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5-Acetyl-3-amino-4-(4-methoxyphenyl)-6-methylthieno[2,3-*b*]pyridine-2-carbonitrile

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Keywords: crystal structure; hydrogen bond; π-stacking; thienopyridines.

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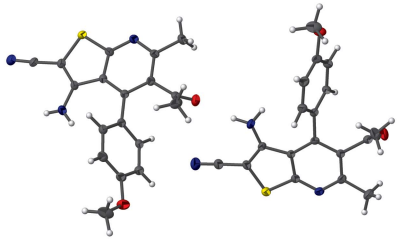
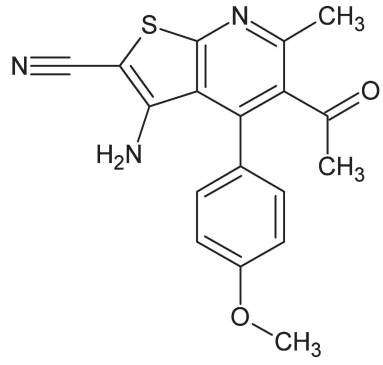
Structural data: full structural data are available from iucrdata.iucr.org

The asymmetric unit of the title compound, $C_{18}H_{15}N_3O_2S$, comprises two independent molecules, which differ primarily in the orientations of the acetyl and *p*-anisyl substituents, each being rotated in opposite directions from the mean plane of the pyridine ring. The major feature of the molecular packing is the formation of a two-dimensional network parallel to the (110) plane, being mediated by amine-N—H···O(carbonyl) hydrogen bonds involving one amine H atom of each independent molecule. The remaining amine-H atoms form significantly weaker N—H···O(methoxy) interactions.

3D view



Chemical scheme



Structure description

Thienopyridines were mentioned for the first time in 1913 (Steinkopf & Lutzkendorf, 1913). After more than a century of investigation, the chemistry of thieno[2,3-*b*]-pyridines is well known; this is primarily because of the great practical importance of many thieno[2,3-*b*]pyridine derivatives (Bakhite, 2003; Litvinov *et al.*, 2005). As part of our studies in this area, we now report the synthesis of the title thienopyridine derivative and its crystal structure.

The asymmetric unit comprises two independent molecules, Fig. 1, differing primarily in the orientations of the acetyl and *p*-anisyl groups. Thus, the C2—C3—C11—C12 and the C3—C2—C9—C10 torsion angles are, respectively, −54.4 (5) and −64.6 (5)°, while the corresponding angles in the second molecule (C20—C21—C29—C30 and C21—C20—C27—C28) are, respectively, 63.9 (4) and 66.2 (5)°. The thieno[2,3-*b*]pyridine core units deviate slightly from planarity, as seen from the dihedral angles of 1.7 (2) and

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O3^{i}	0.88 (5)	2.16 (5)	2.993 (4)	158 (4)
N2—H2B···O2^{ii}	0.84 (5)	2.53 (5)	3.092 (4)	126 (4)
N5—H5A···O1	0.88 (5)	2.04 (5)	2.911 (4)	169 (4)
N5—H5B···O4^{iii}	0.90 (6)	2.49 (6)	3.087 (4)	124 (5)

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

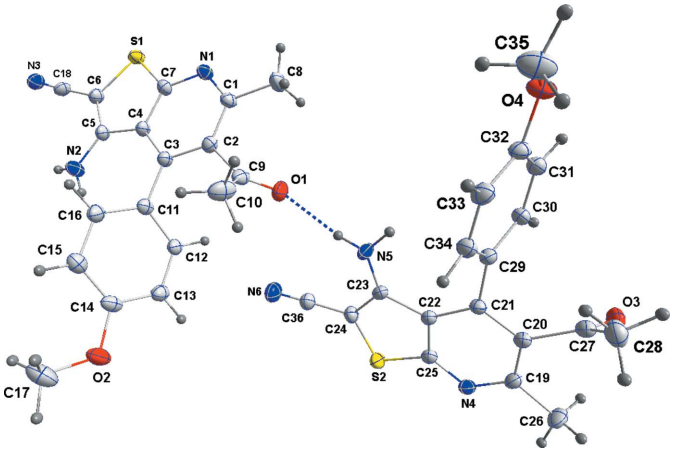


Figure 1
The asymmetric unit with the atom-labelling scheme and 50% probability displacement ellipsoids. The intermolecular N—H···O hydrogen bond is shown as a blue dashed line.

3.0 (2)°, respectively, between the S1/C4–C7 and the C7/N1/C1–C4 rings and between the S2/C22–C25 and the C25/N4/C19–C22 rings. The dihedral angle between the C7/N1/C1–C4 and the C11–C15 rings is 58.2 (1)° while the corresponding angle in the other molecule is 68.0 (1)°.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{18}H_{15}N_3O_2S$
M_r	337.39
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	150
a, b, c (Å)	10.5214 (4), 13.2896 (6), 13.3680 (6)
α, β, γ (°)	107.331 (3), 109.298 (2), 99.272 (3)
V (Å^3)	1612.66 (12)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	1.92
Crystal size (mm)	0.23 × 0.17 × 0.01
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.78, 0.98
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12139, 5977, 4333
R_{int}	0.059
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.066, 0.153, 1.06
No. of reflections	5977
No. of parameters	487
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.39

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

In the crystal, N—H···O hydrogen bonds (Table 1) form a two-dimensional network parallel to the (110) plane. π–π stacking interactions are observed between the thieno-

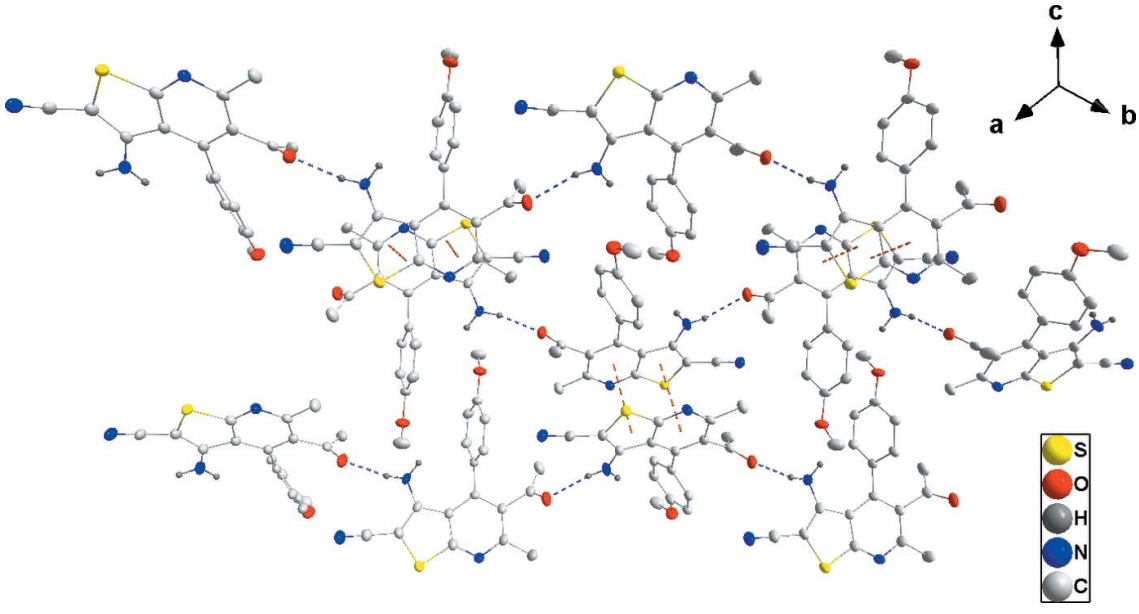


Figure 2
A portion of the packing projected onto (111). The N—H···O hydrogen bonds and the π-stacking interactions are shown, respectively, as blue and orange dashed lines.

[2,3-*b*]pyridine core units (Fig. 2) with $Cg1\cdots Cg2^{iv}$ = 3.643 (2) Å, dihedral angle = 1.86 (2)° and $Cg5\cdots Cg6^{v}$ = 3.645 (2) Å, dihedral angle = 3.0 (2)°. *Cg*1, *Cg*2, *Cg*5 and *Cg*6 are, respectively, the centroids of the S1/C4–C7, C7/N1/C1–C4, S2/C22–C25 and C25/N4/C19-C22 rings [symmetry codes: (iv) $-x+1, -y+2, -z$; (v) $-x+2, -y+1, -z+1$].

Synthesis and crystallization

The title compound was prepared by heating equimolar quantities of 5-acetyl-3-cyano-6-methyl-4-(4-methoxyphenyl)-pyridine-2(1*H*)-thione (2.98 g, 10 mmol) and chloroacetonitrile (0.755 g; 10 mmol) in absolute ethanol (25 ml) containing dissolved sodium (0.40 g) on a steam bath for 30 min. The product that formed on cooling was collected and recrystallized from ethanol solution to give yellow crystals of the title compound. Yield: 92%, m.p. 457 K. IR (KBr) ν = 3490, 3450, 3300, 3200 (NH_2), 2200 (CN), 1690 (C═O) cm^{-1}. ^1H NMR ($CDCl_3$): 7.27–7.29 (*d*, 2H, Ar—H), 7.03–7.06 (*d*, 2H, Ar—H), 4.40 (*s*, 2H, NH_2), 3.89 (*s*, 3H, OCH_3), 2.59 (*s*, 3H, CH_3), 2.00 (*s*, 3H, CH_3) p.p.m.

Refinement

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

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x171700 [https://doi.org/10.1107/S241431461701700X]

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Crystal data

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M_r = 337.39
Triclinic, $P\overline{1}$
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b = 13.2896 (6) Å
c = 13.3680 (6) Å
α = 107.331 (3)°
β = 109.298 (2)°
γ = 99.272 (3)°
V = 1612.66 (12) Å^3
Z = 4
$F(000)$ = 704
D_x = 1.390 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 7503 reflections
θ = 3.6–72.5°
μ = 1.92 mm^{-1}
T = 150 K
Plate, yellow
0.23 × 0.17 × 0.01 mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer
Radiation source: INCOATEC IμS micro-focus source
Mirror monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)
T_{min} = 0.78, T_{max} = 0.98
12139 measured reflections
5977 independent reflections
4333 reflections with $I > 2\sigma(I)$
R_{int} = 0.059
θ_{max} = 72.4°, θ_{min} = 3.6°
h = −12→12
k = −15→16
l = −14→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.153
S = 1.06
5977 reflections
487 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 2.7497P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.
Independent refinement of the hydrogen atoms of the methyl groups led to unsatisfactory geometries so these atoms were included as riding contributions in idealized positions.
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Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.23689 (9)	0.90661 (7)	−0.13718 (7)	0.0231 (2)
O1	0.6522 (3)	0.6773 (2)	0.1498 (2)	0.0351 (7)
O2	0.7270 (3)	1.0382 (2)	0.6220 (2)	0.0353 (7)
N1	0.4244 (3)	0.7950 (2)	−0.1008 (2)	0.0227 (6)
N2	0.3064 (4)	1.0390 (3)	0.1892 (3)	0.0292 (7)
H2A	0.235 (6)	1.065 (4)	0.189 (4)	0.051 (15)*
H2B	0.357 (5)	1.030 (4)	0.247 (4)	0.036 (12)*
N3	0.0500 (4)	1.1062 (3)	−0.0427 (3)	0.0308 (7)
C1	0.5206 (4)	0.7662 (3)	−0.0296 (3)	0.0221 (7)
C2	0.5605 (4)	0.8097 (3)	0.0901 (3)	0.0206 (7)
C3	0.4995 (3)	0.8856 (3)	0.1404 (3)	0.0193 (7)
C4	0.3954 (4)	0.9141 (3)	0.0656 (3)	0.0196 (7)
C5	0.3050 (4)	0.9837 (3)	0.0847 (3)	0.0209 (7)
C6	0.2199 (4)	0.9886 (3)	−0.0158 (3)	0.0230 (7)
C7	0.3657 (4)	0.8670 (3)	−0.0517 (3)	0.0207 (7)
C8	0.5859 (4)	0.6858 (3)	−0.0853 (3)	0.0306 (9)
H8A	0.5503	0.6136	−0.0839	0.046*
H8B	0.6884	0.7121	−0.0434	0.046*
H8C	0.5616	0.6794	−0.1647	0.046*
C9	0.6729 (4)	0.7743 (3)	0.1625 (3)	0.0253 (8)
C10	0.8111 (4)	0.8572 (4)	0.2440 (3)	0.0352 (10)
H10A	0.8538	0.8347	0.3078	0.053*
H10B	0.7964	0.9293	0.2735	0.053*
H10C	0.8738	0.8620	0.2042	0.053*
C11	0.5473 (4)	0.9303 (3)	0.2665 (3)	0.0205 (7)
C12	0.5447 (4)	0.8579 (3)	0.3246 (3)	0.0221 (7)
H12	0.501 (4)	0.779 (3)	0.278 (3)	0.018 (9)*
C13	0.6030 (4)	0.8964 (3)	0.4424 (3)	0.0247 (8)
H13	0.607 (5)	0.846 (4)	0.482 (4)	0.046 (13)*
C14	0.6686 (4)	1.0092 (3)	0.5059 (3)	0.0260 (8)
C15	0.6702 (4)	1.0819 (3)	0.4507 (3)	0.0253 (8)
H15	0.721 (4)	1.157 (4)	0.495 (4)	0.030 (11)*

C16	0.6095 (4)	1.0422 (3)	0.3315 (3)	0.0240 (8)
H16	0.611 (4)	1.097 (3)	0.296 (3)	0.024 (10)*
C17	0.8008 (5)	1.1515 (4)	0.6904 (3)	0.0410 (11)
H17A	0.8761	1.1751	0.6673	0.062*
H17B	0.8415	1.1611	0.7711	0.062*
H17C	0.7354	1.1960	0.6796	0.062*
C18	0.1260 (4)	1.0531 (3)	−0.0285 (3)	0.0240 (8)
S2	0.70225 (10)	0.41261 (8)	0.43430 (8)	0.0259 (2)
O3	1.1091 (3)	0.1552 (2)	0.2571 (2)	0.0335 (6)
O4	1.1927 (3)	0.4897 (2)	−0.0015 (2)	0.0287 (6)
N4	0.8917 (3)	0.3008 (2)	0.4501 (2)	0.0227 (6)
N5	0.8247 (4)	0.5513 (3)	0.2461 (3)	0.0303 (8)
H5A	0.765 (5)	0.586 (4)	0.221 (4)	0.047 (14)*
H5B	0.879 (6)	0.536 (5)	0.207 (5)	0.073 (18)*
N6	0.5335 (4)	0.6134 (3)	0.3391 (3)	0.0376 (8)
C19	0.9927 (4)	0.2682 (3)	0.4203 (3)	0.0223 (7)
C20	1.0409 (4)	0.3055 (3)	0.3468 (3)	0.0209 (7)
C21	0.9875 (4)	0.3811 (3)	0.3055 (3)	0.0188 (7)
C22	0.8835 (4)	0.4179 (3)	0.3385 (3)	0.0188 (7)
C23	0.8047 (4)	0.4922 (3)	0.3093 (3)	0.0224 (7)
C24	0.7053 (4)	0.4970 (3)	0.3559 (3)	0.0234 (7)
C25	0.8386 (4)	0.3710 (3)	0.4071 (3)	0.0214 (7)
C26	1.0517 (4)	0.1910 (3)	0.4715 (3)	0.0324 (9)
H26A	1.1544	0.2204	0.5099	0.049*
H26B	1.0263	0.1188	0.4108	0.049*
H26C	1.0131	0.1835	0.5271	0.049*
C27	1.1437 (4)	0.2550 (3)	0.3080 (3)	0.0245 (8)
C28	1.2866 (4)	0.3253 (3)	0.3390 (3)	0.0339 (9)
H28A	1.3434	0.3456	0.4205	0.051*
H28B	1.2792	0.3920	0.3232	0.051*
H28C	1.3315	0.2845	0.2935	0.051*
C29	1.0364 (4)	0.4152 (3)	0.2243 (3)	0.0204 (7)
C30	1.0068 (4)	0.3365 (3)	0.1162 (3)	0.0223 (7)
H30	0.948 (4)	0.257 (3)	0.091 (3)	0.029 (11)*
C31	1.0592 (4)	0.3648 (3)	0.0434 (3)	0.0233 (7)
H31	1.044 (4)	0.309 (3)	−0.031 (3)	0.024 (10)*
C32	1.1428 (4)	0.4706 (3)	0.0760 (3)	0.0222 (7)
C33	1.1734 (4)	0.5495 (3)	0.1826 (3)	0.0251 (8)
H33	1.232 (4)	0.620 (3)	0.207 (3)	0.024 (10)*
C34	1.1172 (4)	0.5215 (3)	0.2545 (3)	0.0238 (8)
H34	1.147 (4)	0.578 (3)	0.334 (3)	0.025 (10)*
C35	1.3009 (4)	0.5898 (4)	0.0386 (3)	0.0367 (10)
H35A	1.2621	0.6522	0.0541	0.055*
H35B	1.3381	0.5891	−0.0197	0.055*
H35C	1.3767	0.5969	0.1092	0.055*
C36	0.6106 (4)	0.5608 (3)	0.3455 (3)	0.0271 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0245 (5)	0.0287 (5)	0.0189 (4)	0.0118 (4)	0.0080 (3)	0.0112 (4)
O1	0.0442 (17)	0.0367 (17)	0.0394 (15)	0.0266 (14)	0.0216 (13)	0.0213 (13)
O2	0.0397 (16)	0.0409 (17)	0.0186 (12)	0.0116 (14)	0.0073 (12)	0.0073 (12)
N1	0.0217 (15)	0.0276 (16)	0.0193 (14)	0.0096 (13)	0.0081 (12)	0.0081 (12)
N2	0.0328 (19)	0.039 (2)	0.0220 (16)	0.0235 (16)	0.0122 (14)	0.0110 (14)
N3	0.0356 (19)	0.0325 (18)	0.0312 (17)	0.0168 (16)	0.0143 (14)	0.0167 (15)
C1	0.0220 (18)	0.0275 (19)	0.0219 (17)	0.0092 (15)	0.0130 (14)	0.0104 (15)
C2	0.0185 (17)	0.0222 (18)	0.0226 (17)	0.0071 (14)	0.0085 (14)	0.0094 (14)
C3	0.0187 (17)	0.0215 (18)	0.0189 (16)	0.0072 (14)	0.0080 (13)	0.0080 (14)
C4	0.0193 (17)	0.0210 (18)	0.0205 (16)	0.0085 (14)	0.0085 (14)	0.0086 (14)
C5	0.0217 (18)	0.0216 (18)	0.0230 (17)	0.0103 (15)	0.0109 (14)	0.0090 (14)
C6	0.0238 (18)	0.0248 (19)	0.0243 (17)	0.0105 (15)	0.0108 (14)	0.0114 (15)
C7	0.0203 (17)	0.0215 (18)	0.0200 (16)	0.0058 (14)	0.0094 (14)	0.0062 (14)
C8	0.034 (2)	0.035 (2)	0.0276 (19)	0.0198 (18)	0.0155 (17)	0.0100 (17)
C9	0.029 (2)	0.036 (2)	0.0258 (18)	0.0200 (17)	0.0188 (16)	0.0175 (16)
C10	0.025 (2)	0.058 (3)	0.034 (2)	0.019 (2)	0.0137 (17)	0.027 (2)
C11	0.0182 (17)	0.0262 (19)	0.0198 (16)	0.0106 (15)	0.0086 (13)	0.0089 (14)
C12	0.0245 (18)	0.025 (2)	0.0226 (17)	0.0129 (16)	0.0124 (15)	0.0099 (15)
C13	0.0263 (19)	0.031 (2)	0.0230 (18)	0.0133 (16)	0.0120 (15)	0.0126 (16)
C14	0.0241 (19)	0.038 (2)	0.0172 (16)	0.0150 (17)	0.0077 (14)	0.0089 (16)
C15	0.0223 (19)	0.026 (2)	0.0228 (17)	0.0069 (16)	0.0082 (15)	0.0047 (16)
C16	0.0276 (19)	0.025 (2)	0.0253 (18)	0.0126 (16)	0.0137 (15)	0.0115 (16)
C17	0.034 (2)	0.049 (3)	0.0225 (19)	0.001 (2)	0.0076 (17)	0.0003 (19)
C18	0.0252 (19)	0.028 (2)	0.0252 (18)	0.0122 (16)	0.0108 (15)	0.0157 (15)
S2	0.0263 (5)	0.0335 (5)	0.0259 (4)	0.0145 (4)	0.0145 (4)	0.0144 (4)
O3	0.0363 (16)	0.0298 (16)	0.0377 (15)	0.0193 (13)	0.0162 (13)	0.0103 (13)
O4	0.0308 (15)	0.0341 (15)	0.0252 (13)	0.0055 (12)	0.0164 (11)	0.0129 (11)
N4	0.0228 (15)	0.0283 (17)	0.0191 (14)	0.0085 (13)	0.0084 (12)	0.0111 (12)
N5	0.040 (2)	0.039 (2)	0.0326 (17)	0.0274 (17)	0.0211 (16)	0.0256 (16)
N6	0.037 (2)	0.042 (2)	0.044 (2)	0.0217 (17)	0.0195 (16)	0.0204 (17)
C19	0.0224 (18)	0.0239 (19)	0.0199 (16)	0.0083 (15)	0.0050 (14)	0.0102 (14)
C20	0.0232 (18)	0.0240 (18)	0.0160 (15)	0.0102 (15)	0.0072 (13)	0.0071 (14)
C21	0.0200 (17)	0.0225 (18)	0.0165 (15)	0.0073 (14)	0.0084 (13)	0.0089 (14)
C22	0.0198 (17)	0.0213 (17)	0.0153 (15)	0.0082 (14)	0.0063 (13)	0.0067 (13)
C23	0.0280 (19)	0.0250 (19)	0.0162 (15)	0.0134 (16)	0.0072 (14)	0.0092 (14)
C24	0.0227 (18)	0.0266 (19)	0.0236 (17)	0.0112 (15)	0.0116 (14)	0.0086 (15)
C25	0.0223 (18)	0.0236 (18)	0.0161 (16)	0.0086 (15)	0.0057 (14)	0.0059 (14)
C26	0.034 (2)	0.042 (2)	0.036 (2)	0.0201 (19)	0.0164 (18)	0.0272 (19)
C27	0.0288 (19)	0.030 (2)	0.0193 (16)	0.0141 (16)	0.0109 (15)	0.0116 (15)
C28	0.029 (2)	0.037 (2)	0.036 (2)	0.0147 (18)	0.0153 (17)	0.0080 (18)
C29	0.0218 (18)	0.0251 (19)	0.0191 (16)	0.0107 (15)	0.0092 (14)	0.0115 (14)
C30	0.0251 (18)	0.026 (2)	0.0190 (16)	0.0111 (16)	0.0108 (14)	0.0086 (15)
C31	0.0238 (18)	0.028 (2)	0.0206 (17)	0.0097 (15)	0.0105 (14)	0.0091 (15)
C32	0.0208 (18)	0.030 (2)	0.0222 (17)	0.0084 (15)	0.0116 (14)	0.0148 (15)
C33	0.029 (2)	0.021 (2)	0.0258 (18)	0.0064 (16)	0.0109 (15)	0.0109 (15)

C34	0.030 (2)	0.0230 (19)	0.0203 (17)	0.0092 (16)	0.0109 (15)	0.0084 (15)
C35	0.031 (2)	0.042 (2)	0.031 (2)	−0.0029 (19)	0.0138 (17)	0.0113 (19)
C36	0.028 (2)	0.029 (2)	0.0262 (18)	0.0123 (17)	0.0112 (16)	0.0099 (16)

Geometric parameters (Å, º)

S1—C7	1.728 (4)	S2—C25	1.726 (3)
S1—C6	1.747 (3)	S2—C24	1.751 (4)
O1—C9	1.221 (5)	O3—C27	1.224 (4)
O2—C14	1.368 (4)	O4—C32	1.374 (4)
O2—C17	1.428 (5)	O4—C35	1.427 (5)
N1—C1	1.335 (4)	N4—C25	1.338 (4)
N1—C7	1.346 (4)	N4—C19	1.342 (4)
N2—C5	1.365 (4)	N5—C23	1.355 (5)
N2—H2A	0.88 (5)	N5—H5A	0.88 (5)
N2—H2B	0.84 (5)	N5—H5B	0.90 (6)
N3—C18	1.155 (5)	N6—C36	1.151 (5)
C1—C2	1.414 (5)	C19—C20	1.417 (5)
C1—C8	1.507 (4)	C19—C26	1.498 (5)
C2—C3	1.404 (4)	C20—C21	1.393 (5)
C2—C9	1.501 (5)	C20—C27	1.512 (5)
C3—C4	1.407 (5)	C21—C22	1.412 (4)
C3—C11	1.480 (4)	C21—C29	1.496 (5)
C4—C7	1.406 (5)	C22—C25	1.408 (5)
C4—C5	1.459 (4)	C22—C23	1.448 (5)
C5—C6	1.373 (5)	C23—C24	1.384 (5)
C6—C18	1.411 (5)	C24—C36	1.408 (5)
C8—H8A	0.9800	C26—H26A	0.9800
C8—H8B	0.9800	C26—H26B	0.9800
C8—H8C	0.9800	C26—H26C	0.9800
C9—C10	1.496 (6)	C27—C28	1.487 (5)
C10—H10A	0.9800	C28—H28A	0.9800
C10—H10B	0.9800	C28—H28B	0.9800
C10—H10C	0.9800	C28—H28C	0.9800
C11—C16	1.392 (5)	C29—C34	1.388 (5)
C11—C12	1.408 (5)	C29—C30	1.405 (5)
C12—C13	1.378 (5)	C30—C31	1.378 (5)
C12—H12	0.99 (4)	C30—H30	1.02 (4)
C13—C14	1.402 (5)	C31—C32	1.386 (5)
C13—H13	0.97 (5)	C31—H31	0.99 (4)
C14—C15	1.382 (5)	C32—C33	1.390 (5)
C15—C16	1.394 (5)	C33—C34	1.389 (5)
C15—H15	0.95 (4)	C33—H33	0.93 (4)
C16—H16	0.99 (4)	C34—H34	1.01 (4)
C17—H17A	0.9800	C35—H35A	0.9800
C17—H17B	0.9800	C35—H35B	0.9800
C17—H17C	0.9800	C35—H35C	0.9800

C7—S1—C6	89.80 (16)	C25—S2—C24	90.02 (17)
C14—O2—C17	117.2 (3)	C32—O4—C35	116.9 (3)
C1—N1—C7	115.8 (3)	C25—N4—C19	116.5 (3)
C5—N2—H2A	116 (3)	C23—N5—H5A	121 (3)
C5—N2—H2B	120 (3)	C23—N5—H5B	119 (4)
H2A—N2—H2B	121 (4)	H5A—N5—H5B	115 (5)
N1—C1—C2	122.4 (3)	N4—C19—C20	122.1 (3)
N1—C1—C8	115.4 (3)	N4—C19—C26	115.3 (3)
C2—C1—C8	122.2 (3)	C20—C19—C26	122.6 (3)
C3—C2—C1	121.3 (3)	C21—C20—C19	120.6 (3)
C3—C2—C9	120.8 (3)	C21—C20—C27	121.1 (3)
C1—C2—C9	117.9 (3)	C19—C20—C27	118.2 (3)
C2—C3—C4	116.6 (3)	C20—C21—C22	117.7 (3)
C2—C3—C11	119.1 (3)	C20—C21—C29	119.2 (3)
C4—C3—C11	124.3 (3)	C22—C21—C29	123.0 (3)
C7—C4—C3	117.1 (3)	C25—C22—C21	116.7 (3)
C7—C4—C5	110.5 (3)	C25—C22—C23	111.3 (3)
C3—C4—C5	132.4 (3)	C21—C22—C23	131.9 (3)
N2—C5—C6	124.0 (3)	N5—C23—C24	123.4 (3)
N2—C5—C4	124.6 (3)	N5—C23—C22	125.4 (3)
C6—C5—C4	111.4 (3)	C24—C23—C22	111.1 (3)
C5—C6—C18	126.8 (3)	C23—C24—C36	126.7 (3)
C5—C6—S1	114.2 (3)	C23—C24—S2	113.9 (3)
C18—C6—S1	119.0 (3)	C36—C24—S2	119.4 (3)
N1—C7—C4	126.8 (3)	N4—C25—C22	126.2 (3)
N1—C7—S1	119.2 (3)	N4—C25—S2	120.2 (3)
C4—C7—S1	114.0 (2)	C22—C25—S2	113.6 (3)
C1—C8—H8A	109.5	C19—C26—H26A	109.5
C1—C8—H8B	109.5	C19—C26—H26B	109.5
H8A—C8—H8B	109.5	H26A—C26—H26B	109.5
C1—C8—H8C	109.5	C19—C26—H26C	109.5
H8A—C8—H8C	109.5	H26A—C26—H26C	109.5
H8B—C8—H8C	109.5	H26B—C26—H26C	109.5
O1—C9—C10	121.2 (3)	O3—C27—C28	121.5 (3)
O1—C9—C2	119.3 (4)	O3—C27—C20	118.5 (3)
C10—C9—C2	119.3 (3)	C28—C27—C20	119.9 (3)
C9—C10—H10A	109.5	C27—C28—H28A	109.5
C9—C10—H10B	109.5	C27—C28—H28B	109.5
H10A—C10—H10B	109.5	H28A—C28—H28B	109.5
C9—C10—H10C	109.5	C27—C28—H28C	109.5
H10A—C10—H10C	109.5	H28A—C28—H28C	109.5
H10B—C10—H10C	109.5	H28B—C28—H28C	109.5
C16—C11—C12	118.0 (3)	C34—C29—C30	118.5 (3)
C16—C11—C3	121.8 (3)	C34—C29—C21	122.0 (3)
C12—C11—C3	119.8 (3)	C30—C29—C21	119.4 (3)
C13—C12—C11	121.1 (3)	C31—C30—C29	120.2 (4)
C13—C12—H12	121 (2)	C31—C30—H30	119 (2)
C11—C12—H12	117 (2)	C29—C30—H30	121 (2)

C12—C13—C14	119.8 (3)	C30—C31—C32	120.6 (3)
C12—C13—H13	121 (3)	C30—C31—H31	121 (2)
C14—C13—H13	119 (3)	C32—C31—H31	119 (2)
O2—C14—C15	124.8 (3)	O4—C32—C31	116.1 (3)
O2—C14—C13	115.1 (3)	O4—C32—C33	123.8 (3)
C15—C14—C13	120.1 (3)	C31—C32—C33	120.0 (3)
C14—C15—C16	119.6 (4)	C34—C33—C32	119.2 (4)
C14—C15—H15	118 (3)	C34—C33—H33	119 (2)
C16—C15—H15	122 (3)	C32—C33—H33	121 (2)
C11—C16—C15	121.4 (3)	C29—C34—C33	121.4 (3)
C11—C16—H16	122 (2)	C29—C34—H34	120 (2)
C15—C16—H16	117 (2)	C33—C34—H34	118 (2)
O2—C17—H17A	109.5	O4—C35—H35A	109.5
O2—C17—H17B	109.5	O4—C35—H35B	109.5
H17A—C17—H17B	109.5	H35A—C35—H35B	109.5
O2—C17—H17C	109.5	O4—C35—H35C	109.5
H17A—C17—H17C	109.5	H35A—C35—H35C	109.5
H17B—C17—H17C	109.5	H35B—C35—H35C	109.5
N3—C18—C6	177.3 (4)	N6—C36—C24	178.7 (4)
C7—N1—C1—C2	−1.0 (5)	C25—N4—C19—C20	−0.2 (5)
C7—N1—C1—C8	−179.9 (3)	C25—N4—C19—C26	179.0 (3)
N1—C1—C2—C3	0.4 (6)	N4—C19—C20—C21	2.1 (5)
C8—C1—C2—C3	179.2 (3)	C26—C19—C20—C21	−177.0 (3)
N1—C1—C2—C9	−178.2 (3)	N4—C19—C20—C27	−173.6 (3)
C8—C1—C2—C9	0.6 (5)	C26—C19—C20—C27	7.3 (5)
C1—C2—C3—C4	1.2 (5)	C19—C20—C21—C22	−0.6 (5)
C9—C2—C3—C4	179.8 (3)	C27—C20—C21—C22	175.0 (3)
C1—C2—C3—C11	−178.7 (3)	C19—C20—C21—C29	−177.5 (3)
C9—C2—C3—C11	−0.2 (5)	C27—C20—C21—C29	−2.0 (5)
C2—C3—C4—C7	−2.1 (5)	C20—C21—C22—C25	−2.5 (5)
C11—C3—C4—C7	177.8 (3)	C29—C21—C22—C25	174.3 (3)
C2—C3—C4—C5	176.2 (4)	C20—C21—C22—C23	−178.1 (3)
C11—C3—C4—C5	−3.8 (6)	C29—C21—C22—C23	−1.3 (6)
C7—C4—C5—N2	178.6 (3)	C25—C22—C23—N5	178.8 (3)
C3—C4—C5—N2	0.2 (6)	C21—C22—C23—N5	−5.4 (6)
C7—C4—C5—C6	−2.7 (4)	C25—C22—C23—C24	−0.4 (4)
C3—C4—C5—C6	178.9 (4)	C21—C22—C23—C24	175.4 (4)
N2—C5—C6—C18	2.9 (6)	N5—C23—C24—C36	0.5 (6)
C4—C5—C6—C18	−175.9 (4)	C22—C23—C24—C36	179.7 (3)
N2—C5—C6—S1	−178.4 (3)	N5—C23—C24—S2	−179.7 (3)
C4—C5—C6—S1	2.8 (4)	C22—C23—C24—S2	−0.5 (4)
C7—S1—C6—C5	−1.8 (3)	C25—S2—C24—C23	1.0 (3)
C7—S1—C6—C18	177.1 (3)	C25—S2—C24—C36	−179.3 (3)
C1—N1—C7—C4	0.0 (5)	C19—N4—C25—C22	−3.4 (5)
C1—N1—C7—S1	−178.4 (3)	C19—N4—C25—S2	176.8 (3)
C3—C4—C7—N1	1.7 (6)	C21—C22—C25—N4	4.8 (5)
C5—C4—C7—N1	−177.0 (3)	C23—C22—C25—N4	−178.7 (3)

C3—C4—C7—S1	−179.9 (3)	C21—C22—C25—S2	−175.3 (2)
C5—C4—C7—S1	1.4 (4)	C23—C22—C25—S2	1.2 (4)
C6—S1—C7—N1	178.7 (3)	C24—S2—C25—N4	178.7 (3)
C6—S1—C7—C4	0.1 (3)	C24—S2—C25—C22	−1.2 (3)
C3—C2—C9—O1	118.9 (4)	C21—C20—C27—O3	−117.9 (4)
C1—C2—C9—O1	−62.5 (5)	C19—C20—C27—O3	57.7 (5)
C3—C2—C9—C10	−64.6 (5)	C21—C20—C27—C28	66.2 (5)
C1—C2—C9—C10	114.0 (4)	C19—C20—C27—C28	−118.1 (4)
C2—C3—C11—C16	118.5 (4)	C20—C21—C29—C34	−112.7 (4)
C4—C3—C11—C16	−61.5 (5)	C22—C21—C29—C34	70.5 (5)
C2—C3—C11—C12	−54.4 (5)	C20—C21—C29—C30	63.9 (4)
C4—C3—C11—C12	125.6 (4)	C22—C21—C29—C30	−112.9 (4)
C16—C11—C12—C13	−0.5 (5)	C34—C29—C30—C31	1.1 (5)
C3—C11—C12—C13	172.6 (3)	C21—C29—C30—C31	−175.6 (3)
C11—C12—C13—C14	−1.3 (5)	C29—C30—C31—C32	0.6 (5)
C17—O2—C14—C15	−3.2 (5)	C35—O4—C32—C31	−167.6 (3)
C17—O2—C14—C13	177.2 (3)	C35—O4—C32—C33	11.4 (5)
C12—C13—C14—O2	−177.9 (3)	C30—C31—C32—O4	178.4 (3)
C12—C13—C14—C15	2.5 (5)	C30—C31—C32—C33	−0.6 (5)
O2—C14—C15—C16	178.7 (3)	O4—C32—C33—C34	179.9 (3)
C13—C14—C15—C16	−1.7 (5)	C31—C32—C33—C34	−1.2 (5)
C12—C11—C16—C15	1.3 (5)	C30—C29—C34—C33	−2.9 (5)
C3—C11—C16—C15	−171.7 (3)	C21—C29—C34—C33	173.7 (3)
C14—C15—C16—C11	−0.2 (5)	C32—C33—C34—C29	3.0 (5)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O3^{i}	0.88 (5)	2.16 (5)	2.993 (4)	158 (4)
N2—H2*B*···O2^{ii}	0.84 (5)	2.53 (5)	3.092 (4)	126 (4)
N5—H5*A*···O1	0.88 (5)	2.04 (5)	2.911 (4)	169 (4)
N5—H5*B*···O4^{iii}	0.90 (6)	2.49 (6)	3.087 (4)	124 (5)

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