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Crystal structure and Hirshfeld surface analysis of 5-oxo-7-phenyl-2-(phenylamino)-1*H*-[1,2,4]triazolo[1,5-*a*]pyridine-6,8-dicarbonitrile dimethyl sulfoxide monosolvate

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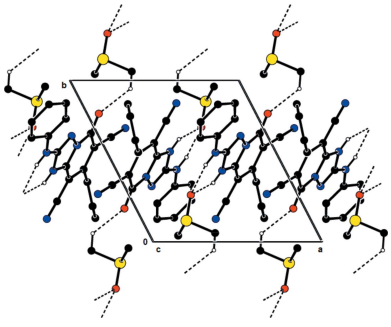
In the title compound, $C_{20}H_{12}N_6O\cdot C_2H_6OS$, the [1,2,4]triazolo[1,5-*a*]pyridine ring system is almost planar and makes dihedral angles of 16.33 (7) and 46.80 (7)°, respectively, with the phenylamino and phenyl rings. In the crystal, molecules are linked by intermolecular N—H···O and C—H···O hydrogen bonds into chains along the *b*-axis direction through the dimethyl sulfoxide solvent molecule, forming $C(10)R_1^2(6)$ motifs. These chains are connected *via* S—O···π interactions, π–π stacking interactions between the pyridine rings [centroid-to-centroid distance = 3.6662 (9) Å] and van der Waals interactions. A Hirshfeld surface analysis of the crystal structure indicates that the most important contributions to the crystal packing are from H···H (28.1%), C···H/H···C (27.2%), N···H/H···N (19.4%) and O···H/H···O (9.8%) interactions.

1. Chemical context

Diverse carbon–carbon and carbon–heteroatom bond-formation reactions are considered fundamental tools in organic synthesis. The reaction has also been amplified, extending these methods to different fields of chemistry, as well to the synthesis of natural products, in medicinal and pharmaceutical chemistry, material science, supramolecular chemistry *etc* (Çelik *et al.*, 2023; Chalkha *et al.*, 2023; Tapera *et al.*, 2022; Gurbanov *et al.*, 2020; Zubkov *et al.*, 2018). Triazolo[1,5-*a*]pyridines are accessible heterocyclic compounds and α-substituted pyridines are among the most widely used starting materials for their synthesis. The most common synthetic pathways to these compounds are well-reviewed in the literature (Jones & Abarca, 2010; Soliman *et al.*, 2014; Kotovshchikov *et al.*, 2021). The triazolo[1,5-*a*]pyridine moiety is a widespread structural motif in various synthetic biologically active compounds, possessing cardiovascular, trypanocidal, nitric oxide synthase inhibitor and antimicrobial activity, and in non-hormonal compounds with antifertility activity and leishmanicidal activity (Jones & Abarca, 2010; Mohamed *et al.*, 2013; Poustforoosh *et al.*, 2022).

A literature survey shows that the title compound **3** was previously synthesized in a two-pot reaction protocol (Barsy *et al.*, 2008), wherein the iminophosphorane 1-amino-6-(triphenylphosphoranylideneamino)-2-oxo-4-phenyl-1,2-dihydropyri-



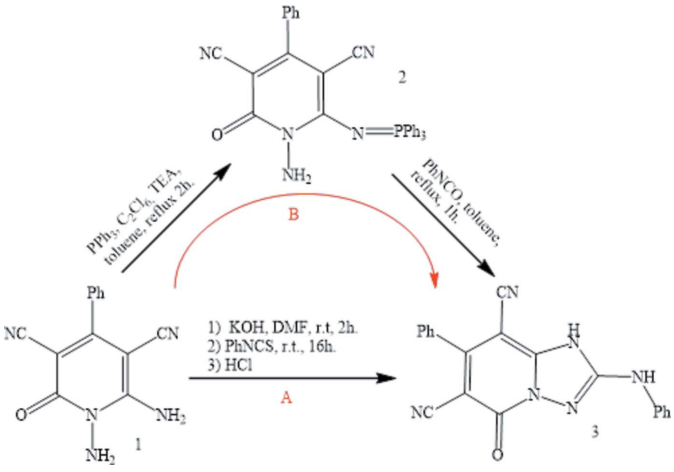
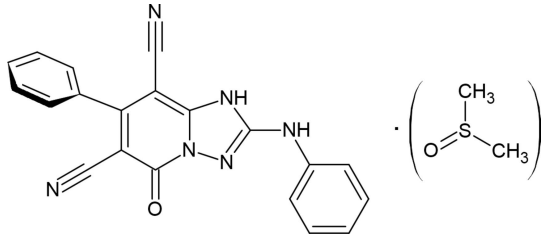


Figure 1
The synthesis routes or the title compound **3**.

dine-3,5-dicarbonitrile **2** prepared from 1,6-diaminopyridine **1** reacted with phenylisocyanate method to prepare **3** (*B* pathway, Fig. 1). Herein, we disclose a more straightforward one-pot synthesis method of **3** using the same starting compound **1** at room temperature (*A* pathway, Fig. 1), but through a different pathway.



Continuing our investigations of heterocyclic systems with biological activity and in the framework of our ongoing structural studies (Maharramov *et al.*, 2021, 2022; Naghiyev *et al.*, 2020, 2021, 2022), we report the crystal structure and Hirshfeld surface analysis of the title compound, 5-oxo-7-phenyl-2-(phenylamino)-1,5-dihydro-[1,2,4]triazolo[1,5-*a*]-pyridine-6,8-dicarbonitrile, which crystallized as a DMSO solvate.

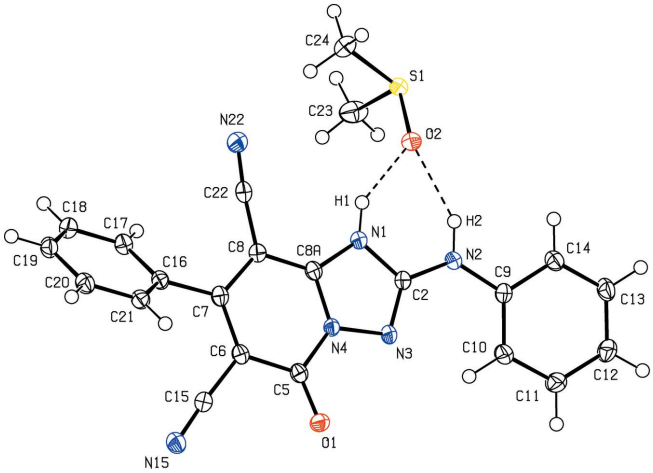


Figure 2
The molecular structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 50% probability level.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.88 (2)	1.84 (2)	2.6249 (16)	146.9 (17)
N2—H2···O2	0.90 (2)	2.07 (2)	2.8680 (16)	147.7 (17)
C10—H10···N3	0.95	2.39	2.9956 (19)	121
C23—H23*B*···O1^{i}	0.98	2.44	3.166 (2)	131
C24—H24*B*···N22	0.98	2.53	3.474 (2)	162

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

2. Structural commentary

In the title compound, (Fig. 2), the [1,2,4]triazolo[1,5-*a*]pyridine ring system (N1/N3/N4/C2/C5–C8/C8*A*) is almost planar [maximum deviation = 0.043 (2) Å for C5] and subtends dihedral angles of 16.33 (7) and 46.80 (7)°, respectively, with the phenylamino and phenyl rings (C9–C14 and C16–C21). The geometric properties of the title compound are normal and consistent with those of the related compounds listed in the *Database survey* (Section 4).

3. Supramolecular features

In the crystal, molecules are linked by intermolecular N—H···O and C—H···O hydrogen bonds into chains along the *b*-axis direction through the dimethyl sulfoxide solvent molecule, forming $C(10)R_1^2(6)$ motifs (Bernstein *et al.*, 1995; Table 1). These chains are connected *via* S—O···π interactions [S1—O2···*Cg*2^{i}: O2···*Cg*2^{i} = 3.1775 (14) Å; S1···*Cg*2^{i} = 4.0054 (8) Å; S1—O2···*Cg*2^{i} = 111.93 (6)°; symmetry code: (i) $1-x, 1-y, 1-z$; *Cg*2 is the centroid of the pyridine ring

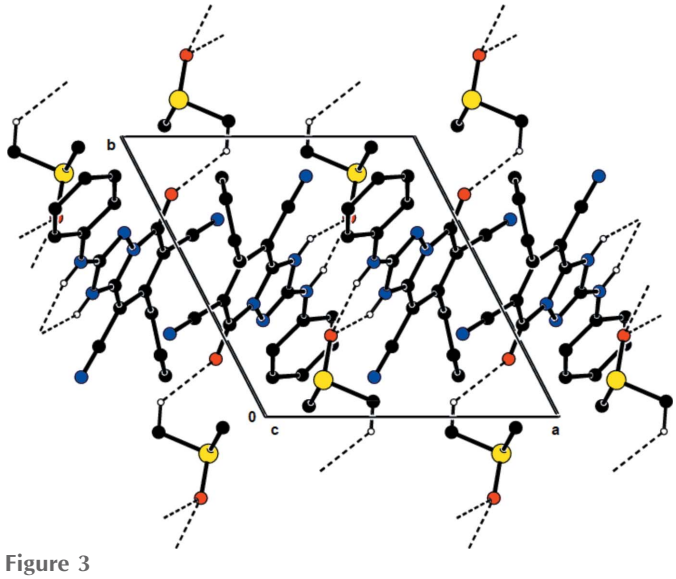


Figure 3
A view along the *c* axis of the N—H···O and C—H···O bonds in the title compound.

Table 2
Summary of short interatomic contacts (Å) in the title compound.

Contact	Distance	Symmetry operation
O1···H23*B*	2.44	−1 + *x*, −1 + *y*, *z*
H17···O1	2.65	−*x*, 1 − *y*, 1 − *z*
O1···H24*A*	2.63	1 − *x*, 1 − *y*, 1 − *z*
H1···O2	1.84	*x*, *y*, *z*
H14···C21	2.98	1 − *x*, 1 − *y*, 1 − *z*
H19···N15	2.73	−*x*, 1 − *y*, 2 − *z*
H18···N22	2.82	1 − *x*, 2 − *y*, 2 − *z*
C22···H23*B*	3.08	1 − *x*, 2 − *y*, 1 − *z*
C9···H20	3.05	*x*, *y*, −1 + *z*
C11···C11	3.53	−*x*, −*y*, −*z*
C12···H18	3.05	*x*, −1 + *y*, −1 + *z*
H19···H23*A*	2.54	*x*, *y*, 1 + *z*
H12···H24*A*	2.41	−1 + *x*, −1 + *y*, −1 + *z*
H12···S1	3.04	1 − *x*, 1 − *y*, −*z*
H23*C*···H23*C*	2.43	1 − *x*, 2 − *y*, 1 − *z*

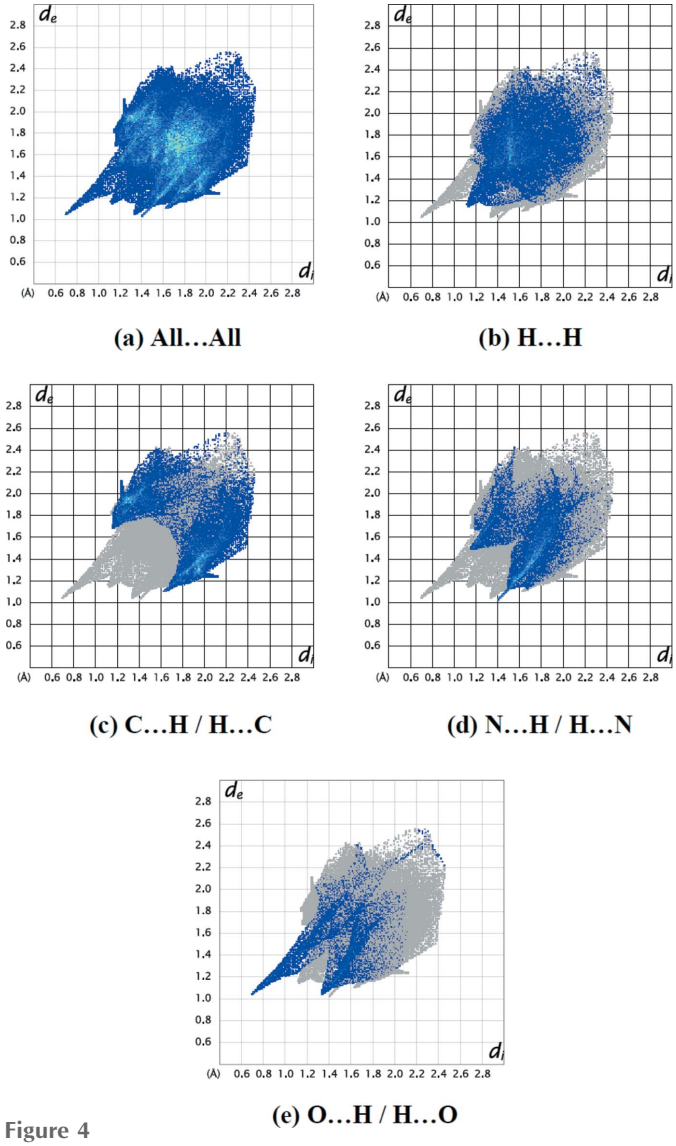


Figure 4
Two-dimensional fingerprint plots for title molecule showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) C···H/H···C, (*d*) N···H/H···N and (*e*) O···H/H···O interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

(N4/C5–C8/C8*A*)], π–π stacking interactions [$Cg2\cdots Cg2^{ii}$ = 3.6662 (9) Å; slippage = 1.468 Å; symmetry code: (ii) $-x, 1-y, 1-z$] and van der Waals interactions (Fig. 3).

CrystalExplorer17.5 (Spackman *et al.*, 2021) was used to compute Hirshfeld surfaces of the title molecule and two-dimensional fingerprints. The Hirshfeld surfaces were mapped over d_{norm} in the range −0.6769 (red) to +1.1190 (blue) a.u. The interactions given in Table 2 play a key role in the molecular packing of the title compound. The most important interatomic contact is H···H as it makes the highest contribution to the crystal packing (28.1%, Fig. 4*b*). Other major contributors are C···H/H···C (27.2%, Fig. 4*c*), N···H/H···N (19.4%, Fig. 4*d*) and N···H/H···N (9.8%, Fig. 4*e*) interactions. Smaller contributions are made by N···C/C···N (6.7%), C···C (3.6%), O···C/C···O(1.7%), N···N (1.5%), S···H/H···S (1.0%), O···N/N···O (0.7%), S···C/C···S(0.2%) and O···S/S···O (0.1%) interactions.

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.42, update of September 2021; Groom *et al.*, 2016) for the central nine-membered ring system '1,5-dihydro[1,2,4]triazolo[1,5-*a*]pyridine' yielded three compounds related to the title compound, *viz*. CSD refcodes HODQEZ (Gumus *et al.*, 2019), HODQID (Gumus *et al.*, 2019) and RETCAX (Aydemir *et al.*, 2018).

In the crystal of HODQEZ, pairs of N—H···N hydrogen bonds link the molecules, forming inversion dimers with an $R_2^2(8)$ ring motif. The dimers are linked by C—H···π and C—Br···π interactions, forming layers parallel to the *bc* plane. In the crystal of HODQID, molecules are linked by N—H···N and C—H···O hydrogen bonds, forming chains propagating along the *b*-axis direction. In the crystal of RETCAX, N—H···N hydrogen bonds link the molecules into supramolecular chains propagating along the *c*-axis direction.

5. Synthesis and crystallization

To a solution of 1,6-diamino-2-oxo-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile (0.82 g, 5.1 mmol) in DMF (25 mL) was added 10 mL of an aqueous solution of potassium hydroxide (0.28 g, 5.1 mmol). The mixture was stirred at room temperature for 2 h. Then an equimolar amount of phenylisothiocyanate (0.51 g, 5.2 mmol) was added to the vigorously stirred reaction mixture and left overnight. After completion of the reaction, monitored by TLC, the reaction mixture was acidified by adding conc. HCl (4 mL). The precipitated solids were separated by filtration and recrystallized from an ethanol/water (1:1) solution (yield 80%; m.p. 557–558 K). Single crystals were grown from a DMSO solution.

^{1}H NMR (300 MHz, DMSO-d_6, p.p.m.): 4.3 (*s*, 1H, NH); 6.9 (*t*, 1H, CH_{arom}, $^3J_{H-H}$ = 7.5 MHz); 7.3 (*t*, 2H, CH_{arom}, $^3J_{H-H}$ = 7.5 MHz); 7.5 (*m*, 5H, CH_{arom}); 7.7 (*d*, 2H, CH_{arom}, $^3J_{H-H}$ = 8.1 MHz); 9.6 (*s*, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6, p.p.m.): 76.4 (C_{quat}), 83.9 (C_{quat}), 117.0 (CH_{arom}), 117.5 (CN), 118.9 (CN), 120.7 (CH_{arom}), 128.9 (CH_{arom}), 129.0 (CH_{arom}),

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{12}N_6O{\cdot}C_2H_6OS$
M_r	430.48
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, b, c (Å)	9.87885 (12), 10.46018 (13), 11.48307 (12)
α, β, γ (°)	100.9305 (10), 105.3054 (11), 112.6790 (12)
V (Å^3)	997.81 (2)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	1.73
Crystal size (mm)	0.22 × 0.16 × 0.12
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2021)
T_{min}, T_{max}	0.660, 0.781
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22299, 4314, 4124
R_{int}	0.037
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.638
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.106, 1.08
No. of reflections	4314
No. of parameters	289
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.41, −0.51

Computer programs: *CrysAlis PRO* (Rigaku OD, 2021), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

129.2 (CH_{arom}), 129.9 (CH_{arom}), 136.3 (C_{arom}), 141.4 (C_{arom}), 152.2 (C_{quat}), 154.9 (C_{quat}), 156.2 (C_{quat}), 161.1 (C═O).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The NH H atoms were located in a difference-Fourier map [N1—H1 = 0.88 (2) Å and N2—H2 = 0.90 (2) Å] and refined with U_{iso}(H) = 1.2U_{eq}(N). Carbon-bound H atoms were positioned geometrically [C—H = 0.95–0.98 Å;] and were included in the refinement in the riding-model approximation with U_{iso}(H) = 1.2 or 1.5U_{eq}(C).

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Authors' contributions are as follows. Conceptualization, ANK and IGM; methodology, ANK, FNN and IGM; investigation, ANK, MA and HMM; writing (original draft), MA and ANK; writing (review and editing of the manuscript), MA and ANK; visualization, MA, ANK and IGM; funding acquisition, VNK, AB and ANK; resources, AB, VNK and HMM; supervision, ANK and MA.

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supporting information

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Computing details

Data collection: *CrysAlis PRO* 1.171.41.117a (Rigaku OD, 2021); cell refinement: *CrysAlis PRO* 1.171.41.117a (Rigaku OD, 2021); data reduction: *CrysAlis PRO* 1.171.41.117a (Rigaku OD, 2021); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

5-Oxo-7-phenyl-2-(phenylamino)-1*H*-[1,2,4]triazolo[1,5-*a*]pyridine-6,8-dicarbonitrile dimethyl sulfoxide monosolvate

Crystal data

$C_{20}H_{12}N_6O\cdot C_2H_6OS$
M_r = 430.48
Triclinic, $P\overline{1}$
a = 9.87885 (12) Å
b = 10.46018 (13) Å
c = 11.48307 (12) Å
α = 100.9305 (10)°
β = 105.3054 (11)°
γ = 112.6790 (12)°
V = 997.81 (2) Å^3
Z = 2
$F(000)$ = 448
D_x = 1.433 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 15870 reflections
θ = 4.8–79.3°
μ = 1.73 mm^{-1}
T = 100 K
Prism, colourless
0.22 × 0.16 × 0.12 mm

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer
Radiation source: micro-focus sealed X-ray tube
φ and ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2021)
T_{min} = 0.660, T_{max} = 0.781
22299 measured reflections
4314 independent reflections
4124 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 79.5°, θ_{min} = 4.2°
h = −12→9
k = −12→13
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.106
S = 1.08
4314 reflections
289 parameters
0 restraints

Primary atom site location: difference Fourier map
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 0.554P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}
Extinction correction: SHELXL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0029 (4)

Special details

Experimental. CrysAlisPro 1.171.41.117a (Rigaku OD, 2021) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

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}
O1	−0.06967 (12)	0.20611 (11)	0.42668 (10)	0.0214 (2)
N1	0.37412 (14)	0.55891 (13)	0.44627 (11)	0.0171 (2)
H1	0.465 (2)	0.635 (2)	0.4612 (18)	0.021*
C2	0.29261 (16)	0.44403 (15)	0.33251 (13)	0.0163 (3)
N2	0.35694 (14)	0.44663 (14)	0.24222 (12)	0.0189 (3)
H2	0.453 (2)	0.523 (2)	0.2678 (18)	0.023*
N3	0.15858 (14)	0.34368 (13)	0.32865 (11)	0.0178 (2)
N4	0.15615 (14)	0.40235 (12)	0.44782 (11)	0.0159 (2)
C5	0.03861 (16)	0.32893 (15)	0.49174 (14)	0.0177 (3)
C6	0.06152 (16)	0.41513 (15)	0.61676 (13)	0.0176 (3)
C7	0.19229 (16)	0.55162 (15)	0.69078 (13)	0.0174 (3)
C8	0.30798 (16)	0.61215 (15)	0.63984 (13)	0.0172 (3)
C8A	0.28510 (16)	0.53211 (15)	0.51784 (13)	0.0167 (3)
C9	0.29501 (17)	0.34391 (15)	0.11906 (13)	0.0179 (3)
C10	0.13802 (18)	0.23723 (17)	0.06025 (15)	0.0227 (3)
H10	0.0659	0.2308	0.1023	0.027*
C11	0.08828 (19)	0.13987 (18)	−0.06143 (15)	0.0262 (3)
H11	−0.0189	0.0670	−0.1026	0.031*
C12	0.19282 (19)	0.14769 (18)	−0.12345 (15)	0.0265 (3)
H12	0.1581	0.0794	−0.2056	0.032*
C13	0.34888 (19)	0.25654 (18)	−0.06421 (15)	0.0242 (3)
H13	0.4208	0.2634	−0.1065	0.029*
C14	0.39982 (17)	0.35488 (17)	0.05611 (14)	0.0211 (3)
H14	0.5062	0.4298	0.0958	0.025*
C15	−0.06863 (17)	0.35194 (15)	0.65539 (13)	0.0186 (3)
N15	−0.18041 (15)	0.29648 (14)	0.67726 (13)	0.0235 (3)
C16	0.21011 (16)	0.63048 (16)	0.82000 (13)	0.0178 (3)
C17	0.25352 (17)	0.78044 (16)	0.85674 (14)	0.0202 (3)
H17	0.2689	0.8319	0.7977	0.024*

C18	0.27428 (18)	0.85436 (16)	0.97909 (14)	0.0223 (3)
H18	0.3041	0.9563	1.0037	0.027*
C19	0.25145 (17)	0.77930 (17)	1.06577 (14)	0.0218 (3)
H19	0.2658	0.8301	1.1495	0.026*
C20	0.20758 (17)	0.62989 (17)	1.03002 (14)	0.0215 (3)
H20	0.1913	0.5788	1.0892	0.026*
C21	0.18757 (17)	0.55538 (16)	0.90782 (14)	0.0195 (3)
H21	0.1587	0.4537	0.8839	0.023*
C22	0.44758 (17)	0.74971 (16)	0.70142 (14)	0.0191 (3)
N22	0.56198 (16)	0.85887 (14)	0.74045 (13)	0.0251 (3)
S1	0.73840 (4)	0.86862 (4)	0.42677 (3)	0.01894 (11)
O2	0.63433 (12)	0.71002 (11)	0.41226 (10)	0.0215 (2)
C23	0.6060 (2)	0.94489 (18)	0.39068 (19)	0.0328 (4)
H23A	0.5447	0.9058	0.2985	0.049*
H23B	0.6662	1.0518	0.4170	0.049*
H23C	0.5340	0.9190	0.4366	0.049*
C24	0.83449 (19)	0.96161 (17)	0.59410 (15)	0.0249 (3)
H24A	0.9001	0.9187	0.6319	0.037*
H24B	0.7551	0.9518	0.6326	0.037*
H24C	0.9013	1.0657	0.6101	0.037*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0204 (5)	0.0187 (5)	0.0200 (5)	0.0048 (4)	0.0082 (4)	0.0039 (4)
N1	0.0170 (6)	0.0169 (5)	0.0174 (6)	0.0073 (5)	0.0079 (4)	0.0045 (4)
C2	0.0179 (6)	0.0170 (6)	0.0160 (6)	0.0096 (5)	0.0072 (5)	0.0054 (5)
N2	0.0173 (6)	0.0196 (6)	0.0181 (6)	0.0065 (5)	0.0089 (5)	0.0037 (5)
N3	0.0193 (6)	0.0192 (6)	0.0162 (6)	0.0087 (5)	0.0095 (5)	0.0049 (5)
N4	0.0174 (6)	0.0156 (5)	0.0157 (5)	0.0075 (5)	0.0080 (4)	0.0046 (4)
C5	0.0187 (6)	0.0193 (6)	0.0191 (7)	0.0108 (5)	0.0086 (5)	0.0083 (5)
C6	0.0195 (7)	0.0199 (7)	0.0177 (7)	0.0109 (6)	0.0091 (5)	0.0081 (5)
C7	0.0198 (7)	0.0198 (7)	0.0178 (7)	0.0128 (6)	0.0077 (5)	0.0080 (5)
C8	0.0181 (6)	0.0175 (6)	0.0172 (7)	0.0089 (5)	0.0073 (5)	0.0058 (5)
C8A	0.0175 (6)	0.0187 (6)	0.0178 (7)	0.0109 (5)	0.0075 (5)	0.0076 (5)
C9	0.0204 (7)	0.0190 (6)	0.0161 (6)	0.0102 (5)	0.0077 (5)	0.0058 (5)
C10	0.0210 (7)	0.0257 (7)	0.0210 (7)	0.0090 (6)	0.0106 (6)	0.0063 (6)
C11	0.0227 (7)	0.0272 (8)	0.0200 (7)	0.0057 (6)	0.0072 (6)	0.0032 (6)
C12	0.0298 (8)	0.0277 (8)	0.0168 (7)	0.0104 (7)	0.0088 (6)	0.0025 (6)
C13	0.0263 (8)	0.0301 (8)	0.0211 (7)	0.0144 (6)	0.0138 (6)	0.0085 (6)
C14	0.0197 (7)	0.0253 (7)	0.0202 (7)	0.0107 (6)	0.0093 (6)	0.0082 (6)
C15	0.0214 (7)	0.0187 (6)	0.0173 (7)	0.0105 (6)	0.0075 (5)	0.0058 (5)
N15	0.0241 (6)	0.0250 (6)	0.0239 (6)	0.0114 (5)	0.0123 (5)	0.0083 (5)
C16	0.0170 (6)	0.0211 (7)	0.0170 (7)	0.0100 (5)	0.0070 (5)	0.0058 (5)
C17	0.0222 (7)	0.0216 (7)	0.0206 (7)	0.0115 (6)	0.0105 (6)	0.0080 (6)
C18	0.0230 (7)	0.0212 (7)	0.0221 (7)	0.0107 (6)	0.0090 (6)	0.0039 (6)
C19	0.0209 (7)	0.0273 (7)	0.0174 (7)	0.0122 (6)	0.0079 (6)	0.0041 (6)
C20	0.0213 (7)	0.0266 (7)	0.0195 (7)	0.0122 (6)	0.0093 (6)	0.0087 (6)

C21	0.0187 (6)	0.0207 (7)	0.0199 (7)	0.0096 (5)	0.0078 (5)	0.0066 (6)
C22	0.0231 (7)	0.0216 (7)	0.0179 (6)	0.0130 (6)	0.0108 (6)	0.0072 (5)
N22	0.0255 (7)	0.0221 (6)	0.0252 (7)	0.0082 (5)	0.0114 (5)	0.0053 (5)
S1	0.01723 (18)	0.01879 (19)	0.01979 (19)	0.00657 (14)	0.00849 (13)	0.00567 (13)
O2	0.0199 (5)	0.0174 (5)	0.0244 (5)	0.0061 (4)	0.0091 (4)	0.0048 (4)
C23	0.0242 (8)	0.0246 (8)	0.0444 (10)	0.0123 (7)	0.0037 (7)	0.0111 (7)
C24	0.0269 (8)	0.0197 (7)	0.0224 (7)	0.0085 (6)	0.0062 (6)	0.0038 (6)

Geometric parameters (Å, º)

O1—C5	1.2277 (18)	C13—C14	1.384 (2)
N1—C8A	1.3439 (18)	C13—H13	0.9500
N1—C2	1.3792 (18)	C14—H14	0.9500
N1—H1	0.88 (2)	C15—N15	1.152 (2)
C2—N3	1.3178 (18)	C16—C17	1.399 (2)
C2—N2	1.3508 (18)	C16—C21	1.403 (2)
N2—C9	1.4102 (18)	C17—C18	1.388 (2)
N2—H2	0.90 (2)	C17—H17	0.9500
N3—N4	1.4000 (16)	C18—C19	1.392 (2)
N4—C8A	1.3504 (18)	C18—H18	0.9500
N4—C5	1.4003 (18)	C19—C20	1.393 (2)
C5—C6	1.4510 (19)	C19—H19	0.9500
C6—C7	1.403 (2)	C20—C21	1.391 (2)
C6—C15	1.4297 (19)	C20—H20	0.9500
C7—C8	1.4088 (19)	C21—H21	0.9500
C7—C16	1.4829 (19)	C22—N22	1.151 (2)
C8—C8A	1.3988 (19)	S1—O2	1.5253 (10)
C8—C22	1.429 (2)	S1—C24	1.7764 (16)
C9—C10	1.390 (2)	S1—C23	1.7788 (16)
C9—C14	1.394 (2)	C23—H23A	0.9800
C10—C11	1.394 (2)	C23—H23B	0.9800
C10—H10	0.9500	C23—H23C	0.9800
C11—C12	1.388 (2)	C24—H24A	0.9800
C11—H11	0.9500	C24—H24B	0.9800
C12—C13	1.391 (2)	C24—H24C	0.9800
C12—H12	0.9500		

C8A—N1—C2	106.74 (12)	C14—C13—H13	119.9
C8A—N1—H1	130.6 (12)	C12—C13—H13	119.9
C2—N1—H1	122.6 (12)	C13—C14—C9	119.96 (14)
N3—C2—N2	128.74 (13)	C13—C14—H14	120.0
N3—C2—N1	112.99 (12)	C9—C14—H14	120.0
N2—C2—N1	118.26 (13)	N15—C15—C6	175.03 (16)
C2—N2—C9	128.42 (13)	C17—C16—C21	119.42 (13)
C2—N2—H2	113.3 (12)	C17—C16—C7	120.65 (13)
C9—N2—H2	118.3 (12)	C21—C16—C7	119.90 (13)
C2—N3—N4	102.08 (11)	C18—C17—C16	120.31 (13)
C8A—N4—N3	112.16 (11)	C18—C17—H17	119.8

C8A—N4—C5	124.35 (12)	C16—C17—H17	119.8
N3—N4—C5	123.34 (11)	C17—C18—C19	120.05 (14)
O1—C5—N4	121.08 (13)	C17—C18—H18	120.0
O1—C5—C6	126.58 (13)	C19—C18—H18	120.0
N4—C5—C6	112.33 (12)	C18—C19—C20	120.12 (14)
C7—C6—C15	122.14 (13)	C18—C19—H19	119.9
C7—C6—C5	124.47 (13)	C20—C19—H19	119.9
C15—C6—C5	113.26 (12)	C21—C20—C19	120.12 (14)
C6—C7—C8	118.34 (13)	C21—C20—H20	119.9
C6—C7—C16	121.23 (13)	C19—C20—H20	119.9
C8—C7—C16	120.43 (13)	C20—C21—C16	119.98 (13)
C8A—C8—C7	117.77 (13)	C20—C21—H21	120.0
C8A—C8—C22	116.44 (12)	C16—C21—H21	120.0
C7—C8—C22	125.79 (13)	N22—C22—C8	173.67 (15)
N1—C8A—N4	106.01 (12)	O2—S1—C24	105.38 (7)
N1—C8A—C8	131.52 (13)	O2—S1—C23	105.07 (7)
N4—C8A—C8	122.47 (13)	C24—S1—C23	99.29 (8)
C10—C9—C14	120.41 (13)	S1—C23—H23A	109.5
C10—C9—N2	123.15 (13)	S1—C23—H23B	109.5
C14—C9—N2	116.43 (13)	H23A—C23—H23B	109.5
C9—C10—C11	118.88 (14)	S1—C23—H23C	109.5
C9—C10—H10	120.6	H23A—C23—H23C	109.5
C11—C10—H10	120.6	H23B—C23—H23C	109.5
C12—C11—C10	121.06 (14)	S1—C24—H24A	109.5
C12—C11—H11	119.5	S1—C24—H24B	109.5
C10—C11—H11	119.5	H24A—C24—H24B	109.5
C11—C12—C13	119.36 (14)	S1—C24—H24C	109.5
C11—C12—H12	120.3	H24A—C24—H24C	109.5
C13—C12—H12	120.3	H24B—C24—H24C	109.5
C14—C13—C12	120.29 (14)		

C8A—N1—C2—N3	−1.59 (16)	N3—N4—C8A—C8	179.38 (12)
C8A—N1—C2—N2	178.85 (12)	C5—N4—C8A—C8	−4.9 (2)
N3—C2—N2—C9	1.7 (2)	C7—C8—C8A—N1	−178.46 (13)
N1—C2—N2—C9	−178.83 (13)	C22—C8—C8A—N1	2.0 (2)
N2—C2—N3—N4	−179.43 (14)	C7—C8—C8A—N4	1.4 (2)
N1—C2—N3—N4	1.07 (15)	C22—C8—C8A—N4	−178.22 (13)
C2—N3—N4—C8A	−0.17 (14)	C2—N2—C9—C10	14.8 (2)
C2—N3—N4—C5	−175.92 (12)	C2—N2—C9—C14	−166.01 (14)
C8A—N4—C5—O1	−174.55 (13)	C14—C9—C10—C11	1.3 (2)
N3—N4—C5—O1	0.7 (2)	N2—C9—C10—C11	−179.53 (14)
C8A—N4—C5—C6	6.19 (19)	C9—C10—C11—C12	0.4 (2)
N3—N4—C5—C6	−178.59 (11)	C10—C11—C12—C13	−1.4 (3)
O1—C5—C6—C7	176.10 (14)	C11—C12—C13—C14	0.8 (2)
N4—C5—C6—C7	−4.69 (19)	C12—C13—C14—C9	0.8 (2)
O1—C5—C6—C15	−7.8 (2)	C10—C9—C14—C13	−1.9 (2)
N4—C5—C6—C15	171.43 (11)	N2—C9—C14—C13	178.89 (13)
C15—C6—C7—C8	−173.97 (12)	C6—C7—C16—C17	−134.34 (14)

C5—C6—C7—C8	1.8 (2)	C8—C7—C16—C17	46.20 (19)
C15—C6—C7—C16	6.6 (2)	C6—C7—C16—C21	47.42 (19)
C5—C6—C7—C16	−177.65 (12)	C8—C7—C16—C21	−132.04 (14)
C6—C7—C8—C8A	0.09 (19)	C21—C16—C17—C18	0.1 (2)
C16—C7—C8—C8A	179.57 (12)	C7—C16—C17—C18	−178.18 (13)
C6—C7—C8—C22	179.62 (13)	C16—C17—C18—C19	−0.2 (2)
C16—C7—C8—C22	−0.9 (2)	C17—C18—C19—C20	−0.1 (2)
C2—N1—C8A—N4	1.35 (14)	C18—C19—C20—C21	0.5 (2)
C2—N1—C8A—C8	−178.81 (14)	C19—C20—C21—C16	−0.6 (2)
N3—N4—C8A—N1	−0.77 (15)	C17—C16—C21—C20	0.3 (2)
C5—N4—C8A—N1	174.93 (12)	C7—C16—C21—C20	178.61 (13)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.88 (2)	1.84 (2)	2.6249 (16)	146.9 (17)
N2—H2···O2	0.90 (2)	2.07 (2)	2.8680 (16)	147.7 (17)
C10—H10···N3	0.95	2.39	2.9956 (19)	121
C23—H23*B*···O1^{i}	0.98	2.44	3.166 (2)	131
C24—H24*B*···N22	0.98	2.53	3.474 (2)	162

Symmetry code: (i) *x*+1, *y*+1, *z*.