
C1—S—C1′	98.2 (4)	H1—C1···C1′	83.30
H1′—C1′···C1	68.8		
H1′—C1′—S—C1	2.7	H1′—C1′···C1—H1	51.6
H1—C1—S—C1′	52.7		

The low fraction of significant reflections is connected with the quality of the crystals giving a large number of weak reflections which contribute substantially to the internal R value. The internal R value calculated from reflections with $I \geq 2\sigma(I)$ is 0.0485. All non-H atoms were refined with anisotropic displacement parameters using a 'rigid-bond' restraint to U_{ij} of two bonded atoms (Rollett, 1970), implemented as the *DELU* instruction in *SHELXL*97 (Sheldrick, 1997). The H atoms were positioned geometrically and allowed to ride during the least-squares refinements. The torsion angles containing H atoms are calculated with geometrically placed H atoms, thereby the s.u.'s of these are of minor significance as the s.u.'s of the H atom positions will be related to the s.u. of the atom to which the H atoms are connected. These geometrical parameters involving H atoms are of considerable value when compared with results from NMR measurements, *etc*. The absolute configuration of the molecule is set by the absolute configuration of the reactant, which is consistent with the Flack parameter calculated from the present model. The calculated Flack parameter alone is not accurate enough to set the absolute configuration of (I), but together with the previous knowledge about the absolute configuration of the constituent monosaccharides, we note that the value of the Flack parameter fits the present structure model. The maximum and minimum residual densities are located near S (min: −1.34 e Å^{-3}, 0.03 Å from S; max: 0.81 e Å^{-3}, 0.58 Å from S) and could be interpreted as ripple in the electron-density map. The number of measured Friedel pairs is 2837, *i.e.* 77% of all unique reflections was also present as their Friedel equivalent. The reason for refining against non-merged Friedel equivalents was the presence of an S atom as an anomalous scatterer.

Data collection: *EXPOSE* (Stoe & Cie, 1997); cell refinement: *CELL* (Stoe & Cie, 1997); data reduction: *INTEGRATE* (Stoe & Cie, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *PLATON*98 (Spek, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1094). Services for accessing these data are described at the back of the journal.

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