Synthesis and crystal structure of topiramate azidosulfate at 90 K and 298 K

Prabhakar Priyanka, a Bidur K. Jayanna, a Haruvegowda Kiran Kumar, b Vinaya, b Thayamma R. Divakara, c Hemmige S. Yathirajan, b* Christopher Glidewell a and Sean Parkine e

a Department of Chemistry, B. N. M. Institute of Technology, Bengaluru-560 070, India, b Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysuru-570 006, India, c T. John Institute of Technology, Bengaluru-560 083, India, d School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, UK, and e Department of Chemistry, University of Kentucky, Lexington, KY, 40506-0055, USA. *Correspondence e-mail: yathirajan@hotmail.com

The low (90 K) and room (298 K) temperature crystal structures of topiramate azidosulfate [systematic name 2,3:4,5-bis-O-(1-methylethylidene)-β-d-fructopyranose azidosulfate], C12H19N3O8S, an intermediate in the synthesis of the anti-convulsant drug topiramate, are described. Topiramate azidosulfate (I) finds use as a reference impurity standard for topiramate. A modified synthesis and some spectroscopic details are also presented.

1. Chemical context
Topiramate, sold under the brand name Topamax (amongst others), is a carbonic anhydrase inhibitor, used alone or with other medications, to treat epilepsy and to prevent migraines (Maryanoff et al., 1987; 1998; Maryanoff, 2009). It is also prescribed for the treatment of bipolar disorder, post-traumatic stress disorder, mood instability disorder, binge-eating disorders, bulimia nervosa and obesity (Silberstein et al., 2005). The vibrational and thermal properties of topiramate were investigated by Sena et al. (2008). Topiramate azidosulfate (a topiramate intermediate) is useful as a reference impurity standard. In view of the importance of topiramate and its derivatives, this paper reports the synthesis, crystal structure, and some spectroscopic data for topiramate azidosulfate, C12H19N3O8S, at low and room temperature (90 K and 298 K).

2. Structural commentary
The molecule of I (see scheme and Fig. 1) has a central core consisting of three fused rings: a pyran ring (labelled A in the scheme) with two fused dioxolane rings (labelled B and C).
Table 1
Cremer–Pople ring-puckering parameters (Å, °) for I at 90 K.

| Pyran | A: O1, C1, C2, C3, C4, C5 | Q | θ | ψ |
|-------|--------------------------|---|---|---|
|       | 0.6368 (16)               | 100.85 (14) | 142.37 (15) |
| Dioxolane | B: O4, C2, C1, O5, C9 | Q | θ | ψ |
|       | 0.3076 (15)               | 4.5 (3) |
| C2: O4, C3, O3, C6 | Q | θ | ψ |
|       | 0.3539 (16)               | 133.4 (15) |

Cremer–Pople ring-puckering parameters were calculated using PLATON (Spek, 2020). For six-membered rings, the θ angles for ideal ‘boat’, ‘twist-boat’, and ‘screw-boat’ conformations are θ = 90° (boat, twist-boat) and θ = 120° (screw-boat). The ψ values, are quantified as either (60k)° (boat) or (60k + 30)° (twist-boat, screw-boat), with the one having k closest to an integer giving the conformation (Boeyens, 1978). Thus, pyran ring A is between ‘twist-boat’ and ‘screw boat’, though marginally closer to the former. For five-membered rings, ψ quantified as either (36k)° (‘envelope’) or (36k + 18)° (‘half-chair’) with k closest to an integer (Cremer & Pople, 1975), assigns dioxolane B as an ‘envelope’ configuration and dioxolane C as between ‘envelope’ and ‘half-chair’ conformations, though somewhat closer to the latter.

Table 2
Selected torsion angles (°) for I at 90 K.

| N1—S1—O6—C12 | 61.39 (12) |
|---------------|------------|
| O6—S1—N1—N2  | 71.03 (13) |
| C2—C1—C12—O6 | 177.58 (12) |

The points of fusion, atoms C1, C2, C3, C4 (Fig. 1), are contiguous chiral centres, the absolute configurations of which were confirmed unambiguously from the anomalous scattering by the sulfur to be L, 2S, 3R, 4R (see Flack, 1983; Hooft et al., 2008; Parsons et al., 2013). All three rings are non-planar, as indicated by their r.m.s. deviations from planarity (pyran A: 0.2597 Å; dioxolanes B, C: 0.1375, 0.1583 Å respectively) and by their Cremer–Pople (1975) ring-puckering parameters (Table 1). The distal carbon atoms of the dioxolane rings (i.e., C6 and C9) each bear two methyl groups. The azidosulfonate group attaches to atom C1 via a methylene linker, with the position of the azide relative to the fused-ring system determined by torsions about four bonds (C1—C12, C12—O6, O6—S1, S1—N1), as summarized in Table 2. The structure was refined against both low-temperature (90 K) and room-

Table 3
Hydrogen bonds and short intermolecular contacts (Å, °) for I at 90 K.

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| C7—H7A···O5′ | 0.98 | 2.50 | 3.456 (2) | 164.8 |
| C7—H7A···O1′ | 0.98 | 2.65 | 3.473 (2) | 141.3 |
| C5—HSB···O8′ | 0.99 | 2.65 | 3.328 (2) | 125.5 |
| C12—H12A···O4′ | 0.99 | 2.58 | 3.163 (2) | 117.4 |

Symmetry codes: (i) x, y−1, z; (ii) x, y−1, z; (iii) x−1, y+1/a, z+1/b.

Figure 1
An ellipsoid plot of I (50% probability) for the structure at 90 K. The structure at 298 K is essentially unchanged, other than having much larger ellipsoids.

Figure 2
Difference-electron density showing the presence of well-ordered hydrogen atoms at both (a) 90 K and (b) 298 K for the methyl group at C7. Ellipsoids are drawn at the 50% probability level. Diagram generated using ShelXle (Hübschle et al., 2011).

3. Supramolecular features
There are no strong intermolecular interactions in crystals of I. The ‘HTAB’ instruction in SHELXL flags four ‘potential hydrogen bonds’ (Table 3), but two of these have very small C—H···O angles, such that the associated interaction energy would be negligible (Wood et al., 2009). The remaining two involve contacts between the methyl group at C7 with O1′ and O5′ of an adjacent molecule [symmetry code: (i) x−1, y, z], the latter being the stronger of the two. During structure analysis, the question arose of whether these contacts would be structurally significant, owing to the possibility of rapid methyl-group rotation at room temperature (Riddell & Rogerson, 1996; 1997). To answer this, the structure was also refined using room-temperature data. At low temperature (90 K) and room temperature (298 K), difference electron density for the three C7 methyl hydrogen atoms is very well resolved (Fig. 2), implying the absence of any disorder, rotational or static. Analysis of the Hirshfeld surface (Spackman & Jayatilaka, 2009) mapped over dnorm for I using CrystalExplorer (Spackman et al., 2021) reveals only two (equivalent) prominent red spots, corresponding to the C7—H7A···O5′ interactions, in which the methyl group at C7 juts into a...
concave recess of an adjacent molecule. These hydrogen bonds link the molecules into chains that extend along the a-axis direction (Fig. 3). There are no especially short contacts involving the azido group; N2 and N3 are 3.118 (2) and 3.166 (2) Å, respectively from a screw-related sulfonyl O7 (via \( \frac{1}{2} + x, \frac{1}{2} - y, 1 - z \)), but these are marginally greater than the sum of van der Waals radii of Bondi (1964). In spite of the lack of extensive intermolecular interactions, the overall packing exhibits segregation of like groups, leading to double layers that extend in the ab plane (Fig. 4). A summary of the various atom–atom contacts obtained using CrystalExplorer fingerprint plots is given in Fig. 5.

4. Database survey

A search of the Cambridge Structural Database (version 5.43 with updates through June 2022; Groom et al., 2016) for the three-ring core of topiramate plus the four methyl groups, but

![Figure 3](image)

A plot of the Hirshfeld surface calculated over \( d_{norm} \) for I at 90 K, showing two adjacent molecules. Hydrogen bonds are drawn as green dashed lines. The red spot at the left corresponds to the C7–H7\( \cdots \)O5i [symmetry code: (i) \( x - 1, y, z \)] hydrogen bond (Table 3). The symmetry-equivalent red spot on the right side of the Hirshfeld surface is obscured from view.

![Figure 4](image)

A packing plot of I viewed in projection down the b-axis, showing segregation of like groups, leading to the formation of double layers parallel to the ab plane. Diagram generated using Mercury (Macrae et al., 2020).

![Figure 5](image)

Fingerprint plots obtained from a Hirshfeld surface analysis for I at 90 K using CrystalExplorer (Spackman et al., 2021). (a) All contacts, (b) O\( \cdots \)H\( \cdots \)O (42.1% coverage), (c) H\( \cdots \)H (38.1%), (d) N\( \cdots \)H\( \cdots \)N (14.5%), (e) N\( \cdots \)O\( \cdots \)N (3.5%), (f) N\( \cdots \)N (1.3%). All other contacts are negligible.
disregarding stereochemistry yielded 239 hits. A search fragment also including –CH2—Z (where Z is not H) attached to the equivalent of C1 in I returned 26 hits (21 excluding duplicates). A search using the keyword ‘topiramate’ gave only three hits, all being the structure of topiramate itself (with NH2 in place of N3 in I): SEQKAA (Maryanoff et al., 1998) and duplicates SEQKAA01 (Kubicki et al., 1999) and SEQKAA02 (Bolte, 2005). An amido derivative (with NHCHMePh in place of N3) is present as entry ZARCEC (Xie et al., 2012). These crystal structures all have the symmetry of P212121, but pack differently from I. SEQKAA (and duplicates) form a tri-periodic hydrogen-bonded supramolecular assembly, while ZARCEC forms C(4) chains (notation after Etter et al., 1990).

5. Synthesis, crystallization and spectroscopic details

Topiramate azidosulfate was synthesized using a modification of procedures found in the literature (Maryanoff et al., 1987; Kankan et al., 2004; Arvai et al., 2006; Koruyucu et al., 2016). The synthesis involved three steps, viz., (1) synthesis of 2,3:4,5-bis-O-(1-methylthiolydine)-β-d-fructopyranose, (2) synthesis of 2,3:4,5-bis-O-(1-methylthiolydine)-1-chlorosulfate-β-d-fructopyranose, and (3) synthesis of topiramate azidosulfate (I), as depicted in Fig. 6. X-ray quality crystals of I were obtained by crystallization from dichloromethane (m.p.: 358–359 K). Some spectroscopic details are as follows:

![Figure 6](https://example.com/figure6.png)

The reaction scheme for the synthesis of I starting from fructose.

**Table 4**

Experimental details.

|                | I at 90 K                           | I at 298 K                           |
|----------------|-------------------------------------|-------------------------------------|
| Chemical data  | C12H19N3O8S                         | C12H19N3O8S                         |
| M              | 365.36                              | 365.36                              |
| Crystal system | Orthorhombic, P212121               | Orthorhombic, P212121               |
| Temperature (K)| 90                                  | 90                                  |
| a, b, c (Å)    | 7.9857 (4), 9.0145 (4), 22.1621 (10)| 8.0717 (8), 9.1135 (12), 22.506 (3) |
| V (Å³)         | 1595.39 (15)                        | 1655.6 (3)                          |
| Z              | 4                                   | 4                                   |
| Radiation type | Mo Ka                               | Mo Ka                               |
| µ (mm⁻¹)       | 0.25                                | 0.24                                |
| Crystal size (mm) | 0.30 × 0.28 × 0.20               | 0.24 × 0.22 × 0.14                  |

Computer programs: APEX3 (Bruker, 2016), SHELXT (Sheldrick, 2015a), SHELXL2015 (Sheldrick, 2015b), XP in SHELXTL (Sheldrick, 2008), SHELXTL (Sheldrick, 2008) and publCIF (Westrip, 2010).
IR (cm⁻¹): 2157 (N≡N=N stretching); 1392 (S=O stretching); 1167 and 1081 (C—O stretching); 1H NMR: CDCl₃ (400 MHz, δ ppm): 1.355 (3H, s, -CH₃); 1.422 (3H, s, -CH₃); 1.489 (3H, s, -CH₃); 1.566 (3H, s, -CH₃); 3.783–3.817 and 3.908–3.945 (2H, dd, -CH₂); 4.246–4.268 (1H, dd, -CH); 4.306–4.332 (2H, m, -CH₂); 4.398–4.424 (1H, dd, -CH); 4.649 (1H, dd, -CH). MS m/z: 364.03 (M-H)⁺

6. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 4. All H atoms were found in difference-Fourier maps, but subsequently included in the refinement using riding models, with constrained distances set to 0.98 Å (RCH₃), 0.99 Å (R₂CH₂) and 1.00 Å (R₃CH). Uequiv(H) parameters were set to values of either 1.2Ueq or 1.5Ueq (RCH₃ only) of the attached atom. The absolute configuration was determined unambiguously from the anomalous scattering by sulfur using established methods (Flack, 1983; Hooft et al., 2008; Parsons et al., 2013).

Acknowledgements

PP is grateful to the B. N. M. Institute of Technology, Bengaluru-560 070, India for research facilities.

Funding information

HSY is grateful to the UGC, New Delhi for a BSR Faculty Fellowship for three years. The D8 Venture diffractometer was funded by the NSF (MRI CHE1625732) and by the University of Kentucky.

References

Arvai, G., Garacci, S., Máté, A. G., Lukacs, F., Viski, Z. & Schneider, G. (2006). US Patent 0040874A1.
Boeyens, J. C. A. (1978). J. Cryst. Mol. Struct. 8, 317–320.
Bolte, M. (2005). CSD Communication (refcode SEQKAA02). CCDC, Cambridge, England.
Bondi, A. (1964). J. Phys. Chem. 68, 441–451.
Bruker (2016). APEX3. Bruker AXS Inc., Madison, Wisconsin, USA.
Cremer, D. & Pople, J. A. (1975). J. Am. Chem. Soc. 97, 1354–1358.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). Acta Cryst. B46, 256–262.

Flack, H. D. (1983). Acta Cryst. A39, 876–881.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). Acta Cryst. B72, 171–179.
Hooft, R. W. W., Straver, L. H. & Spek, A. L. (2008). J. Appl. Cryst. 41, 96–103.
Hübischle, C. B., Sheldrick, G. M. & Dittrich, B. (2011). J. Appl. Cryst. 44, 1281–1284.
Kankan, R. N., Rao, D. R. & Srinivas, P. L. (2004). World Patent WO2004089965A2.
Koruyucu, M., Saltan, F., Kök, G., Akat, H. & Salman, Y. (2016). Iran. Polym. J. 25, 455–463.
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). J. Appl. Cryst. 48, 3–10.
Kubicki, M., Codding, P. W., Litster, S. A., Szkaradzińska, M. B. & Bassouyouni, H. A. R. (1999). J. Mol. Struct. 474, 255–265.
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.
Maryanoff, B. E. (2009). Curr. Top. Med. Chem. 9, 1049–1062.
Maryanoff, B. E., Costanzo, M. J., Nortey, S. O., Greco, M. N., Shank, R. P., Schupsky, J. J., Ortegon, M. P. & Vaught, J. L. (1998). J. Med. Chem. 41, 1315–1343.
Maryanoff, B. E., Nortey, S. O., Gardocki, J. F., Shank, R. P. & Dodgson, S. P. (1987). J. Med. Chem. 30, 880–887.
Parsons, S., Flack, H. D. & Wagner, T. (2013). Acta Cryst. B69, 249–259.
Riddell, F. G. & Rogerson, M. (1996). J. Chem. Soc. Perkin Trans. 2, pp. 493–504.
Riddell, F. G. & Rogerson, M. (1997). J. Chem. Soc. Perkin Trans. 2, pp. 249–256.
Sena, D. M. Jr, Freire, P. T. C., Filho, J. M., Melo, F. E. A., Pontes, F. M., Longo, E., Ferreira, O. P. & Alves, O. L. (2008). J. Braz. Chem. Soc. 19, 1607–1613.
Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.
Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.
Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.
Sliberstein, S. D., Ben-Menachem, E., Shank, R. P. & Wiegand, F. (2005). Clin. Ther. 27, 154–165.
Spackman, M. A. & Jayatilaka, D. (2009). CrystEngComm, 11, 19–32.
Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). J. Appl. Cryst. 54, 1006–1011.
Spek, A. L. (2020). Acta Cryst. E76, 1–11.
Westrip, S. P. (2010). J. Appl. Cryst. 43, 920–925.
Wood, P. A., Allen, F. H. & Pidcock, E. (2009). CrystEngComm, 11, 1563–1571.
Xie, M., Shen, S.-S., Chen, B.-F. & Sha, Y. (2012). Acta Cryst. E68, o1581.
Synthesis and crystal structure of topiramate azidosulfate at 90 K and 298 K

Prabhakar Priyanka, Bidarur K. Jayanna, Haruvegowda Kiran Kumar, Vinaya, Thayamma R. Divakara, Hemmige S. Yathirajan, Christopher Glidewell and Sean Parkin

Computing details

For both structures, data collection: APEX3 (Bruker, 2016); cell refinement: APEX3 (Bruker, 2016); data reduction: APEX3 (Bruker, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2019/2 (Sheldrick, 2015b); molecular graphics: XP in SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL (Sheldrick, 2008) and publCIF (Westrip, 2010).

2,3:4,5-Bis-O-(1-methylethylidene)-β-D-fructopyranose azidosulfate (I-90K)

Crystal data

C₁₂H₁₉N₃O₈S  
Mr = 365.36
Orthorhombic, P2₁2₁2₁
a = 7.9857 (4) Å  
b = 9.0145 (4) Å  
c = 22.1621 (10) Å
V = 1595.39 (13) Å³
Z = 4
F(000) = 768

Data collection

Bruker D8 Venture dual source diffractometer
Radiation source: microsource
Detector resolution: 7.41 pixels mm⁻¹
φ and ω scans
Absorption correction: multi-scan SADABS (Krause et al., 2015)
Tmin = 0.845, Tmax = 0.958
22942 measured reflections
3662 independent reflections
3599 reflections with I > 2σ(I)
Rint = 0.031
θmax = 27.5°, θmin = 2.4°
h = −10→10
k = −11→11
l = −28→28

Refinement

Refinement on F²
Least-squares matrix: full
R(F² > 2σ(F²)) = 0.023
wR(F²) = 0.060
S = 1.07
3662 reflections
221 parameters
0 restraints
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H-atom parameters constrained

w = 1/[σ(²F²) + (0.0311P)² + 0.3897P]
where P = (²F² + 2Fc²)/3
(Δσ)max = 0.001
Δρmax = 0.27 e Å⁻³
Δρmin = −0.27 e Å⁻³

Δρmax = 0.27 e Å⁻³
Δρmin = −0.27 e Å⁻³
Absolute structure: Flack $x$ determined using 1497 quotients $|(I^-)-(I^+)|/(|(I^-)+(I^+)|$ (Parsons et al., 2013)
Absolute structure parameter: −0.006 (18)

Special details

Experimental. The crystal was mounted using polyisobutene oil on the tip of a fine glass fibre, which was fastened in a copper mounting pin with electrical solder. It was placed directly into the cold gas stream of a liquid-nitrogen based cryostat (Hope, 1994; Parkin & Hope, 1998).

Diffraction data were collected with the crystal at 90K, which is standard practice in this laboratory for the majority of flash-cooled crystals.

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 progress was checked using Platon (Spek, 2020) and by an $R$-tensor (Parkin, 2000). The final model was further checked with the IUCr utility checkCIF.

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

|     | x       | y       | z       | $U_{	ext{iso}}$/U$_{eq}$ |
|-----|---------|---------|---------|--------------------------|
| S1  | 0.74373 | 0.79578 | 0.39659 | 0.01482 (10)             |
| O1  | 0.68696 | 0.40140 | 0.39079 | 0.0110 (2)               |
| O2  | 0.37338 | 0.30579 | 0.44523 | 0.0132 (2)               |
| O3  | 0.29357 | 0.40358 | 0.35605 | 0.0140 (2)               |
| O4  | 0.61310 | 0.21617 | 0.27084 | 0.0133 (2)               |
| O5  | 0.82007 | 0.37553 | 0.29850 | 0.0129 (2)               |
| O6  | 0.79097 | 0.66339 | 0.35441 | 0.0131 (2)               |
| O7  | 0.89734 | 0.84031 | 0.42335 | 0.0227 (3)               |
| O8  | 0.63978 | 0.89829 | 0.36559 | 0.0233 (3)               |
| N1  | 0.61434 | 0.72167 | 0.44750 | 0.0176 (3)               |
| N2  | 0.6901  | 0.63604 | 0.48404 | 0.0195 (3)               |
| N3  | 0.7424  | 0.5607  | 0.51895 | 0.0303 (4)               |
| C1  | 0.6742  | 0.42586 | 0.32847 | 0.0111 (3)               |
| C2  | 0.5308  | 0.34038 | 0.29730 | 0.0112 (3)               |
| H2  | 0.47855 | 0.40320 | 0.26522 | 0.013*                   |
| C3  | 0.39740 | 0.28231 | 0.33997 | 0.0121 (3)               |
| H3  | 0.32932 | 0.20420 | 0.31936 | 0.015*                   |
| C4  | 0.46440 | 0.22228 | 0.40096 | 0.0115 (3)               |
| H4  | 0.44009 | 0.11392 | 0.40503 | 0.014*                   |
| C5  | 0.6496  | 0.25192 | 0.40849 | 0.0115 (3)               |
| H5A | 0.68211 | 0.23667 | 0.45114 | 0.014*                   |
| H5B | 0.71454 | 0.18175 | 0.38316 | 0.014*                   |
| C6  | 0.2319  | 0.36980 | 0.41541 | 0.0131 (3)               |
| C7  | 0.0877  | 0.2609  | 0.41185 | 0.0172 (4)               |
| H7A | −0.00062| 0.301745| 0.386016| 0.026*                  |
| H7B | 0.042898| 0.243492| 0.452406| 0.026*                  |
| H7C | 0.127531| 0.166947| 0.394831| 0.026*                  |
| C8  | 0.1871  | 0.5135  | 0.44592 | 0.0196 (4)               |
H8A 0.285516 0.578470 0.446858 0.029*
H8B 0.149912 0.493503 0.487260 0.029*
H8C 0.096764 0.562297 0.423507 0.029*
C9 0.7769 (2) 0.26520 (18) 0.25392 (7) 0.0132 (3)
C10 0.8959 (2) 0.1363 (2) 0.25870 (8) 0.0190 (3)
H10A 0.865031 0.060356 0.229074 0.028*
H10B 0.889904 0.094120 0.299397 0.028*
H10C 1.010288 0.170461 0.250730 0.028*
C11 0.7748 (2) 0.3354 (2) 0.19133 (7) 0.0187 (3)
H11A 0.748270 0.259460 0.161161 0.028*
H11B 0.884938 0.378143 0.182579 0.028*
H11C 0.689687 0.413681 0.190035 0.028*
C12 0.6546 (2) 0.59209 (18) 0.32148 (7) 0.016*
H12A 0.659331 0.619732 0.278277 0.016*
H12B 0.545271 0.624352 0.337951 0.016*

Atomic displacement parameters (Å²)

|      | U¹¹  | U¹²  | U¹³  | U²²  | U²³  | U³³  |
|------|------|------|------|------|------|------|
| S1   | 0.01728 (19) | 0.01052 (18) | 0.01667 (18) | −0.00154 (16) | 0.00150 (16) | −0.00177 (14) |
| O1   | 0.0132 (5) | 0.0106 (5) | 0.0093 (5) | −0.0008 (4) | −0.0014 (4) | 0.0007 (4) |
| O2   | 0.0101 (5) | 0.0190 (6) | 0.0104 (5) | 0.0033 (5) | −0.0002 (4) | −0.0009 (4) |
| O3   | 0.0127 (5) | 0.0181 (6) | 0.0112 (5) | 0.0047 (4) | 0.0029 (4) | 0.0018 (4) |
| O4   | 0.0109 (5) | 0.0147 (5) | 0.0142 (5) | −0.0016 (5) | 0.0031 (4) | −0.0049 (5) |
| O5   | 0.0102 (5) | 0.0154 (6) | 0.0131 (5) | −0.0004 (5) | 0.0011 (4) | −0.0052 (4) |
| O6   | 0.0126 (5) | 0.0120 (5) | 0.0148 (5) | −0.0008 (4) | 0.0007 (4) | −0.0020 (4) |
| O7   | 0.0210 (7) | 0.0223 (7) | 0.0247 (6) | −0.0071 (6) | 0.0008 (5) | −0.0065 (5) |
| O8   | 0.0302 (7) | 0.0121 (6) | 0.0277 (7) | 0.0037 (5) | −0.0002 (6) | 0.0007 (5) |
| N1   | 0.0176 (7) | 0.0187 (7) | 0.0164 (6) | 0.0016 (6) | 0.0027 (6) | −0.0004 (6) |
| N2   | 0.0209 (7) | 0.0195 (7) | 0.0180 (7) | −0.0028 (6) | 0.0044 (6) | −0.0021 (6) |
| N3   | 0.0337 (9) | 0.0329 (9) | 0.0242 (8) | 0.0009 (9) | 0.0026 (8) | 0.0072 (7) |
| C1   | 0.0104 (7) | 0.0127 (8) | 0.0102 (7) | 0.0010 (6) | 0.0016 (6) | 0.0003 (6) |
| C2   | 0.0105 (7) | 0.0133 (7) | 0.0098 (6) | 0.0000 (6) | −0.0005 (6) | −0.0023 (6) |
| C3   | 0.0095 (7) | 0.0155 (8) | 0.0114 (6) | −0.0002 (7) | −0.0003 (6) | −0.0017 (6) |
| C4   | 0.0117 (7) | 0.0118 (7) | 0.0111 (7) | 0.0002 (6) | 0.0008 (6) | −0.0005 (6) |
| C5   | 0.0112 (7) | 0.0102 (7) | 0.0131 (7) | 0.0006 (6) | 0.0002 (5) | 0.0024 (6) |
| C6   | 0.0106 (7) | 0.0187 (8) | 0.0102 (6) | 0.0028 (7) | 0.0006 (6) | 0.0012 (5) |
| C7   | 0.0114 (7) | 0.0264 (9) | 0.0140 (7) | −0.0016 (7) | 0.0006 (6) | 0.0015 (7) |
| C8   | 0.0210 (8) | 0.0187 (9) | 0.0190 (8) | 0.0051 (7) | 0.0052 (7) | −0.0005 (7) |
| C9   | 0.0114 (7) | 0.0151 (7) | 0.0130 (7) | −0.0026 (6) | 0.0028 (6) | −0.0042 (6) |
| C10  | 0.0159 (8) | 0.0192 (8) | 0.0217 (8) | 0.0028 (7) | 0.0026 (7) | −0.0053 (7) |
| C11  | 0.0174 (8) | 0.0256 (9) | 0.0132 (7) | −0.0033 (7) | 0.0025 (6) | −0.0014 (6) |
| C12  | 0.0138 (8) | 0.0122 (7) | 0.0130 (7) | −0.0005 (6) | −0.0021 (6) | 0.0002 (6) |

Geometric parameters (Å, °)

|      |      |      |      |      |      |
|------|------|------|------|------|------|
| S1—O8 | 1.4195 (14) | C4—C5 | 1.512 (2) |
| S1—O7 | 1.4205 (14) | C4—H4 | 1.0000 |
| Bond                  | Distance (Å) | Angle (°)   |
|----------------------|--------------|------------|
| S1—O6                | 1.5622 (12)  |            |
| S1—N1                | 1.6694 (15)  |            |
| O1—C1                | 1.4022 (18)  |            |
| O1—C5                | 1.4347 (19)  |            |
| O2—C6                | 1.4306 (19)  |            |
| O2—C4                | 1.4345 (18)  |            |
| O3—C3                | 1.4176 (19)  |            |
| O3—C6                | 1.4373 (18)  |            |
| O4—C2                | 1.4245 (19)  |            |
| O4—C9                | 1.4306 (18)  |            |
| O5—C1                | 1.4156 (19)  |            |
| O5—C9                | 1.4436 (19)  |            |
| O6—C12               | 1.4600 (19)  |            |
| N1—N2                | 1.272 (2)    |            |
| N2—N3                | 1.111 (2)    |            |
| C1—C12               | 1.515 (2)    |            |
| C1—C2                | 1.543 (2)    |            |
| C2—C3                | 1.518 (2)    |            |
| C2—H2                | 1.0000       |            |
| C3—C4                | 1.551 (2)    |            |
| C3—H3                | 1.0000       |            |

| Bond                  | Distance (Å) | Angle (°)   |
|----------------------|--------------|------------|
| O8—S1—O7             | 121.55 (8)   | H5A—C5—H5B|
| O8—S1—O6             | 110.42 (7)   | O2—C6—O3  |
| O7—S1—O6             | 104.91 (7)   | O2—C6—C8  |
| O8—S1—N1             | 103.04 (8)   | O3—C6—C8  |
| O7—S1—N1             | 111.43 (8)   | O2—C6—C7  |
| O6—S1—N1             | 104.37 (7)   | O3—C6—C7  |
| C1—O1—C5             | 113.70 (12)  | C8—C6—C7  |
| C6—O2—C4             | 107.21 (11)  | C6—C7—H7A |
| C3—O3—C6             | 105.50 (12)  | C6—C7—H7B |
| C2—O4—C9             | 106.66 (12)  | H7A—C7—H7B|
| C1—O5—C9             | 110.20 (12)  | C6—C7—H7C |
| C12—O6—S1            | 117.09 (10)  | H7A—C7—H7C|
| N2—N1—S1             | 112.27 (12)  | H7B—C7—H7C|
| N3—N2—N1             | 173.36 (19)  | C6—C8—H8A |
| O1—C1—O5             | 110.61 (13)  | C6—C8—H8B |
| O1—C1—C12            | 105.31 (13)  | H8A—C8—H8B|
| O5—C1—C12            | 110.74 (13)  | C6—C8—H8C |
| O1—C1—C2             | 114.60 (13)  | H8A—C8—H8C|
| O5—C1—C2             | 103.91 (12)  | H8B—C8—H8C|
| C12—C1—C2            | 111.80 (13)  | O4—C9—O5  |
| O4—C2—C3             | 108.01 (13)  | O4—C9—C10 |
| O4—C2—C1             | 103.56 (12)  | O5—C9—C10 |
| O4—C2—H2             | 110.2        | O5—C9—C11 |
| C3—C2—H2             | 110.2        | C10—C9—C11|
| C1—C2—H2             | 110.2        | C9—C10—H10A|
| Bond  | Value  | Bond  | Value  |
|-------|--------|-------|--------|
| O3—C3—C2 | 107.54 (13) | C9—C10—H10B | 109.5 |
| O3—C3—C4 | 104.57 (12) | H10A—C10—H10B | 109.5 |
| C2—C3—C4 | 114.90 (13) | C9—C10—H10C | 109.5 |
| O3—C3—H3 | 109.9 | H10A—C10—H10C | 109.5 |
| C2—C3—H3 | 109.9 | H10B—C10—H10C | 109.5 |
| C4—C3—H3 | 109.9 | C9—C11—H11A | 109.5 |
| O2—C4—C5 | 109.11 (13) | C9—C11—H11B | 109.5 |
| O2—C4—C3 | 103.78 (12) | C9—C11—H11B | 109.5 |
| C5—C4—C3 | 111.83 (13) | C9—C11—H11C | 109.5 |
| O2—C4—H4 | 110.6 | H11A—C11—H11C | 109.5 |
| C5—C4—H4 | 110.6 | H11B—C11—H11C | 109.5 |
| C3—C4—H4 | 110.6 | O6—C12—C1 | 107.89 (13) |
| O1—C5—C4 | 109.82 (13) | O6—C12—H12A | 110.1 |
| O1—C5—H5A | 109.7 | C11—C12—H12A | 110.1 |
| C4—C5—H5A | 109.7 | O6—C12—H12B | 110.1 |
| O1—C5—H5B | 109.7 | C1—C12—H12B | 110.1 |
| C4—C5—H5B | 109.7 | H12A—C12—H12B | 108.4 |
| O8—Si—O6—C12 | −48.73 (13) | C6—O2—C4—C5 | 136.56 (13) |
| O7—Si—O6—C12 | 178.68 (11) | C6—O2—C4—C3 | 17.21 (15) |
| N1—Si—O6—C12 | 61.39 (12) | O3—C3—C4—O2 | 6.99 (15) |
| O6—Si—N1—N2 | −173.57 (13) | O6—C12—C1 | 52.54 (16) |
| O6—Si—N1—N2 | −41.67 (15) | C1—O5—C9—O4 | −18.10 (16) |
| C5—O1—C1—O5 | 159.94 (12) | C1—O5—C9—C10 | −134.40 (14) |
| C5—O1—C1—C12 | 36.65 (18) | C1—O5—C9—C11 | 100.94 (15) |
| C5—O1—C1—C2 | 121.68 (13) | C6—O3—C3—C2 | −79.67 (16) |
| C9—O5—C1—O1 | −121.96 (14) | C6—O3—C3—C4 | −150.14 (14) |
| C9—O5—C1—C12 | −121.96 (14) | C6—O3—C3—C8 | −150.14 (14) |
| C9—O4—C2—C3 | −154.60 (12) | C6—O3—C3—C7 | 83.68 (15) |
| C9—O4—C2—C1 | −32.84 (15) | C6—O3—C3—C8 | 39.69 (15) |
| O1—C1—C2—O4 | −99.81 (14) | C6—O3—C3—C8 | 155.43 (13) |
| O1—C1—C2—O4 | 21.00 (15) | C2—O4—C9—O5 | 32.11 (15) |
| O5—C1—C2—O4 | 140.47 (13) | C2—O4—C9—C10 | 148.94 (13) |
| O5—C1—C2—C3 | 17.5 (2) | C2—O4—C9—C11 | −86.21 (15) |
| O5—C1—C2—C3 | 138.33 (14) | C1—O5—C9—O4 | −18.10 (16) |
| O1—C1—C2—C3 | −102.20 (16) | C1—O5—C9—C10 | −134.40 (14) |
| O6—C3—C3—C2 | −150.97 (12) | C1—O5—C9—C11 | 100.94 (15) |
| O6—C3—C3—C4 | −28.39 (15) | C1—O5—C9—C11 | −133.17 (11) |
| O4—C2—C3—O3 | −167.78 (12) | O1—C1—C12—O6 | 52.54 (16) |
| O4—C2—C3—O3 | 77.46 (16) | O5—C1—C12—O6 | −67.06 (16) |
| O4—C2—C3—C4 | 76.26 (16) | C2—C1—C12—O6 | 177.58 (12) |
| C1—C2—C3—C4 | −38.49 (19) | | |
Hydrogen-bond geometry (Å, °)

| D—H···A       | D—H | H···A | D···A  | D—H···A |
|---------------|-----|-------|--------|---------|
| C7—H7A···O1i  | 0.98| 2.65  | 3.473 (2) | 141     |
| C7—H7A···O5i  | 0.98| 2.50  | 3.456 (2) | 165     |
| C5—H5B···O8ii | 0.99| 2.65  | 3.328 (2) | 126     |
| C12—H12A···O4iii | 0.99| 2.58  | 3.163 (2) | 117     |

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

(I-298K)

Crystal data

| C12H19N3O8S | Mr = 365.36 |
|             | Orthorhombic, P212121 |
| a = 8.0717 (8) Å | Cell parameters from 9504 reflections |
| b = 9.1135 (12) Å | θ = 3.4–27.5° |
| c = 22.506 (3) Å | μ = 0.24 mm−1 |
| V = 1655.6 (3) Å³ | T = 298 K |
| Z = 4         | Cut block, colourless |
| F(000) = 768  | 0.24 × 0.22 × 0.14 mm |

Data collection

| Bruker D8 Venture dual source diffractometer | 22913 measured reflections |
| Radiation source: microsource | 2986 independent reflections |
| Detector resolution: 7.41 pixels mm−1 | 3523 reflections with I > 2σ(I) |
| φ and ω scans | Rint = 0.067 |
| Absorption correction: multi-scan (SADABS; Krause et al., 2015) | θmax = 27.5°, θmin = 2.4° |
| Tmin = 0.815, Tmax = 0.959 | h = −10→10 |
| l = −29→25 |

Refinement

| Least-squares matrix: full | Hydrogen site location: difference Fourier map |
| R[F² > 2σ(F²)] = 0.036 | H-atom parameters constrained |
| wR(F²) = 0.099 | w = 1/[σ²(Fo²) + (0.0574P)² + 0.1732P] |
| S = 1.04 | where P = (Fo² + 2Fo²)/3 |
| (Δσ/σ)max < 0.001 | Δρmax = 0.20 e Å⁻³ |
| 3786 reflections | Δρmin = −0.27 e Å⁻³ |
| 221 parameters | Absolute structure: Flack x determined using |
| 0 restraints | 1388 quotients [(I⁺)-(I⁻)]/[(I⁺)+(I⁻)] (Parsons et al., 2013) |
| Primary atom site location: structure-invariant direct methods | Absolute structure parameter: 0.07 (5) |
| Secondary atom site location: difference Fourier map |

Special details

**Experimental.** The crystal was mounted glued to the tip of a fine glass fibre, which was fastened in a copper mounting pin with electrical solder.

Data were collected at room temperature to investigate the possibility of the methyl group at C7 undergoing rapid spinning.
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 progress was checked using Platon (Spek, 2020) and by an $R$-tensor (Parkin, 2000). The final model was further checked with the IUCr utility checkCIF.

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

|   | $x$     | $y$     | $z$     | $U_{eq}$/$U_{iso}$ |
|---|---------|---------|---------|---------------------|
| S1| 0.74935 (9) | 0.79040 (6) | 0.39549 (3) | 0.05008 (19) |
| O1| 0.68675 (18) | 0.39774 (16) | 0.38959 (6) | 0.0334 (3) |
| O2| 0.3760 (2) | 0.3015 (2) | 0.44310 (7) | 0.0418 (4) |
| O3| 0.29761 (19) | 0.4019 (2) | 0.35639 (7) | 0.0444 (4) |
| O4| 0.6115 (2) | 0.22006 (19) | 0.27062 (7) | 0.0405 (4) |
| O5| 0.81632 (19) | 0.37532 (19) | 0.29858 (8) | 0.0406 (4) |
| O6| 0.7900 (2) | 0.65798 (18) | 0.35461 (8) | 0.0424 (4) |
| O7| 0.9030 (3) | 0.8324 (3) | 0.42018 (11) | 0.0739 (7) |
| O8| 0.6469 (4) | 0.8910 (2) | 0.36562 (13) | 0.0810 (7) |
| N1| 0.6247 (3) | 0.7208 (3) | 0.44695 (12) | 0.0586 (6) |
| N2| 0.6998 (4) | 0.6366 (3) | 0.48301 (13) | 0.0658 (7) |
| N3| 0.7518 (6) | 0.5639 (5) | 0.51657 (17) | 0.1031 (12) |
| C1| 0.6730 (3) | 0.4242 (2) | 0.32874 (9) | 0.0317 (4) |
| C2| 0.5312 (3) | 0.3413 (3) | 0.29776 (9) | 0.0345 (4) |
| H2| 0.479985 | 0.403642 | 0.267422 | 0.041* |
| C3| 0.3998 (2) | 0.2823 (3) | 0.33972 (9) | 0.0356 (4) |
| H3| 0.333367 | 0.207389 | 0.319499 | 0.043* |
| C4| 0.4662 (3) | 0.2211 (2) | 0.39892 (10) | 0.0349 (4) |
| H4| 0.442711 | 0.115874 | 0.402132 | 0.042* |
| C5| 0.6487 (3) | 0.2499 (2) | 0.40661 (10) | 0.0354 (5) |
| H5A| 0.679702 | 0.234428 | 0.447786 | 0.042* |
| H5B| 0.711710 | 0.181983 | 0.382284 | 0.042* |
| C6| 0.2387 (3) | 0.3687 (3) | 0.41482 (10) | 0.0414 (5) |
| C7| 0.0929 (3) | 0.2650 (4) | 0.41220 (13) | 0.0581 (8) |
| H7A| 0.005298 | 0.309049 | 0.389497 | 0.087* |
| H7B| 0.054350 | 0.245317 | 0.451757 | 0.087* |
| H7C| 0.126270 | 0.174873 | 0.393681 | 0.087* |
| C8| 0.2014 (4) | 0.5115 (4) | 0.44567 (16) | 0.0670 (9) |
| H8A| 0.299085 | 0.571603 | 0.446096 | 0.101* |
| H8B| 0.166869 | 0.492278 | 0.485738 | 0.101* |
| H8C| 0.114454 | 0.561748 | 0.424853 | 0.101* |
| C9| 0.7734 (3) | 0.2684 (3) | 0.25411 (10) | 0.0420 (5) |
| C10| 0.8905 (4) | 0.1406 (3) | 0.25816 (15) | 0.0605 (7) |
| H10A| 0.860101 | 0.067868 | 0.229299 | 0.091* |
| H10B| 0.884762 | 0.098732 | 0.297250 | 0.091* |
| H10C| 1.001458 | 0.173537 | 0.250531 | 0.091* |
| C11| 0.7710 (4) | 0.3396 (4) | 0.19315 (12) | 0.0612 (7) |
| H11A| 0.742453 | 0.267603 | 0.163763 | 0.092* |
### Atomic displacement parameters (Å²)

|     | $U_{11}$   | $U_{22}$   | $U_{33}$   | $U_{12}$   | $U_{13}$   | $U_{23}$   |
|-----|-------------|-------------|-------------|-------------|-------------|-------------|
| S1  | 0.0602 (4)  | 0.0303 (3)  | 0.0598 (4)  | −0.0049 (3) | 0.0056 (3)  | −0.0074 (2) |
| O1  | 0.0365 (7)  | 0.0311 (7)  | 0.0326 (7)  | −0.0014 (6) | −0.0052 (6) | 0.0011 (6)  |
| O2  | 0.0355 (7)  | 0.0565 (10) | 0.0333 (7)  | 0.0088 (8)  | −0.0010 (6) | −0.0008 (7) |
| O3  | 0.0373 (8)  | 0.058 (1)   | 0.0377 (8)  | 0.0136 (7)  | 0.0045 (7)  | 0.0071 (7)  |
| O4  | 0.0382 (7)  | 0.0418 (8)  | 0.0416 (8)  | −0.0060 (7) | 0.0071 (7)  | −0.0148 (7) |
| O5  | 0.0312 (7)  | 0.0451 (9)  | 0.0455 (9)  | −0.0025 (7) | 0.0042 (6)  | −0.0013 (7) |
| O6  | 0.0441 (9)  | 0.0327 (8)  | 0.0505 (9)  | −0.0036 (6) | 0.0048 (7)  | −0.0046 (7) |
| O7  | 0.0710 (14) | 0.0659 (14) | 0.0848 (16) | −0.0266 (12)| 0.0400 (12) | −0.0256 (12)|
| O8  | 0.110 (2)   | 0.0347 (10) | 0.0983 (17) | 0.0140 (12) | −0.0007 (16)| 0.0037 (11) |
| N1  | 0.0585 (13) | 0.0592 (14) | 0.0583 (13) | 0.0015 (12) | 0.0130 (11) | −0.0079 (12)|
| N2  | 0.0774 (18) | 0.0630 (16) | 0.0570 (15) | −0.0066 (14)| 0.0089 (14) | −0.0031 (13)|
| N3  | 0.127 (3)   | 0.105 (3)   | 0.077 (2)   | 0.003 (3)   | 0.000 (3)   | 0.026 (2)   |
| C1  | 0.0312 (9)  | 0.0324 (10) | 0.0315 (10) | 0.0009 (8)  | −0.0007 (8) | −0.0017 (8) |
| C2  | 0.0323 (10) | 0.0420 (11) | 0.0292 (10) | 0.0006 (8)  | −0.0005 (8) | −0.0045 (9) |
| C3  | 0.0276 (8)  | 0.0439 (11) | 0.0353 (10) | −0.0019 (9) | −0.0002 (8) | −0.0058 (9) |
| C4  | 0.0332 (9)  | 0.0333 (10) | 0.0382 (11) | 0.0012 (8)  | 0.0028 (8)  | 0.0009 (9)  |
| C5  | 0.0338 (10) | 0.0305 (10) | 0.0417 (11) | 0.0041 (8)  | −0.0017 (8) | 0.0061 (8)  |
| C6  | 0.0343 (10) | 0.0544 (13) | 0.0354 (11) | 0.0097 (11) | 0.0028 (9)  | 0.0025 (9)  |
| C7  | 0.0346 (11) | 0.091 (2)   | 0.0489 (14) | −0.0055 (13)| 0.0014 (10) | 0.0063 (15) |
| C8  | 0.075 (2)   | 0.0620 (18) | 0.0640 (18) | 0.0221 (16) | 0.0206 (16) | −0.0047 (15)|
| C9  | 0.0373 (11) | 0.0472 (12) | 0.0416 (11) | −0.0022 (10)| 0.0072 (9)  | −0.0013 (1) |
| C10 | 0.0526 (15) | 0.0566 (15) | 0.0722 (18) | 0.0116 (14) | 0.0114 (14) | −0.0184 (14)|
| C11 | 0.0600 (16) | 0.0788 (19) | 0.0449 (14) | −0.0095 (16)| 0.0106 (13) | −0.0052 (13)|
| C12 | 0.0450 (12) | 0.0331 (11) | 0.0415 (12) | 0.0021 (9)  | −0.0049 (9) | 0.0020 (9)  |

### Geometric parameters (Å, °)

|     | S1—O8 | 1.406 (3) | C4—C5 | 1.507 (3) |
|-----|-------|-----------|-------|-----------|
| S1  | 1.412 (2) | C4—H4 | 0.9800 |
| S1  | 1.5527 (17) | C5—H5A | 0.9700 |
| S1  | 1.660 (3) | C5—H5B | 0.9700 |
| O1  | 1.395 (3) | C6—C8 | 1.506 (4) |
| O1  | 1.434 (3) | C6—C7 | 1.511 (4) |
| O2  | 1.417 (3) | C7—H7A | 0.9600 |
| O2  | 1.434 (3) | C7—H7B | 0.9600 |
| O3  | 1.418 (3) | C7—H7C | 0.9600 |
| O3  | 1.431 (3) | C8—H8A | 0.9600 |
| O4  | 1.419 (3) | C8—H8B | 0.9600 |
| O4  | 1.429 (3) | C8—H8C | 0.9600 |

*Supplementary information*
| Bond       | Distance (Å) | Bond       | Distance (Å) | Bond       | Distance (Å) |
|------------|--------------|------------|--------------|------------|--------------|
| O5—C1      | 1.413 (3)    | C9—C10     | 1.503 (4)    | O6—C12     | 1.457 (3)    |
| O5—C9      | 1.439 (3)    | C9—C11     | 1.518 (4)    | N1—N2      | 1.271 (4)    |
| O6—C12     | 1.457 (3)    | C10—H10A   | 0.9600       | N2—N3      | 1.089 (5)    |
| N1—N2      | 1.271 (4)    | C10—H10B   | 0.9600       | C1—C12     | 1.510 (3)    |
| C1—C12     | 1.510 (3)    | C10—H11A   | 0.9600       | C1—C2      | 1.539 (3)    |
| C1—C2      | 1.539 (3)    | C11—H11B   | 0.9600       | C2—C3      | 1.518 (3)    |
| C2—C3      | 1.518 (3)    | C11—H11C   | 0.9600       | C2—H2      | 0.9800       |
| C3—C4      | 1.540 (3)    | C12—H12A   | 0.9700       | C3—H3      | 0.9800       |

| Bond       | Distance (Å) | Bond       | Distance (Å) | Bond       | Distance (Å) |
|------------|--------------|------------|--------------|------------|--------------|
| O8—S1—O7  | 121.86 (16)  | H5A—C5    | H5B—C5      | O8—S1—O6  | 110.36 (14)  |
| O8—S1—O6  | 110.36 (14)  | O2—C6     | O3—C6       | O7—S1—O6  | 104.96 (12)  |
| O7—S1—O6  | 104.96 (12)  | O2—C6     | O3—C6       | O8—S1—N1  | 103.09 (17)  |
| O8—S1—N1  | 103.09 (17)  | O3—C6     | O3—C6       | O7—S1—N1  | 111.19 (15)  |
| O7—S1—N1  | 111.19 (15)  | O2—C6     | O7—S1—N1    | O6—S1—N1  | 104.17 (11)  |
| O6—S1—N1  | 104.17 (11)  | O3—C6     | O7—S1—N1    | C1—O1—C5  | 114.07 (16)  |
| C1—O1—C5  | 114.07 (16)  | O3—C6     | C6—O2—C4    | C6—O2—C4  | 107.84 (16)  |
| C6—O2—C4  | 107.84 (16)  | C6—C7     | H7A—C7—H7B  | C3—O3—C6  | 105.87 (17)  |
| C3—O3—C6  | 105.87 (17)  | H7A—C7—H7B| C6—O4—C9    | C2—O4—C9  | 106.84 (16)  |
| C2—O4—C9  | 106.84 (16)  | H7A—C7—H7B| C1—O5—C9    | 110.53 (16) |
| C1—O5—C9  | 110.53 (16)  | C6—C7     | H7A—C7—H7C  | C12—O6—S1 | 117.92 (14)  |
| C12—O6—S1 | 117.92 (14)  | C6—C7     | H7A—C7—H7C  | N2—N1—S1  | 112.8 (2)    |
| N2—N1—S1  | 112.8 (2)    | C6—C7     | H7B—C7—H7C  | N3—N2—N1  | 173.9 (4)    |
| N3—N2—N1  | 173.9 (4)    | C6—C7     | H7B—C7—H7C  | C3—O1—C5  | 110.61 (17)  |
| C3—O1—C5  | 110.61 (17)  | C6—C8     | H8A—C8—H8B  | C1—O1—C5  | 110.53 (16)  |
| C1—O1—C5  | 110.53 (16)  | C6—C8     | C6—C8—H8B   | C12—C1—C2 | 111.76 (18)  |
| C12—C1—C2 | 111.76 (18)  | C6—C8     | C6—C8—H8C   | O4—C2—C3  | 108.12 (18)  |
| O4—C2—C3  | 108.12 (18)  | C6—C8     | C8—C8—H8C   | O4—C2—C1  | 103.75 (16)  |
| O4—C2—C1  | 103.75 (16)  | C6—C8     | C6—C8—H8C   | C3—C2—C1  | 114.32 (17)  |
| C3—C2—C1  | 114.32 (17)  | C6—C8     | C6—C8—H8C   | O4—C2—H2  | 110.1        |
| O4—C2—H2  | 110.1        | C6—C8     | C6—C8—H8C   | O4—C2—H2  | 110.1        |
| C3—C2—H2  | 110.1        | C6—C8     | C6—C8—H8C   | O4—C2—H2  | 110.1        |
| O4—C2—C2  | 110.1        | C6—C8     | C6—C8—H8C   | O4—C2—C2  | 110.1        |
| O4—C2—C1  | 110.1        | C6—C8     | C6—C8—H8C   | O4—C2—C1  | 110.1        |
| C3—C2—C1  | 110.1        | C6—C8     | C6—C8—H8C   | O3—C3—C2  | 110.1        |
| O3—C3—C2  | 110.1        | C6—C8     | C6—C8—H8C   | O3—C3—C4  | 110.1        |
| O3—C3—C4  | 110.1        | C6—C8     | C6—C8—H8C   | O3—C3—C4  | 110.1        |
| O3—C3—C4  | 110.1        | C6—C8     | C6—C8—H8C   | O3—C3—H3  | 110.1        |
| C2—C3—H3  | 110.1        | C6—C8     | C6—C8—H8C   | C2—C3—H3  | 110.1        |
| O2—C4—C5  | 109.14 (18)  | C6—C8     | C6—C8—H8C   | O2—C4—C3  | 103.79 (16)  |
| O2—C4—C3  | 103.79 (16)  | C6—C8     | C6—C8—H8C   | O2—C4—C3  | 112.11 (18)  |
| O5—C4—C3  | 112.11 (18)  | C6—C8     | C6—C8—H8C   | O5—C4—C3  | 112.11 (18)  |
| O2—C4—H4  | 110.5        | C6—C8     | C6—C8—H8C   | O2—C4—H4  | 110.5        |
C5—C4—H4 110.5  H11B—C11—H11C 109.5
C3—C4—H4 110.5  O6—C12—C1 108.13 (18)
O1—C5—C4  110.00 (17)  O6—C12—H12A 110.1
O1—C5—H5A 109.7  C1—C12—H12A 110.1
O1—C5—H5B 109.7  C1—C12—H12B 110.1
C4—C5—H5B 109.7  H12A—C12—H12B 108.4

O8—S1—O6—C12 −47.7 (2)  C6—O2—C4—C5 135.43 (19)
O7—S1—O6—C12 179.27 (18)  C6—O2—C4—C3 15.7 (2)
N1—S1—O6—C12 62.31 (19)  O3—C3—C4—O2 7.4 (2)
O8—S1—N1—N2 −173.4 (2)  O6—C12—C1—O1 −80.8 (2)
O7—S1—N1—N2 −41.2 (3)  C1—O1—C5—C4 109.7 (2)
O6—S1—N1—N2 71.3 (2)  C4—O2—C6—O3 −33.2 (2)
C5—O1—C1—O5 −80.8 (2)  C1—O1—C5—C4 109.7 (2)
C5—O1—C1—C12 159.36 (17)  O5—C1—C2—O4 76.6 (2)
C5—O1—C1—C2 36.0 (2)  C1—C2—O4—C9 31.7 (2)
C9—O5—C1—O5 121.76 (19)  C1—C2—O4—C9 −148.3 (2)
C9—O5—C1—C12 −154.34 (17)  C1—C2—O4—C9 −148.3 (2)
C9—O5—C1—C2 −32.6 (2)  C1—C2—O4—C9 −148.3 (2)
C9—O4—C2—C3 −150.25 (18)  C1—O5—C9—O4 −17.9 (2)
C9—O4—C2—C1 −32.6 (2)  C1—O5—C9—C10 −134.0 (2)
C12—C1—C2—O4 140.27 (19)  C1—O5—C9—C10 101.1 (2)
C12—C1—C2—C3 176.6 (3)  C1—O5—C9—C10 101.1 (2)
O5—C1—C2—C3 138.32 (19)  C1—O5—C9—C10 101.1 (2)
C12—C1—C2—C3 −102.2 (2)  C1—O5—C9—C10 101.1 (2)
C6—O3—C3—C2 −150.25 (18)  C1—O5—C9—C10 101.1 (2)
C6—O3—C3—C4 −27.6 (2)  S1—O6—C12—C1 135.17 (17)
O4—C2—C3—O3 167.48 (17)  O1—C1—C12—O6 53.4 (2)
O4—C2—C3—C4 77.5 (2)  O5—C1—C12—O6 −66.3 (2)
O4—C2—C3—C4 76.6 (2)  C2—C1—C12—O6 178.62 (17)
O4—C2—C3—C4 76.6 (2)  C2—C1—C12—O6 178.62 (17)
C1—C2—C3—C4 −38.4 (3)

**Hydrogen-bond geometry (Å, °)**

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|------|-------|---------|
| C7—H7.4···O1i | 0.96 | 2.70 | 3.531 (3) | 146 |
| C7—H7.4···O5i | 0.96 | 2.62 | 3.540 (3) | 160 |
| C5—H5B···O8ii | 0.97 | 2.73 | 3.398 (3) | 127 |
| C12—H12A···O4iii | 0.97 | 2.63 | 3.234 (3) | 121 |

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