



Crystal structure and Hirshfeld surface analysis of 4-[4-(1*H*-benzo[*d*]imidazol-2-yl)phenoxy]phthalonitrile dimethyl sulfoxide monosolvate

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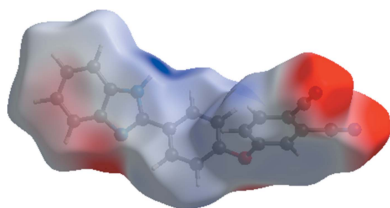
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This work presents the synthesis and structural characterization of [4-(1*H*-benzo[*d*]imidazol-2-yl)phenoxy]phthalonitrile, a phthalonitrile derivative carrying a benzimidazole moiety. The compound crystallizes as its dimethyl sulfoxide monosolvate, C₂₁H₁₂N₄O·(CH₃)₂SO. The dihedral angle between the two fused rings in the heterocyclic ring system is 2.11 (1)°, while the phenyl ring attached to the imidazole moiety is inclined by 20.7 (1)° to the latter. In the crystal structure, adjacent molecules are connected by pairs of weak intermolecular C—H···N hydrogen bonds into inversion dimers. N—H···O and C—H···O hydrogen bonds with R₂¹(7) graph-set motifs are also formed between the organic molecule and the disordered dimethyl sulfoxide solvent [occupancy ratio of 0.623 (5):0.377 (5) for the two sites of the sulfur atom]. Hirshfeld surface analysis and fingerprint plots were used to investigate the intermolecular interactions in the crystalline state.

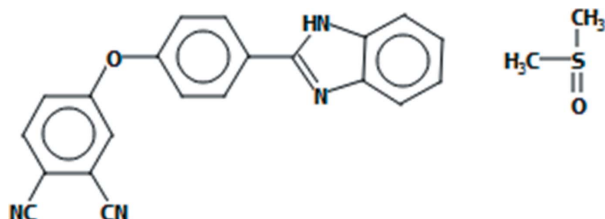
1. Chemical context

Benzimidazole and its derivatives are some of the oldest and chemically most-studied nitrogen-containing aromatic heterocyclic compounds (Srestha *et al.*, 2014). They have a wide range of applications in medicinal chemistry and in biological processes including as anticancer, antiulcer, anti-fungal and anti-inflammatory agents, and exhibit antimicrobial and antioxidant activities (El Rashedy & Aboul-Enein, 2013; Gaba *et al.*, 2014; Kathiravan *et al.*, 2012). They are also used as ligands with fluorescent properties. The fluorescent characteristic of these compounds can be changed by substitution or derivatization of different groups at the NH position of the benzimidazole skeleton.

Phthalonitrile derivatives are some of the most widely used precursors for the preparation of phthalocyanines (Pc). The preparation of phthalocyanines is frequently carried out by a cyclotetramerization reaction of phthalonitriles. The synthesis of the latter compound family, carrying different functional groups, leads to functionalized phthalocyanines that are of great importance with respect to new molecular materials and targeted applications such as catalysis, liquid crystals, photosensitizers for photodynamic therapy (PDT), non-linear optics, nanotechnology or dye-sensitized solar cells (Torre *et*



al., 2004; Martínez-Díaz *et al.*, 2011). In this context, we have recently described a model study, *i.e.* the synthesis, characterization and Hirshfeld surface analysis of zinc phthalocyanines carrying benzimidazole groups through oxygen bridges to a Zn–Pc core (Sen *et al.*, 2018*b*). Here we report the synthesis, structural characterization and Hirshfeld surface analysis of a related ligand that crystallizes as its dimethylsulfoxide monosolvate, $C_{21}H_{12}N_4O \cdot (CH_3)_2SO$.



2. Structural commentary

The molecular components of the title compound are shown in Fig. 1. The molecular structure of the phthalonitrile derivative is constructed from three ring systems, *viz.* a central phenoxy ring, a terminal phthalonitrile system and a terminal benzimidazole ring. The bond lengths of the cyano groups, 1.132 (6) and 1.137 (6) Å, for C21≡N4 and C20≡N3, respectively, conform well with literature values (Saraçoğlu *et al.*, 2011). The corresponding C–C≡N angles [179.4 (6) and 177.9 (7)°] are almost linear and are also in good agreement with literature values (Saraçoğlu *et al.*, 2011; Sen *et al.*, 2018*a*). The C–C bond lengths of the phenyl rings are in the normal range of 1.356 (5)–1.395 (6) Å, *i.e.* characteristic of a delocalized system. The dihedral angle of 2.11 (1)° between the fused C1–C6 and C5/N2/C7/N1/C6 rings in the heterocycle indicate a minute deviation from planarity, whereas the attached C8–C13 ring is inclined by 20.7 (1)° to the C5/N2/C7/N1/C6 ring plane.

3. Supramolecular features

In the crystal structure, N2–H2···O2 and C9–H9···O2 intermolecular hydrogen bonding interactions with an $R_2^1(7)$

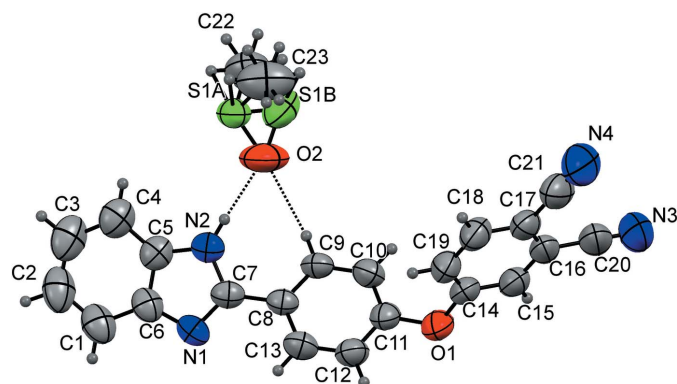


Figure 1
The molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds (Table 1) are shown as dashed lines.

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2–H2···O2	0.86	1.94	2.794 (5)	172
N2–H2···S1A	0.86	2.83	3.614 (4)	152
C9–H9···O2	0.93	2.40	3.175 (5)	141
C23–H23D···N4 ⁱ	0.96	2.63	3.500 (9)	151

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

graph-set motif are present, whereby the O2 atom acts as an acceptor in both cases (Fig. 1). There are also weak intermolecular N2–H2···S1A interactions between the the N–H group of the imidazole ring and the disordered dimethyl sulfate solvent, and a C23–H23D···N4 interaction between one of the methyl groups of the dimethyl sulfoxide solvent and

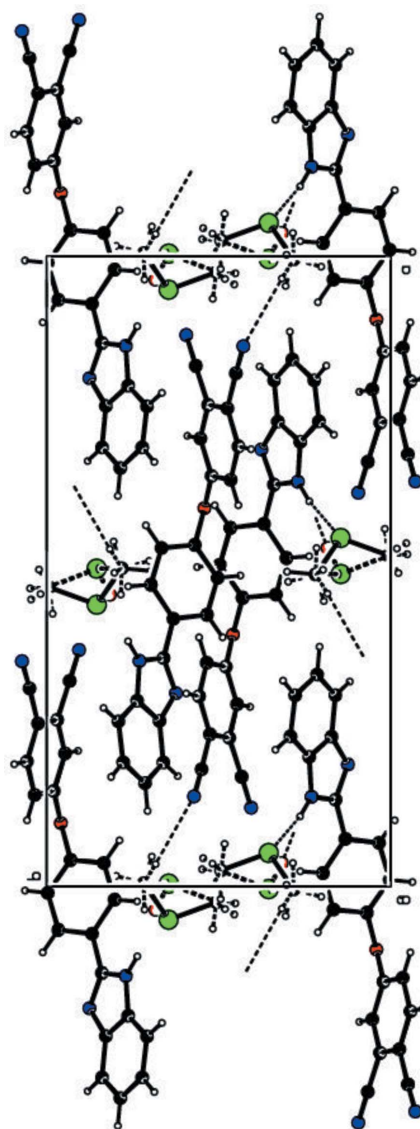


Figure 2
A view of the crystal packing of the title compound. Dashed lines denote the N2–H2···S1A, N2–H2···O2 and C23–H23D···N4 intermolecular hydrogen-bonding interactions.

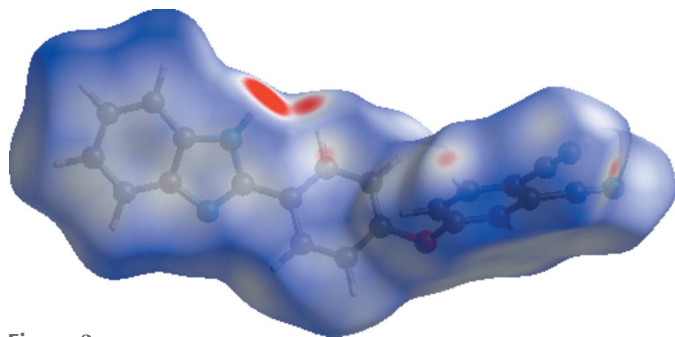


Figure 3
The Hirshfeld surface of the title compound mapped with d_{norm} in the range -0.6328 to 1.3784 a.u.

one of the nitrile N atoms (Table 1, Fig. 2). These interactions lead to the formation of a three-dimensional supramolecular network.

4. Database survey

A search of the Cambridge Structural database (CSD, version 5.40, update November 2018; Groom *et al.*, 2016) for the 4-[4-(1*H*-benzo[*d*]imidazole-2-yl)phenoxy]phthalonitrile moiety revealed two hits. Distinctive bond lengths ($\text{N4}\equiv\text{C21}$, $\text{N3}\equiv\text{C20}$, $\text{C7}-\text{N2}$, $\text{C5}-\text{N2}$) in the title structure are the same within standard uncertainties as the corresponding bond lengths in the structures of 4-[4-(1*H*-benzimidazol-2-yl)phenoxy]benzene-1,2-dicarbonitrile monohydrate (HIDHEK; Sen *et al.*, 2018*b*) or 4-[4-[1-(prop-2-en-1-yl)-1*H*-benzimidazol-2-yl]phenoxy]benzene-1,2-dicarbonitrile (RELBUJ; Sen *et al.*, 2018*a*). In these structures, the C—O bond lengths vary from

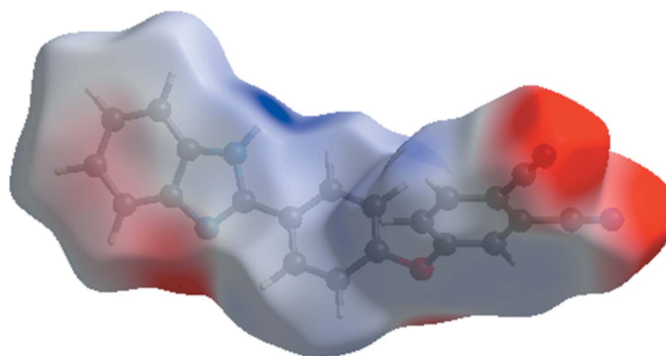


Figure 5
A view of the three-dimensional Hirshfeld surface of the title compound plotted over electrostatic potentials in the range -0.0893 to 0.1930 a.u.

1.363 – 1.407 Å. In the title molecule, the corresponding bond lengths are 1.367 (5) and 1.406 (4) Å, respectively. In all these structures, the molecules are linked into chains by C—H···N hydrogen bonds.

5. Hirshfeld surface analysis

The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and the associated two-dimensional fingerprint plots (McKinnon *et al.*, 2007) were performed with *Crystal-Explorer17* (Turner *et al.*, 2017). The Hirshfeld surfaces were generated using a standard (high) surface resolution with the three-dimensional surfaces mapped over d_{norm} (Fig. 3). For the title molecule, the H···H interactions appear in the middle of the scattered points in the fingerprint plots with a contribution to the overall Hirshfeld surface of 36.1% (Fig. 4). The

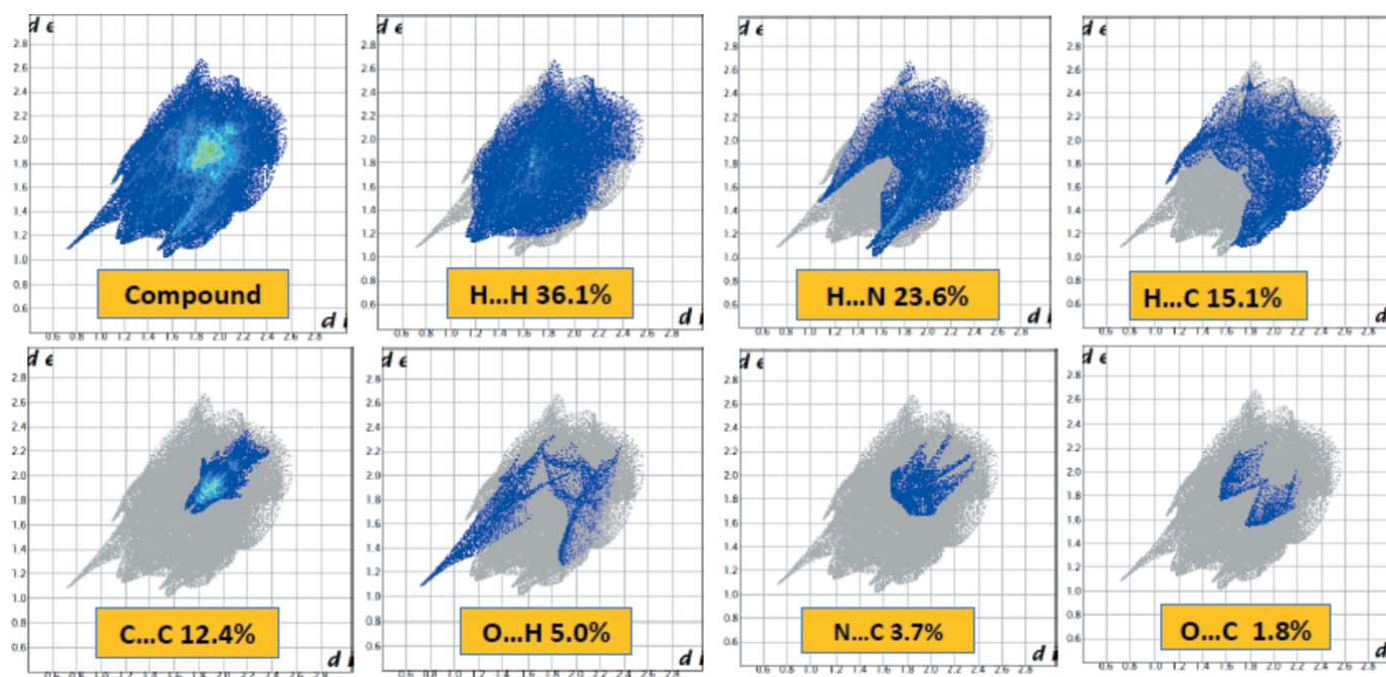


Figure 4
Two-dimensional fingerprint plots with a d_{norm} view of all interactions in the title compound, and subdivided into H···H (36.1%), N···H/H···N (23.6%), C···H/H···C (15.1%), C···C/C···C (12.4%), O···H/H···O (5.0%), C···N/N···C (3.7%), C···O/O···C (1.8%) and S···H/H···S (1.6%) contacts.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₂₁ H ₁₂ N ₄ O·C ₂ H ₆ OS
<i>M_r</i>	414.47
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 ₁
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	20.9154 (11), 11.4208 (6), 8.8938 (6)
<i>V</i> (Å ³)	2124.5 (2)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm ⁻¹)	0.18
Crystal size (mm)	0.65 × 0.56 × 0.47
Data collection	
Diffractometer	Stoe IPDS 2
Absorption correction	Integration (<i>X-RED32</i> ; Stoe & Cie, 2002)
<i>T_{min}</i> , <i>T_{max}</i>	0.966, 0.977
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	15225, 4660, 2281
<i>R_{int}</i>	0.058
(sin θ/λ) _{max} (Å ⁻¹)	0.641
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.042, 0.098, 0.83
No. of reflections	4660
No. of parameters	281
No. of restraints	1
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.20, -0.12
Absolute structure	Flack <i>x</i> determined using 771 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	-0.02 (8)

Computer programs: *X-AREA* and *X-RED32* (Stoe & Cie, 2002), *SHELXT2018* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2006) and *PLATON* (Spek, 2009).

contribution from the N···H/H···N contacts, corresponding to the C—H···N interactions, is represented by a pair of sharp spikes characteristic of a rather strong hydrogen-bonding interaction (23.6%). The whole fingerprint region and all other interactions are displayed in Fig. 4. In particular, the O···H/H···O contacts indicate the presence of intermolecular C—H···O and N—H···O interactions.

A view of the molecular electrostatic potential for the title compound, using the STO-3G basis set at the Hartree–Fock level of theory, is shown in Fig. 5. The N—H···N and C—H···N hydrogen-bond donor and acceptor groups 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

2-(4-Hydroxy-phenyl)-benzimidazole (1.2 g, 5.71 mmol), which was synthesized by the reaction of *o*-phenylenediamine and 4-hydroxybenzaldehyde, and 4-nitrophthalonitrile (0.989 g, 5.71 mmol) were dissolved in DMF (15 ml) and degassed by argon in a dual-bank vacuum-gas manifold system. After stirring for 15 min, finely ground anhydrous K₂CO₃ (0.790 g, 5.71 mmol) was added portion-wise over 2 h

under stirring. The suspension solution was maintained at 333 K for 24 h. After completion of the reaction, the crude product was precipitated by pouring into ice–water. The precipitate was collected by filtration, washed with hot water, ethanol, diethyl ether and was finally dried *in vacuo*. The desired compound was obtained in sufficient purity. The obtained spectroscopic data are accordance with the literature (Khan *et al.*, 2009). Single crystals for structure analysis were obtained from slow evaporation of a DMSO solution.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93 Å for aromatic groups, with N—H = 0.86 Å for the imidazole moiety and with 0.96 Å for methyl groups. *U*_{iso}(H) values were constrained to 1.2–1.5 *U*_{eq} of their carrier atoms. The sulfur atom of the dimethylsulfate solvent is disordered over two sites (S1A and S1B), with an occupancy ratio of 0.623 (5):0.377 (5).

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXT2018* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL2018* (Sheldrick, 2015b), *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

4-[4-(1*H*-Benzo[*d*]imidazol-2-yl)phenoxy]phthalonitrile dimethyl sulfoxide monosolvate

Crystal data

$C_{21}H_{12}N_4O \cdot C_2H_6OS$

$M_r = 414.47$

Orthorhombic, *Pna*2₁

$a = 20.9154$ (11) Å

$b = 11.4208$ (6) Å

$c = 8.8938$ (6) Å

$V = 2124.5$ (2) Å³

$Z = 4$

$F(000) = 864$

$D_x = 1.296$ Mg m⁻³

Mo *K*α radiation, $\lambda = 0.71073$ Å

Cell parameters from 9474 reflections

$\theta = 1.8$ – 27.0°

$\mu = 0.18$ mm⁻¹

$T = 296$ K

Prism, yellow

$0.65 \times 0.56 \times 0.47$ mm

Data collection

Stoe IPDS 2

diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus

Plane graphite monochromator

Detector resolution: 6.67 pixels mm⁻¹

rotation method scans

Absorption correction: integration (X-RED32; Stoe & Cie, 2002)

$T_{\min} = 0.966$, $T_{\max} = 0.977$

15225 measured reflections

4660 independent reflections

2281 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.058$

$\theta_{\max} = 27.1^\circ$, $\theta_{\min} = 2.0^\circ$

$h = -26 \rightarrow 22$

$k = -14 \rightarrow 14$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.098$

$S = 0.83$

4660 reflections

281 parameters

1 restraint

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.20 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.12 \text{ e } \text{\AA}^{-3}$

Absolute structure: Flack x determined using
 771 quotients $[(F^-)-(F)]/[(F^+)+(F)]$ (Parsons *et al.*,
 2013)
 Absolute structure parameter: -0.02 (8)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S1A	0.55296 (11)	0.14556 (16)	0.7814 (2)	0.0869 (9)	0.623 (5)
S1B	0.4957 (2)	0.1452 (4)	0.7420 (4)	0.114 (2)	0.377 (5)
O1	0.39958 (15)	0.4586 (3)	0.0943 (3)	0.0925 (8)	
O2	0.53727 (19)	0.1838 (3)	0.6323 (4)	0.1425 (15)	
N1	0.69349 (16)	0.3756 (2)	0.2997 (4)	0.0751 (8)	
N2	0.64212 (17)	0.2699 (2)	0.4721 (3)	0.0720 (8)	
H2	0.611036	0.236598	0.518771	0.086*	
N3	0.1249 (2)	0.4056 (4)	0.1258 (7)	0.1429 (19)	
N4	0.1428 (2)	0.5716 (5)	0.5187 (7)	0.156 (2)	
C1	0.8034 (2)	0.3391 (4)	0.4030 (6)	0.0968 (13)	
H1	0.824993	0.380986	0.329242	0.116*	
C2	0.8361 (3)	0.2860 (5)	0.5198 (7)	0.1100 (17)	
H2A	0.880352	0.293117	0.526112	0.132*	
C3	0.8032 (3)	0.2223 (5)	0.6272 (7)	0.1098 (16)	
H3	0.826349	0.187242	0.704234	0.132*	
C4	0.7380 (3)	0.2085 (4)	0.6256 (6)	0.0957 (13)	
H4	0.716824	0.165147	0.698781	0.115*	
C5	0.7054 (2)	0.2630 (3)	0.5081 (4)	0.0724 (10)	
C6	0.7375 (2)	0.3280 (3)	0.3992 (5)	0.0748 (10)	
C7	0.6375 (2)	0.3395 (3)	0.3484 (4)	0.0652 (10)	
C8	0.57530 (16)	0.3683 (3)	0.2821 (4)	0.0605 (8)	
C9	0.52110 (19)	0.3027 (3)	0.3118 (4)	0.0679 (10)	
H9	0.523936	0.237162	0.373482	0.081*	
C10	0.46302 (19)	0.3338 (3)	0.2509 (4)	0.0785 (11)	
H10	0.427035	0.288323	0.270114	0.094*	
C11	0.45811 (19)	0.4303 (4)	0.1630 (4)	0.0716 (10)	
C12	0.5104 (2)	0.4970 (4)	0.1317 (5)	0.0783 (11)	
H12	0.506725	0.562819	0.070782	0.094*	
C13	0.5690 (2)	0.4659 (3)	0.1912 (4)	0.0752 (11)	
H13	0.604801	0.511332	0.169824	0.090*	
C14	0.3486 (2)	0.4793 (3)	0.1868 (5)	0.0734 (11)	
C15	0.2890 (2)	0.4466 (3)	0.1358 (5)	0.0804 (11)	
H15	0.284932	0.408992	0.043566	0.096*	
C16	0.2358 (2)	0.4694 (4)	0.2210 (6)	0.0827 (12)	

C17	0.2414 (2)	0.5253 (4)	0.3584 (5)	0.0845 (12)	
C18	0.3018 (2)	0.5574 (4)	0.4094 (5)	0.0890 (12)	
H18	0.306198	0.594294	0.502000	0.107*	
C19	0.3549 (2)	0.5347 (4)	0.3231 (5)	0.0820 (11)	
H19	0.395119	0.556988	0.357067	0.098*	
C20	0.1739 (3)	0.4332 (4)	0.1682 (6)	0.1069 (17)	
C21	0.1857 (3)	0.5498 (5)	0.4466 (6)	0.1113 (17)	
C22	0.5253 (2)	0.0068 (4)	0.8099 (6)	0.1185 (17)	
H22A	0.536012	-0.018040	0.909946	0.178*	0.623 (5)
H22B	0.479713	0.005567	0.797600	0.178*	0.623 (5)
H22C	0.544633	-0.045215	0.738362	0.178*	0.623 (5)
H22D	0.497256	-0.022369	0.886737	0.178*	0.377 (5)
H22E	0.527035	-0.048198	0.728417	0.178*	0.377 (5)
H22F	0.567387	0.017228	0.850914	0.178*	0.377 (5)
C23	0.4951 (4)	0.2180 (5)	0.8988 (7)	0.151 (2)	
H23A	0.502326	0.196930	1.001908	0.227*	0.623 (5)
H23B	0.499347	0.301270	0.887593	0.227*	0.623 (5)
H23C	0.452845	0.194538	0.869547	0.227*	0.623 (5)
H23D	0.464660	0.183633	0.966396	0.227*	0.377 (5)
H23E	0.536893	0.215626	0.943443	0.227*	0.377 (5)
H23F	0.483454	0.297886	0.879270	0.227*	0.377 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1A	0.0892 (19)	0.1040 (13)	0.0676 (11)	-0.0240 (11)	-0.0011 (11)	0.0104 (10)
S1B	0.124 (5)	0.131 (3)	0.087 (3)	0.016 (3)	-0.017 (2)	0.002 (2)
O1	0.081 (2)	0.135 (2)	0.0614 (15)	0.0085 (18)	0.0017 (16)	0.0154 (17)
O2	0.159 (4)	0.159 (3)	0.109 (3)	0.021 (3)	0.056 (3)	0.056 (2)
N1	0.068 (2)	0.0793 (19)	0.078 (2)	-0.0039 (17)	0.0160 (19)	-0.0036 (19)
N2	0.078 (2)	0.0676 (19)	0.070 (2)	-0.0024 (17)	0.0048 (19)	-0.0014 (16)
N3	0.097 (3)	0.166 (4)	0.165 (4)	-0.038 (3)	-0.028 (3)	0.051 (4)
N4	0.102 (4)	0.230 (6)	0.135 (4)	0.061 (4)	0.025 (3)	0.029 (4)
C1	0.080 (3)	0.110 (3)	0.100 (3)	0.005 (3)	0.014 (3)	-0.028 (3)
C2	0.079 (3)	0.138 (5)	0.113 (4)	0.030 (3)	-0.003 (4)	-0.042 (4)
C3	0.111 (5)	0.112 (4)	0.106 (4)	0.052 (3)	-0.008 (4)	-0.028 (3)
C4	0.103 (4)	0.083 (3)	0.101 (3)	0.023 (3)	-0.001 (3)	-0.010 (3)
C5	0.084 (3)	0.062 (2)	0.072 (3)	0.014 (2)	0.001 (3)	-0.011 (2)
C6	0.068 (3)	0.078 (3)	0.078 (3)	0.006 (2)	0.009 (2)	-0.019 (2)
C7	0.079 (3)	0.0538 (19)	0.063 (2)	-0.001 (2)	0.011 (2)	-0.0006 (19)
C8	0.070 (2)	0.0558 (19)	0.0556 (19)	-0.0026 (18)	0.010 (2)	-0.0016 (19)
C9	0.079 (3)	0.064 (2)	0.061 (2)	-0.009 (2)	0.008 (2)	0.0118 (18)
C10	0.075 (3)	0.085 (3)	0.076 (3)	-0.013 (2)	0.008 (2)	0.010 (2)
C11	0.071 (3)	0.087 (3)	0.057 (2)	0.007 (2)	0.006 (2)	0.010 (2)
C12	0.084 (3)	0.076 (3)	0.075 (3)	0.002 (2)	0.007 (2)	0.020 (2)
C13	0.081 (3)	0.067 (2)	0.077 (3)	-0.008 (2)	0.011 (2)	0.007 (2)
C14	0.074 (3)	0.085 (3)	0.062 (2)	0.003 (2)	-0.004 (2)	0.022 (2)
C15	0.084 (3)	0.086 (3)	0.071 (3)	-0.005 (2)	-0.013 (2)	0.020 (2)

C16	0.067 (3)	0.087 (3)	0.094 (3)	-0.004 (2)	-0.007 (3)	0.037 (3)
C17	0.075 (3)	0.099 (3)	0.079 (3)	0.016 (2)	0.000 (3)	0.029 (3)
C18	0.088 (4)	0.106 (3)	0.073 (3)	0.021 (3)	-0.007 (3)	0.007 (3)
C19	0.073 (3)	0.103 (3)	0.071 (3)	0.004 (2)	-0.009 (2)	0.007 (2)
C20	0.085 (3)	0.117 (4)	0.119 (4)	-0.012 (3)	-0.012 (3)	0.050 (3)
C21	0.089 (4)	0.139 (4)	0.106 (4)	0.034 (3)	0.008 (3)	0.034 (3)
C22	0.150 (5)	0.096 (3)	0.110 (4)	-0.009 (3)	0.006 (3)	0.021 (3)
C23	0.231 (7)	0.101 (4)	0.122 (4)	0.003 (4)	0.046 (5)	-0.007 (4)

Geometric parameters (Å, °)

S1A—O2	1.434 (4)	C10—C11	1.356 (5)
S1A—C22	1.706 (5)	C10—H10	0.9300
S1A—C23	1.800 (6)	C11—C12	1.362 (5)
S1B—O2	1.379 (5)	C12—C13	1.381 (5)
S1B—C23	1.624 (7)	C12—H12	0.9300
S1B—C22	1.801 (6)	C13—H13	0.9300
O1—C14	1.367 (5)	C14—C19	1.374 (5)
O1—C11	1.406 (4)	C14—C15	1.378 (5)
N1—C7	1.314 (4)	C15—C16	1.372 (6)
N1—C6	1.388 (5)	C15—H15	0.9300
N2—C7	1.361 (4)	C16—C17	1.384 (6)
N2—C5	1.365 (5)	C16—C20	1.437 (7)
N2—H2	0.8600	C17—C18	1.390 (6)
N3—C20	1.137 (6)	C17—C21	1.433 (7)
N4—C21	1.132 (6)	C18—C19	1.375 (5)
C1—C6	1.384 (6)	C18—H18	0.9300
C1—C2	1.384 (7)	C19—H19	0.9300
C1—H1	0.9300	C22—H22A	0.9600
C2—C3	1.384 (7)	C22—H22B	0.9600
C2—H2A	0.9300	C22—H22C	0.9600
C3—C4	1.372 (7)	C22—H22D	0.9600
C3—H3	0.9300	C22—H22E	0.9600
C4—C5	1.395 (6)	C22—H22F	0.9600
C4—H4	0.9300	C23—H23A	0.9600
C5—C6	1.392 (5)	C23—H23B	0.9600
C7—C8	1.466 (5)	C23—H23C	0.9600
C8—C9	1.384 (5)	C23—H23D	0.9600
C8—C13	1.384 (5)	C23—H23E	0.9600
C9—C10	1.376 (5)	C23—H23F	0.9600
C9—H9	0.9300		
O2—S1A—C22	110.0 (3)	C12—C13—C8	121.0 (4)
O2—S1A—C23	104.1 (3)	C12—C13—H13	119.5
C22—S1A—C23	96.5 (3)	C8—C13—H13	119.5
O2—S1B—C23	116.7 (4)	O1—C14—C19	122.5 (4)
O2—S1B—C22	107.6 (4)	O1—C14—C15	117.4 (4)
C23—S1B—C22	99.4 (3)	C19—C14—C15	120.1 (4)

C14—O1—C11	117.2 (3)	C16—C15—C14	120.1 (4)
C7—N1—C6	104.9 (3)	C16—C15—H15	120.0
C7—N2—C5	106.9 (3)	C14—C15—H15	120.0
C7—N2—H2	126.5	C15—C16—C17	120.3 (4)
C5—N2—H2	126.5	C15—C16—C20	119.8 (5)
C6—C1—C2	118.1 (5)	C17—C16—C20	119.9 (5)
C6—C1—H1	120.9	C16—C17—C18	119.2 (5)
C2—C1—H1	120.9	C16—C17—C21	120.3 (5)
C1—C2—C3	120.1 (5)	C18—C17—C21	120.6 (5)
C1—C2—H2A	120.0	C19—C18—C17	120.1 (4)
C3—C2—H2A	120.0	C19—C18—H18	119.9
C4—C3—C2	123.3 (5)	C17—C18—H18	119.9
C4—C3—H3	118.4	C14—C19—C18	120.2 (4)
C2—C3—H3	118.4	C14—C19—H19	119.9
C3—C4—C5	116.2 (5)	C18—C19—H19	119.9
C3—C4—H4	121.9	N3—C20—C16	179.4 (6)
C5—C4—H4	121.9	N4—C21—C17	177.9 (7)
N2—C5—C6	105.9 (4)	S1A—C22—H22A	109.5
N2—C5—C4	132.5 (4)	S1A—C22—H22B	109.5
C6—C5—C4	121.6 (5)	H22A—C22—H22B	109.5
C1—C6—N1	129.8 (4)	S1A—C22—H22C	109.5
C1—C6—C5	120.7 (4)	H22A—C22—H22C	109.5
N1—C6—C5	109.4 (4)	H22B—C22—H22C	109.5
N1—C7—N2	112.8 (4)	S1B—C22—H22D	109.5
N1—C7—C8	126.0 (3)	S1B—C22—H22E	109.5
N2—C7—C8	121.2 (3)	H22D—C22—H22E	109.5
C9—C8—C13	118.0 (4)	S1B—C22—H22F	109.5
C9—C8—C7	122.0 (3)	H22D—C22—H22F	109.5
C13—C8—C7	120.0 (3)	H22E—C22—H22F	109.5
C10—C9—C8	120.6 (4)	S1A—C23—H23A	109.5
C10—C9—H9	119.7	S1A—C23—H23B	109.5
C8—C9—H9	119.7	H23A—C23—H23B	109.5
C11—C10—C9	120.2 (4)	S1A—C23—H23C	109.5
C11—C10—H10	119.9	H23A—C23—H23C	109.5
C9—C10—H10	119.9	H23B—C23—H23C	109.5
C10—C11—C12	120.8 (4)	S1B—C23—H23D	109.5
C10—C11—O1	120.3 (4)	S1B—C23—H23E	109.5
C12—C11—O1	118.8 (4)	H23D—C23—H23E	109.5
C11—C12—C13	119.4 (4)	S1B—C23—H23F	109.5
C11—C12—H12	120.3	H23D—C23—H23F	109.5
C13—C12—H12	120.3	H23E—C23—H23F	109.5
C6—C1—C2—C3	1.1 (7)	C8—C9—C10—C11	-1.2 (6)
C1—C2—C3—C4	-0.3 (7)	C9—C10—C11—C12	1.0 (6)
C2—C3—C4—C5	-0.2 (7)	C9—C10—C11—O1	176.6 (3)
C7—N2—C5—C6	-1.6 (4)	C14—O1—C11—C10	60.5 (5)
C7—N2—C5—C4	177.2 (4)	C14—O1—C11—C12	-123.7 (4)
C3—C4—C5—N2	-178.8 (4)	C10—C11—C12—C13	-0.4 (6)

C3—C4—C5—C6	-0.1 (6)	O1—C11—C12—C13	-176.1 (4)
C2—C1—C6—N1	177.1 (4)	C11—C12—C13—C8	-0.1 (6)
C2—C1—C6—C5	-1.4 (6)	C9—C8—C13—C12	-0.1 (5)
C7—N1—C6—C1	-178.8 (4)	C7—C8—C13—C12	-177.8 (4)
C7—N1—C6—C5	-0.2 (4)	C11—O1—C14—C19	36.2 (5)
N2—C5—C6—C1	179.9 (3)	C11—O1—C14—C15	-146.4 (3)
C4—C5—C6—C1	0.9 (6)	O1—C14—C15—C16	-177.3 (3)
N2—C5—C6—N1	1.1 (4)	C19—C14—C15—C16	0.1 (6)
C4—C5—C6—N1	-177.9 (3)	C14—C15—C16—C17	0.0 (6)
C6—N1—C7—N2	-0.9 (4)	C14—C15—C16—C20	-178.9 (4)
C6—N1—C7—C8	178.9 (3)	C15—C16—C17—C18	-0.3 (6)
C5—N2—C7—N1	1.6 (4)	C20—C16—C17—C18	178.6 (4)
C5—N2—C7—C8	-178.1 (3)	C15—C16—C17—C21	179.5 (4)
N1—C7—C8—C9	161.5 (3)	C20—C16—C17—C21	-1.6 (6)
N2—C7—C8—C9	-18.8 (5)	C16—C17—C18—C19	0.6 (6)
N1—C7—C8—C13	-20.9 (5)	C21—C17—C18—C19	-179.2 (4)
N2—C7—C8—C13	158.9 (3)	O1—C14—C19—C18	177.5 (4)
C13—C8—C9—C10	0.7 (5)	C15—C14—C19—C18	0.2 (5)
C7—C8—C9—C10	178.3 (3)	C17—C18—C19—C14	-0.6 (6)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2...O2	0.86	1.94	2.794 (5)	172
N2—H2...S1A	0.86	2.83	3.614 (4)	152
C9—H9...O2	0.93	2.40	3.175 (5)	141
C23—H23D...N4 ⁱ	0.96	2.63	3.500 (9)	151

Symmetry code: (i) $-x+1/2, y-1/2, z+1/2$.