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Key indicators

Single-crystal X-ray study
T = 150 K
Mean $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$
Disorder in main residue
R factor = 0.078
wR factor = 0.234
Data-to-parameter ratio = 9.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

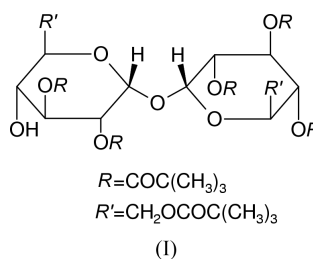
Disordered 2,2',3,3',4,6,6'-hepta-O-pivaloyl- α,α' -trehalose

The structure of the title compound, $\text{C}_{47}\text{H}_{78}\text{O}_{18}$, is characterized by intermolecular hydrogen bonding and a disordered pivaloyl group.

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Comment

In continuation of our recent investigations of the structures and derivatives of the symmetric and non-reducing disaccharide, α,α' -trehalose (Clow *et al.*, 2001; Baddeley *et al.*, 2001, 2002), we have determined the structure of 2,2',3,3',4,6,6'-hepta-O-pivaloyl- α,α' -trehalose, (I). As in the symmetrically substituted derivatives, *e.g.* 2,2',3,3',4,4',6,6'-hexa-O-acetato- α,α' -trehalose EtOAc solvate (Baddeley *et al.*, 2001), 2,2',3,3',4,4'-hexa-O-acetato-6,6'-bis-O-isobutanoyl- α,α' -trehalose 0.7-hydrate (Clow *et al.*, 2001), and 2,2',3,3',4,4'-hexa-O-acetato-6,6'-bis-O-trityl- α,α' -trehalose (Baddeley *et al.*, 2002), both pyranose rings in (I) have near ideal ${}^4\text{C}_1$ conformations. The corresponding puckering parameters (Cremer & Pople, 1975) calculated with *PLATON* (Spek, 2001) are $Q = 0.571(5) \text{ \AA}$, $\theta = 4.5(5)^\circ$ and $\varphi = 319(5)^\circ$ (unprimed atoms), and $Q = 0.568(5) \text{ \AA}$, $\theta = 5.5(5)^\circ$, $\varphi = 317(5)^\circ$ (primed atoms). The arrangement and packing of the bulky pivaloyl groups thus do not lead to any significant changes in the pyranose conformations.



The pseudo-torsion angle $\text{H1}-\text{C1}\cdots\text{C1}'-\text{H1}'$ of the glycosidic linkage is -85.3° . In the ditrityl hexaacetate derivative of α,α' -trehalose, the bridging O atom lies on a twofold axis and the pseudo-torsion angle is -104.7° (Baddeley *et al.*, 2002).

The substitution at $\text{C1}, \text{C1}'$ is α,α' , with $\text{C1}-\text{O1} = 1.423(5) \text{ \AA}$ and $\text{C1}'-\text{O1} = 1.424(5) \text{ \AA}$. The angle subtended at O1 is $111.1(3)^\circ$. The absolute configuration adopted, see below, is *R* at C1, C1', C2, C2', C4, C4', C5 and C5', and *S* at C3 and C3'. Intermolecular hydrogen bonding links the OH group at C4' with a carbonyl oxygen in the $-\text{OCOC}(\text{CH}_3)_3$ group at the C2 position. This results in a hydrogen-bonding motif consisting of chains of molecules along the twofold *b* axis.

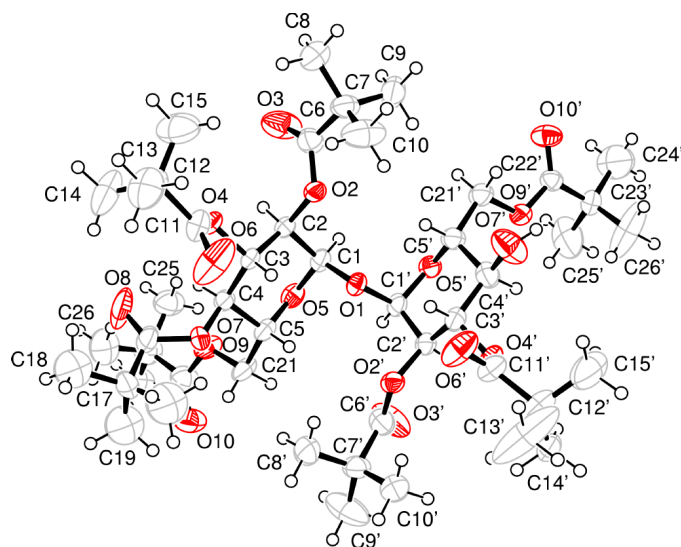


Figure 1
The atomic arrangement in the molecule (disorder excluded). Displacement ellipsoids are drawn at the 50% probability level.

Additional intermolecular C—H...O hydrogen bonding is also present (Table 2). A small peak ($0.69 \text{ e } \text{Å}^{-3}$) in the final difference map may possibly be a disordered oxygen of a water molecule, with a very low occupation factor, but its proximity to C25 (about 2.4 Å) requires disorder at this carbon. Disorder is present in the pivaloyl group, with atoms C18, C19 and C20 each having two sites with occupancies of $0.49 (2)$ and $0.51 (2)$.

Experimental

The title compound was prepared by an esterification method, involving suspension of α, α' -trehalose in pyridine, cooling to 253 K , slow addition of pivaloyl chloride and stirring at room temp for 3 d. The reaction mixture was poured into ice water and extracted into chloroform. Following chromatography using 7:2 light petroleum:diethyl ether, suitable crystals of the isolated product were grown by slow evaporation of a 95% ethanol solution (m.p. $453\text{--}455 \text{ K}$).

Crystal data

$\text{C}_{47}\text{H}_{78}\text{O}_{18}$	$D_x = 1.145 \text{ Mg m}^{-3}$
$M_r = 931.09$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 5000 reflections
$a = 14.1855 (3) \text{ Å}$	$\theta = 1.5\text{--}26.0^\circ$
$b = 10.6390 (2) \text{ Å}$	$\mu = 0.09 \text{ mm}^{-1}$
$c = 18.3343 (4) \text{ Å}$	$T = 150 (2) \text{ K}$
$\beta = 102.5721 (9)^\circ$	Lozenge, colourless
$V = 2700.66 (10) \text{ Å}^3$	$0.55 \times 0.20 \times 0.20 \text{ mm}$
$Z = 2$	

Data collection

Nonius KappaCCD area-detector diffractometer	5812 independent reflections
φ and ω scans	4797 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)	$R_{\text{int}} = 0.072$
$T_{\text{min}} = 0.954$, $T_{\text{max}} = 0.983$	$\theta_{\text{max}} = 26.4^\circ$
45 444 measured reflections	$h = -17 \rightarrow 17$
	$k = -13 \rightarrow 13$
	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1602P)^2 + 1.3102P]$
$R[F^2 > 2\sigma(F^2)] = 0.078$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.234$	$(\Delta/\sigma)_{\text{max}} = 0.013$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.69 \text{ e } \text{Å}^{-3}$
5812 reflections	$\Delta\rho_{\text{min}} = -0.31 \text{ e } \text{Å}^{-3}$
586 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: $0.011 (3)$

Table 1

Selected geometric parameters (Å , $^\circ$).

O1—C1	1.423 (5)	O1—C1'	1.424 (5)
C1—O1—C1'	111.1 (3)	C26—C23—C22	104.1 (6)
O8—C16—C17	126.5 (5)		
C1'—O1—C1—O5	73.1 (4)	C1—O1—C1'—O5'	76.7 (4)
C1'—O1—C1—C2	−165.8 (3)	C1—O1—C1'—C2'	−162.5 (4)

Table 2

Hydrogen-bonding geometry (Å , $^\circ$).

$D\text{—H}\cdots A$	$D\text{—H}$	$H\cdots A$	$D\cdots A$	$D\text{—H}\cdots A$
O7'—H7'...O3 ⁱ	0.84	2.04	2.868 (8)	169
C2—H2A...O10 ⁱⁱⁱ	1.00	2.45	3.352 (6)	149
C9—H9A...O7 ⁱⁱ	0.98	2.49	3.390 (9)	151
C24—H24C...O6 ⁱⁱⁱ	0.98	2.54	3.421 (10)	149

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, -z$; (ii) $1 - x, y - \frac{1}{2}, -z$; (iii) $x, y - 1, z$.

Except for the disordered atoms C18, C18', C19, C19', C20 and C20', which were refined isotropically, all non-H atoms were refined with anisotropic displacement parameters. The H atoms were placed in calculated positions and allowed to ride on their attached atoms with isotropic displacement parameters $1.2U_{\text{eq}}$ of the attached atom. Final R values are higher than normal and several atoms in the disordered structure (*e.g.* O6, C13', C15' and C26') were associated with large displacement parameters. Statistical treatment of these four atom positions was not successful. In the absence of atomic species with atomic number greater than that of oxygen, Friedel pairs were merged prior to refinement. As a consequence, the Flack (1983) parameter and absolute configuration are indeterminate from the intensity data alone. The absolute configuration has therefore been established simply on the basis of the known stereochemistry of the parent trehalose.

Data collection: DENZO (Otwinowski & Minor, 1997) and COLLECT (Hooft, 1998); cell refinement: DENZO and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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