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Molecular and crystal structure of 5,9-dimethyl-5*H*-pyrano[3,2-*c*:5,6-*c*′]bis[2,1-benzothiazin]-7(9*H*)-one 6,6,8,8-tetroxide dimethylformamide monosolvate

Andrii Rybalka,[a]* Svitlana Shishkina,[b] Igor Ukrainets,[c] Lyudmila Sidorenko[c] and Galina Sim[d]

[a]V. N. Karazin Kharkiv National University, 4 Svobody sq., Kharkiv 61077, Ukraine, [b]SSI "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60, Nauky Ave., Kharkiv 61001, Ukraine, [c]National University of Pharmacy, 4 Valentynivska St., Kharkiv 61168, Ukraine, and [d]Far Eastern State Medical University, 35 Murav'eva-Amurskogo St., Khabarovsk, 680000, Russian Federation. *Correspondence e-mail: rybalka19969@gmail.com

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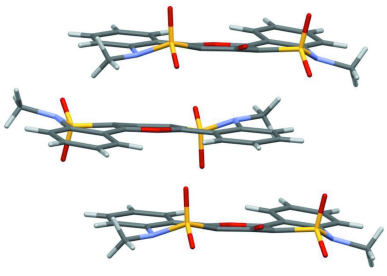
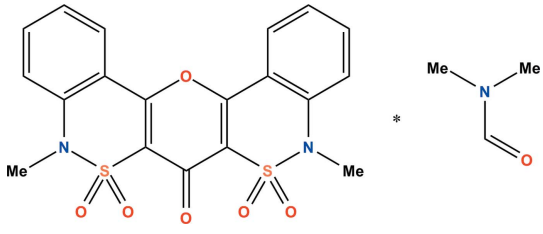
The title molecule crystallizes as a dimethylformamide monosolvate, $C_{19}H_{14}N_2O_6S_2\cdot C_3H_7NO$. The molecule was expected to adopt mirror symmetry but slightly different conformational characteristics of the condensed benzothiazine ring lead to point group symmetry 1. In the crystal, molecules form two types of stacking dimers with distances of 3.464 (2) Å and 3.528 (2) Å between π-systems. As a result, columns extending parallel to [100] are formed, which are connected to intermediate dimethylformamide solvent molecules by C—H···O interactions.

1. Chemical context

Alkyl 1-*R*-4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carboxylates are highly reactive compounds (Ukrainets *et al.*, 2007). They easily form the corresponding amides with primary and many secondary alkyl, aryl or hetarylamines and can be converted to 5,9-di-*R*-6,7,8-trioxodiquinolino [3,4-*b*; 3′,4′-*e*]-4*H*-pyrans in high yields through thermolysis (Ukrainets *et al.*, 2000). The acylating ability is distinctly reduced in alkyl 1-*R*-4-hydroxy-2,2-dioxo-1*H*-2λ^6,1-benzothiazine-3-carboxylates (Ukrainets *et al.*, 2014). However, a similar heterocycle, 5,9-dimethyl-5*H*-pyrano [3,2-*c*:5,6-*c*′]bis[2,1]benzothiazin-7(9*H*)-one 6,6,8,8-tetroxide (I) was synthesized based on methyl 4-hydroxy-1-methyl-2,2-dioxo-1*H*-2λ^6,1-benzothiazine-3-carboxylate (Ukrainets *et al.*, 2013). The molecular and crystal structures of its dimethylformamide solvate are reported in the present communication.





2. Structural commentary

Both thiazine rings adopt a twist-boat conformation (Fig. 1) with slightly different characteristics despite the formally mirror-symmetric molecular structure of (I) in the gas phase.

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

D—H···A	D—H	H···A	D···A	D—H···A
C17—H17A···O3	0.96	2.40	2.885 (2)	111
C18—H18A···O5	0.96	2.41	2.895 (2)	111
C3A—H3AA···O1A	0.96	2.41	2.784 (3)	103
C12—H12···O1	0.93	2.39	2.7106 (17)	100
C16—H16···O1	0.93	2.39	2.7109 (17)	100
C9—H9···O1A^{i}	0.93	2.41	3.324 (2)	169
C18—H18B···O1A^{ii}	0.96	2.46	3.376 (3)	159

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

The puckering parameters (Zefirov *et al.*, 1990) are: $S = 0.51$, $\theta = 44.8°$, $\Psi = 28.9°$ for the C1–C2–C3–C4–N1–S1 ring (1) and $S = 0.48$, $\theta = 50.0°$, $\Psi = 22.8°$ for the C5–C6–C7–C8–N2–S2 ring (2). The S1 and C1 atoms deviate by 0.669 (2) and 0.207 (2) Å, respectively, from the mean-square plane of the remaining atoms in ring (1). The corresponding deviations in ring (2) are 0.668 (2) and 0.270 (2) Å, respectively.

The 4*H*-pyran-4-one ring (3) adopts a sofa conformation with puckering parameters $S = 0.14$, $\theta = 24.7°$, $\Psi = 22.6°$. The deviation of C19 from the plane of the remaining atoms of (3) is 0.087 (2) Å. The C1═C2 and C5═C6 bonds [1.3571 (17) Å and 1.3529 (17) Å] are slightly elongated as compared to the mean value of 1.329 Å for a Csp^2═Csp^2 bond (Bürgi & Dunitz, 1994).

The molecule also contains shortened contacts (the H···O van der Waals radii sum is 2.46 Å; Zefirov, 1997), which can be considered as attractive intramolecular interactions. However, the values of the corresponding C—H···O angles for the pairs C17···O3, C18···O5, C3A···O1A, C12···O1, C16···O1 (Table 1) are too small to allow them to be characterized as intramolecular hydrogen bonds.

A further analysis of the molecular structure revealed the presence of other shortened intramolecular contacts: H9···H17C = 2.21 Å (expected 2.34 Å), H13···H18B = 2.28 Å (expected 2.34 Å), H13···H18C = 2.31 Å (expected 2.34 Å). These shortened contacts affect the very small pyramidalization of the nitrogen atoms; the sums of the bond angles centered at the N1 and N2 atoms are 354 and 356°, respectively.

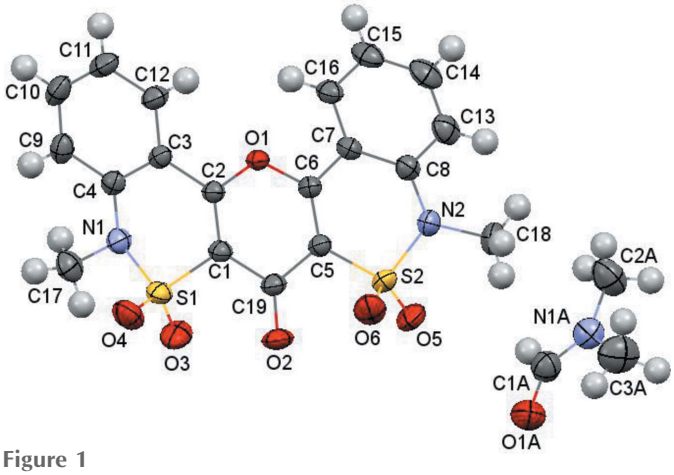


Figure 1
The structures of the molecular entities in solvated (I). Displacement ellipsoids are drawn at the 50% probability level.

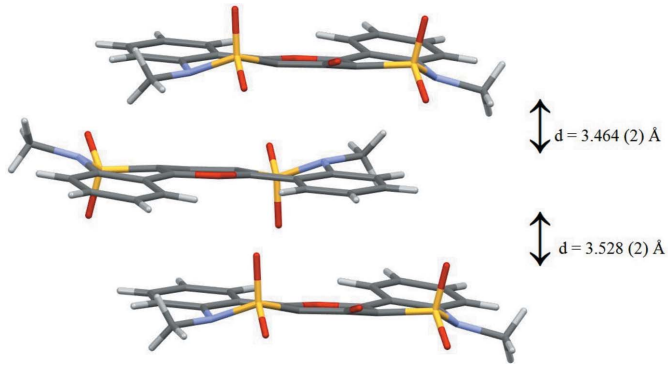


Figure 2
Two types of stacking dimers in the crystal structure of (I).

3. Supramolecular features

In the crystal, molecules of (I) form columns extending parallel to [100] whereby centrosymmetric pairs of molecules within a column interact by π–π stacking interactions (Fig. 2). The plane-to-plane distances between the π-systems in the centrosymmetric dimers are 3.464 (2) and 3.528 (2) Å. The mean-square plane was calculated for O1 and all carbon atoms (with the exception of C19) of the polycyclic entity.

The dimethylformamide solvent molecules are situated between the columns (Fig. 3) and are bound by weak intermolecular hydrogen bonds including C9—H9···O1A^{i} and C18—H18B···O1A^{ii} (Table 2).

4. Database survey

A search of the Cambridge Structural Database (Version 5.38, update February 2019; Groom *et al.*, 2016) for the benzothiazine skeleton revealed 34 hits. In all structures, the conformation of the benzothiazine fragment is similar.

The title compound may be considered as a structural analogue of 5,9-diethyl-6,7,8-trioxodiquinolino[3,4-*b*;3′,4′-*e*]-4*H*-pyran (Ukrainets *et al.*, 2000) with the carbonyl groups being replaced by sulfonyl groups.

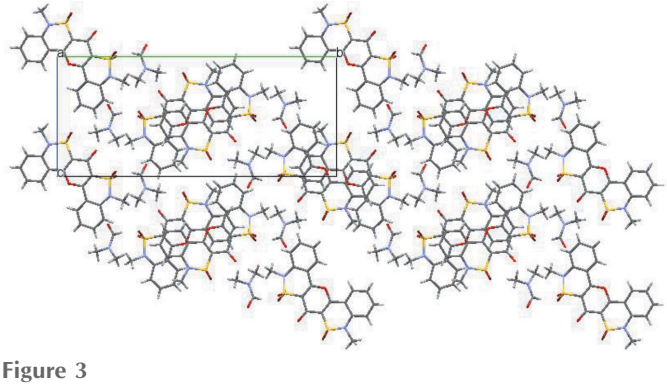


Figure 3
The packing of the molecular entities in the crystal structure of (I) in a view along [100].

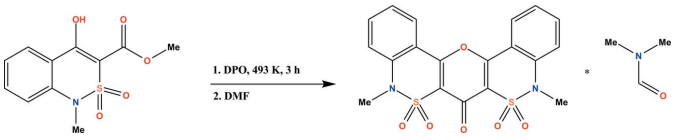


Figure 4
Synthesis scheme for compound (I).

5. Synthesis and crystallization

A mixture of methyl 4-hydroxy-1-methyl-2,2-dioxo-1*H*-2λ^6,1-benzothiazine-3-carboxylate (2.69 g, 0.01 mol) and diphenyl oxide (10 ml) was maintained on a metal bath at 493 K for 3 h, then cooled and diluted with ethanol (Fig. 4). The precipitate was filtered off, washed with ethanol, and recrystallized from DMF. 1.86 g (37% yield) of a colourless substance were obtained, including yellowish crystals of the title solvate; m.p. 640–642 K (decomp.).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms were located from difference-Fourier maps. They were included in calculated positions and treated as riding with C—H = 0.96 Å, U_{iso}(H) = 1.5U_{eq}(C) for methyl groups and with C—H = 0.93 Å, U_{iso}(H) = 1.2U_{eq}(C) for all other hydrogen atoms.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{14}N_2O_6S_2{\cdot}C_3H_7NO$
M_r	503.54
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	7.2678 (2), 26.5667 (7), 11.3590 (3)
β (°)	90.498 (3)
V (Å^3)	2193.13 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.30
Crystal size (mm)	0.20 × 0.20 × 0.18
Data collection	
Diffractometer	Agilent Xcalibur, Sapphire3
Absorption correction	Multi-scan (*CrysAlis RED*; Agilent, 2012)
T_{min}, T_{max}	0.840, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21958, 6370, 5409
R_{int}	0.022
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.703
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.111, 1.06
No. of reflections	6370
No. of parameters	311
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, −0.35

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Agilent, 2012), *SHELXS* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).

Acknowledgements

Any acknowledgements?

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Computing details

Data collection: *CrysAlis CCD* (Agilent, 2012); cell refinement: *CrysAlis RED* (Agilent, 2012); data reduction: *CrysAlis RED* (Agilent, 2012); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

5,9-Dimethyl-5*H*-pyrano[3,2-*c*:5,6-*c*′]bis[2,1-benzothiazin]-7(9*H*)-one 6,6,8,8-tetroxide dimethylformamide monosolvate

Crystal data

$C_{19}H_{14}N_2O_6S_2 \cdot C_3H_7NO$
$M_r = 503.54$
Monoclinic, $P2_1/c$
$a = 7.2678$ (2) Å
$b = 26.5667$ (7) Å
$c = 11.3590$ (3) Å
$\beta = 90.498$ (3)°
$V = 2193.13$ (10) Å^3
$Z = 4$
$F(000) = 1048$
$D_x = 1.525$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8803 reflections
$\theta = 3.3$–$32.1°$
$\mu = 0.30$ mm^{-1}
$T = 293$ K
Block, colourless
0.20 × 0.20 × 0.18 mm

Data collection

Agilent Xcalibur, Sapphire3 diffractometer
Radiation source: Enhance (Mo) X-ray Source
Detector resolution: 16.1827 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis RED*; Agilent, 2012)
$T_{min} = 0.840$, $T_{max} = 1.000$
21958 measured reflections
6370 independent reflections
5409 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 30.0°$, $\theta_{min} = 3.2°$
$h = -9 \rightarrow 10$
$k = -34 \rightarrow 37$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.111$
$S = 1.06$
6370 reflections
311 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.056P)^2 + 0.5564P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.27857 (5)	0.53088 (2)	0.78395 (3)	0.03522 (10)
S2	0.35468 (5)	0.68735 (2)	0.47772 (3)	0.03406 (9)
N1	0.31960 (18)	0.47039 (5)	0.76567 (10)	0.0355 (3)
N2	0.40095 (19)	0.68763 (4)	0.33637 (11)	0.0377 (3)
O1	0.27500 (14)	0.54076 (3)	0.43723 (8)	0.0300 (2)
O2	0.33446 (19)	0.63741 (4)	0.71036 (9)	0.0475 (3)
O3	0.4170 (2)	0.54940 (5)	0.86153 (10)	0.0556 (3)
O4	0.09057 (19)	0.53887 (5)	0.81476 (11)	0.0528 (3)
O5	0.50923 (18)	0.70840 (4)	0.53734 (11)	0.0511 (3)
O6	0.18001 (18)	0.70953 (5)	0.50021 (12)	0.0529 (3)
C1	0.30950 (19)	0.55350 (5)	0.64196 (11)	0.0294 (3)
C2	0.27719 (17)	0.52260 (5)	0.54891 (11)	0.0274 (2)
C3	0.23924 (18)	0.46944 (5)	0.55627 (12)	0.0287 (2)
C4	0.25669 (18)	0.44458 (5)	0.66557 (12)	0.0307 (3)
C5	0.33905 (18)	0.62303 (5)	0.50507 (11)	0.0288 (2)
C6	0.30000 (17)	0.59081 (5)	0.41606 (11)	0.0271 (2)
C7	0.27399 (18)	0.60439 (5)	0.29458 (11)	0.0293 (3)
C8	0.31990 (19)	0.65325 (5)	0.25751 (12)	0.0330 (3)
C9	0.2198 (2)	0.39295 (5)	0.67129 (15)	0.0388 (3)
H9	0.230327	0.375995	0.742662	0.047*
C10	0.1678 (2)	0.36734 (6)	0.57123 (16)	0.0447 (4)
H10	0.144752	0.332967	0.575848	0.054*
C11	0.1491 (2)	0.39142 (6)	0.46392 (16)	0.0445 (4)
H11	0.112482	0.373420	0.397521	0.053*
C12	0.1849 (2)	0.44209 (5)	0.45585 (13)	0.0366 (3)
H12	0.173175	0.458353	0.383672	0.044*
C13	0.2965 (2)	0.66588 (7)	0.13887 (14)	0.0450 (4)
H13	0.327636	0.697916	0.112718	0.054*
C14	0.2274 (2)	0.63092 (8)	0.06068 (14)	0.0489 (4)
H14	0.213819	0.639567	−0.018251	0.059*
C15	0.1778 (2)	0.58326 (7)	0.09716 (13)	0.0443 (4)
H15	0.128749	0.560360	0.043496	0.053*
C16	0.2012 (2)	0.56987 (6)	0.21301 (12)	0.0363 (3)
H16	0.168641	0.537724	0.237646	0.044*
C17	0.3401 (2)	0.44312 (7)	0.87830 (14)	0.0449 (4)
H17C	0.418161	0.414374	0.867349	0.067*
H17B	0.221431	0.432194	0.904561	0.067*
H17A	0.394062	0.465053	0.936211	0.067*
C18	0.4721 (3)	0.73589 (7)	0.29163 (18)	0.0593 (5)

H18C	0.371718	0.755881	0.262233	0.089*
H18B	0.557380	0.729589	0.229276	0.089*
H18A	0.533497	0.753615	0.354267	0.089*
C19	0.3323 (2)	0.60783 (5)	0.62857 (11)	0.0317 (3)
N1A	0.8356 (2)	0.81500 (6)	0.40202 (13)	0.0473 (3)
O1A	0.7557 (2)	0.81809 (6)	0.59460 (13)	0.0654 (4)
C1A	0.8365 (3)	0.79886 (7)	0.51263 (17)	0.0503 (4)
H1A	0.905307	0.770158	0.529054	0.060*
C2A	0.9428 (3)	0.79092 (10)	0.3113 (2)	0.0696 (6)
H2AC	1.005000	0.762143	0.343706	0.104*
H2AB	1.031860	0.814287	0.281574	0.104*
H2AA	0.862751	0.780360	0.248316	0.104*
C3A	0.7312 (4)	0.85925 (9)	0.3696 (2)	0.0769 (7)
H3AC	0.669591	0.853504	0.295690	0.115*
H3AB	0.812776	0.887473	0.362385	0.115*
H3AA	0.641725	0.866160	0.429150	0.115*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0477 (2)	0.03408 (17)	0.02385 (16)	−0.00072 (14)	−0.00252 (13)	−0.00174 (12)
S2	0.04352 (19)	0.02353 (15)	0.03518 (18)	0.00017 (12)	0.00303 (14)	−0.00355 (12)
N1	0.0438 (7)	0.0324 (6)	0.0301 (6)	0.0006 (5)	−0.0039 (5)	0.0038 (5)
N2	0.0502 (7)	0.0283 (6)	0.0346 (6)	−0.0031 (5)	0.0049 (5)	0.0021 (5)
O1	0.0424 (5)	0.0251 (4)	0.0226 (4)	−0.0028 (4)	0.0001 (4)	−0.0031 (3)
O2	0.0785 (9)	0.0336 (5)	0.0304 (5)	0.0003 (5)	−0.0047 (5)	−0.0108 (4)
O3	0.0812 (9)	0.0509 (7)	0.0343 (6)	−0.0151 (6)	−0.0219 (6)	0.0006 (5)
O4	0.0595 (8)	0.0560 (7)	0.0431 (6)	0.0114 (6)	0.0164 (5)	0.0001 (5)
O5	0.0641 (8)	0.0393 (6)	0.0499 (7)	−0.0184 (5)	−0.0046 (6)	−0.0075 (5)
O6	0.0597 (8)	0.0381 (6)	0.0612 (8)	0.0165 (5)	0.0154 (6)	−0.0003 (5)
C1	0.0363 (6)	0.0282 (6)	0.0237 (6)	0.0000 (5)	−0.0018 (5)	−0.0020 (5)
C2	0.0298 (6)	0.0271 (6)	0.0252 (6)	0.0003 (5)	0.0001 (4)	−0.0020 (4)
C3	0.0291 (6)	0.0258 (6)	0.0313 (6)	0.0002 (4)	0.0005 (5)	−0.0028 (5)
C4	0.0280 (6)	0.0288 (6)	0.0352 (7)	0.0016 (5)	0.0024 (5)	−0.0003 (5)
C5	0.0336 (6)	0.0251 (5)	0.0276 (6)	0.0004 (5)	0.0001 (5)	−0.0025 (5)
C6	0.0296 (6)	0.0257 (6)	0.0261 (6)	−0.0006 (4)	0.0012 (4)	−0.0018 (4)
C7	0.0304 (6)	0.0332 (6)	0.0244 (6)	0.0023 (5)	0.0008 (5)	−0.0015 (5)
C8	0.0354 (7)	0.0326 (6)	0.0311 (6)	0.0048 (5)	0.0017 (5)	0.0021 (5)
C9	0.0379 (7)	0.0301 (7)	0.0483 (8)	0.0004 (5)	0.0049 (6)	0.0069 (6)
C10	0.0441 (8)	0.0268 (6)	0.0634 (10)	−0.0044 (6)	0.0050 (7)	−0.0016 (7)
C11	0.0494 (9)	0.0331 (7)	0.0508 (9)	−0.0058 (6)	−0.0023 (7)	−0.0128 (7)
C12	0.0425 (8)	0.0310 (7)	0.0363 (7)	−0.0025 (6)	−0.0033 (6)	−0.0065 (5)
C13	0.0552 (9)	0.0445 (8)	0.0352 (8)	0.0084 (7)	0.0007 (7)	0.0103 (6)
C14	0.0537 (10)	0.0648 (11)	0.0281 (7)	0.0108 (8)	−0.0033 (6)	0.0066 (7)
C15	0.0423 (8)	0.0628 (10)	0.0278 (7)	0.0007 (7)	−0.0038 (6)	−0.0071 (7)
C16	0.0382 (7)	0.0431 (8)	0.0277 (6)	−0.0032 (6)	0.0003 (5)	−0.0058 (6)
C17	0.0520 (9)	0.0474 (9)	0.0352 (8)	0.0035 (7)	−0.0022 (7)	0.0127 (7)
C18	0.0867 (14)	0.0381 (9)	0.0533 (11)	−0.0154 (9)	0.0146 (10)	0.0071 (8)

C19	0.0398 (7)	0.0281 (6)	0.0273 (6)	0.0003 (5)	−0.0030 (5)	−0.0042 (5)
N1A	0.0451 (7)	0.0465 (8)	0.0501 (8)	0.0034 (6)	−0.0014 (6)	0.0010 (6)
O1A	0.0776 (10)	0.0597 (8)	0.0593 (8)	−0.0037 (7)	0.0145 (7)	−0.0117 (7)
C1A	0.0513 (10)	0.0458 (9)	0.0539 (10)	0.0012 (7)	0.0039 (8)	0.0010 (8)
C2A	0.0693 (13)	0.0796 (15)	0.0602 (12)	0.0119 (11)	0.0173 (10)	0.0069 (11)
C3A	0.0933 (18)	0.0628 (13)	0.0744 (15)	0.0251 (12)	−0.0108 (13)	0.0045 (11)

Geometric parameters (Å, º)

S1—O3	1.4197 (12)	C10—C11	1.382 (2)
S1—O4	1.4292 (14)	C10—H10	0.9300
S1—N1	1.6479 (13)	C11—C12	1.374 (2)
S1—C1	1.7375 (13)	C11—H11	0.9300
S2—O5	1.4212 (12)	C12—H12	0.9300
S2—O6	1.4247 (12)	C13—C14	1.377 (3)
S2—N2	1.6433 (13)	C13—H13	0.9300
S2—C5	1.7405 (13)	C14—C15	1.381 (3)
N1—C4	1.4012 (18)	C14—H14	0.9300
N1—C17	1.4767 (18)	C15—C16	1.372 (2)
N2—C8	1.4052 (18)	C15—H15	0.9300
N2—C18	1.474 (2)	C16—H16	0.9300
O1—C2	1.3571 (15)	C17—H17C	0.9600
O1—C6	1.3638 (15)	C17—H17B	0.9600
O2—C19	1.2168 (16)	C17—H17A	0.9600
C1—C2	1.3571 (17)	C18—H18C	0.9600
C1—C19	1.4610 (18)	C18—H18B	0.9600
C2—C3	1.4415 (17)	C18—H18A	0.9600
C3—C12	1.4062 (18)	N1A—C1A	1.328 (2)
C3—C4	1.4110 (19)	N1A—C3A	1.445 (3)
C4—C9	1.3992 (19)	N1A—C2A	1.446 (3)
C5—C6	1.3529 (17)	O1A—C1A	1.217 (2)
C5—C19	1.4611 (18)	C1A—H1A	0.9300
C6—C7	1.4371 (17)	C2A—H2AC	0.9600
C7—C16	1.4039 (19)	C2A—H2AB	0.9600
C7—C8	1.4055 (19)	C2A—H2AA	0.9600
C8—C13	1.398 (2)	C3A—H3AC	0.9600
C9—C10	1.375 (2)	C3A—H3AB	0.9600
C9—H9	0.9300	C3A—H3AA	0.9600
O3—S1—O4	118.06 (9)	C12—C11—H11	120.2
O3—S1—N1	106.74 (7)	C10—C11—H11	120.2
O4—S1—N1	110.49 (7)	C11—C12—C3	120.27 (14)
O3—S1—C1	111.08 (7)	C11—C12—H12	119.9
O4—S1—C1	107.92 (7)	C3—C12—H12	119.9
N1—S1—C1	101.26 (6)	C14—C13—C8	120.03 (16)
O5—S2—O6	116.97 (8)	C14—C13—H13	120.0
O5—S2—N2	107.23 (7)	C8—C13—H13	120.0
O6—S2—N2	111.32 (8)	C13—C14—C15	121.31 (14)

O5—S2—C5	110.72 (7)	C13—C14—H14	119.3
O6—S2—C5	108.33 (7)	C15—C14—H14	119.3
N2—S2—C5	101.13 (6)	C16—C15—C14	119.65 (15)
C4—N1—C17	119.52 (12)	C16—C15—H15	120.2
C4—N1—S1	121.43 (9)	C14—C15—H15	120.2
C17—N1—S1	112.73 (10)	C15—C16—C7	120.43 (15)
C8—N2—C18	119.46 (13)	C15—C16—H16	119.8
C8—N2—S2	122.12 (10)	C7—C16—H16	119.8
C18—N2—S2	114.59 (11)	N1—C17—H17C	109.5
C2—O1—C6	120.73 (10)	N1—C17—H17B	109.5
C2—C1—C19	122.37 (12)	H17C—C17—H17B	109.5
C2—C1—S1	119.40 (10)	N1—C17—H17A	109.5
C19—C1—S1	117.00 (9)	H17C—C17—H17A	109.5
C1—C2—O1	120.90 (12)	H17B—C17—H17A	109.5
C1—C2—C3	125.40 (12)	N2—C18—H18C	109.5
O1—C2—C3	113.69 (11)	N2—C18—H18B	109.5
C12—C3—C4	119.62 (12)	H18C—C18—H18B	109.5
C12—C3—C2	120.78 (12)	N2—C18—H18A	109.5
C4—C3—C2	119.60 (12)	H18C—C18—H18A	109.5
C9—C4—N1	120.23 (13)	H18B—C18—H18A	109.5
C9—C4—C3	118.95 (13)	O2—C19—C1	124.01 (13)
N1—C4—C3	120.73 (12)	O2—C19—C5	123.66 (13)
C6—C5—C19	122.28 (12)	C1—C19—C5	112.20 (11)
C6—C5—S2	120.08 (10)	C1A—N1A—C3A	120.13 (17)
C19—C5—S2	116.45 (9)	C1A—N1A—C2A	122.24 (17)
C5—C6—O1	120.83 (11)	C3A—N1A—C2A	117.58 (18)
C5—C6—C7	125.71 (12)	O1A—C1A—N1A	126.16 (19)
O1—C6—C7	113.42 (11)	O1A—C1A—H1A	116.9
C16—C7—C8	119.64 (12)	N1A—C1A—H1A	116.9
C16—C7—C6	121.02 (12)	N1A—C2A—H2AC	109.5
C8—C7—C6	119.33 (12)	N1A—C2A—H2AB	109.5
C13—C8—N2	120.35 (14)	H2AC—C2A—H2AB	109.5
C13—C8—C7	118.91 (13)	N1A—C2A—H2AA	109.5
N2—C8—C7	120.57 (12)	H2AC—C2A—H2AA	109.5
C10—C9—C4	119.88 (15)	H2AB—C2A—H2AA	109.5
C10—C9—H9	120.1	N1A—C3A—H3AC	109.5
C4—C9—H9	120.1	N1A—C3A—H3AB	109.5
C9—C10—C11	121.62 (14)	H3AC—C3A—H3AB	109.5
C9—C10—H10	119.2	N1A—C3A—H3AA	109.5
C11—C10—H10	119.2	H3AC—C3A—H3AA	109.5
C12—C11—C10	119.67 (14)	H3AB—C3A—H3AA	109.5

O3—S1—N1—C4	−156.20 (12)	C19—C5—C6—O1	−8.4 (2)
O4—S1—N1—C4	74.25 (13)	S2—C5—C6—O1	−175.54 (9)
C1—S1—N1—C4	−39.91 (13)	C19—C5—C6—C7	169.19 (13)
O3—S1—N1—C17	51.92 (13)	S2—C5—C6—C7	2.0 (2)
O4—S1—N1—C17	−77.63 (12)	C2—O1—C6—C5	4.20 (19)
C1—S1—N1—C17	168.21 (11)	C2—O1—C6—C7	−173.67 (11)

O5—S2—N2—C8	154.03 (12)	C5—C6—C7—C16	−168.18 (14)
O6—S2—N2—C8	−76.87 (13)	O1—C6—C7—C16	9.57 (18)
C5—S2—N2—C8	38.02 (13)	C5—C6—C7—C8	10.9 (2)
O5—S2—N2—C18	−48.17 (15)	O1—C6—C7—C8	−171.32 (12)
O6—S2—N2—C18	80.93 (15)	C18—N2—C8—C13	−3.9 (2)
C5—S2—N2—C18	−164.18 (13)	S2—N2—C8—C13	152.83 (12)
O3—S1—C1—C2	141.18 (12)	C18—N2—C8—C7	171.24 (15)
O4—S1—C1—C2	−87.94 (13)	S2—N2—C8—C7	−32.00 (19)
N1—S1—C1—C2	28.13 (13)	C16—C7—C8—C13	−1.8 (2)
O3—S1—C1—C19	−51.17 (13)	C6—C7—C8—C13	179.13 (13)
O4—S1—C1—C19	79.71 (12)	C16—C7—C8—N2	−176.99 (13)
N1—S1—C1—C19	−164.22 (11)	C6—C7—C8—N2	3.9 (2)
C19—C1—C2—O1	3.8 (2)	N1—C4—C9—C10	−176.42 (14)
S1—C1—C2—O1	170.77 (10)	C3—C4—C9—C10	0.1 (2)
C19—C1—C2—C3	−174.90 (13)	C4—C9—C10—C11	−0.6 (2)
S1—C1—C2—C3	−7.95 (19)	C9—C10—C11—C12	0.7 (3)
C6—O1—C2—C1	−1.91 (19)	C10—C11—C12—C3	−0.4 (2)
C6—O1—C2—C3	176.96 (11)	C4—C3—C12—C11	−0.1 (2)
C1—C2—C3—C12	171.94 (13)	C2—C3—C12—C11	179.99 (14)
O1—C2—C3—C12	−6.86 (18)	N2—C8—C13—C14	176.03 (15)
C1—C2—C3—C4	−8.0 (2)	C7—C8—C13—C14	0.8 (2)
O1—C2—C3—C4	173.18 (11)	C8—C13—C14—C15	0.8 (3)
C17—N1—C4—C9	−2.2 (2)	C13—C14—C15—C16	−1.4 (3)
S1—N1—C4—C9	−152.27 (12)	C14—C15—C16—C7	0.4 (2)
C17—N1—C4—C3	−178.74 (13)	C8—C7—C16—C15	1.2 (2)
S1—N1—C4—C3	31.23 (18)	C6—C7—C16—C15	−179.73 (14)
C12—C3—C4—C9	0.2 (2)	C2—C1—C19—O2	168.80 (15)
C2—C3—C4—C9	−179.87 (13)	S1—C1—C19—O2	1.6 (2)
C12—C3—C4—N1	176.72 (13)	C2—C1—C19—C5	−7.13 (19)
C2—C3—C4—N1	−3.32 (19)	S1—C1—C19—C5	−174.38 (10)
O5—S2—C5—C6	−136.55 (12)	C6—C5—C19—O2	−166.55 (15)
O6—S2—C5—C6	93.95 (13)	S2—C5—C19—O2	1.0 (2)
N2—S2—C5—C6	−23.15 (13)	C6—C5—C19—C1	9.40 (19)
O5—S2—C5—C19	55.58 (13)	S2—C5—C19—C1	176.98 (10)
O6—S2—C5—C19	−73.91 (12)	C3A—N1A—C1A—O1A	−0.3 (3)
N2—S2—C5—C19	168.99 (11)	C2A—N1A—C1A—O1A	177.1 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C17—H17*A*···O3	0.96	2.40	2.885 (2)	111
C18—H18*A*···O5	0.96	2.41	2.895 (2)	111
C3*A*—H3*AA*···O1*A*	0.96	2.41	2.784 (3)	103
C12—H12···O1	0.93	2.39	2.7106 (17)	100
C16—H16···O1	0.93	2.39	2.7109 (17)	100

C9—H9···O1*A*^{i}	0.93	2.41	3.324 (2)	169
C18—H18*B*···O1*A*^{ii}	0.96	2.46	3.376 (3)	159

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