research communications

Structures of rac-2,4:3,5-dimethylene xylitol derivatives

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The structures of three racemic (tetrahydro-[1,3]dioxino[5,4-d][1,3]dioxin-4-yl)-methanol derivatives are reported, namely, 4-[(methylsulfonyloxy)methyl]-2,4,4a,6,8,8a-hexahydro-[1,3]dioxino[5,4-d][1,3]dioxine, $C_8H_{14}O_7S$, **1**, 4-[(benzyloxy)methyl]-2,4,4a,6,8,8a-hexahydro-[1,3]dioxino[5,4-d][1,3]dioxine, $C_{14}H_{18}O_5$, **2**, and 4-[(anilinocarbonyl)methyl]-2,4,4a,6,8,8a-hexahydro-[1,3]dioxino[5,4-d]-[1,3]dioxine, $C_{14}H_{17}NO_6$, **3**. Mesylate ester **1** at 173 K has triclinic $P\bar{1}$ symmetry and both benzyl ether **2** at 173 K and phenyl urethane **3** have monoclinic $P2_1/c$ symmetry. These structures are of interest because of the conformation of the cis-fused tetraoxadecalin ring system. This cis-bicyclo[4.4.0]decane ring system, i.e. cis-decalin, can undergo conformational equilibration. In the two most stable conformers, both six-membered rings adopt a chair conformation. However, there are significant consequences in these two stable conformers, with heteroatom substitution at the 1,3,5,7-ring positions as described. Only one conformation, denoted as 'concave' or 'inside', is found in these crystal structures. This is consistent with previously reported structures of the 1,1-geminal dihydroxy aldehyde and tosylate analogs.
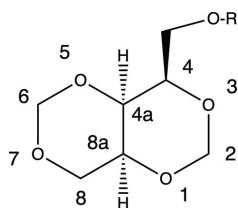
1. Chemical context

Naturally occurring monosaccharides provide an abundant source of inexpensive, often chiral, starting materials for the syntheses of numerous sophisticated natural products, non-natural physiologically active compounds, and ligands for stereoselective catalysts (Ferrier, 2003). Over the past decade or so, a sharply increasing emphasis is seen on the use of these sugars and also on chemical transformations among the various diastereomeric and homologous series of monosaccharides. Despite this flurry of activity, monosaccharide derivatives still provide a rich source of challenging structural and conformational issues due to the anomeric and gauche interactions associated with the O atoms.

concave (inside) convex (outside)

Compound 1   E = CH₃-SO₂-Cl
Compound 2   E = Ph-CH₂-Br
Compound 3   E = Ph-N=C̈=O

In this article, we describe the crystal structures of three cis-fused [4.4.0]bicyclo methylene acetals originally derived from the most inexpensive and readily available five-carbon meso polyalcohol, i.e. xylitol. The chemical structures of these
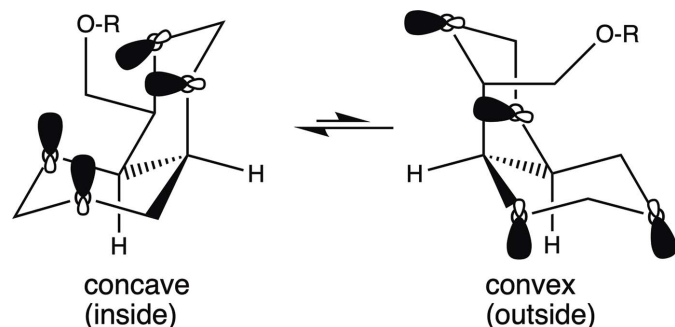
Figure 1
The structures and atom numbering for compounds **1**–**3**. For **1**, $R = SO_2$–CH_3, for **2**, $R = CH_2$–Ph, and for **3**, $R = CO$–NH–Ph.
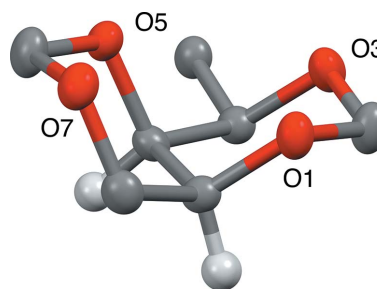
compounds are shown in the scheme. The standard chemical numbering for the 1,3,5,7-tetraoxadecalin ring system is shown in Fig. 1. The atoms in all three crystal structures reported are labeled following this pattern. Compound **1** is a mesylate, with R = mesyl (Zarubinskii & Danilov, 1972), compound **2** is a benzyl ether, with R = benzyl (Che *et al.*, 2017), and compound **3** is an *N*-phenylurethane, with R = –CO–NH–Ph. Since xylitol itself is achiral and we carried out no enantioselective reactions to prepare chiral derivatives, the structures we report are of racemates and hence centrosymmetric, although it is possible to obtain enantiomerically pure compounds from more complicated synthetic routes.

2. Structural commentary

The defining characteristic of the *cis*-1,3,5,7-tetraoxa-[4.4.0]-bicyclodecalin ring system is depicted in Figs. 2 and 3. Fig. 2 illustrates the two lowest-energy all-chair conformations of this skeleton. The O atoms in these conformers adopt a tetrahedral geometry and the axial lone pair of electrons on each of these O atoms within the decalin ring are depicted. This feature was noted previously (Lemieux & Howard, 1963; Burkert, 1980; Taskinen, 2009) and described in detail in a mini-review summarizing over two decades of chemical work largely from one laboratory (Fuchs, 2013). Trivial nomenclature has evolved to describe these two conformations as inside/concave or outside/convex. These descriptions derive from the orientation of the axial lone pairs on the ring O atoms relative to the overall shape of the decalin ring system. For the completely unsubstituted tetraoxydecalin, it is not immediately obvious which of these two conformers is more stable.
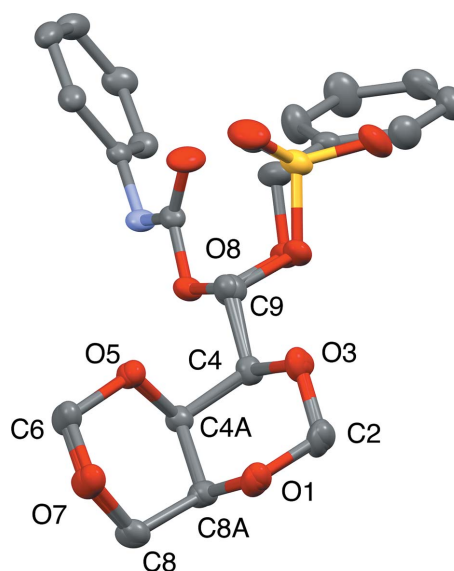

Figure 3
The half-cylinder molecular shape of *cis*-1,3,5,7-tetraoxa-[4.4.0]bicyclo-decalin.

Compounds **1**–**3** also incorporate a derivatized hydroxymethyl substituent at position C4 that is *trans* to both bridgehead H atoms. Consequently, this substituent must be equatorial in the concave/inside conformer and axial in the convex/outside conformer. Conformational analysis suggests that the concave/inside conformer is favored, as seen in all these crystal structures. Fig. 3 highlights this overall geometry found in all three crystal structures. The overall shape of this molecule resembles a cylinder that has been cut in half. It is noteworthy that this molecular shape has been examined for its potential to chelate cations as a polydentate ligand (Ganguly & Fuchs, 2001) and also as a cryptand (Abramson *et al.*, 2003).

Fig. 4 is an overlay of all three crystal structures obtained by minimizing the positional differences of the four ring O atoms in all three structures. No significant difference in the geometry of the tetraoxabicyclic ring in these three structures is discernible. It is noteworthy that a *gauche* conformation is found for the O3—C4—C9—O8 torsion angle, with values of 61.8 (2) and 81.6 (1)° in mesylate **1** and benzyl ether **2**, respectively. However, a relatively antiperiplanar torsion angle of 175.9 (8)° exists in urethane **3**. This is likely the consequence of stabilization by the single intermolecular

Figure 2
Stable conformations of *cis*-1,3,5,7-tetraoxa-[4.4.0]bicyclodecalin.

Figure 4
Structural overlay of compounds **1**–**3**.

Table 1
Hydrogen-bond geometry (Å, °) for **3**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1⋯O9^i	0.863 (16)	1.969 (16)	2.8025 (13)	161.9 (14)
C2—H2B⋯O5^{ii}	0.99	2.51	3.4515 (15)	159

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

hydrogen bond observed in the urethane structure (see below).

Figs. 5–7 display the all-atom displacement ellipsoid plots of compounds **1**–**3**.

3. Supramolecular features

An intramolecular N—H⋯O hydrogen bond is observed in phenyl urethane derivative **3** between the –NH substituent and the carbonyl O atom of the urethane functional group. This is described as $D-H\cdots A$ (N1—H1⋯O9^i), with N1—H1 = 0.863 (16) Å, H1⋯O9^i = 1.969 (16) Å, N1⋯O9^i = 2.8025 (13) Å and N1—H1⋯O9^i = 161.9 (14)° [symmetry code: (i) $x, y-1, z$]. This is shown in Fig. 8.

No other hydrogen-bond interactions are possible in any of the structures, although there are short C—H⋯O interactions between the H2B atom on a methylene acetal and an adjacent acetal O5^{ii} atom [symmetry code: (ii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$] in urethane structure **3** that is characteristically seen in all of the structures. This is characterized in Table 1.

No π-stacking interactions of the aromatic rings are observed.

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.43, update of November 2021; Groom *et al.*, 2016)

Figure 5
Displacement ellipsoid plot (50% probability) of compound **1**.

Figure 6
Displacement ellipsoid plot (50% probability) of compound **2**.

Figure 7
Displacement ellipsoid plot (50% probability) of compound **3**.

Figure 8
Hydrogen bonding in compound **3**.

Table 2
Experimental details.

Experiments were carried out at 173 K with Mo $K\alpha$ radiation. Absorption was corrected for by multi-scan methods (*SADABS*; Krause *et al.*, 2015).

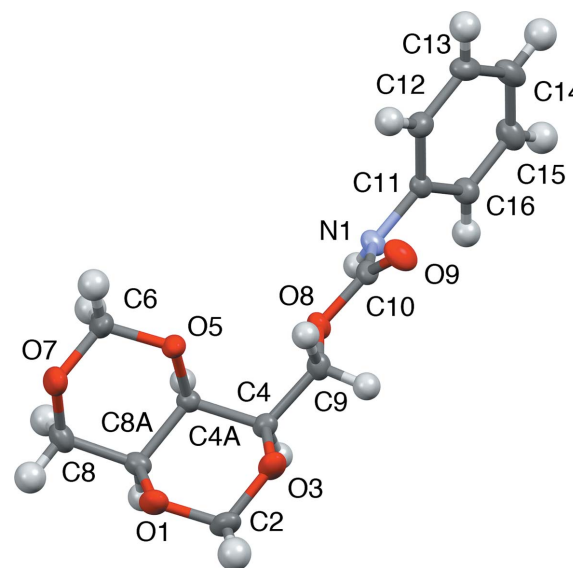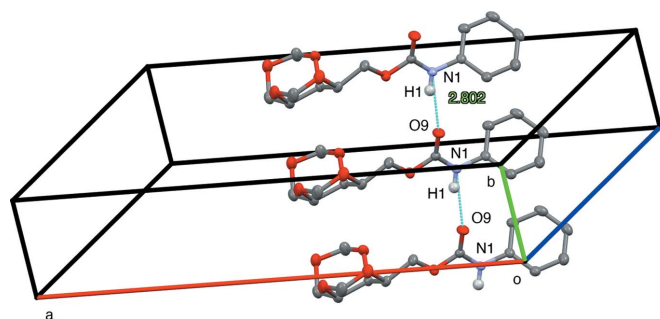|	**1**	**2**	**3**
Crystal data			
Chemical formula	$C_8H_{14}O_7S$	$C_{14}H_{18}O_5$	$C_{14}H_{17}NO_6$
M_r	254.25	266.28	295.28
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a, b, c (Å)	4.7401 (4), 7.3325 (6), 15.9604 (14)	20.5429 (9), 4.4574 (2), 13.9148 (7)	22.909 (2), 4.8973 (5), 12.2331 (14)
α, β, γ (°)	90.019 (3), 93.610 (3), 106.439 (3)	90, 96.651 (2), 90	90, 104.529 (4), 90
V (Å^3)	530.90 (8)	1265.57 (10)	1328.6 (2)
Z	2	4	4
μ (mm^{-1})	0.32	0.11	0.12
Crystal size (mm)	$0.15 \times 0.13 \times 0.09$	$0.20 \times 0.10 \times 0.08$	$0.20 \times 0.15 \times 0.12$
Data collection			
Diffractometer	Bruker D8 Quest	Bruker D8 Quest	Bruker D8 Venture Duo
T_{min}, T_{max}	0.665, 0.748	0.712, 0.746	0.568, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15993, 4823, 2290	32635, 3878, 2759	23485, 3040, 2803
R_{int}	0.084	0.062	0.069
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.929	0.716	0.650
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.070, 0.147, 1.01	0.051, 0.123, 1.04	0.044, 0.107, 1.06
No. of reflections	4823	3878	3040
No. of parameters	146	172	193
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.41, −0.66	0.31, −0.21	0.34, −0.29

Computer programs: *APEX4* and *SAINT* (Bruker, 2022), *SHELXT2019* (Sheldrick, 2015a), *SHELXL2019* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2020), and *publCIF* (Westrip, 2010).

for similar structures returned two relevant entries: 2,4:3,5-di-*O*-methylene-1-*p*-toluenesulfonyl xylitol (CSD refcode HALSAO; Rodier *et al.*, 1993) and dihydroxy-2,4:3,5-di-methylene-L-xylose (SIVHUA; Smith *et al.*, 1991).

5. Synthesis and crystallization

Compounds **1** and **2** were prepared and crystallized by the following general procedure. To a solution of racemic 2,4:3,5-dimethylene xylitol (Hann *et al.*, 1944) in pyridine, 1.1 molar equivalents of either mesyl chloride or benzyl bromide were added and stirred at room temperature until the diacetal dissolved (~4 h). The resulting reaction mixtures were allowed to stand for 18 h at room temperature and then poured onto crushed ice. Solid crystalline material formed upon slow evaporation of the reaction mixture on sitting in a fume hood overnight. Recrystallization from ethanol produced diffraction-quality crystals. ^{1}H and ^{13}C NMR spectra of the crystalline samples indicated no discernible impurities and are provided in the supporting information.

Compound **1**, ^{13}C{^{1}H} NMR (298 K, CDCl$_3$, 100.5 MHz): δ 93.07, 92.85, 75.49, 70.13, 69.42, 69.32, 68.30, 37.36.

Compound **2**, ^{13}C{^{1}H} NMR (298 K, CDCl$_3$, 100.5 MHz): δ 137.94, 128.44, 127.85, 127.79, 93.21, 93.16, 77.24, 73.67, 70.63, 70.16, 69.52, 68.49.

For urethane derivative **3**, a solution of racemic 2,4:3,5-dimethylene xylitol, 1.1 molar equivalents of phenyl isocyanate, and pyridine was heated to reflux for 2 h protected

from atmospheric moisture by a drying tube. On cooling, the derivative precipitated from the solution and was collected by filtration. Recrystallization from acetone yielded diffraction-quality crystals. ^{1}H and ^{13}C NMR spectra of the crystalline samples indicated no discernible impurities and are provided in the supporting information.

Compound **3**, ^{13}C{^{1}H} NMR (298 K, d_6-DMSO, 100.5 MHz): δ 153.76, 139.49, 129.21, 122.92, 118.64, 92.56, 92.17, 75.57, 69.98, 69.93, 69.12, 63.86.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were added automatically using a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$. The H atom on N1 in urethane **3** was located in a difference Fourier map and refined freely.

Funding information

research communications

References

Abramson, S., Ashkenazi, E., Frische, K., Goldberg, I., Golender, L., Greenwald, M., Lemcoff, N. G., Madar, R., Weinman, S. & Fuchs, B. (2003). *Chem. Eur. J.* **9**, 6071–6082.

Bruker (2022). *APEX4* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Burkert, U. (1980). *J. Comput. Chem.* **1**, 192–198.

Che, R., Zhu, Q., Yu, J., Li, J., Yu, J. & Lu, W. (2017). *Tetrahedron*, **73**, 6172–6180.

Ferrier, R. J. (2003). *Carbohydrate Chemistry*, Vol. 34, pp. 338–366. London: Royal Society of Chemistry.

Fuchs, B. (2013). *Isr. J. Chem.* **53**, 45–52.

Ganguly, B. & Fuchs, B. (2001). *J. Phys. Org. Chem.* **14**, 488–494.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Hann, R. M., Ness, A. T. & Hudson, C. S. (1944). *J. Am. Chem. Soc.* **66**, 670–673.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

Lemieux, R. U. & Howard, J. (1963). *Can. J. Chem.* **41**, 393–398.

Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.

Rodier, N., Ronco, G., Julien, R., Postel, D. & Villa, P. (1993). *Acta Cryst.* C**49**, 2032–2033.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Smith, D. A., Baker, D. & Rahman, A. F. M. M. (1991). *Struct. Chem.* **2**, 65–70.

Taskinen, E. (2009). *J. Phys. Org. Chem.* **22**, 761–768.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Zarubinskii, G. M. & Danilov, S. N. (1972). *Zh. Obshch. Khim.* **42**, 2758–2763.

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Computing details

For all structures, data collection: *APEX4* (Bruker, 2022); cell refinement: *SAINT* (Bruker, 2022); data reduction: *SAINT* (Bruker, 2022); program(s) used to solve structure: SHELXT2019 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2019* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

4-[(Methylsulfonyloxy)methyl]-2,4,4a,6,8,8a-hexahydro-[1,3]dioxino[5,4-*d*][1,3]dioxine (1)

Crystal data

$C_8H_{14}O_7S$	$Z = 2$
$M_r = 254.25$	$F(000) = 268$
Triclinic, $P\overline{1}$	$D_x = 1.590$ Mg m^{-3}
$a = 4.7401$ (4) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 7.3325$ (6) Å	Cell parameters from 1351 reflections
$c = 15.9604$ (14) Å	$\theta = 8.9$–35.3°
$\alpha = 90.019$ (3)°	$\mu = 0.32$ mm^{-1}
$\beta = 93.610$ (3)°	$T = 173$ K
$\gamma = 106.439$ (3)°	Cube, colorless
$V = 530.90$ (8) Å^3	$0.15 \times 0.13 \times 0.09$ mm

Data collection

Bruker D8 Quest diffractometer	4823 independent reflections
Kappa Diffractometer scans	2290 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)	$R_{int} = 0.084$
	$\theta_{max} = 41.3°$, $\theta_{min} = 2.6°$
$T_{min} = 0.665$, $T_{max} = 0.748$	$h = -8\rightarrow7$
15993 measured reflections	$k = -11\rightarrow11$
	$l = -25\rightarrow21$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.070$	$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2 + 0.2188P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.147$	
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
4823 reflections	$\Delta\rho_{max} = 0.41$ e Å^{-3}
146 parameters	$\Delta\rho_{min} = -0.65$ e Å^{-3}
0 restraints	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	0.60628 (13)	0.80009 (9)	0.58781 (4)	0.02721 (16)
O1	0.6927 (3)	0.4016 (2)	0.93342 (9)	0.0266 (4)
O3	0.6751 (3)	0.6081 (2)	0.82311 (9)	0.0260 (4)
O5	0.4827 (3)	0.2098 (2)	0.76954 (9)	0.0243 (3)
O7	0.4434 (3)	0.0034 (2)	0.88198 (10)	0.0289 (4)
O8	0.7865 (3)	0.7367 (2)	0.66251 (9)	0.0261 (4)
O9	0.3104 (4)	0.6800 (3)	0.58398 (11)	0.0398 (5)
O10	0.6589 (4)	0.9992 (2)	0.60079 (10)	0.0373 (4)
C2	0.7642 (6)	0.5925 (3)	0.90849 (14)	0.0309 (5)
H2A	0.979758	0.650217	0.917189	0.037*
H2B	0.666347	0.663938	0.943971	0.037*
C4	0.8303 (5)	0.5179 (3)	0.77023 (13)	0.0227 (4)
H4	1.045638	0.585886	0.776752	0.027*
C4A	0.7829 (5)	0.3113 (3)	0.79322 (13)	0.0216 (4)
H4A	0.917530	0.256771	0.761967	0.026*
C6	0.4217 (6)	0.0183 (3)	0.79414 (14)	0.0304 (5)
H6A	0.220286	−0.052390	0.772201	0.036*
H6B	0.562188	−0.040402	0.769413	0.036*
C8	0.7415 (5)	0.0902 (3)	0.91348 (14)	0.0275 (5)
H8A	0.871338	0.019144	0.891627	0.033*
H8B	0.754402	0.083849	0.975507	0.033*
C8A	0.8461 (5)	0.2954 (3)	0.88766 (13)	0.0228 (4)
H8AA	1.062871	0.346026	0.901998	0.027*
C9	0.7183 (5)	0.5344 (3)	0.68109 (13)	0.0240 (5)
H9A	0.815314	0.469652	0.642238	0.029*
H9B	0.502868	0.474287	0.674387	0.029*
C10	0.7686 (5)	0.7580 (3)	0.49760 (14)	0.0280 (5)
H10A	0.666135	0.795460	0.448192	0.042*
H10B	0.754631	0.622437	0.493002	0.042*
H10C	0.976420	0.832549	0.500840	0.042*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0286 (3)	0.0314 (3)	0.0257 (3)	0.0142 (2)	0.0054 (2)	0.0082 (2)
O1	0.0368 (9)	0.0221 (8)	0.0199 (8)	0.0062 (7)	0.0049 (7)	0.0028 (6)
O3	0.0357 (9)	0.0248 (8)	0.0203 (8)	0.0130 (7)	0.0034 (6)	0.0021 (6)
O5	0.0261 (8)	0.0208 (8)	0.0242 (8)	0.0038 (6)	0.0000 (6)	−0.0001 (6)
O7	0.0339 (9)	0.0239 (9)	0.0257 (8)	0.0023 (7)	0.0056 (7)	0.0034 (6)

O8	0.0320 (9)	0.0231 (8)	0.0226 (8)	0.0067 (7)	0.0026 (6)	0.0073 (6)
O9	0.0237 (9)	0.0517 (12)	0.0463 (11)	0.0140 (8)	0.0052 (8)	0.0153 (9)
O10	0.0571 (12)	0.0318 (10)	0.0316 (10)	0.0246 (9)	0.0116 (8)	0.0086 (7)
C2	0.0457 (15)	0.0230 (12)	0.0222 (11)	0.0073 (10)	0.0006 (10)	0.0011 (9)
C4	0.0237 (11)	0.0212 (11)	0.0228 (11)	0.0056 (8)	0.0026 (8)	0.0038 (8)
C4A	0.0222 (11)	0.0229 (11)	0.0214 (11)	0.0087 (8)	0.0046 (8)	0.0035 (8)
C6	0.0416 (14)	0.0206 (12)	0.0262 (12)	0.0042 (10)	0.0021 (10)	0.0012 (9)
C8	0.0339 (13)	0.0262 (12)	0.0236 (11)	0.0100 (10)	0.0039 (9)	0.0068 (9)
C8A	0.0233 (11)	0.0221 (11)	0.0223 (11)	0.0051 (9)	0.0015 (8)	0.0047 (8)
C9	0.0303 (12)	0.0194 (11)	0.0218 (11)	0.0060 (9)	0.0021 (9)	0.0042 (8)
C10	0.0310 (13)	0.0306 (13)	0.0240 (12)	0.0111 (10)	0.0026 (9)	0.0043 (9)

Geometric parameters (Å, º)

S1—O10	1.4228 (18)	C4—C4A	1.516 (3)
S1—O9	1.4270 (18)	C4—H4	1.0000
S1—O8	1.5698 (15)	C4A—C8A	1.529 (3)
S1—C10	1.742 (2)	C4A—H4A	1.0000
O1—C2	1.408 (3)	C6—H6A	0.9900
O1—C8A	1.434 (3)	C6—H6B	0.9900
O3—C2	1.415 (3)	C8—C8A	1.511 (3)
O3—C4	1.430 (3)	C8—H8A	0.9900
O5—C6	1.412 (3)	C8—H8B	0.9900
O5—C4A	1.433 (3)	C8A—H8AA	1.0000
O7—C6	1.406 (3)	C9—H9A	0.9900
O7—C8	1.434 (3)	C9—H9B	0.9900
O8—C9	1.461 (2)	C10—H10A	0.9800
C2—H2A	0.9900	C10—H10B	0.9800
C2—H2B	0.9900	C10—H10C	0.9800
C4—C9	1.504 (3)		

O10—S1—O9	119.11 (11)	O7—C6—H6A	109.3
O10—S1—O8	104.77 (10)	O5—C6—H6A	109.3
O9—S1—O8	108.86 (9)	O7—C6—H6B	109.3
O10—S1—C10	109.80 (11)	O5—C6—H6B	109.3
O9—S1—C10	108.16 (12)	H6A—C6—H6B	108.0
O8—S1—C10	105.28 (10)	O7—C8—C8A	111.14 (18)
C2—O1—C8A	111.28 (17)	O7—C8—H8A	109.4
C2—O3—C4	110.29 (17)	C8A—C8—H8A	109.4
C6—O5—C4A	110.55 (17)	O7—C8—H8B	109.4
C6—O7—C8	109.65 (17)	C8A—C8—H8B	109.4
C9—O8—S1	118.45 (13)	H8A—C8—H8B	108.0
O1—C2—O3	111.64 (18)	O1—C8A—C8	107.96 (18)
O1—C2—H2A	109.3	O1—C8A—C4A	110.20 (17)
O3—C2—H2A	109.3	C8—C8A—C4A	110.23 (18)
O1—C2—H2B	109.3	O1—C8A—H8AA	109.5
O3—C2—H2B	109.3	C8—C8A—H8AA	109.5
H2A—C2—H2B	108.0	C4A—C8A—H8AA	109.5

O3—C4—C9	107.43 (17)	O8—C9—C4	107.50 (17)
O3—C4—C4A	110.85 (17)	O8—C9—H9A	110.2
C9—C4—C4A	110.92 (18)	C4—C9—H9A	110.2
O3—C4—H4	109.2	O8—C9—H9B	110.2
C9—C4—H4	109.2	C4—C9—H9B	110.2
C4A—C4—H4	109.2	H9A—C9—H9B	108.5
O5—C4A—C4	108.19 (17)	S1—C10—H10A	109.5
O5—C4A—C8A	110.03 (17)	S1—C10—H10B	109.5
C4—C4A—C8A	110.15 (18)	H10A—C10—H10B	109.5
O5—C4A—H4A	109.5	S1—C10—H10C	109.5
C4—C4A—H4A	109.5	H10A—C10—H10C	109.5
C8A—C4A—H4A	109.5	H10B—C10—H10C	109.5
O7—C6—O5	111.57 (18)		

O10—S1—O8—C9	163.58 (16)	C4A—O5—C6—O7	64.7 (2)
O9—S1—O8—C9	35.15 (18)	C6—O7—C8—C8A	56.9 (2)
C10—S1—O8—C9	−80.62 (17)	C2—O1—C8A—C8	−176.03 (18)
C8A—O1—C2—O3	63.0 (2)	C2—O1—C8A—C4A	−55.6 (2)
C4—O3—C2—O1	−63.2 (2)	O7—C8—C8A—O1	70.2 (2)
C2—O3—C4—C9	178.21 (17)	O7—C8—C8A—C4A	−50.2 (2)
C2—O3—C4—C4A	56.9 (2)	O5—C4A—C8A—O1	−69.6 (2)
C6—O5—C4A—C4	−176.51 (17)	C4—C4A—C8A—O1	49.6 (2)
C6—O5—C4A—C8A	−56.1 (2)	O5—C4A—C8A—C8	49.5 (2)
O3—C4—C4A—O5	69.7 (2)	C4—C4A—C8A—C8	168.64 (18)
C9—C4—C4A—O5	−49.6 (2)	S1—O8—C9—C4	−159.17 (14)
O3—C4—C4A—C8A	−50.7 (2)	O3—C4—C9—O8	61.8 (2)
C9—C4—C4A—C8A	−169.91 (18)	C4A—C4—C9—O8	−176.93 (17)
C8—O7—C6—O5	−64.3 (2)		

4-[(Benzyloxy)methyl]-2,4,4a,6,8,8a-hexahydro-[1,3]dioxino[5,4-*d*][1,3]dioxine (2)

Crystal data

$C_{14}H_{18}O_5$	$F(000) = 568$
$M_r = 266.28$	$D_x = 1.398$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 20.5429$ (9) Å	Cell parameters from 665 reflections
$b = 4.4574$ (2) Å	$\theta = 7.0$–$30.6°$
$c = 13.9148$ (7) Å	$\mu = 0.11$ mm^{-1}
$\beta = 96.651$ (2)°	$T = 173$ K
$V = 1265.57$ (10) Å^3	Block, colorless
$Z = 4$	$0.20 \times 0.10 \times 0.08$ mm

Data collection

Bruker D8 Quest diffractometer	3878 independent reflections
Kappa Diffractometer scans	2759 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)	$R_{int} = 0.062$
	$\theta_{max} = 30.6°$, $\theta_{min} = 2.0°$
$T_{min} = 0.712$, $T_{max} = 0.746$	$h = -29 \rightarrow 28$
32635 measured reflections	$k = -6 \rightarrow 6$
	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.051$	H-atom parameters constrained
$wR(F^2) = 0.123$	$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.495P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	
3878 reflections	$(\Delta/\sigma)_{max} < 0.001$
172 parameters	$\Delta\rho_{max} = 0.31$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
O3	0.14034 (5)	0.5880 (2)	0.31935 (7)	0.0230 (2)
O5	0.18458 (5)	0.5729 (2)	0.12265 (7)	0.0205 (2)
O7	0.09777 (5)	0.5175 (2)	0.00055 (7)	0.0244 (2)
O8	0.27719 (5)	0.4412 (3)	0.40210 (7)	0.0277 (2)
O1	0.05578 (5)	0.4848 (2)	0.19753 (7)	0.0223 (2)
C2	0.07448 (7)	0.4955 (4)	0.29813 (10)	0.0250 (3)
H2A	0.068982	0.294409	0.326277	0.030*
H2B	0.045623	0.637039	0.328068	0.030*
C13	0.37677 (9)	0.4540 (4)	0.69810 (12)	0.0369 (4)
H13	0.360471	0.499754	0.757563	0.044*
C4	0.18415 (7)	0.3773 (3)	0.28339 (10)	0.0202 (3)
H4	0.181883	0.184159	0.319425	0.024*
C14	0.43189 (9)	0.2806 (4)	0.69818 (12)	0.0362 (4)
H14	0.453646	0.206011	0.757327	0.043*
C15	0.45538 (10)	0.2158 (5)	0.61234 (14)	0.0488 (5)
H15	0.493685	0.096685	0.611887	0.059*
C16	0.42333 (9)	0.3238 (5)	0.52620 (13)	0.0405 (4)
H16	0.439881	0.276927	0.467000	0.049*
C4A	0.16574 (7)	0.3179 (3)	0.17607 (10)	0.0191 (3)
H4A	0.190262	0.137749	0.157023	0.023*
C6	0.16623 (7)	0.5295 (3)	0.02246 (10)	0.0247 (3)
H6A	0.183747	0.696081	−0.013987	0.030*
H6B	0.185645	0.340146	0.001883	0.030*
C8	0.07206 (7)	0.2614 (3)	0.04578 (10)	0.0238 (3)
H8A	0.087998	0.076190	0.016981	0.029*
H8B	0.023629	0.263209	0.033288	0.029*
C9	0.25236 (7)	0.5044 (3)	0.30451 (10)	0.0239 (3)
H9A	0.281348	0.414262	0.260268	0.029*
H9B	0.251289	0.724063	0.293854	0.029*
C12	0.34453 (8)	0.5633 (4)	0.61206 (12)	0.0355 (4)

H12	0.306381	0.683312	0.612870	0.043*
C8A	0.09237 (7)	0.2591 (3)	0.15380 (10)	0.0204 (3)
H8AA	0.081985	0.058431	0.180316	0.024*
C10	0.33439 (8)	0.6145 (4)	0.43094 (12)	0.0334 (4)
H10A	0.322121	0.827277	0.438450	0.040*
H10B	0.364623	0.603076	0.380580	0.040*
C11	0.36794 (7)	0.4977 (3)	0.52499 (11)	0.0263 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3	0.0214 (5)	0.0255 (5)	0.0220 (5)	0.0013 (4)	0.0020 (4)	−0.0051 (4)
O5	0.0249 (5)	0.0202 (5)	0.0162 (4)	−0.0022 (4)	0.0016 (4)	0.0004 (4)
O7	0.0285 (5)	0.0231 (5)	0.0204 (5)	−0.0008 (4)	−0.0027 (4)	0.0034 (4)
O8	0.0248 (5)	0.0345 (6)	0.0219 (5)	−0.0064 (4)	−0.0057 (4)	0.0041 (4)
O1	0.0213 (5)	0.0238 (5)	0.0216 (5)	0.0014 (4)	0.0010 (4)	0.0002 (4)
C2	0.0207 (7)	0.0325 (8)	0.0221 (7)	0.0003 (6)	0.0038 (5)	0.0011 (6)
C13	0.0387 (10)	0.0449 (10)	0.0272 (8)	−0.0007 (8)	0.0036 (7)	−0.0043 (7)
C4	0.0226 (7)	0.0190 (6)	0.0186 (6)	0.0027 (5)	0.0005 (5)	0.0001 (5)
C14	0.0366 (9)	0.0401 (10)	0.0289 (8)	−0.0014 (7)	−0.0090 (7)	0.0027 (7)
C15	0.0406 (11)	0.0617 (13)	0.0427 (11)	0.0242 (10)	−0.0014 (8)	−0.0011 (9)
C16	0.0391 (10)	0.0533 (11)	0.0292 (9)	0.0116 (8)	0.0045 (7)	−0.0039 (8)
C4A	0.0234 (7)	0.0148 (6)	0.0187 (6)	0.0024 (5)	0.0007 (5)	0.0008 (5)
C6	0.0291 (8)	0.0281 (7)	0.0171 (6)	0.0003 (6)	0.0032 (5)	0.0005 (6)
C8	0.0281 (7)	0.0188 (6)	0.0231 (7)	−0.0016 (6)	−0.0037 (6)	−0.0013 (5)
C9	0.0233 (7)	0.0283 (7)	0.0194 (6)	0.0009 (6)	−0.0005 (5)	0.0019 (6)
C12	0.0265 (8)	0.0430 (10)	0.0365 (9)	0.0068 (7)	0.0020 (7)	−0.0028 (8)
C8A	0.0252 (7)	0.0149 (6)	0.0203 (6)	−0.0014 (5)	−0.0010 (5)	0.0012 (5)
C10	0.0286 (8)	0.0382 (9)	0.0310 (8)	−0.0100 (7)	−0.0071 (6)	0.0060 (7)
C11	0.0217 (7)	0.0294 (8)	0.0265 (7)	−0.0058 (6)	−0.0031 (6)	−0.0012 (6)

Geometric parameters (Å, º)

O3—C2	1.4125 (17)	C15—C16	1.385 (3)
O3—C4	1.4307 (17)	C15—H15	0.9500
O5—C6	1.4146 (16)	C16—C11	1.375 (2)
O5—C4A	1.4354 (16)	C16—H16	0.9500
O7—C6	1.4051 (18)	C4A—C8A	1.526 (2)
O7—C8	1.4336 (17)	C4A—H4A	1.0000
O8—C9	1.4223 (16)	C6—H6A	0.9900
O8—C10	1.4247 (18)	C6—H6B	0.9900
O1—C2	1.4089 (17)	C8—C8A	1.5127 (19)
O1—C8A	1.4329 (17)	C8—H8A	0.9900
C2—H2A	0.9900	C8—H8B	0.9900
C2—H2B	0.9900	C9—H9A	0.9900
C13—C14	1.371 (3)	C9—H9B	0.9900
C13—C12	1.388 (2)	C12—C11	1.385 (2)
C13—H13	0.9500	C12—H12	0.9500

C4—C9	1.509 (2)	C8A—H8AA	1.0000
C4—C4A	1.5206 (19)	C10—C11	1.500 (2)
C4—H4	1.0000	C10—H10A	0.9900
C14—C15	1.370 (3)	C10—H10B	0.9900
C14—H14	0.9500		
C2—O3—C4	111.19 (11)	O7—C6—H6A	109.3
C6—O5—C4A	110.19 (10)	O5—C6—H6A	109.3
C6—O7—C8	110.21 (11)	O7—C6—H6B	109.3
C9—O8—C10	110.75 (11)	O5—C6—H6B	109.3
C2—O1—C8A	110.46 (11)	H6A—C6—H6B	108.0
O1—C2—O3	111.22 (11)	O7—C8—C8A	111.62 (11)
O1—C2—H2A	109.4	O7—C8—H8A	109.3
O3—C2—H2A	109.4	C8A—C8—H8A	109.3
O1—C2—H2B	109.4	O7—C8—H8B	109.3
O3—C2—H2B	109.4	C8A—C8—H8B	109.3
H2A—C2—H2B	108.0	H8A—C8—H8B	108.0
C14—C13—C12	120.68 (16)	O8—C9—C4	109.50 (11)
C14—C13—H13	119.7	O8—C9—H9A	109.8
C12—C13—H13	119.7	C4—C9—H9A	109.8
O3—C4—C9	107.03 (11)	O8—C9—H9B	109.8
O3—C4—C4A	111.27 (11)	C4—C9—H9B	109.8
C9—C4—C4A	112.12 (12)	H9A—C9—H9B	108.2
O3—C4—H4	108.8	C11—C12—C13	120.07 (16)
C9—C4—H4	108.8	C11—C12—H12	120.0
C4A—C4—H4	108.8	C13—C12—H12	120.0
C15—C14—C13	119.51 (16)	O1—C8A—C8	108.61 (11)
C15—C14—H14	120.2	O1—C8A—C4A	110.34 (11)
C13—C14—H14	120.2	C8—C8A—C4A	110.66 (12)
C14—C15—C16	120.08 (17)	O1—C8A—H8AA	109.1
C14—C15—H15	120.0	C8—C8A—H8AA	109.1
C16—C15—H15	120.0	C4A—C8A—H8AA	109.1
C11—C16—C15	121.06 (16)	O8—C10—C11	109.77 (13)
C11—C16—H16	119.5	O8—C10—H10A	109.7
C15—C16—H16	119.5	C11—C10—H10A	109.7
O5—C4A—C4	108.63 (11)	O8—C10—H10B	109.7
O5—C4A—C8A	110.50 (11)	C11—C10—H10B	109.7
C4—C4A—C8A	110.90 (11)	H10A—C10—H10B	108.2
O5—C4A—H4A	108.9	C16—C11—C12	118.60 (15)
C4—C4A—H4A	108.9	C16—C11—C10	120.14 (15)
C8A—C4A—H4A	108.9	C12—C11—C10	121.26 (15)
O7—C6—O5	111.39 (11)		
C8A—O1—C2—O3	64.95 (15)	C4A—C4—C9—O8	−156.09 (11)
C4—O3—C2—O1	−63.31 (15)	C14—C13—C12—C11	0.0 (3)
C2—O3—C4—C9	176.82 (11)	C2—O1—C8A—C8	−178.47 (11)
C2—O3—C4—C4A	54.02 (14)	C2—O1—C8A—C4A	−57.01 (14)
C12—C13—C14—C15	0.2 (3)	O7—C8—C8A—O1	73.36 (15)

C13—C14—C15—C16	−0.3 (3)	O7—C8—C8A—C4A	−47.90 (15)
C14—C15—C16—C11	0.3 (3)	O5—C4A—C8A—O1	−71.99 (13)
C6—O5—C4A—C4	−178.11 (11)	C4—C4A—C8A—O1	48.53 (14)
C6—O5—C4A—C8A	−56.24 (14)	O5—C4A—C8A—C8	48.25 (14)
O3—C4—C4A—O5	74.48 (14)	C4—C4A—C8A—C8	168.77 (11)
C9—C4—C4A—O5	−45.35 (15)	C9—O8—C10—C11	−167.65 (13)
O3—C4—C4A—C8A	−47.14 (15)	C15—C16—C11—C12	−0.1 (3)
C9—C4—C4A—C8A	−166.97 (11)	C15—C16—C11—C10	179.44 (19)
C8—O7—C6—O5	−64.20 (15)	C13—C12—C11—C16	−0.1 (3)
C4A—O5—C6—O7	65.18 (14)	C13—C12—C11—C10	−179.57 (16)
C6—O7—C8—C8A	55.30 (15)	O8—C10—C11—C16	102.95 (19)
C10—O8—C9—C4	−166.65 (13)	O8—C10—C11—C12	−77.6 (2)
O3—C4—C9—O8	81.64 (14)		

4-[(Anilinocarbonyl)methyl]-2,4,4a,6,8,8a-hexahydro-[1,3]dioxino[5,4-*d*][1,3]dioxine (3)

Crystal data

$C_{14}H_{17}NO_6$	$F(000) = 624$
$M_r = 295.28$	$D_x = 1.476$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 22.909$ (2) Å	Cell parameters from 2795 reflections
$b = 4.8973$ (5) Å	$\theta = 7.0–41.7°$
$c = 12.2331$ (14) Å	$\mu = 0.12$ mm^{-1}
$\beta = 104.529$ (4)°	$T = 173$ K
$V = 1328.6$ (2) Å^3	Block, colorless
$Z = 4$	$0.20 \times 0.15 \times 0.12$ mm

Data collection

Bruker D8 Venture Duo diffractometer	3040 independent reflections
Kappa Diffractometer scans	2803 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)	$R_{int} = 0.069$
	$\theta_{max} = 27.5°$, $\theta_{min} = 2.8°$
$T_{min} = 0.568$, $T_{max} = 0.746$	$h = −29 \rightarrow 29$
23485 measured reflections	$k = −6 \rightarrow 6$
	$l = −15 \rightarrow 15$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.044$	
$wR(F^2) = 0.107$	$w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 0.442P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
3040 reflections	$(\Delta/\sigma)_{max} = 0.001$
193 parameters	$\Delta\rho_{max} = 0.34$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = −0.29$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.60997 (4)	0.50342 (19)	0.58605 (7)	0.0310 (2)
O3	0.70830 (4)	0.62699 (19)	0.58784 (7)	0.0302 (2)
O5	0.63244 (4)	0.55251 (17)	0.35740 (7)	0.0258 (2)
O7	0.53139 (4)	0.48658 (19)	0.35638 (8)	0.0324 (2)
O8	0.77058 (3)	0.32337 (15)	0.37519 (7)	0.02338 (19)
O9	0.82960 (4)	0.63477 (16)	0.31909 (8)	0.0330 (2)
N1	0.82836 (4)	0.19036 (18)	0.26368 (8)	0.0225 (2)
H1	0.8209 (7)	0.027 (3)	0.2824 (13)	0.027*
C2	0.66883 (6)	0.5438 (3)	0.65284 (10)	0.0347 (3)
H2A	0.683838	0.371609	0.692421	0.042*
H2B	0.668196	0.684296	0.710706	0.042*
C4	0.71453 (5)	0.4155 (2)	0.51082 (9)	0.0230 (2)
H4	0.733167	0.251744	0.554844	0.028*
C4A	0.65326 (5)	0.3365 (2)	0.43578 (9)	0.0215 (2)
H4A	0.657592	0.166324	0.393308	0.026*
C6	0.57349 (5)	0.4990 (3)	0.29052 (10)	0.0320 (3)
H6A	0.561531	0.644689	0.233139	0.038*
H6B	0.573382	0.323456	0.250366	0.038*
C8	0.54503 (5)	0.2626 (3)	0.43325 (11)	0.0318 (3)
H8A	0.540811	0.089413	0.390230	0.038*
H8B	0.515926	0.259346	0.480937	0.038*
C9	0.75822 (5)	0.5321 (2)	0.44922 (10)	0.0242 (2)
H9A	0.740477	0.694399	0.404957	0.029*
H9B	0.795986	0.587944	0.503863	0.029*
C8A	0.60852 (5)	0.2844 (2)	0.50798 (10)	0.0262 (2)
H8AA	0.619336	0.109986	0.550758	0.031*
C10	0.81139 (5)	0.4021 (2)	0.31843 (9)	0.0208 (2)
C11	0.87120 (5)	0.2165 (2)	0.19801 (9)	0.0210 (2)
C12	0.86405 (5)	0.4148 (2)	0.11452 (10)	0.0265 (2)
H12	0.831260	0.539301	0.102868	0.032*
C13	0.90499 (6)	0.4305 (3)	0.04823 (10)	0.0310 (3)
H13	0.900295	0.566736	−0.008600	0.037*
C14	0.95263 (6)	0.2486 (3)	0.06448 (11)	0.0333 (3)
H14	0.980372	0.258761	0.018488	0.040*
C15	0.95972 (6)	0.0516 (3)	0.14805 (12)	0.0323 (3)
H15	0.992606	−0.072340	0.159664	0.039*
C16	0.91903 (5)	0.0342 (2)	0.21495 (10)	0.0256 (2)
H16	0.923900	−0.101674	0.271959	0.031*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0299 (4)	0.0412 (5)	0.0242 (4)	0.0067 (4)	0.0111 (3)	−0.0022 (3)
O3	0.0292 (4)	0.0361 (5)	0.0248 (4)	0.0022 (3)	0.0056 (3)	−0.0100 (3)
O5	0.0216 (4)	0.0324 (4)	0.0222 (4)	0.0004 (3)	0.0032 (3)	0.0065 (3)

O7	0.0209 (4)	0.0425 (5)	0.0336 (5)	0.0030 (3)	0.0064 (3)	0.0023 (4)
O8	0.0225 (4)	0.0208 (4)	0.0287 (4)	−0.0030 (3)	0.0100 (3)	−0.0040 (3)
O9	0.0438 (5)	0.0157 (4)	0.0454 (5)	−0.0033 (3)	0.0221 (4)	−0.0004 (3)
N1	0.0248 (4)	0.0156 (4)	0.0291 (5)	−0.0020 (3)	0.0107 (4)	0.0010 (3)
C2	0.0344 (7)	0.0503 (8)	0.0194 (5)	0.0081 (6)	0.0068 (5)	−0.0035 (5)
C4	0.0227 (5)	0.0246 (5)	0.0211 (5)	0.0042 (4)	0.0043 (4)	−0.0016 (4)
C4A	0.0220 (5)	0.0225 (5)	0.0206 (5)	0.0023 (4)	0.0066 (4)	0.0006 (4)
C6	0.0220 (6)	0.0482 (7)	0.0241 (6)	0.0007 (5)	0.0025 (4)	0.0031 (5)
C8	0.0256 (6)	0.0345 (6)	0.0381 (6)	−0.0027 (5)	0.0135 (5)	−0.0003 (5)
C9	0.0217 (5)	0.0224 (5)	0.0284 (5)	0.0003 (4)	0.0064 (4)	−0.0052 (4)
C8A	0.0280 (6)	0.0273 (5)	0.0258 (5)	0.0031 (4)	0.0115 (4)	0.0037 (4)
C10	0.0196 (5)	0.0179 (5)	0.0240 (5)	0.0004 (4)	0.0040 (4)	0.0025 (4)
C11	0.0220 (5)	0.0188 (5)	0.0222 (5)	−0.0040 (4)	0.0057 (4)	−0.0025 (4)
C12	0.0291 (6)	0.0230 (5)	0.0263 (5)	−0.0026 (4)	0.0046 (4)	0.0020 (4)
C13	0.0417 (7)	0.0277 (6)	0.0242 (5)	−0.0089 (5)	0.0093 (5)	0.0015 (4)
C14	0.0406 (7)	0.0318 (6)	0.0336 (6)	−0.0095 (5)	0.0204 (5)	−0.0064 (5)
C15	0.0316 (6)	0.0275 (6)	0.0418 (7)	0.0002 (5)	0.0165 (5)	−0.0037 (5)
C16	0.0279 (6)	0.0209 (5)	0.0288 (6)	−0.0005 (4)	0.0086 (4)	0.0006 (4)

Geometric parameters (Å, º)

O1—C2	1.4042 (16)	C4A—H4A	1.0000
O1—C8A	1.4309 (14)	C6—H6A	0.9900
O3—C2	1.4059 (16)	C6—H6B	0.9900
O3—C4	1.4313 (13)	C8—C8A	1.5152 (17)
O5—C6	1.4168 (14)	C8—H8A	0.9900
O5—C4A	1.4272 (13)	C8—H8B	0.9900
O7—C6	1.4046 (15)	C9—H9A	0.9900
O7—C8	1.4275 (16)	C9—H9B	0.9900
O8—C10	1.3530 (13)	C8A—H8AA	1.0000
O8—C9	1.4400 (13)	C11—C16	1.3881 (16)
O9—C10	1.2129 (13)	C11—C12	1.3891 (15)
N1—C10	1.3436 (14)	C12—C13	1.3873 (17)
N1—C11	1.4215 (14)	C12—H12	0.9500
N1—H1	0.863 (16)	C13—C14	1.384 (2)
C2—H2A	0.9900	C13—H13	0.9500
C2—H2B	0.9900	C14—C15	1.3852 (18)
C4—C9	1.5079 (15)	C14—H14	0.9500
C4—C4A	1.5219 (15)	C15—C16	1.3888 (16)
C4—H4	1.0000	C15—H15	0.9500
C4A—C8A	1.5330 (15)	C16—H16	0.9500
C2—O1—C8A	110.61 (9)	C8A—C8—H8B	109.4
C2—O3—C4	110.31 (9)	H8A—C8—H8B	108.0
C6—O5—C4A	111.13 (9)	O8—C9—C4	107.79 (9)
C6—O7—C8	110.06 (9)	O8—C9—H9A	110.1
C10—O8—C9	113.00 (8)	C4—C9—H9A	110.1
C10—N1—C11	122.64 (9)	O8—C9—H9B	110.1

C10—N1—H1	118.9 (10)	C4—C9—H9B	110.1
C11—N1—H1	116.4 (10)	H9A—C9—H9B	108.5
O1—C2—O3	111.82 (9)	O1—C8A—C8	108.28 (9)
O1—C2—H2A	109.3	O1—C8A—C4A	110.67 (9)
O3—C2—H2A	109.3	C8—C8A—C4A	110.10 (9)
O1—C2—H2B	109.3	O1—C8A—H8AA	109.3
O3—C2—H2B	109.3	C8—C8A—H8AA	109.3
H2A—C2—H2B	107.9	C4A—C8A—H8AA	109.3
O3—C4—C9	104.08 (9)	O9—C10—N1	125.90 (10)
O3—C4—C4A	110.60 (8)	O9—C10—O8	123.03 (10)
C9—C4—C4A	114.97 (9)	N1—C10—O8	111.08 (9)
O3—C4—H4	109.0	C16—C11—C12	120.17 (10)
C9—C4—H4	109.0	C16—C11—N1	119.26 (10)
C4A—C4—H4	109.0	C12—C11—N1	120.52 (10)
O5—C4A—C4	108.61 (9)	C13—C12—C11	119.75 (11)
O5—C4A—C8A	110.56 (8)	C13—C12—H12	120.1
C4—C4A—C8A	110.09 (9)	C11—C12—H12	120.1
O5—C4A—H4A	109.2	C14—C13—C12	120.31 (11)
C4—C4A—H4A	109.2	C14—C13—H13	119.8
C8A—C4A—H4A	109.2	C12—C13—H13	119.8
O7—C6—O5	111.66 (9)	C13—C14—C15	119.77 (11)
O7—C6—H6A	109.3	C13—C14—H14	120.1
O5—C6—H6A	109.3	C15—C14—H14	120.1
O7—C6—H6B	109.3	C14—C15—C16	120.39 (11)
O5—C6—H6B	109.3	C14—C15—H15	119.8
H6A—C6—H6B	108.0	C16—C15—H15	119.8
O7—C8—C8A	111.20 (10)	C11—C16—C15	119.60 (11)
O7—C8—H8A	109.4	C11—C16—H16	120.2
C8A—C8—H8A	109.4	C15—C16—H16	120.2
O7—C8—H8B	109.4		
C8A—O1—C2—O3	64.04 (13)	O7—C8—C8A—C4A	−49.89 (13)
C4—O3—C2—O1	−64.56 (13)	O5—C4A—C8A—O1	−71.14 (11)
C2—O3—C4—C9	−179.25 (9)	C4—C4A—C8A—O1	48.87 (12)
C2—O3—C4—C4A	56.74 (11)	O5—C4A—C8A—C8	48.53 (12)
C6—O5—C4A—C4	−175.73 (9)	C4—C4A—C8A—C8	168.54 (9)
C6—O5—C4A—C8A	−54.84 (11)	C11—N1—C10—O9	0.04 (18)
O3—C4—C4A—O5	71.73 (11)	C11—N1—C10—O8	−179.59 (9)
C9—C4—C4A—O5	−45.78 (12)	C9—O8—C10—O9	−8.87 (15)
O3—C4—C4A—C8A	−49.46 (12)	C9—O8—C10—N1	170.76 (9)
C9—C4—C4A—C8A	−166.96 (9)	C10—N1—C11—C16	130.24 (11)
C8—O7—C6—O5	−63.89 (13)	C10—N1—C11—C12	−52.41 (15)
C4A—O5—C6—O7	63.36 (13)	C16—C11—C12—C13	−0.13 (16)
C6—O7—C8—C8A	57.21 (13)	N1—C11—C12—C13	−177.46 (10)
C10—O8—C9—C4	−177.55 (8)	C11—C12—C13—C14	0.38 (17)
O3—C4—C9—O8	175.86 (8)	C12—C13—C14—C15	−0.58 (19)
C4A—C4—C9—O8	−63.01 (12)	C13—C14—C15—C16	0.53 (19)
C2—O1—C8A—C8	−176.28 (10)	C12—C11—C16—C15	0.09 (17)

| C2—O1—C8A—C4A | −55.53 (12) | N1—C11—C16—C15 | 177.45 (10) |
| O7—C8—C8A—O1 | 71.22 (12) | C14—C15—C16—C11 | −0.29 (18) |

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O9[i]	0.863 (16)	1.969 (16)	2.8025 (13)	161.9 (14)
C2—H2*B*···O5[ii]	0.99	2.51	3.4515 (15)	159

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) *x*, −*y*+3/2, *z*+1/2.