Non-classical hydrogen bonding involving bound diazides in an inositol derivative

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Key indicators

Single-crystal X-ray study
T = 88 K
Mean σ(C–C) = 0.016 Å
Disorder in solvent or counterion
R factor = 0.053
wR factor = 0.127
Data-to-parameter ratio = 9.3

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

The inositol derivative 1D-1,2-diazido-1,2-dideoxy-3,4,5,6-tetra-O-benzyl-myo-inositol diethyl ether 0.6-solvate, $C_{34}H_{34}N_6O_4 \cdot 0.6C_4H_{10}O$, packs with weak and unusual C—H$\cdots$N,O hydrogen bonds and C—H$\cdots\pi$ interactions.

Comment

The title compound, (I), was prepared as part of a programme aimed at generating new hydrogenation catalyst ligands from inositol molecules (Gainsford *et al.*, 2000; Falshaw *et al.*, 1999).
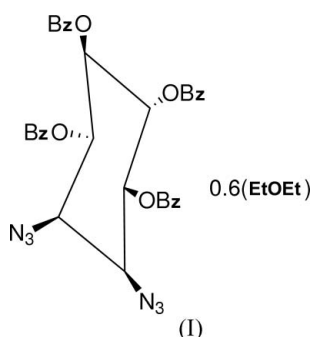
The asymmetric unit of (I) contains one independent molecule, as shown in Fig. 1, together with a partial-occupancy solvent molecule. The absolute configuration shown is that determined from the chemical synthesis route. There are few cyclohexane structures in the Cambridge Structural Database (CSD, Version 5.26; Allen, 2002) with adjacent azide and O substituents, namely CSD refcodes QAPSAB and QAPSEF (Akai, Nakamura *et al.*, 1999; Akai, Sugita *et al.*, 1999),
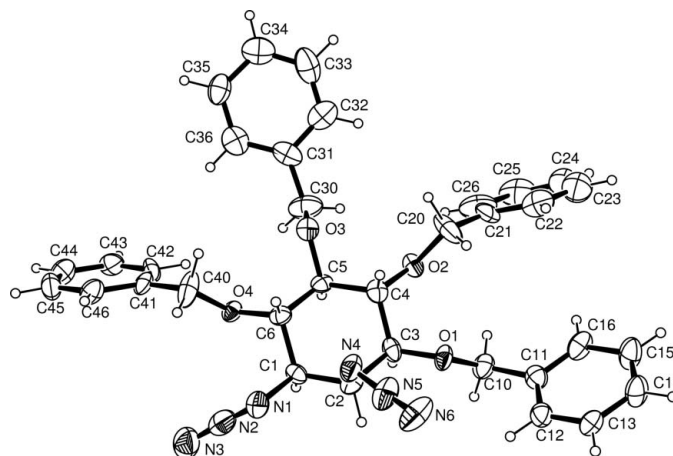

Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. The solvent molecule has been omitted.
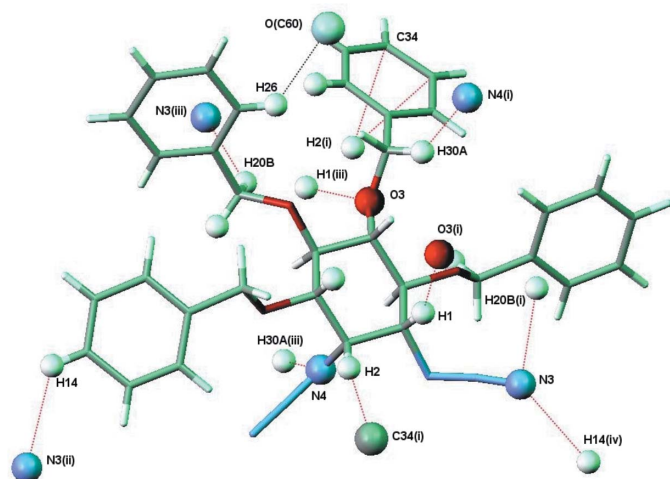
Figure 2
Intermolecular interactions (dotted lines) in (I). Contact atoms are shown as spheres. See text for discussion of O(C60). [Symmetry codes are as given in Table 2; additionally: (iv) $\frac{3}{2} - x$, $1 - y$, $-\frac{1}{2} + z$].

AZUZAW (Busscher *et al.*, 2004) and IXEVAI (Carballido *et al.*, 2004). The azide angular geometries C—N—N and N—N—N in (I) all fall within the previously observed ranges of 114–119° and 170–174°, respectively. The cyclohexane ring adopts a chair conformation, with puckering parameters (Cremer & Pople, 1975) $Q = 0.573$ (9) Å, $\theta = 2.6$ (9)° and $\varphi = 347$ (20)°.

Normally, inositol derivatives are strongly hydrogen-bonded, utilizing all available bound groups, *e.g.* O—H···O (GEGWIY; Dietrich *et al.*, 1999) and C—H···O=C (HADKIG; Steiner *et al.*, 1993). Although the crystals of (I) were weakly diffracting, the crystal packing stability has again been assisted by definite, though weak, non-classical hydrogen bonding involving C—H···X (where X is O or N_{azide}) and C—H···π interactions, as detailed in Table 2. These forces are sufficient to stabilize a partial molecule of the crystallizing solvent diethyl ether in the crystal structure (estimated as 0.6 of a molecule).

There are two types of C—H···N_{azide} interactions in the structure of (I). One was unexpected, being to the inositol ring-bound atom N4, while the other two were to the terminal azide atom N3. The former have rarely been observed, according to a CSD search, with only one occurrence noted in SUMRAT (Goulaouic *et al.*, 1993), with H···N = 2.67 Å and C—H···N = 131°. There are currently five instances of C—H···$N_{terminal}$ interactions. Three examples are ZDGPLN (Schmidt *et al.*, 1980), MIYKIO (Barnes *et al.*, 2002) and YASBAW (Humphreys *et al.*, 2005) with H···N values of 2.62, 2.59 and 2.47 Å, respectively, and C—H···N angles of 127, 146 and 161°, respectively. In the last of these structures, the interaction was apparently insufficient to reduce the disorder found in the azide group.

The C—H···π interactions listed in Table 2 fit within the normal applied H···Cg limit of 3 Å. From the interaction distances, it seems highly likely that there is also a C—H···O hydrogen bond to the disordered diethyl ether solvent molecule, with C26—H26···O(C60) = 2.49 Å, C26···O =

3.17 (9) Å and C—H···O = 138°.

The combined weak interactions give three-dimensional stability to the crystal structure, although it is difficult to show this meaningfully in a packing diagram. Instead, Fig. 2 (*MERCURY*; Bruno *et al.*, 2002), shows the full interaction commitments of all the groups bound to the inositol as dotted bonds, with the disordered solvent molecule represented by one atom, O(C60) (see *Experimental*).

Experimental

1D-3,4,5,6-Tetra-*O*-benzy-*myo*-inositol (2.50 g, 4.62 mmol) was treated with methanesulfonyl chloride (3.60 ml, 46.2 mmol) in pyridine (20 ml) overnight at room temperature to give the 1,2-dimesylate (3.12 g, 97%). The 1,2-dimesylate (4.88 g, 7.00 mmol) was then subjected to a displacement reaction using sodium azide (6.83 g, 105 mmol) in dimethylformamide (50 ml) overnight at 383 K to give the 1,2-diazide (2.88 g, 70%). Crystals of the title compound were isolated from diethyl ether.

Crystal data

$C_{34}H_{34}N_6O_4 \cdot 0.6C_4H_{10}O$	Mo $K\alpha$ radiation
$M_r = 655.53$	Cell parameters from 895
Orthorhombic, $P2_12_12_1$	reflections
$a = 9.006$ (3) Å	$\theta = 2.6$–14.6°
$b = 15.324$ (6) Å	$\mu = 0.08$ mm^{-1}
$c = 25.424$ (11) Å	$T = 88$ (2) K
$V = 3509$ (2) Å^3	Needle, colourless
$Z = 4$	$0.50 \times 0.22 \times 0.18$ mm
$D_x = 1.241$ Mg m^{-3}	

Data collection

Bruker SMART CCD area-detector diffractometer	4038 independent reflections
	908 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.328$
Absorption correction: multi-scan (*SADABS*; Blessing, 1995; Sheldrick, 1996)	$\theta_{max} = 26.4°$
	$h = -10 \rightarrow 11$
	$k = -19 \rightarrow 19$
$T_{min} = 0.597$, $T_{max} = 0.986$	$l = -31 \rightarrow 28$
19603 measured reflections	

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.053$	
$wR(F^2) = 0.127$	
$S = 0.77$	$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2]$
4038 reflections	where $P = (F_o^2 + 2F_c^2)/3$
432 parameters	$(\Delta/\sigma)_{max} = 0.001$
	$\Delta\rho_{max} = 0.16$ e Å^{-3}
	$\Delta\rho_{min} = -0.20$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C3	1.429 (8)	N1—C1	1.482 (10)
N1—N2	1.194 (11)	N2—N3	1.180 (11)
C10—O1—C3	114.4 (6)	N3—N2—N1	172.9 (13)
N2—N1—C1	111.9 (10)	N1—C1—C2	105.8 (8)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2···Cg1[i]	1.0	2.64	3.510 (10)	146
C43—H43···Cg2[i]	0.95	2.82	3.597 (11)	140
C1—H1···O3[i]	1.00	2.57	3.514 (10)	157
C30—H30A···N4[i]	0.99	2.53	3.282 (13)	132
C14—H14···N3[ii]	0.95	2.70	3.353 (16)	126
C20—H20B···N3[iii]	0.99	2.65	3.474 (16)	141

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, -z$; (ii) $-x+\frac{3}{2}, -y+1, z+\frac{1}{2}$; (iii) $x+\frac{1}{2}, -y+\frac{1}{2}, -z$.

All non-H atoms except C23 and C24 were refined with anisotropic displacement parameters. In the absence of significant anomalous scattering effects, Friedel-related reflections were merged. The H atoms of the amino (N1) and hydroxyl (O1) atoms were positionally refined. All C-bound H atoms were constrained to their expected geometries, with C—H(methyl) = 0.98 Å and the remaining C—H = 1.0 Å. For all H atoms, $U_{iso}(H) = 1.2U_{eq}$(parent atom). The disordered diethyl ether was modelled with density at 11 atomic sites using C atoms only and a common U_{iso}; no extra O or H atoms were included for the ether solvent molecule. Models of diethyl ether in two main orientations fit these positions, but no rational model could be constructed. On the basis of the total electron density, about 0.62 of a diethyl ether molecule per asymmetric unit was found.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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