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Bis[4-(5-anilino-1,3,4-thiadiazol-2-yl)pyridinium] sulfate

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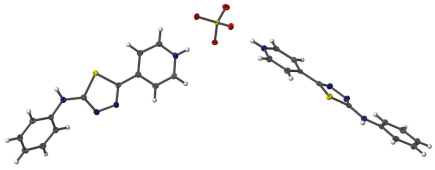
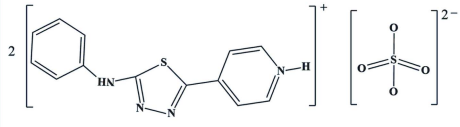
Structural data: full structural data are available from iucrdata.iucr.org

The asymmetric unit of the title salt, $2C_{13}H_{11}N_4S^+\cdot SO_4^{-}$, comprises two 4-(5-anilino-1,3,4-thiadiazol-2-yl)pyridinium cations and one sulfate anion. In one cation, the phenyl ring is inclined to the pyridinium ring at a dihedral angle of 34.82 (6)°, while in other cation the rings are almost coplanar with a corresponding dihedral angle 5.33 (10)°. Strong N—H···O hydrogen bonds link the cations to the sulfate anion in the asymmetric unit. Additional N—H···O, C—H···N, C—H···O and C—H···S hydrogen bonds further stabilize the crystal structure. Weak C—H···π and π–π interactions are also observed in the crystal structure.

3D view



Chemical scheme



Structure description

Derivatives of 1,3,4-thiadiazoles belong to an extensively studied and important class of heterocyclic compounds, which have diverse biological applications. These include antibacterial, antifungal, antimicrobial, antitumor, antioxidant, antitubercular and anti-convulsant activities (Shawali, 2014). Aroyl hydrazide reacts with phenyl isothiocynate to form thiosemicarbazide derivatives (Singh *et al.*, 2014), which can be subsequently cyclized to form the corresponding thiadiazole derivative in the presence of strong acid (Bharti *et al.*, 2013; Dulare *et al.*, 2010). Aroyl thiosemicarbazide derivatives generally convert to oxadiazoles in the presence of a weak acid or $Mn(OAc)_2$ (Paswan *et al.*, 2015).

The title compound is a salt containing two 4-(5-anilino-1,3,4-thiadiazol-2-yl)pyridinium cations with a sulfate anion balancing the charge (Fig. 1) (Abdel-Aziz *et al.*, 2015). The N1,C1–C5 pyridinium and C8–C13 phenyl rings are inclined an angle of 34.82 (6)° in one cation while the second cation is closer to planar, with a corresponding dihedral angle of 5.33 (10)°. An intramolecular C22—H22*A*···N7 hydrogen bond contributes to the

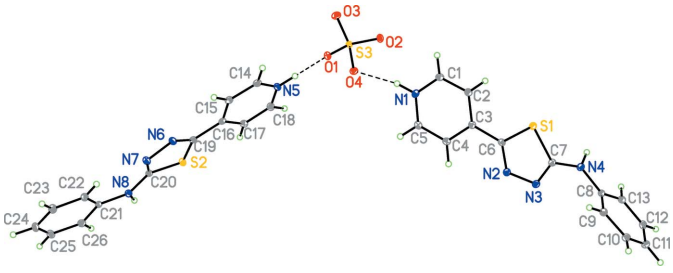


Figure 1
Molecular structure of the title compound, $C_{26}H_{22}N_8O_4S_3$, showing 50% probability displacement ellipsoids.

planarity of this cation. The C—N bond lengths, N2—C6 1.310 (2), N3—C7 1.324 (2), N6—C19 1.299 (2) and N7—C20 1.320 (2) Å, are well within the reported range (Singh *et al.*, 2007) and similar to standard C═N, 1.28 Å, bond lengths. The endocyclic C—S bonds S1—C6 1.7338 (17), S1—C7 1.7495 (18), S2—C19 1.7350 (17) and S2—C20 1.7399 (17) Å are intermediate in length between single and double bonds, suggesting considerable delocalization of charge in the thiadiazole ring.

In the crystal structure, N1—H1*B*···O2, N1—H1*B*···O4, and N5—H5*B*···O1 hydrogen bonds link the sulfate anion to the two cations in the asymmetric unit, Fig. 2. An extensive series of N4—H4*B*···O2, N8—H8*A*···O4, C1—H1*A*···N2, C4—H4*A*···O2, C4—H4*A*···S2, C5—H5*A*···O3, C15—H15*A*···O3 and C17—H17*A*···N2 hydrogen bonds also stabilize the crystal structure. The crystal packing is further reinforced by a weak C—H···π interaction (Table 1). An extensive series of π–π stacking interactions between the thiadiazole, phenyl and pyridinium rings is also observed with centroid-to-centroid distances *Cg*1···*Cg*1^{i} = 3.612 (7) Å; *Cg*3..*Cg*3^{ii} = 3.633 (3) Å; *Cg*4..*Cg*4^{iii} = 3.946 (5) Å; *Cg*4..*Cg*4^{iv} = 3.592 (5) Å; *Cg*5..*Cg*6^{iii} = 3.745 (6) Å; *Cg*5..*Cg*6^{iv} = 3.730 (7) Å. Ring centroids: *Cg*1 = S1/C6/N2/N3/C7; *Cg*3 = C8–C13; *Cg*4 = S2/C19/N6/N7/C20; *Cg*5 = N5/C14–C18; *Cg*6 = C21–C26; symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, 1-y, -z$; (iii) $1-x, -y, 1-z$; (iv) $2-x, -y, 1-z$. These contacts lead to a three-dimensional structure.

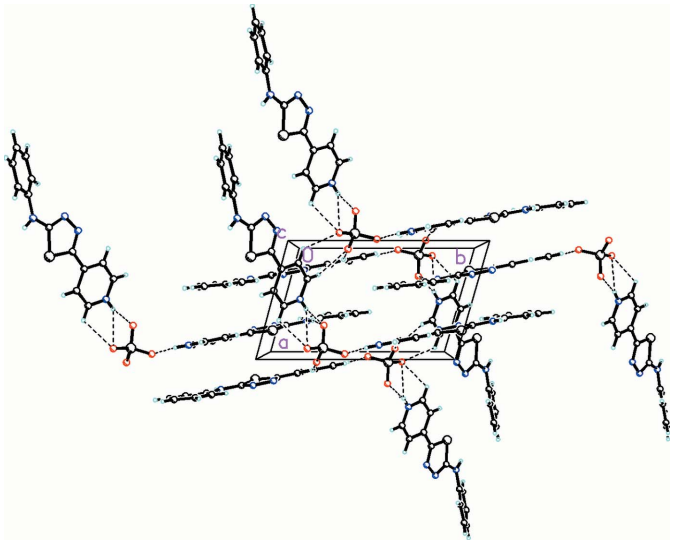


Figure 2
Molecular packing of $C_{26}H_{22}N_8O_4S_3$ viewed along the *c* axis. Dashed lines indicate pyridinium N—H···$O_{sulfate}$ and phenyl C—H···$N_{thiadiazole}$ interactions.

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

*Cg*2 is the centroid of the pyridine ring, N1/C1–C5.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···O2	0.88	2.50	3.054 (2)	122
N1—H1*B*···O4	0.88	1.86	2.730 (2)	168
N4—H4*B*···O2^{i}	0.88	1.98	2.7506 (19)	146
C1—H1*A*···N2^{ii}	0.95	2.66	3.490 (2)	146
C4—H4*A*···S2^{iii}	0.95	3.00	3.6835 (18)	130
C4—H4*A*···O2^{iv}	0.95	2.44	3.158 (2)	132
C5—H5*A*···O3^{iv}	0.95	2.45	3.242 (2)	140
N5—H5*B*···O1	0.88	1.67	2.5459 (19)	172
N8—H8*A*···O4^{v}	0.88	1.92	2.7875 (19)	167
C15—H15*A*···O3^{vi}	0.95	2.38	3.297 (2)	162
C17—H17*A*···N2^{vii}	0.95	2.50	3.240 (2)	135
C22—H22*A*···N7	0.95	2.30	2.933 (2)	123
C22—H22*A*···*Cg*2^{iv}	0.95	2.94	3.790 (5)	149

Symmetry codes: (i) $-x+1, -y+2, -z$; (ii) $x-1, y, z$; (iii) $x+1, y+1, z$; (iv) $x+1, y, z$; (v) $x, y-1, z$; (vi) $-x, -y+1, -z+1$; (vii) $x-1, y-1, z$.

Synthesis and crystallization

A mixture of isonicotinic acid hydrazide (2.740 g, 20.00 mmol) and phenyl isothiocyanate (2.4 ml, 20.00 mmol) in absolute ethanol (30 ml) was refluxed for 8 h (Fig. 3). The white precipitate of 1-isonicotinoyl-4-phenylthiosemicarbazide obtained upon cooling was filtered off and washed with water and ether (50:50 *v*/*v*). 1-Isonicotinoyl-4-phenyl thiosemicarbazide (2.72 g, 10.00 mmol) was added slowly to 10 ml conc. H_2SO_4 and stirred for 2 h with cooling. The mixture was poured over crushed ice and a yellow precipitate of bis-4-(5-phenylamino-[1,3,4]thiadiazol-2-yl)pyridinium sulfate was

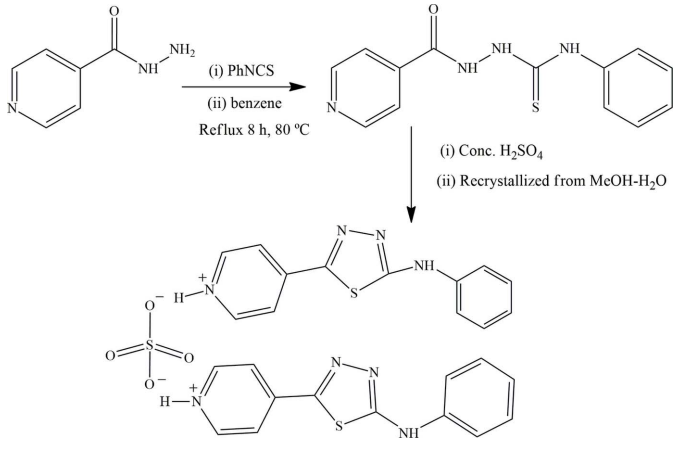


Figure 3
Reaction scheme showing the synthesis of the title compound, $C_{26}H_{22}N_8O_4S_3$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$2C_{13}H_{11}N_4S^+\cdot SO_4^{2-}$
M_r	606.69
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, b, c (Å)	7.4551 (8), 11.9212 (13), 15.1931 (16)
α, β, γ (°)	90.605 (6), 99.245 (5), 105.408 (6)
V (Å^3)	1282.8 (2)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.34
Crystal size (mm)	0.2 × 0.2 × 0.2
Data collection	
Diffractometer	Bruker SMART APEX CCD area-detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.675, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13929, 4529, 3975
R_{int}	0.030
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.074, 1.07
No. of reflections	4529
No. of parameters	370
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.39

Computer programs: *SMART* (Bruker, 2012), *SAINT* (Bruker, 2012), *SHELXS2013* (Sheldrick, 2008), *SHELXL2014/7* (Sheldrick, 2015), *SHELXTL* (Sheldrick, 2008).

obtained. It was filtered off, washed with cold water, dried. and recrystallized from a methanol–water mixture. Yellow crystals suitable for X-ray analysis were obtained by slow evaporation of the methanol–water solution over a period of 10–15 days. Yield: 85%; m.p. 497–499 K. Anal. Calc. for $C_{26}H_{22}N_8O_4S_3$ (%): C, 51.47; H, 3.65; N, 18.47; S, 15.86. Found: C, 51.75; H, 3.80; N, 18.86; S, 15.42. ^{1}H NMR (DMSO-d_6), δ (p.p.m.) = 10.76 (*s*, 2H, NH); 7.04 (*t*, 2H, phenyl H); 7.38 (*t*, 4H, phenyl H); 7.64 (*d*, 4H, phenyl H); 7.81 (*d*, 4H, pyridyl H); 8.67 (*d*, 4H, pyridyl H); 3.36 (*s*, 2H, pyridinium NH). ^{13}C NMR (DMSO-d_6), δ (p.p.m.) = 117.7 (C9, C13, C22, C26); 120.6 (C2, C4, C15, C17); 122.5 (C11, C24); 129.2 (C10, C12, C23, C25); 137.1 (C8, C21); 140.2 (C3, C16); 150.6 (C1, C5, C14, C18); 155.2 (C6, C19); 165.3 (C7, C20). IR (selected, KBr) 3200 [ν(N—H, pyridinium)], 3129 [ν(N—H, amine)], 1540 [ν(C=N)], 1120; [ν(N—N)], 754 [ν(C—S)] cm^{-1}.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x160446 [doi:10.1107/S2414314616004466]

Bis[4-(5-anilino-1,3,4-thiadiazol-2-yl)pyridinium] sulfate

Akhilesh Bharti, Paras Nath, Pooja Bharati, Sushil K. Gupta and Manoj K. Bharty

Bis[4-(5-anilino-1,3,4-thiadiazol-2-yl)pyridinium] sulfate

Crystal data

$2C_{13}H_{11}N_4S^+\cdot SO_4^{2-}$
M_r = 606.69
Triclinic, $P\overline{1}$
a = 7.4551 (8) Å
b = 11.9212 (13) Å
c = 15.1931 (16) Å
α = 90.605 (6)°
β = 99.245 (5)°
γ = 105.408 (6)°
V = 1282.8 (2) Å^3
Z = 2
$F(000)$ = 628
D_x = 1.571 Mg m^{-3}
Melting point = 497–499 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6650 reflections
θ = 2.9–34.1°
μ = 0.34 mm^{-1}
T = 100 K
Block, yellow
0.2 × 0.2 × 0.2 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Radiation source: sealed tube
Detector resolution: 8 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.675, T_{max} = 0.747
13929 measured reflections
4529 independent reflections
3975 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 25.0°, θ_{min} = 2.3°
h = −8→8
k = −14→14
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.074
S = 1.07
4529 reflections
370 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0311P)^2 + 0.7088P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.86656 (6)	1.16414 (4)	0.01533 (3)	0.01666 (12)
N1	0.5081 (2)	0.87361 (13)	0.24034 (9)	0.0152 (3)
H1B	0.4244	0.8302	0.2694	0.018*
N2	1.0918 (2)	1.07959 (13)	0.12273 (10)	0.0160 (3)
N3	1.2061 (2)	1.15163 (13)	0.07287 (10)	0.0169 (3)
N4	1.1793 (2)	1.27474 (13)	−0.04811 (10)	0.0167 (3)
H4B	1.0973	1.2920	−0.0905	0.020*
C1	0.4531 (3)	0.94483 (16)	0.18063 (11)	0.0166 (4)
H1A	0.3258	0.9487	0.1708	0.020*
C2	0.5815 (3)	1.01274 (16)	0.13334 (11)	0.0161 (4)
H2A	0.5432	1.0634	0.0909	0.019*
C3	0.7690 (2)	1.00609 (15)	0.14859 (11)	0.0140 (4)
C4	0.8198 (3)	0.93160 (15)	0.21186 (11)	0.0152 (4)
H4A	0.9461	0.9260	0.2236	0.018*
C5	0.6868 (3)	0.86629 (15)	0.25720 (11)	0.0153 (4)
H5A	0.7214	0.8157	0.3007	0.018*
C6	0.9129 (2)	1.07610 (15)	0.10135 (11)	0.0142 (4)
C7	1.1087 (2)	1.20118 (15)	0.01211 (11)	0.0149 (4)
C8	1.3723 (2)	1.32689 (15)	−0.04979 (12)	0.0152 (4)
C9	1.5098 (3)	1.35018 (16)	0.02694 (12)	0.0171 (4)
H9A	1.4763	1.3282	0.0833	0.021*
C10	1.6951 (3)	1.40552 (16)	0.02058 (13)	0.0201 (4)
H10A	1.7880	1.4233	0.0731	0.024*
C11	1.7473 (3)	1.43550 (16)	−0.06159 (13)	0.0211 (4)
H11A	1.8758	1.4703	−0.0658	0.025*
C12	1.6093 (3)	1.41396 (16)	−0.13740 (12)	0.0188 (4)
H12A	1.6435	1.4352	−0.1937	0.023*
C13	1.4219 (3)	1.36171 (15)	−0.13185 (12)	0.0164 (4)
H13A	1.3278	1.3497	−0.1838	0.020*
S2	0.23101 (6)	−0.01835 (4)	0.39241 (3)	0.01541 (11)
N5	0.1036 (2)	0.39691 (13)	0.32752 (10)	0.0170 (3)
H5B	0.0829	0.4592	0.3019	0.020*
N6	0.2292 (2)	0.09266 (13)	0.53715 (10)	0.0164 (3)
N7	0.2674 (2)	−0.00908 (13)	0.56431 (10)	0.0171 (3)
N8	0.3111 (2)	−0.18121 (13)	0.49976 (9)	0.0146 (3)
H8A	0.3196	−0.2130	0.4486	0.018*
C14	0.1019 (2)	0.38726 (16)	0.41526 (12)	0.0172 (4)
H14A	0.0773	0.4478	0.4486	0.021*
C15	0.1348 (2)	0.29209 (16)	0.45807 (12)	0.0165 (4)
H15A	0.1335	0.2865	0.5203	0.020*
C16	0.1704 (2)	0.20354 (15)	0.40815 (12)	0.0146 (4)
C17	0.1705 (3)	0.21536 (16)	0.31685 (12)	0.0168 (4)
H17A	0.1940	0.1562	0.2815	0.020*
C18	0.1365 (3)	0.31296 (16)	0.27849 (12)	0.0183 (4)
H18A	0.1362	0.3210	0.2163	0.022*

C19	0.2077 (2)	0.10113 (15)	0.45117 (11)	0.0143 (4)
C20	0.2736 (2)	−0.07629 (15)	0.49586 (11)	0.0141 (4)
C21	0.3381 (2)	−0.24591 (15)	0.57507 (11)	0.0144 (4)
C22	0.3396 (3)	−0.20759 (16)	0.66238 (12)	0.0168 (4)
H22A	0.3269	−0.1320	0.6746	0.020*
C23	0.3599 (3)	−0.28141 (17)	0.73117 (12)	0.0208 (4)
H23A	0.3616	−0.2554	0.7907	0.025*
C24	0.3777 (3)	−0.39180 (17)	0.71503 (13)	0.0216 (4)
H24A	0.3886	−0.4418	0.7627	0.026*
C25	0.3796 (3)	−0.42896 (16)	0.62851 (13)	0.0211 (4)
H25A	0.3930	−0.5045	0.6169	0.025*
C26	0.3619 (3)	−0.35642 (16)	0.55884 (12)	0.0180 (4)
H26A	0.3659	−0.3818	0.4999	0.022*
S3	0.08058 (6)	0.68673 (4)	0.27783 (3)	0.01258 (11)
O1	0.02984 (18)	0.56462 (10)	0.23978 (8)	0.0167 (3)
O2	0.08188 (17)	0.76412 (11)	0.20296 (8)	0.0169 (3)
O3	−0.05074 (18)	0.70046 (11)	0.33570 (8)	0.0202 (3)
O4	0.27727 (17)	0.71575 (11)	0.33018 (8)	0.0162 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0133 (2)	0.0196 (2)	0.0172 (2)	0.00468 (18)	0.00223 (17)	0.00663 (18)
N1	0.0154 (8)	0.0165 (8)	0.0134 (7)	0.0020 (6)	0.0049 (6)	0.0006 (6)
N2	0.0159 (8)	0.0166 (8)	0.0156 (7)	0.0041 (6)	0.0037 (6)	0.0035 (6)
N3	0.0147 (8)	0.0198 (8)	0.0170 (8)	0.0047 (6)	0.0043 (6)	0.0048 (6)
N4	0.0139 (8)	0.0214 (8)	0.0142 (7)	0.0040 (6)	0.0012 (6)	0.0065 (6)
C1	0.0152 (9)	0.0184 (10)	0.0165 (9)	0.0060 (7)	0.0011 (7)	−0.0003 (7)
C2	0.0163 (9)	0.0169 (9)	0.0150 (9)	0.0054 (7)	0.0005 (7)	0.0012 (7)
C3	0.0167 (9)	0.0127 (9)	0.0122 (8)	0.0033 (7)	0.0026 (7)	−0.0027 (7)
C4	0.0147 (9)	0.0160 (9)	0.0145 (8)	0.0051 (7)	0.0004 (7)	−0.0015 (7)
C5	0.0196 (10)	0.0147 (9)	0.0120 (8)	0.0060 (7)	0.0012 (7)	−0.0004 (7)
C6	0.0158 (9)	0.0138 (9)	0.0137 (8)	0.0055 (7)	0.0023 (7)	0.0005 (7)
C7	0.0148 (9)	0.0155 (9)	0.0141 (8)	0.0036 (7)	0.0026 (7)	−0.0009 (7)
C8	0.0148 (9)	0.0124 (9)	0.0196 (9)	0.0046 (7)	0.0047 (7)	0.0004 (7)
C9	0.0175 (10)	0.0180 (9)	0.0165 (9)	0.0050 (7)	0.0040 (7)	0.0034 (7)
C10	0.0169 (10)	0.0193 (10)	0.0229 (10)	0.0049 (8)	−0.0006 (8)	0.0004 (8)
C11	0.0146 (9)	0.0200 (10)	0.0293 (10)	0.0042 (8)	0.0060 (8)	0.0014 (8)
C12	0.0229 (10)	0.0165 (9)	0.0197 (9)	0.0064 (8)	0.0094 (8)	0.0030 (7)
C13	0.0177 (10)	0.0158 (9)	0.0166 (9)	0.0061 (7)	0.0027 (7)	−0.0002 (7)
S2	0.0192 (2)	0.0154 (2)	0.0125 (2)	0.00660 (18)	0.00193 (17)	0.00194 (17)
N5	0.0148 (8)	0.0134 (8)	0.0227 (8)	0.0041 (6)	0.0020 (6)	0.0032 (6)
N6	0.0173 (8)	0.0165 (8)	0.0165 (8)	0.0067 (6)	0.0022 (6)	0.0025 (6)
N7	0.0201 (8)	0.0169 (8)	0.0155 (7)	0.0077 (6)	0.0019 (6)	0.0022 (6)
N8	0.0164 (8)	0.0164 (8)	0.0117 (7)	0.0055 (6)	0.0026 (6)	0.0012 (6)
C14	0.0130 (9)	0.0161 (9)	0.0220 (9)	0.0032 (7)	0.0032 (7)	−0.0013 (7)
C15	0.0135 (9)	0.0179 (9)	0.0167 (9)	0.0020 (7)	0.0028 (7)	−0.0006 (7)
C16	0.0077 (8)	0.0165 (9)	0.0182 (9)	0.0013 (7)	0.0012 (7)	0.0019 (7)

C17	0.0163 (9)	0.0173 (9)	0.0171 (9)	0.0051 (7)	0.0023 (7)	−0.0002 (7)
C18	0.0185 (10)	0.0187 (10)	0.0171 (9)	0.0045 (8)	0.0022 (7)	0.0025 (8)
C19	0.0101 (9)	0.0169 (9)	0.0151 (9)	0.0025 (7)	0.0014 (7)	0.0003 (7)
C20	0.0100 (9)	0.0175 (9)	0.0139 (8)	0.0028 (7)	0.0013 (7)	0.0024 (7)
C21	0.0088 (9)	0.0155 (9)	0.0170 (9)	0.0011 (7)	0.0005 (7)	0.0038 (7)
C22	0.0152 (9)	0.0170 (9)	0.0171 (9)	0.0033 (7)	0.0011 (7)	0.0024 (7)
C23	0.0201 (10)	0.0246 (10)	0.0168 (9)	0.0051 (8)	0.0022 (7)	0.0034 (8)
C24	0.0190 (10)	0.0215 (10)	0.0222 (10)	0.0033 (8)	0.0007 (8)	0.0098 (8)
C25	0.0186 (10)	0.0153 (10)	0.0285 (10)	0.0047 (8)	0.0008 (8)	0.0038 (8)
C26	0.0142 (9)	0.0193 (10)	0.0194 (9)	0.0039 (7)	0.0006 (7)	0.0001 (8)
S3	0.0126 (2)	0.0137 (2)	0.0123 (2)	0.00470 (17)	0.00261 (16)	0.00257 (16)
O1	0.0199 (7)	0.0134 (6)	0.0168 (6)	0.0042 (5)	0.0035 (5)	0.0021 (5)
O2	0.0174 (7)	0.0162 (7)	0.0162 (6)	0.0037 (5)	0.0014 (5)	0.0057 (5)
O3	0.0180 (7)	0.0253 (7)	0.0200 (7)	0.0078 (6)	0.0074 (5)	0.0007 (6)
O4	0.0133 (6)	0.0215 (7)	0.0142 (6)	0.0057 (5)	0.0013 (5)	0.0034 (5)

Geometric parameters (Å, º)

S1—C6	1.7338 (17)	N5—C18	1.338 (2)
S1—C7	1.7495 (18)	N5—C14	1.341 (2)
N1—C1	1.339 (2)	N5—H5B	0.8800
N1—C5	1.342 (2)	N6—C19	1.299 (2)
N1—H1B	0.8800	N6—N7	1.371 (2)
N2—C6	1.310 (2)	N7—C20	1.320 (2)
N2—N3	1.367 (2)	N8—C20	1.352 (2)
N3—C7	1.324 (2)	N8—C21	1.404 (2)
N4—C7	1.345 (2)	N8—H8A	0.8800
N4—C8	1.412 (2)	C14—C15	1.372 (3)
N4—H4B	0.8800	C14—H14A	0.9500
C1—C2	1.382 (3)	C15—C16	1.399 (2)
C1—H1A	0.9500	C15—H15A	0.9500
C2—C3	1.403 (2)	C16—C17	1.396 (3)
C2—H2A	0.9500	C16—C19	1.461 (2)
C3—C4	1.391 (2)	C17—C18	1.372 (3)
C3—C6	1.465 (3)	C17—H17A	0.9500
C4—C5	1.373 (3)	C18—H18A	0.9500
C4—H4A	0.9500	C21—C22	1.396 (3)
C5—H5A	0.9500	C21—C26	1.400 (3)
C8—C13	1.393 (3)	C22—C23	1.389 (3)
C8—C9	1.394 (2)	C22—H22A	0.9500
C9—C10	1.384 (3)	C23—C24	1.381 (3)
C9—H9A	0.9500	C23—H23A	0.9500
C10—C11	1.389 (3)	C24—C25	1.386 (3)
C10—H10A	0.9500	C24—H24A	0.9500
C11—C12	1.387 (3)	C25—C26	1.386 (3)
C11—H11A	0.9500	C25—H25A	0.9500
C12—C13	1.387 (3)	C26—H26A	0.9500
C12—H12A	0.9500	S3—O3	1.4550 (13)

C13—H13A	0.9500	S3—O2	1.4717 (13)
S2—C19	1.7350 (17)	S3—O1	1.4885 (13)
S2—C20	1.7399 (17)	S3—O4	1.5008 (12)
C6—S1—C7	86.67 (8)	C14—N5—H5B	119.6
C1—N1—C5	122.10 (16)	C19—N6—N7	113.61 (14)
C1—N1—H1B	118.9	C20—N7—N6	111.60 (14)
C5—N1—H1B	118.9	C20—N8—C21	128.25 (15)
C6—N2—N3	113.95 (14)	C20—N8—H8A	115.9
C7—N3—N2	111.76 (15)	C21—N8—H8A	115.9
C7—N4—C8	126.25 (15)	N5—C14—C15	121.58 (16)
C7—N4—H4B	116.9	N5—C14—H14A	119.2
C8—N4—H4B	116.9	C15—C14—H14A	119.2
N1—C1—C2	120.00 (16)	C14—C15—C16	118.60 (17)
N1—C1—H1A	120.0	C14—C15—H15A	120.7
C2—C1—H1A	120.0	C16—C15—H15A	120.7
C1—C2—C3	119.33 (16)	C17—C16—C15	118.74 (16)
C1—C2—H2A	120.3	C17—C16—C19	120.84 (16)
C3—C2—H2A	120.3	C15—C16—C19	120.42 (16)
C4—C3—C2	118.58 (16)	C18—C17—C16	119.50 (17)
C4—C3—C6	119.12 (16)	C18—C17—H17A	120.3
C2—C3—C6	122.29 (16)	C16—C17—H17A	120.3
C5—C4—C3	119.74 (16)	N5—C18—C17	120.82 (17)
C5—C4—H4A	120.1	N5—C18—H18A	119.6
C3—C4—H4A	120.1	C17—C18—H18A	119.6
N1—C5—C4	120.24 (16)	N6—C19—C16	122.64 (16)
N1—C5—H5A	119.9	N6—C19—S2	114.22 (13)
C4—C5—H5A	119.9	C16—C19—S2	123.13 (13)
N2—C6—C3	122.10 (15)	N7—C20—N8	126.48 (16)
N2—C6—S1	113.74 (13)	N7—C20—S2	114.25 (13)
C3—C6—S1	124.14 (13)	N8—C20—S2	119.27 (13)
N3—C7—N4	126.24 (17)	C22—C21—C26	119.51 (16)
N3—C7—S1	113.85 (13)	C22—C21—N8	124.35 (16)
N4—C7—S1	119.91 (13)	C26—C21—N8	116.14 (15)
C13—C8—C9	119.77 (17)	C23—C22—C21	119.11 (17)
C13—C8—N4	117.24 (16)	C23—C22—H22A	120.4
C9—C8—N4	122.89 (16)	C21—C22—H22A	120.4
C10—C9—C8	119.66 (17)	C24—C23—C22	121.51 (17)
C10—C9—H9A	120.2	C24—C23—H23A	119.2
C8—C9—H9A	120.2	C22—C23—H23A	119.2
C9—C10—C11	120.90 (17)	C23—C24—C25	119.31 (17)
C9—C10—H10A	119.6	C23—C24—H24A	120.3
C11—C10—H10A	119.6	C25—C24—H24A	120.3
C12—C11—C10	119.10 (18)	C26—C25—C24	120.30 (17)
C12—C11—H11A	120.5	C26—C25—H25A	119.8
C10—C11—H11A	120.5	C24—C25—H25A	119.8
C11—C12—C13	120.72 (18)	C25—C26—C21	120.21 (17)
C11—C12—H12A	119.6	C25—C26—H26A	119.9

C13—C12—H12A	119.6	C21—C26—H26A	119.9
C12—C13—C8	119.75 (17)	O3—S3—O2	112.11 (7)
C12—C13—H13A	120.1	O3—S3—O1	110.58 (8)
C8—C13—H13A	120.1	O2—S3—O1	107.89 (7)
C19—S2—C20	86.32 (8)	O3—S3—O4	109.81 (7)
C18—N5—C14	120.77 (16)	O2—S3—O4	107.61 (7)
C18—N5—H5B	119.6	O1—S3—O4	108.73 (7)

C6—N2—N3—C7	−1.1 (2)	C19—N6—N7—C20	−0.1 (2)
C5—N1—C1—C2	0.8 (2)	C18—N5—C14—C15	0.5 (3)
N1—C1—C2—C3	0.0 (3)	N5—C14—C15—C16	−0.2 (3)
C1—C2—C3—C4	−0.6 (2)	C14—C15—C16—C17	−0.2 (3)
C1—C2—C3—C6	−179.57 (16)	C14—C15—C16—C19	179.49 (16)
C2—C3—C4—C5	0.4 (2)	C15—C16—C17—C18	0.2 (3)
C6—C3—C4—C5	179.41 (15)	C19—C16—C17—C18	−179.48 (17)
C1—N1—C5—C4	−1.0 (2)	C14—N5—C18—C17	−0.5 (3)
C3—C4—C5—N1	0.4 (2)	C16—C17—C18—N5	0.1 (3)
N3—N2—C6—C3	−178.51 (15)	N7—N6—C19—C16	−178.58 (15)
N3—N2—C6—S1	−0.15 (19)	N7—N6—C19—S2	0.4 (2)
C4—C3—C6—N2	−6.8 (2)	C17—C16—C19—N6	172.31 (17)
C2—C3—C6—N2	172.17 (16)	C15—C16—C19—N6	−7.3 (3)
C4—C3—C6—S1	175.01 (13)	C17—C16—C19—S2	−6.6 (2)
C2—C3—C6—S1	−6.0 (2)	C15—C16—C19—S2	173.74 (14)
C7—S1—C6—N2	0.94 (13)	C20—S2—C19—N6	−0.51 (14)
C7—S1—C6—C3	179.26 (15)	C20—S2—C19—C16	178.50 (15)
N2—N3—C7—N4	−178.79 (16)	N6—N7—C20—N8	178.81 (16)
N2—N3—C7—S1	1.79 (18)	N6—N7—C20—S2	−0.35 (19)
C8—N4—C7—N3	−10.2 (3)	C21—N8—C20—N7	5.0 (3)
C8—N4—C7—S1	169.24 (13)	C21—N8—C20—S2	−175.91 (14)
C6—S1—C7—N3	−1.55 (14)	C19—S2—C20—N7	0.48 (14)
C6—S1—C7—N4	178.98 (15)	C19—S2—C20—N8	−178.74 (15)
C7—N4—C8—C13	155.55 (17)	C20—N8—C21—C22	−3.4 (3)
C7—N4—C8—C9	−28.2 (3)	C20—N8—C21—C26	175.62 (17)
C13—C8—C9—C10	−1.4 (3)	C26—C21—C22—C23	−1.6 (3)
N4—C8—C9—C10	−177.54 (16)	N8—C21—C22—C23	177.37 (17)
C8—C9—C10—C11	−1.7 (3)	C21—C22—C23—C24	−0.3 (3)
C9—C10—C11—C12	2.9 (3)	C22—C23—C24—C25	1.5 (3)
C10—C11—C12—C13	−0.9 (3)	C23—C24—C25—C26	−0.6 (3)
C11—C12—C13—C8	−2.1 (3)	C24—C25—C26—C21	−1.3 (3)
C9—C8—C13—C12	3.3 (3)	C22—C21—C26—C25	2.4 (3)
N4—C8—C13—C12	179.68 (15)	N8—C21—C26—C25	−176.64 (16)

Hydrogen-bond geometry (Å, º)

Cg2 is the centroid of pyridine ring, N1/C1–C5.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···O2	0.88	2.50	3.054 (2)	122
N1—H1*B*···O4	0.88	1.86	2.730 (2)	168

N4—H4*B*···O2^{i}	0.88	1.98	2.7506 (19)	146
C1—H1*A*···N2^{ii}	0.95	2.66	3.490 (2)	146
C4—H4*A*···S2^{iii}	0.95	3.00	3.6835 (18)	130
C4—H4*A*···O2^{iv}	0.95	2.44	3.158 (2)	132
C5—H5*A*···O3^{iv}	0.95	2.45	3.242 (2)	140
N5—H5*B*···O1	0.88	1.67	2.5459 (19)	172
N8—H8*A*···O4^{v}	0.88	1.92	2.7875 (19)	167
C15—H15*A*···O3^{vi}	0.95	2.38	3.297 (2)	162
C17—H17*A*···N2^{vii}	0.95	2.50	3.240 (2)	135
C22—H22*A*···N7	0.95	2.30	2.933 (2)	123
C22—H22*A*···*Cg2*^{iv}	0.95	2.94	3.790 (5)	149

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