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Disordered 4,4′-di-*O*-isobutyroyl-2,2′,-3,3′,6,6′-hex-*O*-acetyl-α,α′-trehalose

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.053
wR factor = 0.154
Data-to-parameter ratio = 7.9

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

The twofold symmetry of the title compound, $C_{32}H_{46}O_{19}$, coincides with a crystallographic twofold axis. Weak C—H···O hydrogen bonding and a disordered isobutyroyl group are present.

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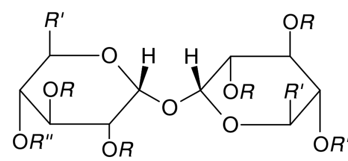
Comment

Recently we have determined the structures of a number of substituted trehalose derivatives. These have included hydrated or solvated forms, such as 2,2′,3,3′,4,4′-hexa-*O*-acetato-6,6′-bis-*O*-isobutanoyl-α,α′-trehalose 0.7-hydrate (Clow *et al.*, 2001), 2,2′,3,3′,4,6,6′-hepta-*O*-pivaloyl-α,α′-trehalose (Baddeley *et al.*, 2003) and 2,2′,3,3′,4,4′,6,6′-hexa-*O*-acetato-α,α′-trehalose ethyl acetate solvate (Baddeley *et al.*, 2001). The anyhdrous symmetrically substituted 2,2′,3,3′,4,4′-hexa-*O*-acetato-6,6′-bis-*O*-trityl-α,α′-trehalose (Baddeley *et al.*, 2002) possesses molecular twofold symmetry, coinciding with a crystallographic twofold axis.



(I)

The disordered structure reported here, 2,2′,3,3′,4,6,6′-hepta-*O*-pivaloyl-α,α′-trehalose, (I), also possesses molecular twofold symmetry, coinciding with a crystallographic twofold axis. As this axis passes through the bridging oxygen at $(-x+\frac{1}{2}, \frac{1}{2}+x, \frac{1}{4})$, the molecular geometry shown in Table 1 applies to both halves of the molecule. As expected, the pyranose ring has a $^4C_1$ conformation, as indicated by the puckering parameters (Cremer & Pople, 1975), calculated with *PLATON* (Spek, 2001), Q = 0.556 (4) Å, θ = 1.5 (4)° and φ = 52 (8)°.

The pseudo-torsion angle H1—C1···C1′—H1′ of the glycosidic linkage is −89.1°. In the ditrityl hexaacetate derivative of α,α′-trehalose, where the bridging oxygen also lies on a twofold axis, the pseudo-torsion angle is −104.7° (Baddeley *et al.*, 2002).

The substitution at C1,C1′ is α,α′, with C1—O1 = 1.417 (4) Å and the angle subtended at O1 = 113.1 (4)°. The absolute configuration adopted (see below) is *R* at C1, C2, C3, C4 and C5. Disorder is present in the isobutyroyl group, with atoms O8, C13, C14, C15 and C16 disordered over two sites

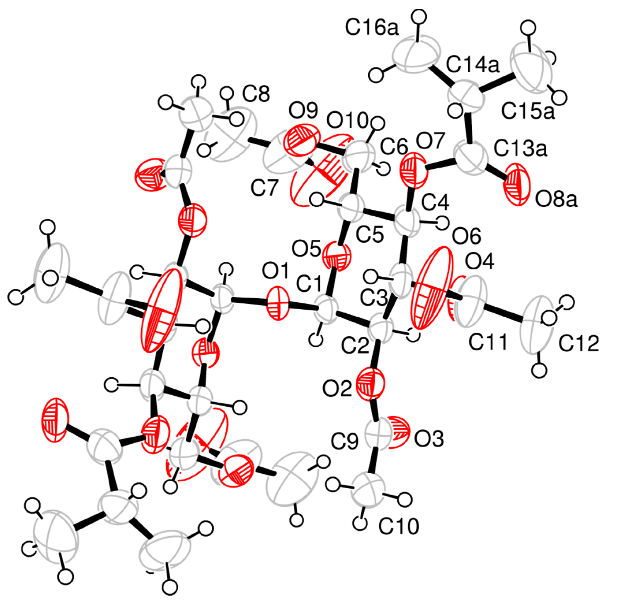


Figure 1
The atomic arrangement in the molecule (disorder excluded). Displacement ellipsoids are drawn at the 50% probability level.

with fixed occupancies of 0.5. There are no O—H···O hydrogen bonds, but there are weak C—H···O hydrogen bonds which are listed in Table 2 (disordered atoms excluded). The disordered structure of 2,2′,3,3′4,6,6′-hepta-*O*-pivaloyl-α,α′-trehalose (Baddeley *et al.*, 2003) also possesses C—H···O hydrogen bonds.

Experimental

2,2′,3,3′,4,4′-Hexaacetyl-α,α′-trehalose, prepared according to the method of Bredereck (1930), was dissolved in 1:1 pyridine–water and stirred at room temperature for 48 h. At this time, thin-layer chromatography (EtOAc) showed the acyl migration to be complete. The solvent was removed under vacuum and the resulting solid recrystallized from DCM/MTBE. 2,2′,3,3′,6,6′-Hexaacetyl-α,α′-trehalose was dissolved in pyridine and 2.1 equivalents of isobutyroyl chloride added with stirring. After 4 h the solution was added to water. The resulting solid was collected, washed with water and dried. Recrystallization from ethanol gave 4,4′-di-*O*-isobutyroyl-2,2′,3,3′,6,6′-hexa-*O*-acetyl-α,α′-trehalose (m.p. 397–399 K).

Crystal data

$C_{32}H_{46}O_{19}$
$M_r = 734.69$
Tetragonal, $P4_12_12$
$a = 14.9188$ (9) Å
$c = 17.8355$ (6) Å
$V = 3969.7$ (4) Å^3
$Z = 4$
$D_x = 1.229$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5000 reflections
$\theta = 1.9$–$25.7°$
$\mu = 0.10$ mm^{-1}
$T = 150$ (2) K
Lozenge, colourless
0.45 × 0.15 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{min} = 0.956$, $T_{max} = 0.985$
50356 measured reflections
2206 independent reflections
1414 reflections with $I > 2\sigma(I)$
$R_{int} = 0.132$
$\theta_{max} = 25.7°$
$h = -17 \rightarrow 18$
$k = -18 \rightarrow 18$
$l = -20 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.155$
$S = 1.01$
2206 reflections
281 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1016P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0117 (18)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.417 (4)	C2—C3	1.514 (5)
O5—C5	1.432 (5)	C3—C4	1.515 (6)
C1—C2	1.499 (5)		
C1—O1—C1^{i}	113.1 (4)		
H1—C1—C1^{i}—H1^{i}	−89.1		

Symmetry code: (i) $1-y, 1-x, \frac{1}{2}-z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O4^{ii}	1.00	2.53	3.487 (4)	161
C6—H6A···O6^{iii}	0.99	2.37	3.217 (8)	143
C8—H8B···O10^{iv}	0.98	2.53	3.412 (10)	150
C8—H8C···O3^{i}	0.98	2.59	3.528 (8)	161
C12—H12B···O5^{ii}	0.98	2.58	3.454 (5)	148

Symmetry codes: (i) $1-y, 1-x, \frac{1}{2}-z$ (ii) $y, x, -z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{4}-z$; (iv) $\frac{1}{2}-y, x-\frac{1}{2}, \frac{1}{4}+z$;.

The H atoms were initially placed in calculated positions and thereafter allowed to ride on their attached atoms, with isotropic displacement parameters 1.2 times U_{eq} of the attached atom. The weakly diffracting and disordered structure resulted in a low reflection/parameter ratio, and several atoms in the disordered structure were associated with large displacement parameters where the statistical distributions could not be assigned.

A similar refinement in the alternative space group ($P4_32_12$) cannot be discounted. Further, the choice of the disorder (A or B) in the affected chain is not random, as atom O8B is separated from its symmetry-equivalent by only 1.76 (1) Å across $y, x, -z$. Hence the x, y, z and the $y, x, -z$ sites must be occupied by different orientations of the side chain. In the absence of atomic species with an atomic number greater than that of oxygen, Friedel pairs were merged prior to refinement. As a consequence, the Flack (1983) x parameter and absolute configuration are indeterminate from the intensity data alone. The latter 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: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1998); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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