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Crystal structure of 4-nitrophenyl 6-O-ethyl-β-D-galactopyranoside monohydrate

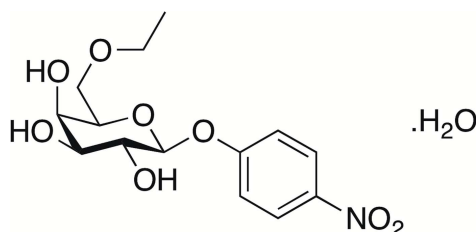
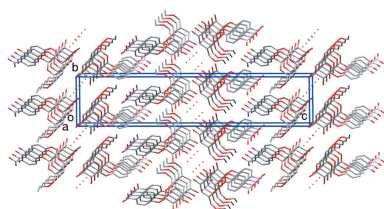
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The synthesis and crystal structure of the title compound, C₁₄H₁₉NO₈·H₂O, prepared in three steps from 6-*O*-ethyl-1,2;3,4-di-*O*-isopropylidene-α-D-galactopyranose using protecting-group strategies employed in carbohydrate chemistry, is reported. The asymmetric unit consists of a single galactoside molecule, in which the pyranoid ring has a ⁴C₁ conformation and the 4-nitrophenyl moiety is essentially planar. In the crystal, each carbohydrate is surrounded by other D-galactose residues and water molecules, linked by O—H···O hydrogen bonds involving all hydroxy groups, giving a two-dimensional substructure lying parallel to (100) and extended into three dimensions by C—H···O interactions.

1. Chemical context

Small molecules containing D-galactose moieties substituted at non-anomeric positions have been assayed against galactosidases (Viana *et al.*, 2011; McCarter *et al.*, 1992; Huber & Gaunt, 1983) and lectins (Butera *et al.*, 2009; Salameh *et al.*, 2005). *Trypanosoma cruzi* trans-sialidase (TcTS) (Mendonça-Previato *et al.*, 2010), an enzyme involved in Chagas's disease infection, is inhibited by β-D-galactopyranosides substituted at the C6 ring site, which are in general more potent than the corresponding analogues modified at other ring positions of the carbohydrate (Harrison *et al.*, 2011). In this context, the title compound C₁₄H₁₉NO₈ was designed and synthesized to be evaluated against TcTS and *T. cruzi* invasion of host cells. The synthesis and crystal structure of this compound as the monohydrate (I) is reported herein.



2. Structural commentary

In the structure of the title monohydrated compound (I) (Fig. 1), the pyranoid ring adopts a ⁴C₁ conformation, with puckering parameters $Q = 0.569$ (2) Å, $\theta = 4.6$ (2)° and $\varphi = 51$ (3)°. The anomeric *beta* form and D-galacto configuration of the carbohydrate with C1(*S*), C2(*R*), C3(*S*), C4(*R*) and

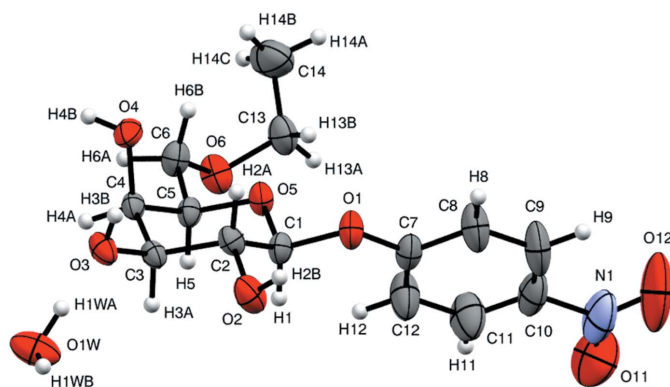


Figure 1
The molecular structure of the title compound with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

C5(*R*) are consistent with that expected from the synthesis. The length of the glycosidic bond is 1.408 (2) Å and the bond angles around the anomeric carbon atom (C1) range from 106.40 (16) to 111.35 (17)°. The 4-nitrophenyl substituent at C1 located in an equatorial position is essentially planar, with a r.m.s. deviation of 0.02 Å for non-hydrogen atoms [torsion angle C9–C10–N1–O11 = 179.0 (4)°]. The angle between the mean plane of the 4-nitrophenyl substituent (defined by atoms C7–C12/N1/O11/O12) and the mean sugar plane (defined by C1–C5/O5 atoms) is 57.45 (11)° [torsion angle O5–C1–O1–O7 = –79.8 (2)°]. An intramolecular C13–H13B···O5 interaction is also present (Table 1).

3. Supramolecular features

In the crystal, a carbohydrate moiety is connected to eight neighboring *D*-galactose residues by several direct and water-mediated classical hydrogen bonds (Table 1), establishing a network of interactions (Fig. 2). Regarding only the O–H···O interaction type, there are O2–H2B···O6ⁱ, O3–H3B···O1Wⁱⁱ and O4–H4B···O3ⁱⁱⁱ hydrogen bonds. In addition, there is a single-water bridge connecting O3 to O2 of

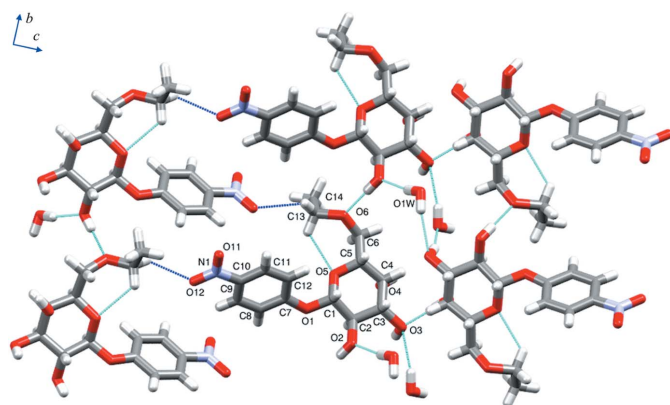


Figure 2
Selected interactions in the crystal lattice with O–H···O hydrogen bonds shown as turquoise dashed lines and C–H···O interactions shown as blue dashed lines.

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O2–H2B···O6 ⁱ	0.82	1.85	2.670 (2)	179
O3–H3B···O1W ⁱⁱ	0.82	1.91	2.711 (2)	167
O4–H4B···O3 ⁱⁱⁱ	0.82	1.97	2.785 (2)	170
O1W–H1WA···O2 ^{iv}	0.89	1.90	2.776 (3)	166
O1W–H1WB···O3 ^v	0.89	2.39	3.208 (2)	154
C3–H3A···O4 ^{vi}	0.98	2.35	3.283 (3)	158
C13–H13A···O12 ^{vii}	0.97	2.55	3.167 (3)	121
C13–H13B···O5	0.97	2.53	3.173 (3)	123

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

a nearby galactoside molecule (O1W–H1WA···O2^{iv} and O1W–H1WB···O3^v; for symmetry codes, see Table 1). A two-dimensional substructure in the form of a sheet lying parallel to (100) is formed. The overall three-dimensional supramolecular aggregation is completed by intermolecular C–H···O interactions: C3–H3A···O4^{vi} connects carbohydrate rings stacked along the *a* axis and C13–H13A···O12^{vii} connects ethyl and nitro groups along the *c* axis. The 4-nitrophenyl substituent groups are arranged in parallel planes (Fig. 3), with an interplanar distance of 3.4355 (14) Å, but the slip angle (48.3°) prevents overlapping and therefore no π – π interactions are present [ring-centroid separation = 5.163 (2) Å].

4. Database survey

To the best of our knowledge, this is the first report of the crystal structure of an aryl 6-*O*-substituted- β -*D*-galactopyranoside in the literature. In the Cambridge Structural Database (Version 5.38; Groom *et al.*, 2016), the structural data for the closely related analogue 4-nitrophenyl β -*D*-galactopyranoside have been deposited (CSD Refcode VUCYO1; Gubica *et al.*, 2009). Both galactosides are monohydrates and their molecular geometry and intermolecular interaction profiles in the crystal lattice are quite similar. The aromatic ring of the 6-unsubstituted galactoside is less planar

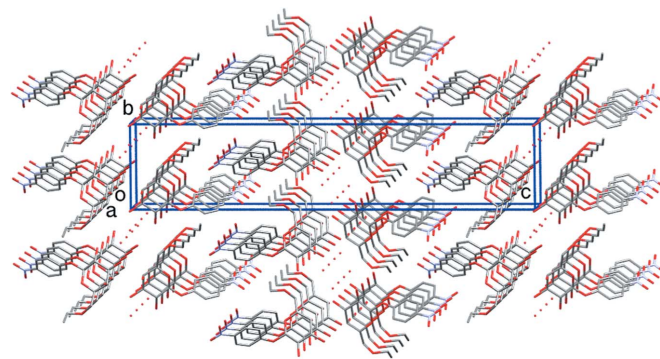


Figure 3
Crystal packing of the title compound, showing the stacked galactoside molecules along the *a* axis. For clarity, H atoms are not shown.

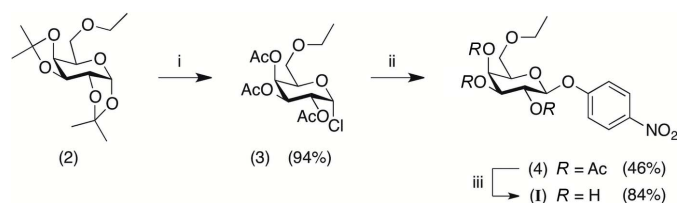


Figure 4

Synthesis of the title compound (I): (i) AcCl, MeOH, HCl_(aq), room temperature, closed system; (ii) 4-nitrophenol, LiOH·H₂O, acetone/H₂O, room temperature; (iii) MeONa/MeOH, CH₂Cl₂, 273 K. The water molecule of crystallization of (I) is not represented.

due to the increased rotation of the N1—C10 bond, since the angle between the mean planes of the phenyl and nitro groups is *ca.* 5.1°, compared to 2.6 (5)° in the title compound. According to the authors (Gubica *et al.*, 2009), the deviation from coplanarity of these fragments in the 4-nitrophenyl β-D-galactopyranoside structure is due to intermolecular interactions involving the nitro group. In our crystallographic study on compound (I) we did not observe classical hydrogen bonds to 4-nitrophenyl O-atom acceptors, but only the weak C13—H13A···O12 interaction noted above.

5. Synthesis and crystallization

The chemical synthesis of 4-nitrophenyl 6-O-ethyl-β-D-galactopyranoside monohydrate (I) was achieved in three steps, as shown in Fig. 4.

Initially the *O*-alkylation of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose was carried out as reported in the literature furnishing the 6-*O*-alkylated derivative (2) (Cironi & Varela, 2001; McKeown & Hayward, 1960). Next, the peracetylated α-D-galactopyranosyl chloride (3) was prepared in a three-step one-pot reaction as follows. To a solution of (2) (0.59 g, 2.06 mmol) in acetyl chloride (2.92 mL, 41.13 mmol) was added methanol (0.42 mL) under ice-bath conditions. The mixture was stirred at room temperature for 2 h in a closed system and concentrated hydrochloric acid (0.34 mL) was then added and the resulting mixture was stirred at room temperature for 24 h, also in a closed system. The reaction was quenched with crushed ice (about 30 mL) and the mixture was extracted with dichloromethane (3 × 25 mL). The organic layers were washed with a saturated aqueous sodium bicarbonate solution (2 × 60 mL) and water (60 mL), then dried over anhydrous sodium sulfate and concentrated. The brown oil obtained (0.68 g, 94% yield) was used in the next step without further purification.

Classical procedures in carbohydrate chemistry were employed in the next two steps (Conchie *et al.*, 1957). The glycosylation of 4-nitrophenol with (3) in alkaline medium gave (4) in 46% yield. Treatment with sodium methoxide to remove the acetyl groups furnished (I) (as the monohydrate), in 84% yield. Colorless crystals of (I) (m.p. 424.1–424.9 K) suitable for X-ray diffraction analysis were obtained by slow evaporation of an acetone solution (about 0.7 mg/mL) at room temperature.

Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₄ H ₁₉ NO ₈ ·H ₂ O
<i>M_r</i>	347.32
Crystal system, space group	Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.1628 (3), 8.1593 (3), 38.5755 (16)
<i>V</i> (Å ³)	1624.99 (13)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm ⁻¹)	0.12
Crystal size (mm)	0.20 × 0.15 × 0.10
Data collection	
Diffractometer	Rigaku OD Xcalibur, Atlas, Gemini Ultra
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.835, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	26976, 4265, 3597
<i>R</i> _{int}	0.038
(sin θ/λ) _{max} (Å ⁻¹)	0.704
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.046, 0.108, 1.08
No. of reflections	4265
No. of parameters	218
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.20, -0.23

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Spectrometric data. [α]_D²⁸ -46 (*c* 1.0, DMSO). IR $\bar{\nu}_{\max}$ (cm⁻¹): 3354 (O—H), 1608, 1592, 1493 (C=C), 1511, 1349 (NO₂), 1249, 1074 (C—O), 846 (C—H aromatic out-of-plane bending). ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 8.20 (*d*, 2H, *J*_{ortho} 9.2 Hz, *CHCNO*₂), 7.22 (*d*, 2H, *J*_{ortho} 9.2 Hz, *OCCH*), 5.28 (*d*, 1H, *J*_{OH-2,2} 5.2 Hz, OH-2), 5.05 (*d*, 1H, *J*_{1,2} 7.6 Hz, H-1), 4.91 (*d*, 1H, *J*_{OH-3,3} 5.7 Hz, OH-3), 4.64 (*d*, 1H, *J*_{OH-4,4} 4.6 Hz, OH-4), 3.85 (*t*, 1H, *J*_{5,6a} 5.4 Hz, *J*_{5,6b} 5.4 Hz, H-5), 3.71–3.66 (*m*, 1H, H-4), 3.63 (*ddd*, 1H, *J*_{2,1} 7.6 Hz, *J*_{2,OH-2} 5.2 Hz, *J*_{2,3} 9.2 Hz, H-2), 3.55 (*dd*, 1H, *J*_{6a,5} 5.4 Hz, *J*_{6a,6b} 10.2 Hz, H-6a), 3.50–3.39 (*m*, 4H, H-3, H-6b and *OCH*₂CH₃), 1.09 (*t*, 3H, *J*_{ortho} 6.9 Hz, *OCH*₂CH₃). ¹³C NMR (100 MHz, DMSO-*d*₆): δ_C 162.4 (*OCCH*), 141.6 (*CHCNO*₂), 125.6 (*CHCNO*₂), 116.5 (*OCCH*), 100.3 (C-1), 73.8 (C-5), 73.0 (C-3), 70.0 (C-2), 69.1 (C-6), 68.3 (C-4), 65.7 (*OCH*₂CH₃), 15.1 (*OCH*₂CH₃).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Oxygen-bound H atoms were located in a difference-Fourier map and refined with distance restraints of 0.82 Å (hydroxy group H) and 0.89 Å (water H) with *U*_{iso}(H) = 1.5 *U*_{eq}(O). Carbon-bound H atoms were constrained to an ideal geometry with C—H distances in the range 0.93–0.98 Å, *U*_{iso}(H) = 1.5 *U*_{eq}(C) for methyl H atoms and *U*_{iso}(H) = 1.2 *U*_{eq}(C) for other H atoms. In the absence of significant anomalous scattering effects, the Flack structure parameter (Flack, 1983) is essentially meaningless in this

analysis and the absolute configuration is inferred from the known D-galacto configuration of the starting material, and remained unchanged during the synthesis. The *beta* configuration of C1 is confirmed by the coupling constant $J_{1,2} = 7.6$ Hz, obtained from NMR spectroscopy.

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Crystal structure of 4-nitrophenyl 6-O-ethyl- β -D-galactopyranoside monohydrate

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *pubCIF* (Westrip, 2010).

4-Nitrophenyl 6-O-ethyl- β -D-galactopyranoside monohydrate

Crystal data

$C_{14}H_{19}NO_8 \cdot H_2O$

$M_r = 347.32$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 5.1628$ (3) Å

$b = 8.1593$ (3) Å

$c = 38.5755$ (16) Å

$V = 1624.99$ (13) Å³

$Z = 4$

$F(000) = 736$

$D_x = 1.420$ Mg m⁻³

Melting point: 424.5 K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 8847 reflections

$\theta = 2.5$ – 28.5°

$\mu = 0.12$ mm⁻¹

$T = 293$ K

Rod, colourless

$0.20 \times 0.15 \times 0.10$ mm

Data collection

Rigaku OD Xcalibur, Atlas, Gemini Ultra diffractometer

Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 10.4186 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Rigaku OD, 2015)

$T_{\min} = 0.835$, $T_{\max} = 1.000$

26976 measured reflections

4265 independent reflections

3597 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 30.0^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -7 \rightarrow 7$

$k = -11 \rightarrow 11$

$l = -54 \rightarrow 52$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.108$

$S = 1.08$

4265 reflections

218 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 0.4091P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.20 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$$

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.2973 (3)	0.04259 (19)	0.13258 (4)	0.0359 (4)
O2	0.3964 (4)	-0.11807 (19)	0.06875 (4)	0.0413 (4)
H2B	0.3333	-0.1933	0.0800	0.062*
O3	0.1726 (3)	0.0335 (2)	0.00904 (4)	0.0331 (4)
H3B	0.0444	-0.0206	0.0142	0.050*
O4	-0.1450 (3)	0.2630 (2)	0.04353 (4)	0.0340 (4)
H4B	-0.2160	0.3194	0.0287	0.051*
O5	0.1951 (3)	0.27596 (18)	0.10442 (3)	0.0300 (3)
O6	0.1929 (4)	0.63541 (19)	0.10524 (4)	0.0388 (4)
O11	1.0131 (8)	0.2628 (5)	0.25526 (8)	0.1100 (12)
O12	0.7670 (9)	0.0893 (4)	0.28005 (6)	0.1237 (14)
N1	0.8375 (8)	0.1651 (4)	0.25473 (7)	0.0748 (10)
C1	0.3383 (4)	0.1298 (3)	0.10156 (5)	0.0285 (4)
H1	0.5228	0.1538	0.0984	0.034*
C2	0.2387 (5)	0.0236 (3)	0.07205 (5)	0.0283 (4)
H2A	0.0581	-0.0078	0.0762	0.034*
C3	0.2607 (4)	0.1215 (2)	0.03863 (5)	0.0257 (4)
H3A	0.4454	0.1433	0.0350	0.031*
C4	0.1277 (4)	0.2877 (3)	0.04194 (5)	0.0254 (4)
H4A	0.1685	0.3539	0.0215	0.030*
C5	0.2224 (4)	0.3771 (2)	0.07412 (5)	0.0266 (4)
H5	0.4057	0.4049	0.0711	0.032*
C6	0.0717 (5)	0.5319 (3)	0.08045 (6)	0.0340 (5)
H6A	0.0534	0.5910	0.0588	0.041*
H6B	-0.1005	0.5037	0.0886	0.041*
C7	0.4348 (5)	0.0860 (3)	0.16169 (6)	0.0350 (5)
C8	0.3682 (7)	-0.0008 (3)	0.19102 (6)	0.0521 (7)
H8	0.2354	-0.0778	0.1902	0.062*
C9	0.5004 (8)	0.0274 (4)	0.22159 (7)	0.0629 (9)
H9	0.4563	-0.0297	0.2416	0.076*
C10	0.6952 (6)	0.1392 (4)	0.22221 (6)	0.0515 (7)
C11	0.7581 (8)	0.2284 (5)	0.19380 (7)	0.0651 (9)

H11	0.8884	0.3069	0.1950	0.078*
C12	0.6266 (7)	0.2019 (4)	0.16305 (7)	0.0596 (9)
H12	0.6684	0.2623	0.1434	0.072*
C13	0.0993 (6)	0.6211 (3)	0.14011 (6)	0.0431 (6)
H13A	0.2266	0.6673	0.1558	0.052*
H13B	0.0799	0.5059	0.1458	0.052*
C14	-0.1538 (7)	0.7057 (5)	0.14554 (9)	0.0696 (10)
H14A	-0.1984	0.7024	0.1697	0.104*
H14B	-0.2858	0.6514	0.1323	0.104*
H14C	-0.1400	0.8177	0.1381	0.104*
O1W	0.7487 (4)	0.8396 (2)	0.01513 (5)	0.0579 (6)
H1WA	0.6231	0.8390	0.0309	0.087*
H1WB	0.7808	0.7339	0.0114	0.087*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0504 (10)	0.0340 (8)	0.0232 (7)	-0.0048 (8)	-0.0058 (7)	0.0061 (6)
O2	0.0589 (11)	0.0259 (8)	0.0391 (9)	0.0043 (8)	0.0131 (8)	0.0045 (7)
O3	0.0378 (8)	0.0389 (8)	0.0226 (7)	-0.0109 (7)	0.0029 (6)	-0.0054 (6)
O4	0.0266 (8)	0.0428 (9)	0.0326 (8)	-0.0055 (7)	-0.0060 (7)	0.0056 (7)
O5	0.0428 (9)	0.0267 (7)	0.0205 (6)	0.0025 (7)	-0.0005 (7)	0.0016 (6)
O6	0.0548 (11)	0.0289 (8)	0.0326 (8)	-0.0085 (8)	0.0020 (8)	-0.0043 (7)
O11	0.101 (2)	0.158 (3)	0.0708 (18)	-0.019 (3)	-0.0407 (17)	-0.029 (2)
O12	0.211 (4)	0.120 (2)	0.0396 (12)	-0.013 (3)	-0.0491 (19)	0.0032 (15)
N1	0.104 (3)	0.082 (2)	0.0393 (14)	0.021 (2)	-0.0273 (16)	-0.0178 (14)
C1	0.0346 (11)	0.0263 (10)	0.0247 (9)	-0.0019 (9)	-0.0023 (9)	0.0051 (8)
C2	0.0335 (11)	0.0256 (9)	0.0258 (9)	-0.0022 (9)	0.0035 (9)	0.0010 (8)
C3	0.0283 (10)	0.0289 (10)	0.0199 (8)	-0.0053 (9)	0.0013 (8)	-0.0012 (8)
C4	0.0275 (10)	0.0287 (10)	0.0200 (9)	-0.0053 (8)	-0.0007 (8)	0.0044 (8)
C5	0.0305 (11)	0.0259 (9)	0.0234 (9)	-0.0055 (9)	-0.0031 (8)	0.0034 (8)
C6	0.0435 (13)	0.0289 (10)	0.0296 (10)	0.0001 (10)	-0.0060 (9)	0.0001 (9)
C7	0.0494 (14)	0.0309 (11)	0.0248 (10)	0.0063 (10)	-0.0055 (10)	-0.0004 (9)
C8	0.085 (2)	0.0448 (15)	0.0267 (11)	-0.0106 (15)	-0.0050 (13)	0.0029 (10)
C9	0.109 (3)	0.0573 (17)	0.0229 (11)	-0.002 (2)	-0.0065 (15)	0.0044 (12)
C10	0.071 (2)	0.0533 (16)	0.0296 (12)	0.0133 (16)	-0.0161 (13)	-0.0103 (12)
C11	0.074 (2)	0.079 (2)	0.0422 (15)	-0.024 (2)	-0.0151 (15)	-0.0040 (15)
C12	0.076 (2)	0.069 (2)	0.0341 (13)	-0.0261 (18)	-0.0139 (14)	0.0098 (13)
C13	0.0567 (16)	0.0445 (14)	0.0282 (11)	-0.0012 (13)	0.0004 (11)	-0.0034 (11)
C14	0.0544 (19)	0.097 (3)	0.0570 (18)	0.0062 (19)	0.0048 (15)	-0.0203 (18)
O1W	0.0500 (11)	0.0482 (11)	0.0753 (13)	-0.0145 (10)	0.0207 (11)	-0.0187 (10)

Geometric parameters (Å, °)

O1—C1	1.408 (2)	C5—H5	0.9800
O1—C7	1.375 (3)	C5—C6	1.504 (3)
O2—H2B	0.8200	C6—H6A	0.9700
O2—C2	1.420 (3)	C6—H6B	0.9700

O3—H3B	0.8201	C7—C8	1.379 (3)
O3—C3	1.423 (2)	C7—C12	1.370 (4)
O4—H4B	0.8199	C8—H8	0.9300
O4—C4	1.424 (3)	C8—C9	1.382 (4)
O5—C1	1.408 (3)	C9—H9	0.9300
O5—C5	1.438 (2)	C9—C10	1.358 (5)
O6—C6	1.421 (3)	C10—C11	1.355 (4)
O6—C13	1.434 (3)	C11—H11	0.9300
O11—N1	1.207 (5)	C11—C12	1.384 (4)
O12—N1	1.212 (4)	C12—H12	0.9300
N1—C10	1.469 (4)	C13—H13A	0.9700
C1—H1	0.9800	C13—H13B	0.9700
C1—C2	1.520 (3)	C13—C14	1.493 (4)
C2—H2A	0.9800	C14—H14A	0.9600
C2—C3	1.521 (3)	C14—H14B	0.9600
C3—H3A	0.9800	C14—H14C	0.9600
C3—C4	1.526 (3)	O1W—H1WA	0.8898
C4—H4A	0.9800	O1W—H1WB	0.8902
C4—C5	1.520 (3)		
C7—O1—C1	119.10 (18)	C6—C5—H5	108.9
C2—O2—H2B	109.5	O6—C6—C5	112.37 (18)
C3—O3—H3B	109.5	O6—C6—H6A	109.1
C4—O4—H4B	109.4	O6—C6—H6B	109.1
C1—O5—C5	111.77 (15)	C5—C6—H6A	109.1
C6—O6—C13	115.74 (19)	C5—C6—H6B	109.1
O11—N1—O12	123.3 (3)	H6A—C6—H6B	107.9
O11—N1—C10	119.0 (3)	O1—C7—C8	114.2 (2)
O12—N1—C10	117.7 (4)	C12—C7—O1	125.6 (2)
O1—C1—H1	110.5	C12—C7—C8	120.2 (2)
O1—C1—C2	107.33 (16)	C7—C8—H8	120.3
O5—C1—O1	106.40 (16)	C7—C8—C9	119.5 (3)
O5—C1—H1	110.5	C9—C8—H8	120.3
O5—C1—C2	111.35 (17)	C8—C9—H9	120.2
C2—C1—H1	110.5	C10—C9—C8	119.5 (3)
O2—C2—C1	109.70 (18)	C10—C9—H9	120.2
O2—C2—H2A	110.3	C9—C10—N1	118.8 (3)
O2—C2—C3	107.99 (16)	C11—C10—N1	119.6 (3)
C1—C2—H2A	110.3	C11—C10—C9	121.6 (3)
C1—C2—C3	108.08 (16)	C10—C11—H11	120.3
C3—C2—H2A	110.3	C10—C11—C12	119.4 (3)
O3—C3—C2	113.03 (16)	C12—C11—H11	120.3
O3—C3—H3A	106.8	C7—C12—C11	119.7 (3)
O3—C3—C4	111.82 (17)	C7—C12—H12	120.1
C2—C3—H3A	106.8	C11—C12—H12	120.1
C2—C3—C4	111.25 (16)	O6—C13—H13A	109.0
C4—C3—H3A	106.8	O6—C13—H13B	109.0
O4—C4—C3	108.80 (17)	O6—C13—C14	112.9 (2)

O4—C4—H4A	109.0	H13A—C13—H13B	107.8
O4—C4—C5	110.55 (17)	C14—C13—H13A	109.0
C3—C4—H4A	109.0	C14—C13—H13B	109.0
C5—C4—C3	110.47 (17)	C13—C14—H14A	109.5
C5—C4—H4A	109.0	C13—C14—H14B	109.5
O5—C5—C4	110.93 (16)	C13—C14—H14C	109.5
O5—C5—H5	108.9	H14A—C14—H14B	109.5
O5—C5—C6	107.41 (17)	H14A—C14—H14C	109.5
C4—C5—H5	108.9	H14B—C14—H14C	109.5
C6—C5—C4	111.64 (17)	H1WA—O1W—H1WB	104.0
O1—C1—C2—O2	-67.1 (2)	C1—O5—C5—C6	-177.75 (17)
O1—C1—C2—C3	175.37 (17)	C1—C2—C3—O3	179.94 (18)
O1—C7—C8—C9	177.4 (3)	C1—C2—C3—C4	-53.3 (2)
O1—C7—C12—C11	-177.0 (3)	C2—C3—C4—O4	-70.0 (2)
O2—C2—C3—O3	61.3 (2)	C2—C3—C4—C5	51.5 (2)
O2—C2—C3—C4	-171.91 (17)	C3—C4—C5—O5	-53.3 (2)
O3—C3—C4—O4	57.4 (2)	C3—C4—C5—C6	-173.06 (17)
O3—C3—C4—C5	178.97 (16)	C4—C5—C6—O6	-166.46 (18)
O4—C4—C5—O5	67.2 (2)	C5—O5—C1—O1	179.69 (16)
O4—C4—C5—C6	-52.6 (2)	C5—O5—C1—C2	-63.7 (2)
O5—C1—C2—O2	176.81 (16)	C6—O6—C13—C14	-77.1 (3)
O5—C1—C2—C3	59.3 (2)	C7—O1—C1—O5	-79.8 (2)
O5—C5—C6—O6	71.7 (2)	C7—O1—C1—C2	160.93 (19)
O11—N1—C10—C9	179.0 (4)	C7—C8—C9—C10	-0.5 (5)
O11—N1—C10—C11	-2.0 (5)	C8—C7—C12—C11	1.6 (5)
O12—N1—C10—C9	-2.8 (5)	C8—C9—C10—N1	-178.7 (3)
O12—N1—C10—C11	176.2 (4)	C8—C9—C10—C11	2.3 (5)
N1—C10—C11—C12	178.9 (3)	C9—C10—C11—C12	-2.1 (5)
C1—O1—C7—C8	176.3 (2)	C10—C11—C12—C7	0.1 (6)
C1—O1—C7—C12	-4.9 (4)	C12—C7—C8—C9	-1.4 (5)
C1—O5—C5—C4	60.0 (2)	C13—O6—C6—C5	-96.4 (2)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2B \cdots O6 ⁱ	0.82	1.85	2.670 (2)	179
O3—H3B \cdots O1W ⁱⁱ	0.82	1.91	2.711 (2)	167
O4—H4B \cdots O3 ⁱⁱⁱ	0.82	1.97	2.785 (2)	170
O1W—H1WA \cdots O2 ^{iv}	0.89	1.90	2.776 (3)	166
O1W—H1WB \cdots O3 ^v	0.89	2.39	3.208 (2)	154
C3—H3A \cdots O4 ^{vi}	0.98	2.35	3.283 (3)	158
C13—H13A \cdots O12 ^{vii}	0.97	2.55	3.167 (3)	121
C13—H13B \cdots O5	0.97	2.53	3.173 (3)	123

Symmetry codes: (i) $x, y-1, z$; (ii) $x-1, y-1, z$; (iii) $x-1/2, -y+1/2, -z$; (iv) $x, y+1, z$; (v) $x+1/2, -y+1/2, -z$; (vi) $x+1, y, z$; (vii) $-x+1, y+1/2, -z+1/2$.