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Crystal structure and Hirshfeld surface analysis of 10-hydroxy-2-(4-methoxyphenyl)-3-oxo-2,3,3a,4,10,10a-hexahydro-1*H*-9-thia-2-azacyclopenta[*b*]fluorene-4-carboxylic acid dimethyl sulfoxide-d_6 monosolvate

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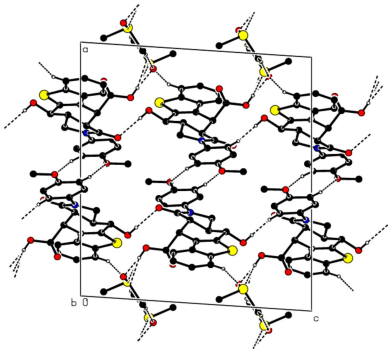
In the title compound, $C_{22}H_{19}NO_5S\cdot C_2D_6OS$, the central six-membered ring has a slightly distorted boat conformation, while the fused pyrrolidine ring adopts an envelope conformation. These conformations are stabilized by O—H···O hydrogen bonds between the main compound and solvent molecules. In addition, intramolecular C—H···O hydrogen bonds in the main molecule form two $S(6)$ rings. Molecules are connected by pairs of intermolecular C—H···O hydrogen bonds, forming dimers with a $R_2^2(8)$ motif. These dimers form a three-dimensional network through O—H···O, O—H···S and C—H···O hydrogen bonds with each other directly and through solvent molecules. In addition, weak π–π stacking interactions [centroid-to-centroid distances = 3.9937 (10) and 3.9936 (10) Å, slippages of 2.034 and 1.681 Å] are observed. The intermolecular contacts were quantified using Hirshfeld surface analysis and two-dimensional fingerprint plots, revealing the relative contributions of the contacts to the crystal packing to be H···H 41.7%, O···H/H···O 27.7%, C···H/H···C 17.0%, and S···H/H···S 7.5%.

1. Chemical context

Intermolecular non-covalent interactions play a critical role in determining the crystal packing and orientation of organic and coordination compounds, leading to significant changes in their properties and actions (Gurbanov *et al.*, 2018, 2020; Kopylovich *et al.*, 2011*a*,*b*,*c*; Mahmoudi *et al.*, 2019, 2021; Mahmudov *et al.*, 2013). In fact, various types of non-covalent bond donors and acceptors determine the supramolecular packing of heterocyclic and coordination compounds, which is a fundamental molecular descriptor for predicting the oral bioavailability as well as biocatalytic activity of small drug candidates (Abdelhamid *et al.*, 2011; Akbari Afkhami *et al.*, 2017; Khalilov *et al.*, 2021; Safavora *et al.*, 2019). This work is a continuation of studies of properties of vinylarene systems, previously obtained by the tandem acylation/[4 + 2]-cyclo-addition between 3-(aryl)allylamines and maleic anhydrides as an example of an IMDAV (Intra Molecular Diels–Alder



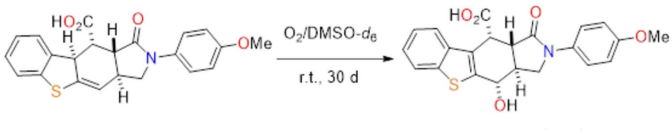
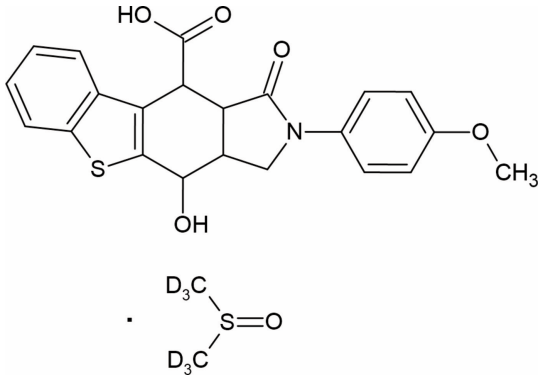


Figure 1
Synthesis of 10-hydroxy-2-(4-methoxy-phenyl)-3-oxo-2,3,3a,4,10,10*a*-hexahydro-1*H*-9-thia-2-aza-cyclopenta[*b*]fluorene-4-carboxylic acid.

Vinylarene) reaction. The IMDAV reaction is a useful tool for the one-step synthesis of benzofurans, indoles and benzothiophenes annalated with other carbo- or heterocycles (Horak *et al.*, 2015, 2017; Krishna *et al.*, 2022; Nadirova *et al.*, 2020; Zubkov *et al.*, 2016).

We report here the first case of a spontaneous oxidation reaction of an IMDAV adduct (Fig. 1) in air in DMSO at room temperature. Presumably, the DMSO acts as a mild oxidant, as it is observed in a number of other oxidation reactions – Pfitzner-Moffatt, Corey–Kim, Swern, and Kornblum oxidation (Epstein *et al.*, 1967). The slow oxidation of (3a*RS*,9b*RS*,10*RS*,10a*RS*)-2-(4-methoxyphenyl)-1-oxo-2,3,3a,4,10,10a-hexahydro-1*H*-benzo[4,5]thieno[2,3-*f*]isoindole-10-carboxylic acid occurs under stirring of the solution in DMSO-d_6 for a month. The title compound was isolated in 67% yield after a standard treatment of the reaction mixture. It should be noted that in this case, the reaction does not stop at the formation of an alcohol, but leads to the formation of an aromatic product as a result of proton migration.



2. Structural commentary

In the title compound (Fig. 2), the central six-membered ring (C3*A*/C4*B*/C4*A*/C9*B*/C10/C10*A*) has a slightly distorted boat conformation, with puckering parameters (Cremer & Pople, 1975) of Q_T = 0.5290 (17) Å, θ = 129.87 (18)° and φ = 156.7 (2)°. The fused pyrrolidine ring (N2/C1/C10*A*/C3*A*/C3) adopts an envelope conformation with the C3*A* atom as the flap [the puckering parameters are $Q(2)$ = 0.3523 (17) Å and $\varphi(2)$ = 290.0 (3)°], while the fused thiophene ring (S5/C4*A*/C9*B*/C9*A*/C5*A*) is essentially planar (r.m.s. deviation = 0.002 Å). The molecular conformation is stabilized by an O—H···O hydrogen bond (O3—H3···O6*A*) between the main compound and solvent molecules, as well as two intramolecular C—H···O hydrogen bonds (C17—H17*A*···O1 and C3*A*—H3*AA*···O2) in the main molecule, which form *S*(6) rings (O1/C1/N2/C12/C17/H17*A* and O2/C11/C10/C10*A*/C3*A*/H3*AA*; Table 1; Fig. 2; Bernstein *et al.*, 1995). All bond lengths and angles in the main compound are comparable to those of the analogous compound ethyl 2-methyl-5,8-dioxo-6-phenyl-4a,5,6,7,7a,8-hexahydro-4*H*-furo[2,3-*f*]isoindole-4-carboxylate (CSD refcode OJIPUV; Zaytsev *et al.*, 2021).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···S1*A*	0.84	2.72	3.4846 (15)	152
O3—H3···O6*A*	0.84	1.72	2.563 (2)	176
O3—H3···O6*B*	0.84	2.06	2.852 (16)	158
O5*A*—H5*A*···O1^{i}	0.84	1.96	2.763 (2)	160
C3*A*—H3*AA*···O2	1.00	2.49	3.202 (2)	127
C3—H3*A*···O5*B*	0.99	2.54	2.887 (4)	100
C6—H6*A*···O6*A*^{ii}	0.95	2.48	3.307 (3)	145
C14—H14*A*···O4^{iii}	0.95	2.54	3.445 (2)	159
C17—H17*A*···O1	0.95	2.33	2.868 (2)	116
C17—H17*A*···O5*B*^{iv}	0.95	2.46	3.289 (4)	146
C18—H18*C*···O5*B*^{v}	0.98	2.43	2.922 (4)	110
C20*A*—D20*A*···O6*A*^{vi}	0.98	2.46	3.434 (3)	173
C20*A*—D20*A*···O6*B*^{vi}	0.98	1.87	2.839 (13)	168

Symmetry codes: (i) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (ii) $x, -y+\frac{5}{2}, z+\frac{1}{2}$; (iii) $-x+1, -y, -z+1$; (iv) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (v) $-x+1, -y+1, -z+1$; (vi) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$.

3. Supramolecular features and Hirshfeld surface analysis

In the crystal structure of the title compound, molecules are connected by pairs of intermolecular C—H···O hydrogen bonds, forming dimers with an $R_2^2(8)$ motif (Table 1, Fig. 3). These dimers form a three-dimensional network through O—H···O, O—H···S and C—H···O hydrogen bonds, directly with each other and through solvent molecules (Table 1). In addition, weak π–π stacking interactions are observed [*Cg*5···*Cg*6(x, 1 + y, z) = 3.9937 (10) Å with slippage of 2.034 Å and *Cg*6···*Cg*5(x, −1 + y, z) = 3.9936 (10) Å with slippage of 1.681 Å; *Cg*5 and *Cg*6 are the centroids of the C5*A*/C6/C7/C8/C9/C9*A* and C12–C17 benzene rings, respectively].

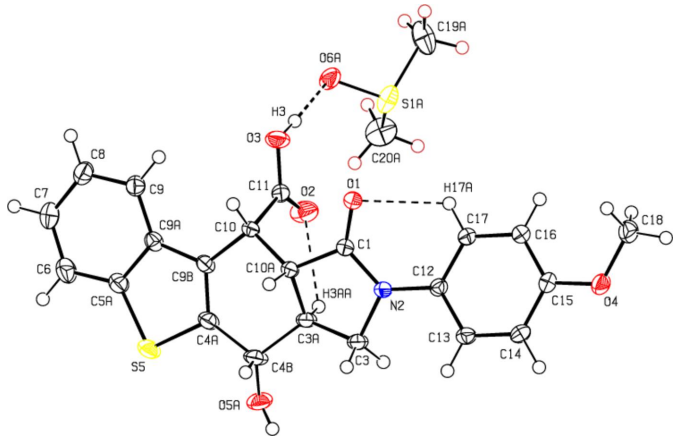


Figure 2
The molecular structure of the title compound, with atom labeling. Displacement ellipsoids are drawn at the 50% probability level. Only the major component of the disordered DMSO molecule is shown.

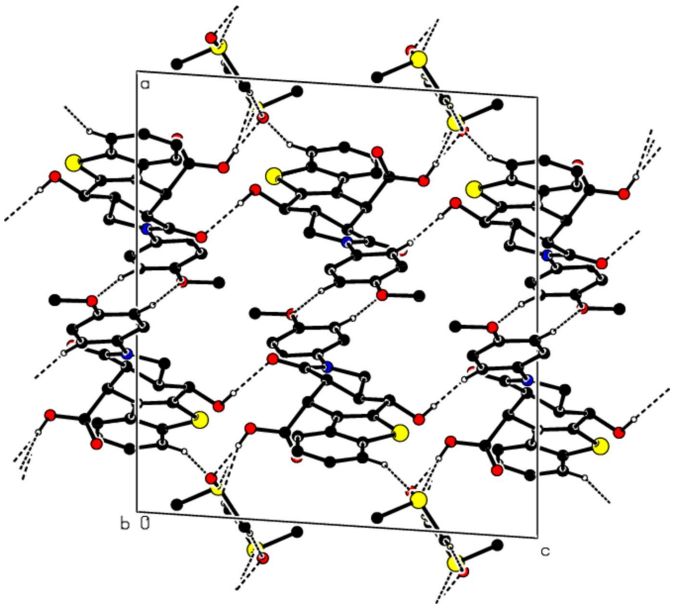


Figure 3
A view along the *b*-axis of the crystal packing of the title compound. The O—H···O, O—H···S and C—H···O hydrogen bonds are shown as dashed lines. Only the major component of the disordered DMSO molecule is shown.

Hirshfeld surfaces and their associated two-dimensional fingerprint plots were used to quantify the various intermolecular interactions, and were generated using *Crystal Explorer* 17.5 (Spackman *et al.*, 2021). The 3D d_{norm} surfaces are plotted over a fixed color scale of −0.7960 (red) and 1.2965 (blue) a.u.

Two-dimensional fingerprint plots together with their percentage contributions are shown in Fig. 4. The crystal packing is dominated by H···H contacts, representing van der Waals interactions (41.7% contribution to the overall surface), followed by O···H/H···O, C···H/H···C and S···H/H···S interactions, which contribute to 27.7%, 17.0% and 7.5%, respectively. The other contacts (C···C 4.2%, N···C/C···N 1.3%, O···O 0.7%, N···H/H···N 0.1% and S···C/C···S 0.1%) only make a minor contribution to the crystal packing.

4. Database survey

A search of the Cambridge Crystallographic Database (CSD version 5.40, update of September 2019; Groom *et al.*, 2016) yielded six entries closely related to the title compound, *viz*. OJIPUV (Zaytsev *et al.*, 2021), JOGYIP (Zhou *et al.*, 2014), LESXIS (Horak *et al.*, 2013), QAFSUO (Zubkov *et al.*, 2016), QAFTAV (Zubkov *et al.*, 2016) and QUKPAP (Horak *et al.*, 2015).

In OJIPUV and JOGYIP, space group $P\overline{1}$, molecules are bonded by intermolecular C—H···O hydrogen bonds, C—H···π interactions, and π–π stacking interactions, forming three-dimensional networks. In the crystal of LESXIS (*Pbca*), which contains two similar molecules per asymmetric unit, O—H···O hydrogen bonds connect the molecules into chains parallel to the *b*-axis. There are also weak C—H···π interactions in the crystal. In the crystal structures of QAFSUO ($P2_1/c$) and QAFTAV ($P2_1/n$), the three-dimensional packings are stabilized by O—H···O hydrogen bonds, C—H···O contacts and C—H···π interactions. The asymmetric unit of QUKPAP ($P2_1/c$) comprises two similar molecules, *A* and *B*, of the same chirality. The only considerable difference concerns the conformation of the allyl group. The carboxyl hydrogen atoms are involved in strong hydrogen bonds with the carbonyl atoms of neighboring molecules, giving rise to $(A\cdots B\cdots)_n$ chains.

In the six structures, the different groups bonded to the central twelve-membered ring systems account for the distinct intermolecular interactions in the crystals.

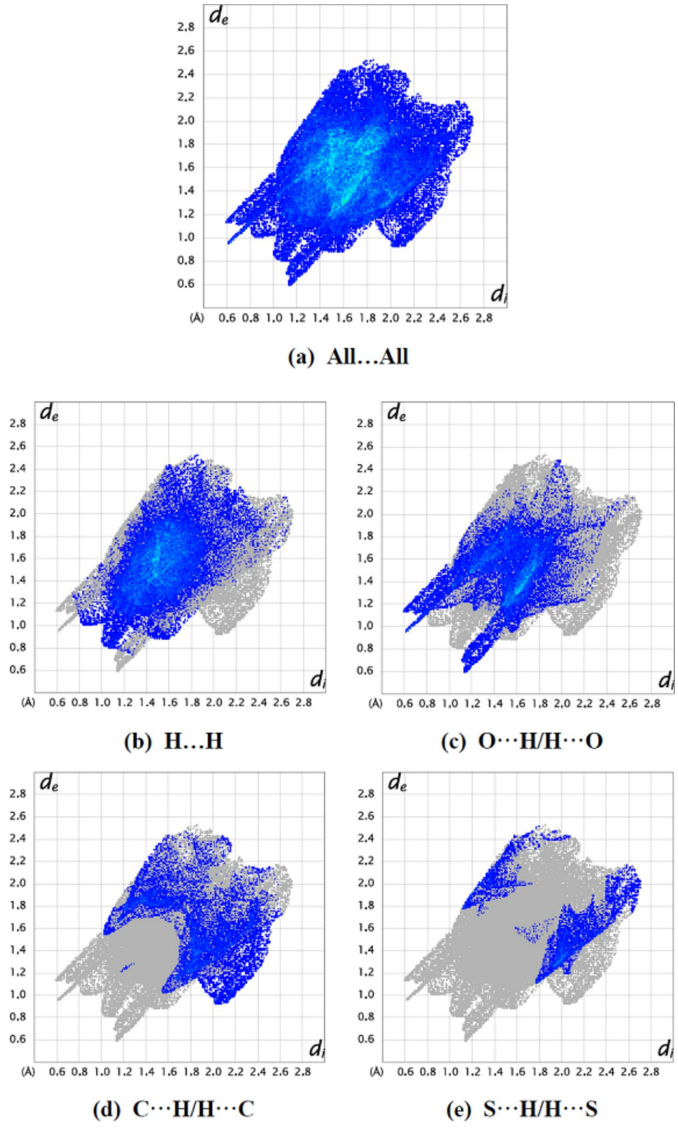


Figure 4
The two-dimensional fingerprint plots of the title compound, showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) O···H/H···O, (*d*) C···H/H···C and (*e*) S···H/H···S interactions. [d_e and d_i represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

5. Synthesis and crystallization

A solution of (3a*RS*,9b*RS*,10*RS*,10a*RS*)-2-(4-methoxyphenyl)-1-oxo-2,3,3a,4,10,10a-hexahydro-1*H*-benzo[4,5]thieno[2,3-*f*]-isoindole-10-carboxylic acid (30.0 mg, 0.08 mmol) in 0.5 ml of DMSO-d_6 was stirred for 30 days in an open flask. The reaction mixture was concentrated, diluted with EtOH (0.5 mL), and the solid was filtered, washed with Et_2O (3 × 1 mL), and air dried. The title compound was obtained as a colorless powder, yield 67%, 25.2 mg; m.p. > 523 K (with decomp.). IR (KBr), ν (cm^{-1}): 1722 (CO_2), 1644 (N—C═O), 1514. ^{1}H NMR (700.2 MHz, DMSO-d_6): δ (*J*, Hz) *there are no OH peaks* 12.78 (*s*, 1H, CO_2H), 8.04 (*d*, *J* = 7.6, 1H, H Ar), 7.92 (*d*, *J* = 7.6, 1H, H Ar), 7.59 (*d*, *J* = 9.1, 2H, H Ar), 7.42 (*t*, *J* = 7.6, 1H, H Ar), 7.34 (*t*, *J* = 7.6, 1H, H Ar), 6.97 (*d*, *J* = 9.1, 2H, H Ar), 2.47–2.44 (*m*, 1H, H-4) 4.28 (*d*, *J* = 4.8, 1H, H-10), 4.00 (*t*, *J* = 8.7, 1H, H-3A), 3.75 (*s*, 3H, CH_3), 3.73 (*t*, *J* = 8.7, 1H, H-3B), 3.40–3.37 (*m*, 1H, H-3a), 3.21 (*dd*, *J* = 16.0, 4.8, 1H, H-10a). ^{13}C {^{1}H} NMR (176.1 MHz, DMSO-d_6): δ 172.7, 172.2, 156.1, 139.6, 138.8, 138.4, 133.5, 126.7, 124.7, 124.6, 122.9, 122.7, 121.1 (2C), 114.3 (2C), 68.2, 55.7, 52.2, 47.8, 40.5, 32.7. MS (ESI) *m/z*: $[M + H]^+$ 494. Elemental analysis calculated (%) for $C_{22}H_{19}NO_5S{\cdot}C_2D_6OS$: C 58.40, H 6.33, N 2.84, S 12.99; found: C 58.13, H 6.47, N 3.07, S 13.20.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms of the OH groups were placed in geometrically idealized positions and constrained to ride on their parent atoms, with O—H = 0.84 Å and U_{iso}(H) = 1.5U_{eq}(O). H atoms bound to C atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.95–1.00 Å and U_{iso}(H) = 1.2 or 1.5U_{eq}(C). The dimethyl sulfoxide solvent molecule exhibits disorder at two positions in the ratio 0.8903 (18):0.1097 (18). All the methyl hydrogen atoms of the solvent molecule were assigned as deuterium and refined. The C4*B* and C4*C* atoms of the two parts of the disordered solvent molecule were refined using EADP and EXYZ commands, and other similar bond lengths of the disordered solvent molecule were refined using SADI.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{22}H_{19}NO_5S{\cdot}C_2D_6OS$
M_r	493.61
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, *b*, *c* (Å)	16.3178 (4), 9.2747 (2), 14.8720 (4)
β (°)	93.771 (1)
V (Å^3)	2245.89 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.28
Crystal size (mm)	0.40 × 0.28 × 0.22
Data collection	
Diffractometer	Bruker Kappa APEXII area-detector diffractometer
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.847, 0.941
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	69078, 6531, 5693
R_{int}	0.032
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.703
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.049, 0.129, 1.12
No. of reflections	6531
No. of parameters	324
No. of restraints	15
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.54, −0.47

Computer programs: *APEX4* and *SAINT* (Bruker, 2008), *SHELXT2016/6* (Sheldrick, 2015*a*), *SHELXL2016/6* (Sheldrick, 2015*b*, *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

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Crystal structure and Hirshfeld surface analysis of 10-hydroxy-2-(4-methoxyphenyl)-3-oxo-2,3,3a,4,10,10a-hexahydro-1*H*-9-thia-2-azacyclopenta[*b*]fluorene-4-carboxylic acid dimethyl sulfoxide-d_6 monosolvate

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Computing details

10-Hydroxy-2-(4-methoxyphenyl)-3-oxo-2,3,3a,4,10,10a-hexahydro-1*H*-9-thia-2-azacyclopenta[*b*]fluorene-4-carboxylic acid dimethyl sulfoxide-d_6 monosolvate

Crystal data

$C_{22}H_{19}NO_5S·C_2D_6OS$
$M_r = 493.61$
Monoclinic, $P2_1/c$
$a = 16.3178$ (4) Å
$b = 9.2747$ (2) Å
$c = 14.8720$ (4) Å
$\beta = 93.771$ (1)°
$V = 2245.89$ (10) Å^3
$Z = 4$
$F(000) = 1024$
$D_x = 1.460$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9765 reflections
$\theta = 2.6$–30.1°
$\mu = 0.28$ mm^{-1}
$T = 100$ K
Fragment, colourless
0.40 × 0.28 × 0.22 mm

Data collection

Bruker Kappa APEXII area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
$T_{min} = 0.847$, $T_{max} = 0.941$
69078 measured reflections
6531 independent reflections
5693 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 30.0°$, $\theta_{min} = 4.2°$
$h = -22\rightarrow22$
$k = -13\rightarrow13$
$l = -20\rightarrow20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.129$
$S = 1.12$
6531 reflections
324 parameters
15 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 1.8241P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ 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}	Occ. (<1)
S1A	0.06873 (3)	0.67027 (5)	0.20351 (4)	0.03201 (16)	0.8903 (18)
S1B	−0.0094 (3)	0.7350 (5)	0.2022 (3)	0.0386 (13)*	0.1097 (18)
S5	0.21789 (3)	1.16195 (5)	0.65744 (3)	0.03355 (13)	
O1	0.36715 (8)	0.72156 (13)	0.33936 (8)	0.0253 (3)	
O2	0.14801 (9)	0.83115 (17)	0.39946 (10)	0.0367 (3)	
O3	0.20598 (9)	0.93552 (15)	0.28380 (8)	0.0338 (3)	
H3	0.165707	0.899140	0.253855	0.041*	
O4	0.47133 (8)	0.05607 (13)	0.38739 (8)	0.0275 (3)	
O5A	0.25163 (15)	0.8579 (2)	0.70428 (13)	0.0338 (6)	0.637 (4)
H5A	0.283755	0.813423	0.741012	0.041*	0.637 (4)
O5B	0.3604 (2)	0.9025 (4)	0.6728 (2)	0.0282 (9)	0.363 (4)
H5B	0.358402	0.867406	0.724666	0.034*	0.363 (4)
O6A	0.08659 (10)	0.82728 (16)	0.18542 (11)	0.0337 (4)	0.8903 (18)
O6B	0.0447 (10)	0.8676 (13)	0.2106 (10)	0.044 (3)*	0.1097 (18)
N2	0.35684 (8)	0.60178 (14)	0.47516 (9)	0.0193 (3)	
C1	0.35193 (10)	0.71814 (17)	0.41916 (10)	0.0193 (3)	
C3A	0.29022 (10)	0.77925 (18)	0.55483 (10)	0.0218 (3)	
H3AA	0.232017	0.752657	0.536985	0.026*	
C3	0.34047 (11)	0.64061 (18)	0.56878 (10)	0.0231 (3)	
H3A	0.392113	0.658285	0.605867	0.028*	
H3B	0.308591	0.564525	0.597492	0.028*	
C4B	0.29054 (12)	0.8898 (2)	0.63036 (11)	0.0302 (4)	0.637 (4)
H4A	0.349158	0.910797	0.649808	0.036*	0.637 (4)
C4C	0.29054 (12)	0.8898 (2)	0.63036 (11)	0.0302 (4)	0.363 (4)
H4B	0.251734	0.853878	0.674610	0.036*	0.363 (4)
C4A	0.25370 (11)	1.02578 (19)	0.58966 (11)	0.0258 (3)	
C5A	0.19138 (11)	1.26951 (19)	0.56388 (11)	0.0264 (3)	
C6	0.15675 (13)	1.4072 (2)	0.56345 (14)	0.0338 (4)	
H6A	0.143922	1.452519	0.618055	0.041*	
C7	0.14169 (12)	1.4755 (2)	0.48199 (14)	0.0331 (4)	
H7A	0.117404	1.568665	0.480419	0.040*	
C8	0.16150 (12)	1.41029 (19)	0.40123 (13)	0.0295 (4)	
H8A	0.151707	1.460284	0.345810	0.035*	
C9B	0.24595 (10)	1.06021 (17)	0.50055 (10)	0.0204 (3)	
C9A	0.21054 (10)	1.20072 (17)	0.48381 (11)	0.0213 (3)	
C9	0.19531 (10)	1.27320 (18)	0.40184 (11)	0.0238 (3)	
H9A	0.208082	1.228670	0.346961	0.029*	
C10A	0.32805 (9)	0.84675 (16)	0.47404 (10)	0.0187 (3)	
H10A	0.380248	0.894315	0.497193	0.022*	

C10	0.27474 (9)	0.96355 (16)	0.42751 (10)	0.0184 (3)	
H10B	0.309492	1.021507	0.387981	0.022*	
C11	0.20217 (10)	0.90191 (17)	0.36979 (11)	0.0216 (3)	
C12	0.38481 (9)	0.46286 (16)	0.45148 (10)	0.0189 (3)	
C13	0.42078 (10)	0.37136 (18)	0.51699 (11)	0.0218 (3)	
H13A	0.426719	0.402232	0.577975	0.026*	
C14	0.44797 (10)	0.23566 (18)	0.49391 (11)	0.0224 (3)	
H14A	0.471177	0.173102	0.539320	0.027*	
C15	0.44140 (10)	0.19057 (16)	0.40438 (11)	0.0206 (3)	
C16	0.40420 (10)	0.28012 (17)	0.33900 (11)	0.0227 (3)	
H16A	0.398353	0.249190	0.278021	0.027*	
C17	0.37553 (10)	0.41479 (17)	0.36268 (10)	0.0214 (3)	
H17A	0.349271	0.474921	0.317799	0.026*	
C18	0.46796 (13)	0.0111 (2)	0.29506 (13)	0.0319 (4)	
H18A	0.490909	−0.086181	0.291209	0.048*	
H18B	0.410733	0.010725	0.270532	0.048*	
H18C	0.499947	0.078007	0.260286	0.048*	
C19A	0.02185 (17)	0.6061 (3)	0.0999 (2)	0.0471 (7)	0.8903 (18)
D19A	0.008139	0.503811	0.105923	0.071*	0.8903 (18)
D19B	−0.028387	0.661165	0.084572	0.071*	0.8903 (18)
D19C	0.059929	0.617892	0.052192	0.071*	0.8903 (18)
C20A	−0.01808 (16)	0.6679 (3)	0.26878 (19)	0.0470 (6)	0.8903 (18)
D20A	−0.032251	0.567942	0.282401	0.070*	0.8903 (18)
D20B	−0.005525	0.720540	0.325154	0.070*	0.8903 (18)
D20C	−0.064553	0.713967	0.234952	0.070*	0.8903 (18)
C19B	0.0423 (13)	0.6018 (18)	0.2686 (12)	0.049 (4)*	0.1097 (18)
D19D	0.010074	0.512543	0.265939	0.074*	0.1097 (18)
D19E	0.096287	0.583660	0.245646	0.074*	0.1097 (18)
D19F	0.049335	0.635024	0.331200	0.074*	0.1097 (18)
C20B	0.0041 (16)	0.666 (2)	0.0930 (9)	0.049 (4)*	0.1097 (18)
D20D	−0.029537	0.579159	0.082990	0.074*	0.1097 (18)
D20E	−0.012775	0.738825	0.047762	0.074*	0.1097 (18)
D20F	0.062047	0.641717	0.087819	0.074*	0.1097 (18)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1A	0.0229 (2)	0.0222 (2)	0.0503 (3)	−0.00093 (17)	−0.0028 (2)	0.0081 (2)
S5	0.0489 (3)	0.0338 (2)	0.01792 (19)	0.0139 (2)	0.00149 (17)	−0.00626 (16)
O1	0.0395 (7)	0.0201 (5)	0.0168 (5)	0.0014 (5)	0.0053 (5)	−0.0001 (4)
O2	0.0332 (7)	0.0444 (8)	0.0314 (7)	−0.0135 (6)	−0.0070 (6)	0.0084 (6)
O3	0.0458 (8)	0.0352 (7)	0.0188 (6)	−0.0119 (6)	−0.0097 (5)	0.0031 (5)
O4	0.0368 (7)	0.0202 (6)	0.0260 (6)	0.0073 (5)	0.0066 (5)	0.0023 (4)
O5A	0.0472 (13)	0.0372 (12)	0.0179 (9)	0.0081 (9)	0.0094 (8)	0.0081 (8)
O5B	0.0288 (18)	0.036 (2)	0.0193 (16)	−0.0038 (14)	−0.0041 (12)	−0.0009 (13)
O6A	0.0408 (9)	0.0232 (7)	0.0346 (8)	−0.0094 (6)	−0.0158 (7)	0.0074 (6)
N2	0.0236 (6)	0.0192 (6)	0.0149 (5)	0.0026 (5)	−0.0004 (5)	0.0004 (5)
C1	0.0218 (7)	0.0183 (7)	0.0174 (6)	0.0003 (5)	−0.0009 (5)	−0.0003 (5)

C3A	0.0264 (7)	0.0258 (7)	0.0131 (6)	0.0056 (6)	0.0004 (5)	0.0014 (5)
C3	0.0288 (8)	0.0258 (8)	0.0146 (6)	0.0067 (6)	0.0007 (6)	0.0018 (6)
C4B	0.0406 (10)	0.0370 (9)	0.0127 (7)	0.0155 (8)	−0.0008 (6)	−0.0016 (6)
C4C	0.0406 (10)	0.0370 (9)	0.0127 (7)	0.0155 (8)	−0.0008 (6)	−0.0016 (6)
C4A	0.0320 (8)	0.0278 (8)	0.0172 (7)	0.0080 (7)	−0.0010 (6)	−0.0045 (6)
C5A	0.0312 (8)	0.0256 (8)	0.0222 (7)	0.0038 (7)	0.0006 (6)	−0.0037 (6)
C6	0.0391 (10)	0.0281 (9)	0.0345 (10)	0.0060 (8)	0.0054 (8)	−0.0086 (7)
C7	0.0355 (9)	0.0217 (8)	0.0424 (11)	0.0042 (7)	0.0044 (8)	−0.0021 (7)
C8	0.0324 (9)	0.0221 (8)	0.0337 (9)	0.0021 (7)	0.0005 (7)	0.0032 (7)
C9B	0.0212 (7)	0.0220 (7)	0.0179 (7)	0.0023 (6)	−0.0005 (5)	−0.0041 (5)
C9A	0.0196 (7)	0.0221 (7)	0.0218 (7)	0.0002 (5)	−0.0009 (5)	−0.0037 (6)
C9	0.0249 (7)	0.0215 (7)	0.0249 (8)	0.0006 (6)	0.0014 (6)	−0.0008 (6)
C10A	0.0212 (7)	0.0193 (7)	0.0153 (6)	0.0022 (5)	−0.0004 (5)	−0.0011 (5)
C10	0.0213 (7)	0.0192 (7)	0.0144 (6)	0.0011 (5)	−0.0015 (5)	−0.0012 (5)
C11	0.0248 (7)	0.0186 (7)	0.0205 (7)	0.0014 (6)	−0.0047 (6)	−0.0001 (5)
C12	0.0187 (6)	0.0182 (7)	0.0196 (7)	0.0002 (5)	−0.0009 (5)	0.0014 (5)
C13	0.0233 (7)	0.0239 (7)	0.0177 (7)	0.0020 (6)	−0.0023 (5)	0.0015 (6)
C14	0.0217 (7)	0.0228 (7)	0.0224 (7)	0.0036 (6)	−0.0015 (6)	0.0049 (6)
C15	0.0197 (7)	0.0176 (7)	0.0248 (7)	0.0006 (5)	0.0033 (6)	0.0018 (6)
C16	0.0289 (8)	0.0196 (7)	0.0195 (7)	−0.0010 (6)	0.0013 (6)	0.0004 (6)
C17	0.0261 (7)	0.0186 (7)	0.0188 (7)	0.0000 (6)	−0.0026 (6)	0.0018 (5)
C18	0.0453 (11)	0.0226 (8)	0.0289 (9)	0.0050 (7)	0.0111 (8)	−0.0007 (7)
C19A	0.0414 (14)	0.0399 (14)	0.0605 (17)	−0.0108 (11)	0.0066 (12)	−0.0198 (12)
C20A	0.0358 (12)	0.0560 (16)	0.0497 (15)	−0.0034 (11)	0.0075 (11)	0.0072 (12)

Geometric parameters (Å, º)

S1A—O6A	1.5127 (15)	C7—C8	1.401 (3)
S1A—C20A	1.769 (3)	C7—H7A	0.9500
S1A—C19A	1.777 (3)	C8—C9	1.386 (2)
S1B—O6B	1.515 (12)	C8—H8A	0.9500
S1B—C19B	1.762 (12)	C9B—C9A	1.441 (2)
S1B—C20B	1.774 (13)	C9B—C10	1.507 (2)
S5—C4A	1.7407 (17)	C9A—C9	1.400 (2)
S5—C5A	1.7434 (18)	C9—H9A	0.9500
O1—C1	1.2288 (19)	C10A—C10	1.526 (2)
O2—C11	1.207 (2)	C10A—H10A	1.0000
O3—C11	1.322 (2)	C10—C11	1.527 (2)
O3—H3	0.8400	C10—H10B	1.0000
O4—C15	1.3692 (19)	C12—C13	1.392 (2)
O4—C18	1.433 (2)	C12—C17	1.393 (2)
O5A—C4B	1.338 (3)	C13—C14	1.385 (2)
O5A—H5A	0.8400	C13—H13A	0.9500
O5B—C4C	1.271 (4)	C14—C15	1.393 (2)
O5B—H5B	0.8400	C14—H14A	0.9500
N2—C1	1.362 (2)	C15—C16	1.388 (2)
N2—C12	1.419 (2)	C16—C17	1.387 (2)
N2—C3	1.479 (2)	C16—H16A	0.9500

C1—C10A	1.511 (2)	C17—H17A	0.9500
C3A—C4C	1.521 (2)	C18—H18A	0.9800
C3A—C4B	1.521 (2)	C18—H18B	0.9800
C3A—C10A	1.521 (2)	C18—H18C	0.9800
C3A—C3	1.532 (2)	C19A—D19A	0.9800
C3A—H3AA	1.0000	C19A—D19B	0.9800
C3—H3A	0.9900	C19A—D19C	0.9800
C3—H3B	0.9900	C20A—D20A	0.9800
C4B—C4A	1.507 (2)	C20A—D20B	0.9800
C4B—H4A	1.0000	C20A—D20C	0.9800
C4C—C4A	1.507 (2)	C19B—D19D	0.9800
C4C—H4B	1.0000	C19B—D19E	0.9800
C4A—C9B	1.361 (2)	C19B—D19F	0.9800
C5A—C6	1.396 (3)	C20B—D20D	0.9800
C5A—C9A	1.404 (2)	C20B—D20E	0.9800
C6—C7	1.375 (3)	C20B—D20F	0.9800
C6—H6A	0.9500		

O6A—S1A—C20A	106.26 (13)	C8—C9—C9A	119.61 (16)
O6A—S1A—C19A	104.20 (12)	C8—C9—H9A	120.2
C20A—S1A—C19A	99.03 (13)	C9A—C9—H9A	120.2
O6B—S1B—C19B	105.6 (8)	C1—C10A—C3A	103.55 (12)
O6B—S1B—C20B	105.2 (8)	C1—C10A—C10	118.36 (12)
C19B—S1B—C20B	100.2 (9)	C3A—C10A—C10	113.66 (13)
C4A—S5—C5A	91.61 (8)	C1—C10A—H10A	106.9
C11—O3—H3	109.5	C3A—C10A—H10A	106.9
C15—O4—C18	116.77 (13)	C10—C10A—H10A	106.9
C4B—O5A—H5A	109.5	C9B—C10—C10A	106.90 (12)
C4C—O5B—H5B	109.5	C9B—C10—C11	111.15 (13)
C1—N2—C12	125.06 (13)	C10A—C10—C11	112.76 (13)
C1—N2—C3	112.06 (13)	C9B—C10—H10B	108.6
C12—N2—C3	122.38 (13)	C10A—C10—H10B	108.6
O1—C1—N2	127.11 (15)	C11—C10—H10B	108.6
O1—C1—C10A	125.25 (14)	O2—C11—O3	124.33 (15)
N2—C1—C10A	107.58 (13)	O2—C11—C10	123.87 (15)
C4C—C3A—C10A	108.91 (14)	O3—C11—C10	111.81 (14)
C4B—C3A—C10A	108.91 (14)	C13—C12—C17	118.87 (14)
C4C—C3A—C3	119.35 (13)	C13—C12—N2	120.50 (14)
C4B—C3A—C3	119.35 (13)	C17—C12—N2	120.62 (13)
C10A—C3A—C3	102.18 (12)	C14—C13—C12	120.51 (15)
C4B—C3A—H3AA	108.6	C14—C13—H13A	119.7
C10A—C3A—H3AA	108.6	C12—C13—H13A	119.7
C3—C3A—H3AA	108.6	C13—C14—C15	120.25 (14)
N2—C3—C3A	101.83 (12)	C13—C14—H14A	119.9
N2—C3—H3A	111.4	C15—C14—H14A	119.9
C3A—C3—H3A	111.4	O4—C15—C16	124.11 (15)
N2—C3—H3B	111.4	O4—C15—C14	116.36 (14)
C3A—C3—H3B	111.4	C16—C15—C14	119.51 (14)

H3A—C3—H3B	109.3	C17—C16—C15	120.02 (15)
O5A—C4B—C4A	108.46 (16)	C17—C16—H16A	120.0
O5A—C4B—C3A	118.61 (19)	C15—C16—H16A	120.0
C4A—C4B—C3A	106.60 (13)	C16—C17—C12	120.76 (14)
O5A—C4B—H4A	107.6	C16—C17—H17A	119.6
C4A—C4B—H4A	107.6	C12—C17—H17A	119.6
C3A—C4B—H4A	107.6	O4—C18—H18A	109.5
O5B—C4C—C4A	116.3 (2)	O4—C18—H18B	109.5
O5B—C4C—C3A	112.9 (2)	H18A—C18—H18B	109.5
C4A—C4C—C3A	106.60 (13)	O4—C18—H18C	109.5
O5B—C4C—H4B	106.9	H18A—C18—H18C	109.5
C4A—C4C—H4B	106.9	H18B—C18—H18C	109.5
C3A—C4C—H4B	106.9	S1A—C19A—D19A	109.5
C9B—C4A—C4C	126.63 (15)	S1A—C19A—D19B	109.5
C9B—C4A—C4B	126.63 (15)	D19A—C19A—D19B	109.5
C9B—C4A—S5	112.36 (13)	S1A—C19A—D19C	109.5
C4C—C4A—S5	120.99 (12)	D19A—C19A—D19C	109.5
C4B—C4A—S5	120.99 (12)	D19B—C19A—D19C	109.5
C6—C5A—C9A	121.61 (17)	S1A—C20A—D20A	109.5
C6—C5A—S5	127.31 (14)	S1A—C20A—D20B	109.5
C9A—C5A—S5	111.07 (13)	D20A—C20A—D20B	109.5
C7—C6—C5A	118.33 (17)	S1A—C20A—D20C	109.5
C7—C6—H6A	120.8	D20A—C20A—D20C	109.5
C5A—C6—H6A	120.8	D20B—C20A—D20C	109.5
C6—C7—C8	121.20 (17)	S1B—C19B—D19D	109.5
C6—C7—H7A	119.4	S1B—C19B—D19E	109.5
C8—C7—H7A	119.4	D19D—C19B—D19E	109.5
C9—C8—C7	120.31 (17)	S1B—C19B—D19F	109.5
C9—C8—H8A	119.8	D19D—C19B—D19F	109.5
C7—C8—H8A	119.8	D19E—C19B—D19F	109.5
C4A—C9B—C9A	113.02 (14)	S1B—C20B—D20D	109.5
C4A—C9B—C10	123.29 (14)	S1B—C20B—D20E	109.5
C9A—C9B—C10	123.65 (14)	D20D—C20B—D20E	109.5
C9—C9A—C5A	118.92 (15)	S1B—C20B—D20F	109.5
C9—C9A—C9B	129.13 (15)	D20D—C20B—D20F	109.5
C5A—C9A—C9B	111.94 (15)	D20E—C20B—D20F	109.5

C12—N2—C1—O1	3.3 (3)	C10—C9B—C9A—C9	0.6 (3)
C3—N2—C1—O1	175.30 (16)	C4A—C9B—C9A—C5A	−0.6 (2)
C12—N2—C1—C10A	−174.00 (13)	C10—C9B—C9A—C5A	−178.18 (15)
C3—N2—C1—C10A	−1.96 (18)	C7—C8—C9—C9A	−0.8 (3)
C1—N2—C3—C3A	23.14 (17)	C5A—C9A—C9—C8	−0.3 (2)
C12—N2—C3—C3A	−164.58 (14)	C9B—C9A—C9—C8	−179.02 (17)
C4C—C3A—C3—N2	−154.00 (15)	O1—C1—C10A—C3A	162.34 (16)
C4B—C3A—C3—N2	−154.00 (15)	N2—C1—C10A—C3A	−20.34 (16)
C10A—C3A—C3—N2	−33.89 (15)	O1—C1—C10A—C10	35.5 (2)
C10A—C3A—C4B—O5A	172.66 (17)	N2—C1—C10A—C10	−147.14 (14)
C3—C3A—C4B—O5A	−70.7 (2)	C4C—C3A—C10A—C1	160.51 (13)

C10A—C3A—C4B—C4A	50.03 (19)	C4B—C3A—C10A—C1	160.51 (13)
C3—C3A—C4B—C4A	166.67 (15)	C3—C3A—C10A—C1	33.35 (15)
C10A—C3A—C4C—O5B	−78.8 (2)	C4C—C3A—C10A—C10	−69.78 (17)
C3—C3A—C4C—O5B	37.8 (3)	C4B—C3A—C10A—C10	−69.78 (17)
C10A—C3A—C4C—C4A	50.03 (19)	C3—C3A—C10A—C10	163.06 (13)
C3—C3A—C4C—C4A	166.67 (15)	C4A—C9B—C10—C10A	−12.4 (2)
O5B—C4C—C4A—C9B	107.8 (3)	C9A—C9B—C10—C10A	165.01 (14)
C3A—C4C—C4A—C9B	−19.0 (3)	C4A—C9B—C10—C11	111.08 (18)
O5B—C4C—C4A—S5	−70.3 (3)	C9A—C9B—C10—C11	−71.54 (19)
C3A—C4C—C4A—S5	162.82 (13)	C1—C10A—C10—C9B	168.32 (13)
O5A—C4B—C4A—C9B	−147.8 (2)	C3A—C10A—C10—C9B	46.52 (17)
C3A—C4B—C4A—C9B	−19.0 (3)	C1—C10A—C10—C11	45.88 (19)
O5A—C4B—C4A—S5	34.0 (2)	C3A—C10A—C10—C11	−75.93 (17)
C3A—C4B—C4A—S5	162.82 (13)	C9B—C10—C11—O2	−57.9 (2)
C5A—S5—C4A—C9B	0.01 (15)	C10A—C10—C11—O2	62.1 (2)
C5A—S5—C4A—C4C	178.43 (16)	C9B—C10—C11—O3	122.07 (15)
C5A—S5—C4A—C4B	178.43 (16)	C10A—C10—C11—O3	−117.90 (15)
C4A—S5—C5A—C6	−179.43 (19)	C1—N2—C12—C13	152.25 (16)
C4A—S5—C5A—C9A	−0.33 (14)	C3—N2—C12—C13	−19.0 (2)
C9A—C5A—C6—C7	−0.2 (3)	C1—N2—C12—C17	−28.8 (2)
S5—C5A—C6—C7	178.84 (16)	C3—N2—C12—C17	159.92 (15)
C5A—C6—C7—C8	−0.9 (3)	C17—C12—C13—C14	1.0 (2)
C6—C7—C8—C9	1.4 (3)	N2—C12—C13—C14	179.89 (15)
C4C—C4A—C9B—C9A	−178.00 (17)	C12—C13—C14—C15	1.6 (2)
C4B—C4A—C9B—C9A	−178.00 (17)	C18—O4—C15—C16	4.1 (2)
S5—C4A—C9B—C9A	0.3 (2)	C18—O4—C15—C14	−177.49 (15)
C4C—C4A—C9B—C10	−0.4 (3)	C13—C14—C15—O4	178.70 (15)
C4B—C4A—C9B—C10	−0.4 (3)	C13—C14—C15—C16	−2.8 (2)
S5—C4A—C9B—C10	177.93 (13)	O4—C15—C16—C17	179.86 (15)
C6—C5A—C9A—C9	0.8 (3)	C14—C15—C16—C17	1.5 (2)
S5—C5A—C9A—C9	−178.38 (13)	C15—C16—C17—C12	1.1 (2)
C6—C5A—C9A—C9B	179.71 (17)	C13—C12—C17—C16	−2.3 (2)
S5—C5A—C9A—C9B	0.55 (19)	N2—C12—C17—C16	178.78 (15)
C4A—C9B—C9A—C9	178.24 (17)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···S1*A*	0.84	2.72	3.4846 (15)	152
O3—H3···O6*A*	0.84	1.72	2.563 (2)	176
O3—H3···O6*B*	0.84	2.06	2.852 (16)	158
O5*A*—H5*A*···O1^{i}	0.84	1.96	2.763 (2)	160
C3*A*—H3*AA*···O2	1.00	2.49	3.202 (2)	127
C3—H3*A*···O5*B*	0.99	2.54	2.887 (4)	100
C6—H6*A*···O6*A*^{ii}	0.95	2.48	3.307 (3)	145
C14—H14*A*···O4^{iii}	0.95	2.54	3.445 (2)	159
C17—H17*A*···O1	0.95	2.33	2.868 (2)	116
C17—H17*A*···O5*B*^{iv}	0.95	2.46	3.289 (4)	146

C18—H18*C*···O5*B*^{v}	0.98	2.43	2.922 (4)	110
C20*A*—D20*A*···O6*A*^{vi}	0.98	2.46	3.434 (3)	173
C20*A*—D20*A*···O6*B*^{vi}	0.98	1.87	2.839 (13)	168

Symmetry codes: (i) *x*, −*y*+3/2, *z*+1/2; (ii) *x*, −*y*+5/2, *z*+1/2; (iii) −*x*+1, −*y*, −*z*+1; (iv) *x*, −*y*+3/2, *z*−1/2; (v) −*x*+1, −*y*+1, −*z*+1; (vi) −*x*, *y*−1/2, −*z*+1/2.