Crystal structure and Hirshfeld surface analysis of N,N'-[ethane-1,2-diylbis(oxy)]bis(4-methylbenzene-sulfonamide)

Seher Meral,[a] Sevgi Kansiz,[b] Necmi Dege,[b] Aysen Alaman Agar[a] and Galyna G. Tsapyuk[c]*

[a]Ondokuz Mayıs University, Faculty of Arts and Sciences, Department of Chemistry, 55139, Samsun, Turkey, [b]Ondokuz Mayıs University, Faculty of Arts and Sciences, Department of Physics, 55139, Kurupelit, Samsun, Turkey, and [c]Taras Shevchenko National University of Kyiv, Department of Chemistry, 64, Vladimirska Str., Kiev 01601, Ukraine. *Correspondence e-mail: tsapyuk@ukr.net

In the molecule of the title compound, $C_{16}H_{20}N_2O_6S_2$, the mid-point of the C—C bond of the central ethane moiety is located on a twofold rotation axis. In the crystal, molecules are linked by N—H$\cdots$O hydrogen bonds into supramolecular chains propagating along the [101] direction. Hirshfeld surface analysis and two-dimensional fingerprint plots indicate that the most important contributions to the crystal packing are from H$\cdots$H (43.1%), O$\cdots$H/H$\cdots$O (40.9%), C$\cdots$H/H$\cdots$C (8.8%) and C$\cdots$C (5.5%) interactions.

1. Chemical context

Sulfonamides are synthetic molecules which include the SO_2–NH group and are called sulfa drugs. These effective drug molecules have an important role in the medical field, including as promising chemotherapeutic agents, and have been used in the treatment of many bacterial infections due to their physical, chemical and biological properties (Mahmood et al., 2016; Ghorab et al., 2018). Recently, sulfonamides have also been used in the organic synthesis reactions for the synthesis of linear or cyclic oligomers and the introduction of nucleophilic heteroatom functionality to the synthesized molecule (Ni et al., 2015). N,N'-ditosylalkane diamine is a disulfonamide synthesized by the tosylation of diamine, and this synthetic molecule has antibacterial properties (Alyar et al., 2011) and has also been used in many organic synthesis reactions (Rong et al., 1998). In this study, the synthesis, crystal structure and Hirshfeld surface analysis are reported for the new potential sulfa drug, N,N'-[ethane-1,2-diylbis(oxy)]bis(4-methylbenzenesulfonamide).
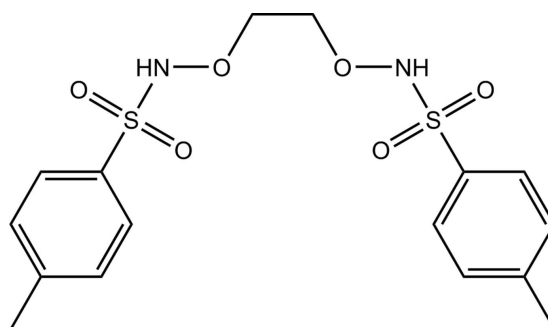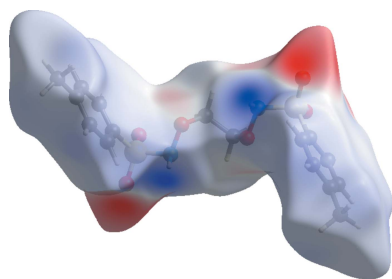
https://doi.org/10.1107/S2056989018017437

research communications

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O3^{i}	0.83 (3)	2.17 (3)	2.974 (3)	162 (3)
C1—H1$A\cdots$O2^{ii}	0.97	2.56	3.401 (4)	146

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

2. Structural commentary

The molecular structure of the title compound is illustrated in Fig. 1. The molecular point group symmetry is C_{2v} (*mm*2) (H atoms excluded), with the twofold rotation axis bisecting the central C1—C1^{i} bond. The molecule is Z-shaped with the N1—S1—C2—C3 torsion angle being −60.6 (3)°. The C1—O1 bond length of 1.429 (3) Å and the O1—N1 bond length of 1.426 (2) Å are close to the values reported for similar compounds (see the *Database survey*). The S1—O2 and S1—O3 distances are 1.4376 (17) and 1.4168 (19) Å, respectively while the S1—N1 and S1—C2 distances are 1.647 (3) Å and 1.747 (3) Å, respectively.

3. Supramolecular features

The crystal packing of the title compound features inter-molecular N—H$\cdots$O hydrogen bonds (Table 1 and Fig. 2), which connect the molecules into supramolecular chains propagating along the [101] direction. The chains are linked by pairs of C—H$\cdots$O hydrogen bonds (Table 1, Fig. 3), forming a framework with small cavities of 99 Å^3, *ca* 5% of the unit-cell volume.

4. Database survey

A search of the Cambridge Structural database (CSD, version 5.39, update May 2018; Groom *et al.*, 2016) for structures similar to the title compound gave hits including (1*S*,2*S*,4*S*,5*S*)-2,5-bis[(*p*-toluenesulfonyl)amino]bicyclo(2.2.1)heptane (Berkessel *et al.*, 2004), 1,6-anhydro-2,5-dideoxy-3,4-*O*-isopropyl-idene-2,5-bis[(4-methylbenzenesulfonyl)amino]-1-thiohexitol (Sureshkumar *et al.*, 2005), (1*R*,3*S*)-1-(toluenesulfonylamido)-
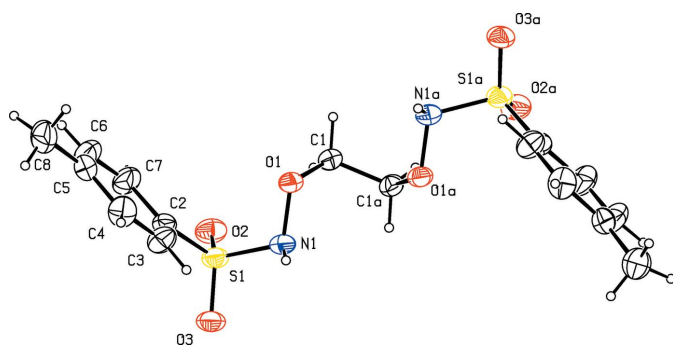

Figure 2
A view of the chain structure formed by N—H$\cdots$O hydrogen bonding.

3-(toluenesulfonylamidomethyl)-3,5,5-trimethylcyclohexane (Berkessel *et al.*, 2006) and *N*,*N*′-propylenedioxybis(2,4,6-tri-methylbenzenesulfonamide) (Wardell *et al.*, 2004). In the latter compound, the C1—O1 bond length is 1.4448 (19) Å, in agreement with the value found in this study. In addition, the S1—O11 and S1—O12 distances are 1.4312 (12) and 1.4263 (13) Å, respectively and the S1—N1 and S1—C11 distances are 1.6608 (14) and 1.7799 (16) Å, respectively.

5. Hirshfeld surface analysis

Hirshfeld surface analysis is a method for visualizing the interactions present in the crystal structure and providing quantitative information about them. The d_{norm} representation of the Hirshfeld surface reveals the close contacts of hydrogen-bond donors and acceptors, but other close contacts are also evident. The molecular Hirshfeld surfaces were generated using a standard (high) surface resolution with the three-dimensional d_{norm} surfaces mapped over a fixed colour scale of −0.464 (red) to 2.052 (blue) Å using the *Crystal-Explorer* (Turner *et al.*, 2017). The red spots on the surface indicate the intermolecular contacts involved in the hydrogen

Figure 1
The molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 20% probability level. Symmetry code: (a) $-x, y, -z-\frac{1}{2}$.
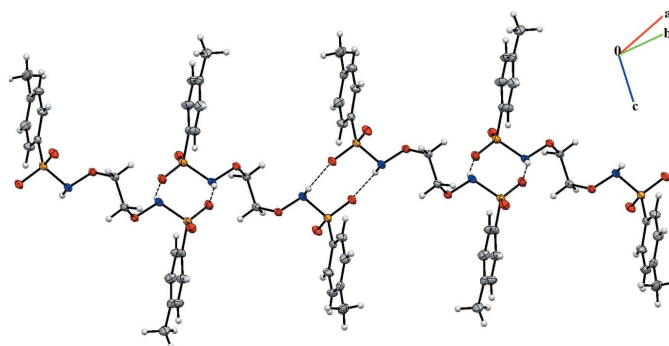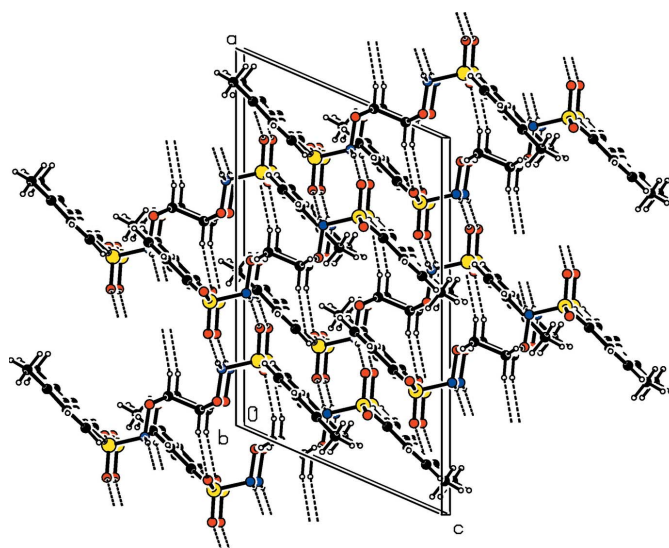

Figure 3
A view along the *b*-axis of the crystal packing of the title compound. The hydrogen bonds (Table 1) are shown as dashed lines.

Figure 6
The overall fingerprint plot for the title compound.

Fig. 6 shows the two-dimensional fingerprint of the sum of the contacts contributing to the Hirshfeld surface represented in normal mode. The second plot shown in Fig. 7 represents the O···H/H···O contacts (40.9%) between the oxygen atoms inside the surface and the hydrogen atoms outside the surface.
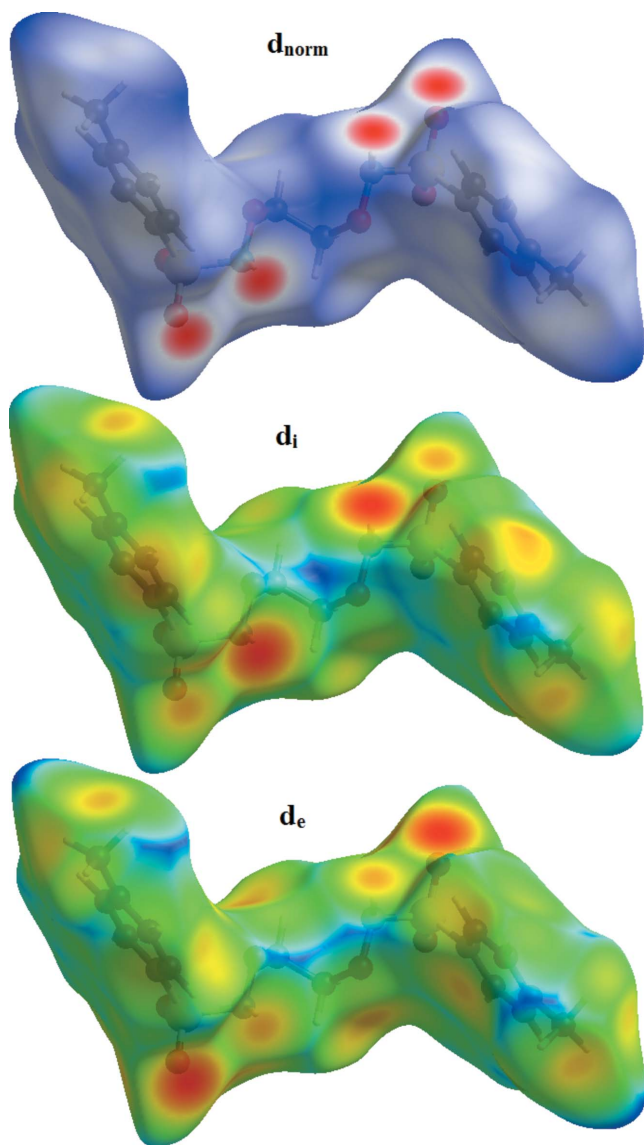

Figure 4
The Hirshfeld surface of the title compound mapped over d_{norm}, d_i and d_e.

bonds. In Figs. 4 and 5, the identified red spot is attributed to the H···O close contacts which are due to the N—H···O hydrogen bonds (Table 1).
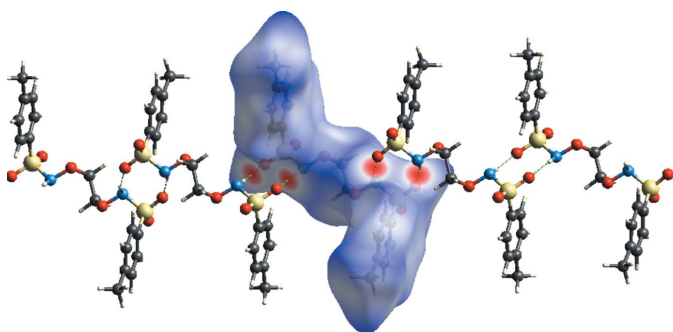

Figure 5
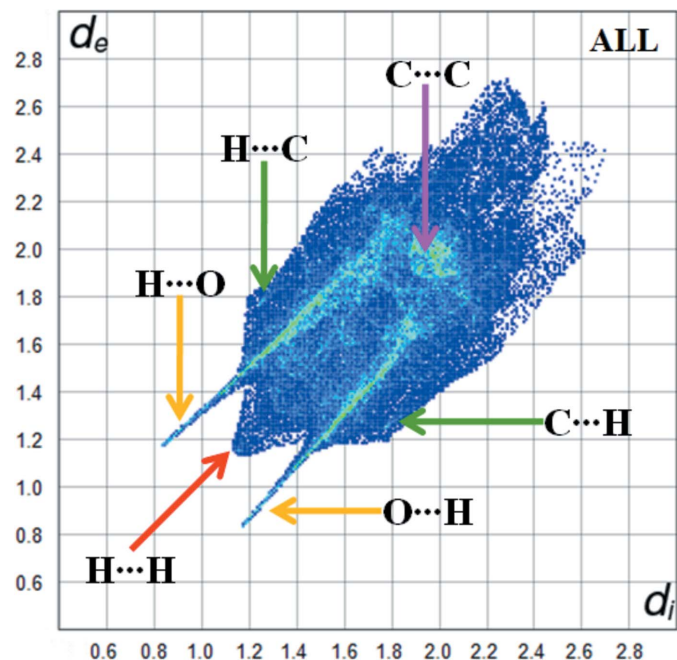Hirshfeld surface mapped over d_{norm} to visualize the intermolecular interactions in the title compound.

Figure 7
Two-dimensional fingerprint plots with a d_{norm} view of the H···H (43.1%), O···H/H···O (40.9%), C···H/H···C (8.8%) and C···C (5.5%) contacts in the title compound.

Figure 8
A view of the three-dimensional Hirshfeld surface plotted over electrostatic potential energy.

$d_e + d_i \sim 2.0$ Å and has two symmetrical points at the top, bottom left and right, which is characteristic of an N—H···O hydrogen bond.

The H···H plot shown in Fig. 7 shows the two-dimensional fingerprint of the (d_i, d_e) points associated with hydrogen atoms. It is characterized by an end point that points to the origin and corresponds to $d_i = d_e = 1.08$ Å, which indicates the presence of the H···H contacts in this study (43.1%). The C···H/H···C plot in Fig. 7 shows the contact between the carbon atoms inside the surface and the hydrogen atoms outside the surface of Hirshfeld and *vice versa*. There are two symmetrical wings on the left and right sides (8.8%). Furthermore, there are C···C (5.5%), N···H/H···N (1.4%), O···C/C···O (0.1%) and S···H/H···S (0.1%) contacts in the title structure.

A view of the three-dimensional Hirshfeld surface of the title compound plotted over electrostatic potential energy in the range −0.095 to 0.123 a.u. using the STO-3G basis set at the Hartree–Fock level of theory is shown in Fig. 8 where the N—H···O hydrogen-bond donors and acceptors are shown as blue and red areas around the atoms related with positive (hydrogen-bond donors) and negative (hydrogen-bond acceptors) electrostatic potentials, respectively.

6. Synthesis and crystallization

The title compound was synthesized according to the method of Bauer & Suresh (1963). Single crystals (m.p. 414–415 K) were obtained from an ethanol solution (yield 93%)

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. C-bound H atoms were positioned geometrically (C—H = 0.93–0.97 Å) and refined as riding, with $U_{iso}(H) = 1.5U_{eq}$(C-methyl) and $1.2U_{eq}$(C) for other H atoms. The NH H atom was located in a difference-Fourier maps and freely refined.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{20}N_2O_6S_2$
M_r	400.46
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	296
a, b, c (Å)	16.3393 (18), 13.4977 (19), 9.7461 (11)
β (°)	113.442 (8)
V (Å^3)	1972.0 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.30
Crystal size (mm)	$0.56 \times 0.36 \times 0.13$
Data collection	
Diffractometer	Stoe IPDS 2
Absorption correction	Integration (*X-RED32*; Stoe & Cie, 2002)
T_{min}, T_{max}	0.873, 0.973
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6561, 1938, 1070
R_{int}	0.086
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.116, 0.90
No. of reflections	1938
No. of parameters	123
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.14, −0.25

Computer programs: *X-AREA* and *X-RED32* (Stoe & Cie, 2002), *SHELXL2017* (Sheldrick, 2015), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

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Crystal structure and Hirshfeld surface analysis of *N,N′*-[ethane-1,2-diylbis(-oxy)]bis(4-methylbenzenesulfonamide)

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *WinGX* (Farrugia, 2012); program(s) used to refine structure: *SHELXL2017* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

N,N′-**[Ethane-1,2-diylbis(oxy)]bis(4-methylbenzenesulfonamide)**

Crystal data

$C_{16}H_{20}N_2O_6S_2$	$F(000) = 840$
$M_r = 400.46$	$D_x = 1.349$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 16.3393\ (18)$ Å	Cell parameters from 6407 reflections
$b = 13.4977\ (19)$ Å	$\theta = 2.0$–$27.2°$
$c = 9.7461\ (11)$ Å	$\mu = 0.30$ mm^{-1}
$\beta = 113.442\ (8)°$	$T = 296$ K
$V = 1972.0\ (4)$ Å^3	Prism, colorless
$Z = 4$	$0.56 \times 0.36 \times 0.13$ mm

Data collection

Stoe IPDS 2 diffractometer	6561 measured reflections
	1938 independent reflections
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus	1070 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.086$
Detector resolution: 6.67 pixels mm^{-1}	$\theta_{max} = 26.0°$, $\theta_{min} = 2.0°$
rotation method scans	$h = -20 \rightarrow 20$
Absorption correction: integration (X-RED32; Stoe & Cie, 2002)	$k = -16 \rightarrow 16$
	$l = -12 \rightarrow 9$
$T_{min} = 0.873$, $T_{max} = 0.973$	

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.047$	
$wR(F^2) = 0.116$	$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2]$
$S = 0.90$	where $P = (F_o^2 + 2F_c^2)/3$
1938 reflections	$(\Delta/\sigma)_{max} < 0.001$
123 parameters	$\Delta\rho_{max} = 0.14$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.25$ e Å^{-3}

Special details

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

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

	x	y	z	U_{iso}*/U_{eq}
S1	0.19812 (4)	0.13241 (6)	0.11223 (9)	0.0759 (3)
O1	0.04273 (10)	0.15963 (13)	−0.0863 (2)	0.0722 (5)
C1	0.00029 (17)	0.0748 (2)	−0.1731 (3)	0.0698 (7)
H1A	−0.060770	0.071765	−0.181199	0.084*
H1B	0.030688	0.015643	−0.121023	0.084*
O3	0.28617 (11)	0.15543 (15)	0.1220 (3)	0.0907 (7)
O2	0.17825 (13)	0.03371 (14)	0.1379 (3)	0.0928 (7)
N1	0.13462 (14)	0.1594 (2)	−0.0629 (3)	0.0751 (7)
C2	0.16891 (16)	0.2121 (2)	0.2267 (3)	0.0705 (8)
C5	0.1182 (2)	0.3366 (3)	0.4043 (4)	0.0929 (10)
C7	0.1370 (2)	0.1733 (3)	0.3271 (4)	0.1030 (11)
H7	0.131947	0.105133	0.335264	0.124*
C4	0.1518 (2)	0.3736 (3)	0.3067 (4)	0.1041 (11)
H4	0.157573	0.441748	0.299978	0.125*
C6	0.1129 (3)	0.2367 (4)	0.4145 (5)	0.1153 (13)
H6	0.092328	0.210422	0.483059	0.138*
C3	0.1774 (2)	0.3119 (3)	0.2180 (4)	0.0954 (10)
H3	0.200335	0.338428	0.152627	0.115*
C8	0.0890 (3)	0.4066 (4)	0.4973 (5)	0.1375 (16)
H8A	0.083016	0.370639	0.577813	0.206*
H8B	0.032607	0.435597	0.435712	0.206*
H8C	0.132692	0.457942	0.537350	0.206*
H1	0.146 (2)	0.217 (2)	−0.080 (4)	0.089 (11)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0600 (4)	0.0881 (5)	0.0859 (6)	−0.0056 (4)	0.0356 (4)	0.0138 (4)
O1	0.0565 (9)	0.0901 (13)	0.0773 (13)	−0.0033 (9)	0.0344 (9)	−0.0099 (10)
C1	0.0658 (14)	0.0790 (17)	0.0728 (19)	−0.0063 (14)	0.0365 (15)	0.0007 (16)
O3	0.0572 (11)	0.1173 (16)	0.1016 (17)	−0.0056 (10)	0.0358 (11)	0.0226 (13)
O2	0.0875 (13)	0.0809 (13)	0.1204 (19)	−0.0012 (10)	0.0523 (13)	0.0201 (13)
N1	0.0571 (13)	0.0913 (19)	0.0849 (19)	−0.0072 (12)	0.0367 (12)	0.0028 (15)
C2	0.0576 (14)	0.084 (2)	0.0694 (19)	−0.0124 (13)	0.0251 (13)	0.0098 (15)
C5	0.0732 (19)	0.131 (3)	0.065 (2)	−0.008 (2)	0.0175 (16)	−0.010 (2)
C7	0.122 (3)	0.108 (2)	0.100 (3)	−0.038 (2)	0.066 (2)	0.000 (2)
C4	0.124 (3)	0.089 (2)	0.100 (3)	−0.008 (2)	0.044 (2)	0.000 (2)
C6	0.127 (3)	0.148 (4)	0.097 (3)	−0.040 (3)	0.071 (3)	−0.014 (3)
C3	0.107 (2)	0.094 (2)	0.101 (3)	−0.0100 (18)	0.059 (2)	0.011 (2)

C8	0.123 (3)	0.192 (4)	0.093 (3)	0.006 (3)	0.038 (2)	−0.044 (3)

Geometric parameters (Å, º)

S1—O2	1.4168 (19)	C5—C6	1.357 (5)
S1—O3	1.4376 (17)	C5—C4	1.368 (5)
S1—N1	1.647 (3)	C5—C8	1.512 (5)
S1—C2	1.747 (3)	C7—C6	1.371 (5)
O1—N1	1.426 (2)	C7—H7	0.9300
O1—C1	1.429 (3)	C4—C3	1.379 (5)
C1—C1^i	1.494 (5)	C4—H4	0.9300
C1—H1A	0.9700	C6—H6	0.9300
C1—H1B	0.9700	C3—H3	0.9300
N1—H1	0.83 (3)	C8—H8A	0.9600
C2—C3	1.361 (4)	C8—H8B	0.9600
C2—C7	1.381 (4)	C8—H8C	0.9600
O2—S1—O3	119.02 (12)	C6—C5—C8	122.2 (4)
O2—S1—N1	107.29 (15)	C4—C5—C8	120.0 (4)
O3—S1—N1	102.83 (12)	C6—C7—C2	119.1 (3)
O2—S1—C2	109.02 (13)	C6—C7—H7	120.5
O3—S1—C2	110.20 (13)	C2—C7—H7	120.5
N1—S1—C2	107.80 (13)	C5—C4—C3	121.4 (3)
N1—O1—C1	108.99 (19)	C5—C4—H4	119.3
O1—C1—C1^i	113.68 (15)	C3—C4—H4	119.3
O1—C1—H1A	108.8	C5—C6—C7	122.2 (3)
C1^i—C1—H1A	108.8	C5—C6—H6	118.9
O1—C1—H1B	108.8	C7—C6—H6	118.9
C1^i—C1—H1B	108.8	C2—C3—C4	119.7 (3)
H1A—C1—H1B	107.7	C2—C3—H3	120.2
O1—N1—S1	110.82 (17)	C4—C3—H3	120.2
O1—N1—H1	106 (2)	C5—C8—H8A	109.5
S1—N1—H1	108 (2)	C5—C8—H8B	109.5
C3—C2—C7	119.7 (3)	H8A—C8—H8B	109.5
C3—C2—S1	120.6 (2)	C5—C8—H8C	109.5
C7—C2—S1	119.7 (3)	H8A—C8—H8C	109.5
C6—C5—C4	117.9 (3)	H8B—C8—H8C	109.5
N1—O1—C1—C1^i	−63.7 (3)	C3—C2—C7—C6	1.2 (5)
C1—O1—N1—S1	−108.3 (2)	S1—C2—C7—C6	−178.9 (3)
O2—S1—N1—O1	65.1 (2)	C6—C5—C4—C3	1.8 (6)
O3—S1—N1—O1	−168.64 (18)	C8—C5—C4—C3	−178.7 (3)
C2—S1—N1—O1	−52.2 (2)	C4—C5—C6—C7	−2.4 (6)
O2—S1—C2—C3	−176.8 (3)	C8—C5—C6—C7	178.1 (3)
O3—S1—C2—C3	50.9 (3)	C2—C7—C6—C5	0.9 (6)
N1—S1—C2—C3	−60.6 (3)	C7—C2—C3—C4	−1.7 (5)
O2—S1—C2—C7	3.3 (3)	S1—C2—C3—C4	178.4 (3)

| O3—S1—C2—C7 | −129.0 (2) | C5—C4—C3—C2 | 0.2 (6) |
| N1—S1—C2—C7 | 119.5 (3) | | |

Symmetry code: (i) −*x*, *y*, −*z*−1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O3[ii]	0.83 (3)	2.17 (3)	2.974 (3)	162 (3)
C1—H1*A*···O2[iii]	0.97	2.56	3.401 (4)	146

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