Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure of 4,6-dimethyl-2-[(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)sulfanyl]pyrimidine

Mamdouh A. Abu-Zaied,[a] Galal H. Elgemeie[b] and Peter G. Jones[c]*

[a]Green Chemistry Department, National Research Centre, 33 El Bohouth Street, Dokki, Giza, Egypt, [b]Chemistry Department, Faculty of Science, Helwan University, Cairo, Egypt, and [c]Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany. *Correspondence e-mail: p.jones@tu-bs.de

Received 17 October 2019
Accepted 24 October 2019

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: crystal structure; galactose; pyrimidine; weak hydrogen bond.

CCDC reference: 1962352

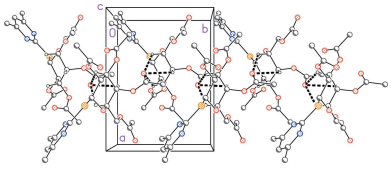
Supporting information: this article has supporting information at journals.iucr.org/e

In the title compound, $C_{20}H_{26}N_2O_9S$, the S atom is attached equatorially to the sugar ring. The C—S bond lengths are unequal, with S—C_s = 1.8018 (13) Å and S—C_p = 1.7662 (13) Å (s = sugar and p = pyrimidyl). In the crystal, a system of three weak hydrogen bonds, sharing an oxygen acceptor, links the molecules to form chains propagating parallel to the *b*-axis direction.

1. Chemical context

Nucleosides are building blocks of biological systems and display a wide range of biological activities (Ding *et al.*, 2003). Pyrimidine nucleoside analogues provide diverse and novel moieties for pharmacological targets, and they play basic and comprehensive roles in the field of medicinal chemistry (Xu *et al.*, 2017). Different strategies for the synthesis of many pyrimidine nucleoside analogues have been developed to access new and potent pharmacological agents (Cao *et al.*, 2011). Many such derivatives are manufactured as potential chemotherapeutic agents and have a significant impact on current medicinal research (Ohkubo *et al.*, 2012). Recently, thioglycosides have proved to be important in the production of medically important carbohydrate compounds, because of their ease of preparation and chemical stability (Gourdain *et al.*, 2011).

We have recently described the preparation of various pyrimidine and pyridine thioglycosides that displayed antagonistic activity (Hammad *et al.*, 2018; Elgemeie *et al.*, 2010). We have also reported the use of dihydropyridine thioglycosides as substrates or inhibitors of protein glycosylation (Scale *et al.*, 1997; Elgemeie *et al.*, 2015, 2016, 2017) and the use of pyrimidine thioglycosides as antihepatocellular carcinoma agents (Elgemeie & Farag, 2017). Continuing our efforts to develop simple and cost-effective methodologies for the synthesis of pyrimidine thioglycosides, we report here the one-step synthesis of a pyrimidine-2-thiogalactoside derivative by the reaction of 4,6-dimethylpyrimidine-2(1*H*)-thione (**1**) with 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**2**). This reaction in NaH/DMF at room temperature gave a product for which two isomeric structures seemed possible, corresponding to two possible modes of glysosylation to give the pyrimidine-*N*-galactoside (**3**) or its regioisomer pyrimidine-2-thiogalactoside **4** (see Scheme). Spectroscopic data cannot differentiate between these structures. It has been suggested that **1** reacts with **2** *via* a simple S_N2 reaction to give the β-glycoside product **4** (Davis, 2000).



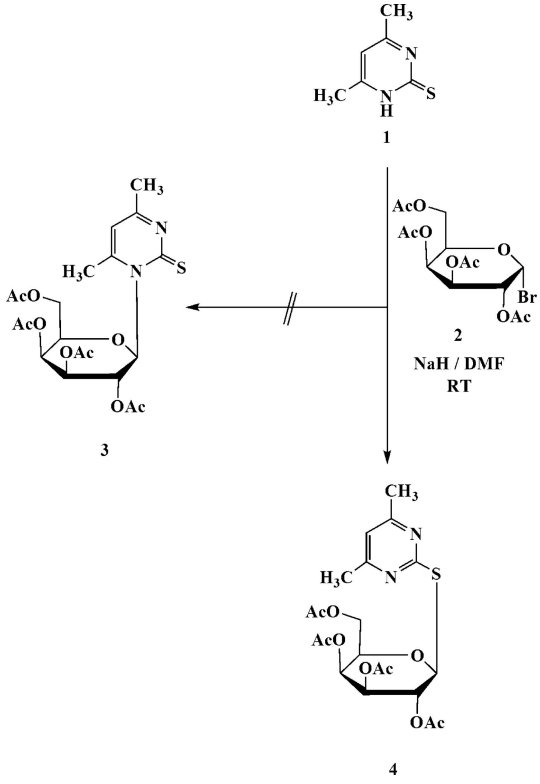
OPEN ACCESS

Table 1
Selected torsion angles (°).

S1—C11—C12—C13	178.21 (9)	C22—C21—O4—C14	177.90 (11)
S1—C11—O1—C15	171.60 (8)	C24—C23—O5—C16	178.85 (13)
C18—C17—O2—C12	176.21 (11)	C15—C16—O5—C23	174.82 (12)
C20—C19—O3—C13	−173.83 (12)		

2. Structural commentary

The crystal structure determination indicated unambiguously the formation of the pyrimidine-2-thiogalactoside, **4**, as the only product in the solid state.



The molecular structure of **4** is shown in Fig. 1 (for selected torsion angles, see Table 1) and the S atom is attached equatorially to the sugar ring. Similar to the structure of a related glucose derivative (Masoud *et al.*, 2017), the C—S bond lengths are unequal, with S—C_s = 1.8018 (13) Å and S—C_p = 1.7662 (13) Å (s = sugar and p = pyrimidyl). The relative orientation of the pyridyl ring and the sugar moiety is defined by the torsion angles N2—C1—S1—C11 [−7.85 (12)°] and C1—S1—C11—C12 [165.01 (9)°]. All the acetyl groups show extended conformations, with absolute C—O—C—C torsion angles in the range 173–179°.

3. Supramolecular features

Some short C—H···O and C—H···S contacts are listed in Table 2, but these are at best borderline 'weak' hydrogen bonds, particularly in view of their narrow angles. The molecular packing is thus rather featureless. However, a motif of three sugar-ring C—H groups (C13—H13, C14—H14 and C15—H15) sharing a common acceptor (O8) can be recognized (Fig. 2). Neighbouring molecules are connected *via* the 2_1 operator, leading to chains of molecules propagating parallel to the *b*-axis direction.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7*C*···O9^{i}	0.98	2.57	3.495 (2)	157
C8—H8*B*···O1^{ii}	0.98	2.52	3.2499 (18)	131
C13—H13···O8^{iii}	1.00	2.65	3.2998 (16)	123
C14—H14···O8^{iii}	1.00	2.53	3.0626 (16)	113
C15—H15···O8^{iii}	1.00	2.50	3.1759 (16)	124
C18—H18*B*···S1^{iv}	0.98	2.95	3.7876 (19)	144
C22—H22*C*···O6^{v}	0.98	2.51	3.1911 (19)	127

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

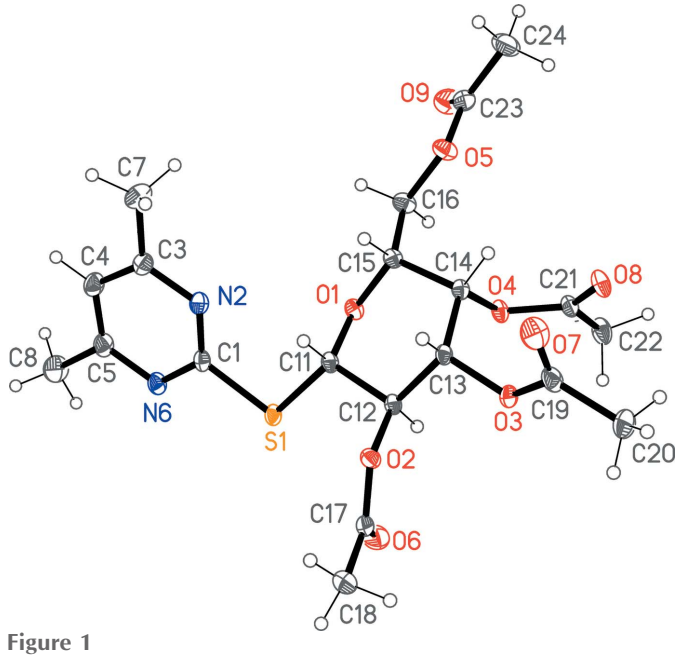


Figure 1
The molecular structure of the title compound, **4**, in the crystal. Displacement ellipsoids represent 50% probability levels.

4. Database survey

A search of the Cambridge Structural Database (Vwersion 2.0.0; Groom *et al.*, 2016) for tetraacetyl thioglycosides with an S-bonded heterocycle [linkage S—C(—N)$_2$, restricted to hexoses] gave one hit, a 1,2,4-triazole derivative of tetra-acetylglucose (refcode HEKPUL; El Ashry *et al.*, 2018).

5. Synthesis and crystallization

To a solution of pyrimidine-2(1*H*)-thione (**1**; 1.40 g, 0.01 mol) in dry DMF (20 ml), NaH (15 mmol) was added gradually over a period of 15 min and the solution was stirred at room temperature for another 30 min. A solution of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**2**; 4.52 g, 0.011 mol) in DMF (20 ml) was then added dropwise over a period of 30 min and the reaction mixture was stirred at room

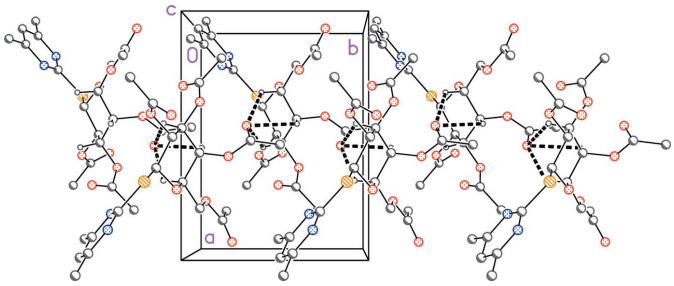


Figure 2
Packing diagram of **4** projected parallel to the *ab* plane in the region $z \simeq 1$. Dashed lines indicate weak C—H···O hydrogen bonds. H atoms not involved in this hydrogen bonding system have been omitted.

temperature until the reaction was judged complete by thin-layer chromatography (3–6 h). The mixture was evaporated under reduced pressure at 333 K and the residue was washed with distilled water to remove potassium bromide. The crude solid was collected by filtration and purified using column chromatography (the solvent system was petroleum ether/ethyl acetate, 3:1 *v*/*v*; R_F = 0.35); after evaporation of the solvent, this afforded compound **4** as colourless crystals in 85% yield (m.p. 441.2 K). IR (KBr, cm^{-1}): ν 1752 (C═O); ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.11 (*s*, 12H, 4 × OAc), 2.45 (*s*, 6H, 2CH$_3$), 4.01–4.12 (*m*, 2H, 2H-6′), 4.35–4.37 (*m*, 1H, H-5′), 5.21 (*t*, 1H, $J_{4'\text{-}3'}$ = 2.6, $J_{4'\text{-}5'}$ = 2.4 Hz, H-4′), 5.42–5.46 (*m*, 2H, H-3′, H-2′), 5.98 (*d*, 1H, $J_{1'\text{-}2'}$ = 10.65 Hz, H-1′), 7.01 (*s*, 1H, pyrimidine H-5); ^{13}C NMR: δ 21.43 (4 × OAc), 22.4 (2CH$_3$), 62.13 (C-6′), 68.41 (C-5′), 71.12 (C-4′), 74.43 (C-3′), 77.56 (C-2′), 82.12 (C-1′), 118.41 (C-5), 168.35 (C-4), 170.45 (C-6), 172.78 (4 × C═O). Analysis calculated (%) for $C_{20}H_{26}N_2O_9S$: C 51.06, H 5.57, N 5.95, S 6.82; found: C 51.16, H 5.46, N 5.82, S 6.75.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Methyl groups were refined as idealized rigid groups allowed to rotate but not tip (C—H = 0.98 Å and H—C—H = 109.5°). Other H atoms were included using a riding model starting from calculated positions (aromatic C—H = 0.95 Å, methylene C—H = 0.99 Å and methine C—H = 1.00 Å).

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{26}N_2O_9S$
M_r	470.49
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	100
a, *b*, *c* (Å)	11.4868 (2), 8.6444 (2), 11.5561 (2)
β (°)	91.3762 (16)
V (Å^3)	1147.14 (4)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.19
Crystal size (mm)	0.40 × 0.40 × 0.08
Data collection	
Diffractometer	Oxford Diffraction Xcalibur Eos
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.896, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	107162, 7825, 7530
R_{int}	0.034
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.757
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.073, 1.04
No. of reflections	7825
No. of parameters	295
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.21
Absolute structure	Flack *x* determined using 3355 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	−0.003 (11)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXS97* (Sheldrick, 2008), *SHELXL2017* (Sheldrick, 2015) and *XP* (Siemens, 1994).

Acknowledgements

GHE would like to thank the Egyptian Academy of Scientific Research & Technology (ASRT), Jesor program, for awarding a grant.

References

Cao, S., Okamoto, I., Tsunoda, H., Ohkubo, A., Seio, K. & Sekine, M. (2011). *Tetrahedron Lett.* **52**, 407–410.
Davis, B. G. (2000). *J. Chem. Soc. Perkin Trans. 1*, **14**, 2137–2160.
Ding, Y., Hofstadler, S. A., Swayze, E. E., Risen, L. & Griffey, R. H. (2003). *Angew. Chem. Int. Ed.* **42**, 3409–3412.
El Ashry El, S. H., Awad, L. F., Al Moaty, M. N. A., Ghabbour, H. A. & Barakwat, A. (2018). *J. Mol. Struct.* **1152**, 87–95.
Elgemeie, G. H., Abou-Zeid, M., Alsaid, S., Hebishy, A. & Essa, H. (2015). *Nucleosides Nucleotides*, **34**, 659–673.
Elgemeie, G. H., Abu-Zaied, M. A. & Azzam, R. (2016). *Nucleosides Nucleotides*, **35**, 211–222.
Elgemeie, G. H., Abu-Zaied, M. A. & Loutfy, S. A. (2017). *Tetrahedron*, **73**, 5853–5861.
Elgemeie, G. H. & Farag, A. B. (2017). *Nucleosides Nucleotides*, **36**, 328–342.
Elgemeie, G. H., Mahdy, E. M., Elgawish, M. A., Ahmed, M. M., Shousha, W. G. & Eldin, M. E. (2010). *Z. Naturforsch. Teil C*, **65**, 577–587.
Gourdain, S., Petermann, C., Martinez, A., Harakat, D. & Clivio, P. (2011). *J. Org. Chem.* **76**, 1906–1909.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Hammad, S. F., Masoud, D. M., Elgemeie, G. H. & Jones, P. G. (2018). *Acta Cryst.* E**74**, 853–856.
Masoud, D. M., Hammad, S. F., Elgemeie, G. H. & Jones, P. G. (2017). *Acta Cryst.* E**73**, 1751–1754.
Ohkubo, A., Nishino, Y., Ito, Y., Tsunoda, H., Seio, K. & Sekine, M. (2012). *Org. Biomol. Chem.* **10**, 2008–2010.
Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.
Rigaku OD (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
Scale, S., Akhmed, N., Rao, U. S., Paul, K., Lan, L., Dickstein, B., Lee, J., Elgemeie, G. H., Stein, W. D. & Bates, S. E. P. (1997). *Mol. Pharmacol.* **51**, 1024–1033.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Siemens (1994). *XP*. Siemens Analytical X-ray Instruments, Madison, Wisconsin, USA.
Xu, J., Tsanakopoulou, M., Magnani, C. J., Szabla, R., Šponer, J. E., Šponer, J., Góra, R. W. & Sutherland, J. D. (2017). *Nat. Chem.* **9**, 303–309.

supporting information

Acta Cryst. (2019). E**75**, 1820-1823 [https://doi.org/10.1107/S205698901901449X]

Crystal structure of 4,6-dimethyl-2-[(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)sulfanyl]pyrimidine

Mamdouh A. Abu-Zaied, Galal H. Elgemeie and Peter G. Jones

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: *SHELXL2017* (Sheldrick, 2015); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL2017* (Sheldrick, 2015).

4,6-Dimethyl-2-[(2,3,4,6-tetra-*O*-acetyl-*β*-*D*-galactopyranosyl)sulfanyl]pyrimidine

Crystal data

$C_{20}H_{26}N_2O_9S$
$M_r = 470.49$
Monoclinic, $P2_1$
$a = 11.4868$ (2) Å
$b = 8.6444$ (2) Å
$c = 11.5561$ (2) Å
$\beta = 91.3762$ (16)°
$V = 1147.14$ (4) Å^3
$Z = 2$
$F(000) = 496$
$D_x = 1.362$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 34705 reflections
$\theta = 2.5$–31.9°
$\mu = 0.19$ mm^{-1}
$T = 100$ K
Plate, colourless
0.40 × 0.40 × 0.08 mm

Data collection

Oxford Diffraction Xcalibur Eos diffractometer
Radiation source: fine-focus sealed X-ray tube
Detector resolution: 16.1419 pixels mm^{-1}
ω–scan
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2015)
$T_{min} = 0.896$, $T_{max} = 1.000$
107162 measured reflections
7825 independent reflections
7530 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 32.6°$, $\theta_{min} = 2.5°$
$h = -16\rightarrow17$
$k = -13\rightarrow12$
$l = -17\rightarrow17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.073$
$S = 1.04$
7825 reflections
295 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 0.1562P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Absolute structure: Flack *x* determined using 3355 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: −0.003 (11)

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}
S1	0.31717 (3)	0.37712 (4)	0.52391 (3)	0.01490 (7)
C1	0.20586 (11)	0.24276 (15)	0.55326 (12)	0.0142 (2)
N2	0.19449 (10)	0.18868 (14)	0.65991 (10)	0.0157 (2)
C3	0.10603 (12)	0.08858 (17)	0.67531 (12)	0.0172 (2)
C4	0.03201 (12)	0.04670 (18)	0.58372 (14)	0.0206 (3)
H4	−0.030920	−0.022627	0.594791	0.025*
C5	0.05295 (11)	0.10958 (19)	0.47507 (13)	0.0199 (3)
N6	0.14080 (10)	0.20913 (15)	0.45864 (10)	0.0171 (2)
C7	0.09350 (14)	0.0274 (2)	0.79576 (14)	0.0245 (3)
H7A	0.168605	−0.013057	0.824151	0.037*
H7B	0.035507	−0.055784	0.795217	0.037*
H7C	0.068210	0.110957	0.846639	0.037*
C8	−0.02150 (15)	0.0695 (3)	0.37087 (15)	0.0321 (4)
H8A	−0.006740	0.143333	0.308590	0.048*
H8B	−0.103788	0.074109	0.391103	0.048*
H8C	−0.002582	−0.035284	0.344863	0.048*
C11	0.36873 (11)	0.41461 (15)	0.66971 (11)	0.0131 (2)
H11	0.375290	0.314664	0.712943	0.016*
C12	0.48727 (11)	0.49574 (15)	0.67193 (11)	0.0128 (2)
H12	0.483420	0.593888	0.626193	0.015*
C13	0.52391 (10)	0.52856 (15)	0.79714 (11)	0.0126 (2)
H13	0.543513	0.428968	0.837101	0.015*
C14	0.42901 (11)	0.61209 (15)	0.86310 (10)	0.0125 (2)
H14	0.450359	0.615925	0.947450	0.015*
C15	0.31396 (11)	0.52721 (16)	0.84512 (11)	0.0134 (2)
H15	0.320387	0.421966	0.880626	0.016*
C16	0.21073 (12)	0.61091 (19)	0.89541 (11)	0.0182 (2)
H16A	0.199582	0.712822	0.857662	0.022*
H16B	0.138732	0.549329	0.883778	0.022*
C17	0.60600 (13)	0.42066 (17)	0.51651 (12)	0.0189 (3)
C18	0.70211 (15)	0.3144 (2)	0.48332 (15)	0.0268 (3)
H18A	0.701248	0.301910	0.399020	0.040*
H18B	0.691163	0.213438	0.520012	0.040*
H18C	0.777016	0.358241	0.509150	0.040*
C19	0.70586 (11)	0.60977 (19)	0.88007 (12)	0.0195 (3)

C20	0.80074 (13)	0.7270 (2)	0.86755 (15)	0.0289 (3)
H20A	0.777357	0.824463	0.903511	0.043*
H20B	0.814694	0.744261	0.785231	0.043*
H20C	0.872252	0.688885	0.905729	0.043*
C21	0.47753 (11)	0.87850 (18)	0.87510 (11)	0.0161 (2)
C22	0.46064 (15)	1.03358 (18)	0.81936 (13)	0.0229 (3)
H22A	0.484169	1.114920	0.874164	0.034*
H22B	0.378397	1.047057	0.797118	0.034*
H22C	0.508294	1.040209	0.750322	0.034*
C23	0.15859 (13)	0.71433 (19)	1.07533 (13)	0.0219 (3)
C24	0.19319 (16)	0.7243 (3)	1.20142 (14)	0.0306 (4)
H24A	0.135476	0.785614	1.242427	0.046*
H24B	0.269721	0.773711	1.209540	0.046*
H24C	0.196923	0.619929	1.234481	0.046*
O1	0.28647 (8)	0.51166 (12)	0.72429 (8)	0.01402 (17)
O2	0.57416 (8)	0.39412 (12)	0.62726 (8)	0.01502 (18)
O3	0.62667 (8)	0.62251 (13)	0.79139 (8)	0.01642 (18)
O4	0.41523 (8)	0.76733 (12)	0.81822 (8)	0.01450 (18)
O5	0.23709 (9)	0.63008 (14)	1.01710 (9)	0.0198 (2)
O6	0.56194 (12)	0.51912 (15)	0.45620 (10)	0.0278 (2)
O7	0.69797 (10)	0.51640 (16)	0.95647 (10)	0.0266 (2)
O8	0.53897 (9)	0.85198 (13)	0.95903 (9)	0.0201 (2)
O9	0.07262 (10)	0.76925 (17)	1.03075 (11)	0.0295 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01701 (13)	0.01501 (14)	0.01247 (12)	−0.00376 (11)	−0.00397 (9)	−0.00027 (11)
C1	0.0126 (5)	0.0123 (6)	0.0177 (5)	0.0001 (4)	−0.0024 (4)	−0.0023 (4)
N2	0.0156 (5)	0.0138 (5)	0.0176 (5)	0.0000 (4)	−0.0019 (4)	0.0000 (4)
C3	0.0151 (5)	0.0148 (6)	0.0218 (6)	0.0007 (4)	0.0013 (4)	0.0003 (5)
C4	0.0143 (5)	0.0210 (7)	0.0265 (7)	−0.0033 (5)	−0.0001 (5)	−0.0024 (5)
C5	0.0136 (5)	0.0224 (7)	0.0235 (6)	−0.0022 (5)	−0.0030 (5)	−0.0043 (5)
N6	0.0144 (5)	0.0191 (6)	0.0177 (5)	−0.0013 (4)	−0.0037 (4)	−0.0033 (4)
C7	0.0223 (6)	0.0257 (8)	0.0257 (7)	−0.0023 (6)	0.0014 (5)	0.0072 (6)
C8	0.0232 (7)	0.0468 (11)	0.0260 (7)	−0.0135 (7)	−0.0066 (6)	−0.0073 (7)
C11	0.0139 (5)	0.0129 (6)	0.0123 (5)	−0.0003 (4)	−0.0036 (4)	−0.0004 (4)
C12	0.0139 (5)	0.0126 (6)	0.0120 (5)	−0.0005 (4)	−0.0026 (4)	−0.0009 (4)
C13	0.0118 (5)	0.0136 (6)	0.0122 (5)	−0.0016 (4)	−0.0029 (4)	−0.0008 (4)
C14	0.0142 (5)	0.0118 (5)	0.0114 (5)	0.0002 (4)	−0.0031 (4)	0.0011 (4)
C15	0.0139 (5)	0.0149 (6)	0.0112 (5)	0.0009 (4)	−0.0027 (4)	0.0009 (4)
C16	0.0159 (5)	0.0242 (7)	0.0142 (5)	0.0030 (5)	−0.0017 (4)	−0.0005 (5)
C17	0.0222 (6)	0.0199 (7)	0.0148 (5)	−0.0085 (5)	0.0028 (4)	−0.0051 (5)
C18	0.0255 (7)	0.0288 (8)	0.0266 (7)	−0.0049 (6)	0.0080 (6)	−0.0112 (6)
C19	0.0132 (5)	0.0263 (7)	0.0188 (6)	0.0007 (5)	−0.0036 (4)	−0.0079 (5)
C20	0.0169 (6)	0.0392 (10)	0.0303 (8)	−0.0094 (6)	−0.0020 (5)	−0.0098 (7)
C21	0.0202 (5)	0.0137 (6)	0.0142 (5)	−0.0009 (5)	−0.0014 (4)	−0.0028 (5)
C22	0.0356 (8)	0.0137 (6)	0.0189 (6)	−0.0028 (6)	−0.0062 (5)	0.0010 (5)

C23	0.0187 (6)	0.0250 (7)	0.0221 (6)	−0.0031 (5)	0.0056 (5)	−0.0031 (5)
C24	0.0286 (7)	0.0445 (11)	0.0189 (7)	−0.0026 (7)	0.0045 (6)	−0.0080 (7)
O1	0.0138 (4)	0.0156 (4)	0.0125 (4)	0.0015 (3)	−0.0042 (3)	−0.0007 (3)
O2	0.0156 (4)	0.0163 (5)	0.0131 (4)	−0.0001 (3)	0.0001 (3)	−0.0018 (3)
O3	0.0141 (4)	0.0201 (5)	0.0149 (4)	−0.0046 (4)	−0.0029 (3)	−0.0025 (4)
O4	0.0195 (4)	0.0108 (4)	0.0129 (4)	−0.0004 (3)	−0.0055 (3)	0.0005 (3)
O5	0.0183 (4)	0.0270 (6)	0.0142 (4)	0.0031 (4)	−0.0005 (3)	−0.0020 (4)
O6	0.0396 (6)	0.0273 (6)	0.0167 (5)	−0.0032 (5)	0.0034 (4)	0.0030 (4)
O7	0.0231 (5)	0.0330 (7)	0.0233 (5)	0.0017 (5)	−0.0102 (4)	0.0011 (5)
O8	0.0243 (5)	0.0184 (5)	0.0173 (4)	0.0006 (4)	−0.0076 (4)	−0.0046 (4)
O9	0.0207 (5)	0.0371 (7)	0.0310 (6)	0.0060 (5)	0.0038 (4)	−0.0013 (5)

Geometric parameters (Å, º)

S1—C1	1.7662 (13)	C23—O9	1.201 (2)
S1—C11	1.8018 (13)	C23—O5	1.3511 (18)
C1—N2	1.3275 (18)	C23—C24	1.504 (2)
C1—N6	1.3414 (17)	C4—H4	0.9500
N2—C3	1.3497 (18)	C7—H7A	0.9800
C3—C4	1.390 (2)	C7—H7B	0.9800
C3—C7	1.499 (2)	C7—H7C	0.9800
C4—C5	1.394 (2)	C8—H8A	0.9800
C5—N6	1.3432 (18)	C8—H8B	0.9800
C5—C8	1.501 (2)	C8—H8C	0.9800
C11—O1	1.4223 (15)	C11—H11	1.0000
C11—C12	1.5314 (17)	C12—H12	1.0000
C12—O2	1.4349 (16)	C13—H13	1.0000
C12—C13	1.5239 (17)	C14—H14	1.0000
C13—O3	1.4356 (15)	C15—H15	1.0000
C13—C14	1.5267 (18)	C16—H16A	0.9900
C14—O4	1.4460 (16)	C16—H16B	0.9900
C14—C15	1.5214 (17)	C18—H18A	0.9800
C15—O1	1.4305 (15)	C18—H18B	0.9800
C15—C16	1.5168 (19)	C18—H18C	0.9800
C16—O5	1.4409 (16)	C20—H20A	0.9800
C17—O6	1.204 (2)	C20—H20B	0.9800
C17—O2	1.3591 (16)	C20—H20C	0.9800
C17—C18	1.493 (2)	C22—H22A	0.9800
C19—O7	1.201 (2)	C22—H22B	0.9800
C19—O3	1.3583 (16)	C22—H22C	0.9800
C19—C20	1.498 (2)	C24—H24A	0.9800
C21—O8	1.2077 (16)	C24—H24B	0.9800
C21—O4	1.3584 (16)	C24—H24C	0.9800
C21—C22	1.498 (2)		
C1—S1—C11	99.32 (6)	H7A—C7—H7C	109.5
N2—C1—N6	127.96 (13)	H7B—C7—H7C	109.5
N2—C1—S1	119.85 (10)	C5—C8—H8A	109.5

N6—C1—S1	112.19 (10)	C5—C8—H8B	109.5
C1—N2—C3	116.07 (12)	H8A—C8—H8B	109.5
N2—C3—C4	121.02 (13)	C5—C8—H8C	109.5
N2—C3—C7	115.98 (13)	H8A—C8—H8C	109.5
C4—C3—C7	123.00 (13)	H8B—C8—H8C	109.5
C3—C4—C5	117.95 (13)	O1—C11—H11	109.3
N6—C5—C4	121.56 (13)	C12—C11—H11	109.3
N6—C5—C8	116.76 (14)	S1—C11—H11	109.3
C4—C5—C8	121.68 (14)	O2—C12—H12	110.6
C1—N6—C5	115.43 (12)	C13—C12—H12	110.6
O1—C11—C12	108.80 (10)	C11—C12—H12	110.6
O1—C11—S1	108.29 (8)	O3—C13—H13	109.4
C12—C11—S1	111.73 (9)	C12—C13—H13	109.4
O2—C12—C13	106.07 (10)	C14—C13—H13	109.4
O2—C12—C11	109.85 (10)	O4—C14—H14	109.9
C13—C12—C11	109.05 (10)	C15—C14—H14	109.9
O3—C13—C12	105.66 (10)	C13—C14—H14	109.9
O3—C13—C14	110.69 (10)	O1—C15—H15	109.1
C12—C13—C14	112.20 (10)	C16—C15—H15	109.1
O4—C14—C15	108.14 (10)	C14—C15—H15	109.1
O4—C14—C13	109.47 (10)	O5—C16—H16A	110.5
C15—C14—C13	109.39 (10)	C15—C16—H16A	110.5
O1—C15—C16	105.22 (10)	O5—C16—H16B	110.5
O1—C15—C14	110.44 (10)	C15—C16—H16B	110.5
C16—C15—C14	113.71 (11)	H16A—C16—H16B	108.7
O5—C16—C15	106.32 (10)	C17—C18—H18A	109.5
O6—C17—O2	123.07 (14)	C17—C18—H18B	109.5
O6—C17—C18	126.10 (14)	H18A—C18—H18B	109.5
O2—C17—C18	110.82 (13)	C17—C18—H18C	109.5
O7—C19—O3	123.23 (13)	H18A—C18—H18C	109.5
O7—C19—C20	126.41 (14)	H18B—C18—H18C	109.5
O3—C19—C20	110.37 (13)	C19—C20—H20A	109.5
O8—C21—O4	123.04 (13)	C19—C20—H20B	109.5
O8—C21—C22	125.63 (13)	H20A—C20—H20B	109.5
O4—C21—C22	111.33 (11)	C19—C20—H20C	109.5
O9—C23—O5	123.46 (14)	H20A—C20—H20C	109.5
O9—C23—C24	126.07 (15)	H20B—C20—H20C	109.5
O5—C23—C24	110.45 (14)	C21—C22—H22A	109.5
C11—O1—C15	110.79 (9)	C21—C22—H22B	109.5
C17—O2—C12	116.15 (11)	H22A—C22—H22B	109.5
C19—O3—C13	117.11 (11)	C21—C22—H22C	109.5
C21—O4—C14	115.54 (10)	H22A—C22—H22C	109.5
C23—O5—C16	114.90 (11)	H22B—C22—H22C	109.5
C3—C4—H4	121.0	C23—C24—H24A	109.5
C5—C4—H4	121.0	C23—C24—H24B	109.5
C3—C7—H7A	109.5	H24A—C24—H24B	109.5
C3—C7—H7B	109.5	C23—C24—H24C	109.5
H7A—C7—H7B	109.5	H24A—C24—H24C	109.5

C3—C7—H7C	109.5	H24B—C24—H24C	109.5
C11—S1—C1—N2	−7.85 (12)	C12—C13—C14—C15	49.77 (14)
C11—S1—C1—N6	171.73 (10)	O4—C14—C15—O1	63.93 (13)
N6—C1—N2—C3	−0.6 (2)	C13—C14—C15—O1	−55.22 (14)
S1—C1—N2—C3	178.90 (10)	O4—C14—C15—C16	−54.09 (13)
C1—N2—C3—C4	−0.2 (2)	C13—C14—C15—C16	−173.24 (11)
C1—N2—C3—C7	179.87 (13)	O1—C15—C16—O5	−179.18 (11)
N2—C3—C4—C5	0.9 (2)	C14—C15—C16—O5	−58.19 (14)
C7—C3—C4—C5	−179.23 (15)	C12—C11—O1—C15	−66.76 (12)
C3—C4—C5—N6	−0.8 (2)	S1—C11—O1—C15	171.60 (8)
C3—C4—C5—C8	179.22 (15)	C16—C15—O1—C11	−171.37 (11)
N2—C1—N6—C5	0.7 (2)	C14—C15—O1—C11	65.52 (13)
S1—C1—N6—C5	−178.84 (10)	O6—C17—O2—C12	−2.78 (19)
C4—C5—N6—C1	0.1 (2)	C18—C17—O2—C12	176.21 (11)
C8—C5—N6—C1	−179.96 (14)	C13—C12—O2—C17	−140.59 (11)
C1—S1—C11—O1	−75.17 (9)	C11—C12—O2—C17	101.70 (12)
C1—S1—C11—C12	165.01 (9)	O7—C19—O3—C13	6.0 (2)
O1—C11—C12—O2	174.55 (9)	C20—C19—O3—C13	−173.83 (12)
S1—C11—C12—O2	−65.93 (12)	C12—C13—O3—C19	−150.10 (11)
O1—C11—C12—C13	58.70 (13)	C14—C13—O3—C19	88.21 (13)
S1—C11—C12—C13	178.21 (9)	O8—C21—O4—C14	−1.39 (18)
O2—C12—C13—O3	69.45 (12)	C22—C21—O4—C14	177.90 (11)
C11—C12—C13—O3	−172.30 (10)	C15—C14—O4—C21	146.97 (11)
O2—C12—C13—C14	−169.84 (10)	C13—C14—O4—C21	−93.93 (12)
C11—C12—C13—C14	−51.59 (14)	O9—C23—O5—C16	0.4 (2)
O3—C13—C14—O4	49.20 (13)	C24—C23—O5—C16	178.85 (13)
C12—C13—C14—O4	−68.56 (13)	C15—C16—O5—C23	174.82 (12)
O3—C13—C14—C15	167.53 (10)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7*C*···O9^{i}	0.98	2.57	3.495 (2)	157
C8—H8*B*···O1^{ii}	0.98	2.52	3.2499 (18)	131
C13—H13···O8^{iii}	1.00	2.65	3.2998 (16)	123
C14—H14···O8^{iii}	1.00	2.53	3.0626 (16)	113
C15—H15···O8^{iii}	1.00	2.50	3.1759 (16)	124
C18—H18*B*···S1^{iv}	0.98	2.95	3.7876 (19)	144
C22—H22*C*···O6^{v}	0.98	2.51	3.1911 (19)	127

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