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Ethyl 3-amino-2-cyano-4-(4-methoxyphenyl)-6-methylthieno[2,3-*b*]pyridine-5-carboxylate

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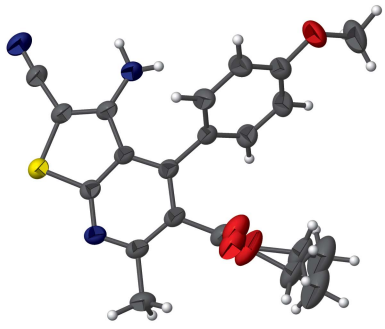
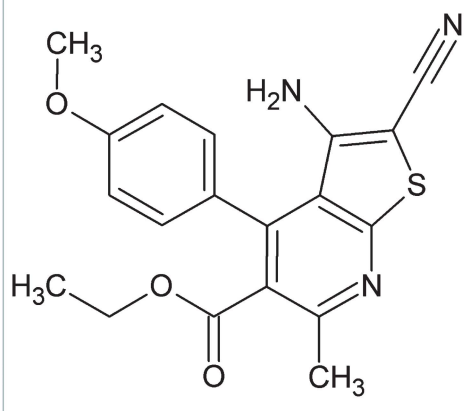
Structural data: full structural data are available from iucrdata.iucr.org

In the title molecule, $C_{19}H_{17}N_3O_3S$, the bicyclic core is planar [maximum deviation = 0.0205 (1) Å] In the crystal, the molecules stack along the *a*-axis direction through π–π-stacking interactions between the bicyclic units with a small alternation in the interplanar distances along the stack. The stacks are held together by N—H···N and C—H···O hydrogen bonds. The carboethoxy substituent is disordered over several closely spaced sites and was modeled as having two-component disorder [occupancy ratio 0.548 (16):0.452 (16)]. The final refinement was as a two-component twin.

3D view



Chemical scheme



Structure description

The spectrum of biological activities of thienopyridine derivatives is rather broad and includes antiviral (Schnute *et al.*, 2007; Attaby *et al.*, 2007), antidiabetic (Bahekar *et al.* 2007), antimicrobial (Abdel-Rahman *et al.*, 2003; Hussein *et al.* 2000), anti-inflammatory (Madhusudana *et al.*, 2012), antihypertensive (Ribichini *et al.*, 2007), antitumor (Hayakawa *et al.*, 2004), and neurotropic activities (Krauze *et al.*, 1999). As part of our studies in this area, we undertook the synthesis and crystal structure of the title compound (Fig. 1).

As expected, the bicyclic unit is planar [maximum deviations of −0.0151 (1) and 0.0205 (1) Å for atoms C1 and C6, respectively] while the dihedral angle between the mean planes of the C1/C2/C3/N3/C4/C7 unit and the C8–C13 ring is 65.71 (17)°. In the crystal, the molecules stack in a head-to-tail fashion along the *a*-axis direction through π–π-stacking interactions between the bicyclic units with the centroid–centroid distances alternating between 3.693 (2) and 3.637 (2) Å along the stack (Fig. 2). The stacks are

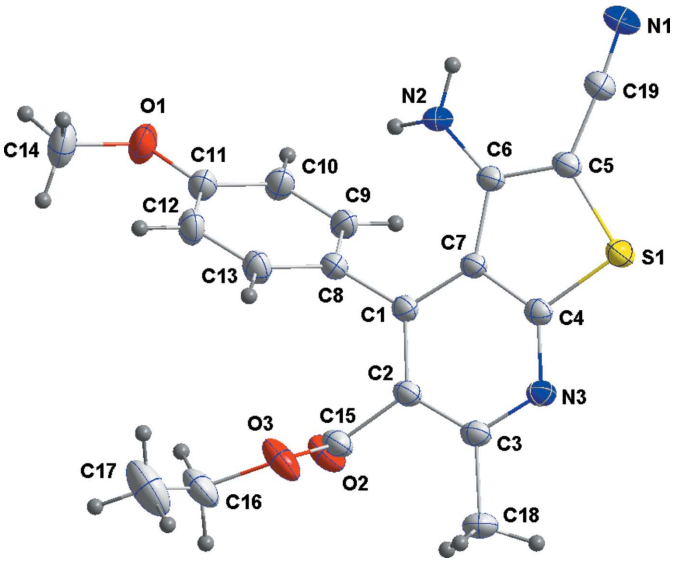


Figure 1
The title molecule with labeling scheme and 50% probability ellipsoids. Only one orientation of the disordered ester group is shown.

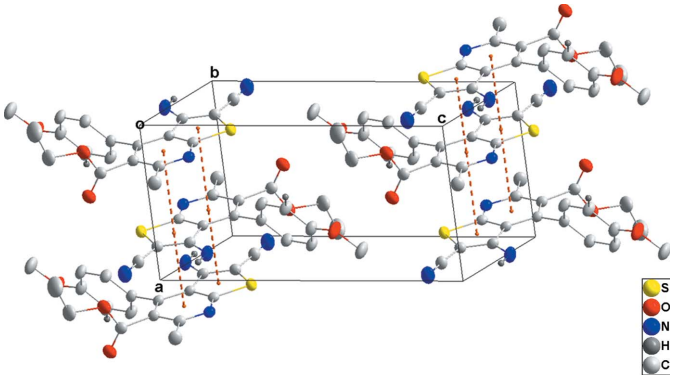


Figure 2
Oblique view of the packing showing two of the π–π-stacks.

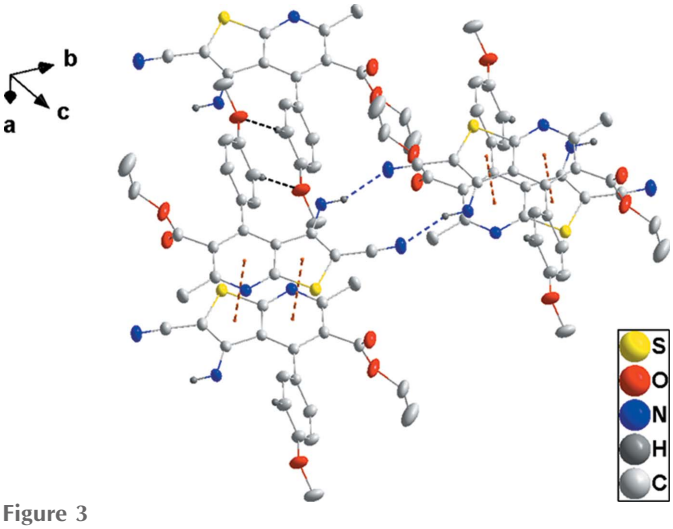


Figure 3
Oblique view of the intermolecular interactions. C—H···O and N—H···N hydrogen bonds are shown, respectively, as black and blue dashed lines while the π–π-stacking interactions are shown as orange dashed lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2B···N1^{i}	0.91	2.17	3.030 (4)	159
C10—H10···O1^{ii}	0.94	2.46	3.366 (4)	162
C16A—H16D···O1^{iii}	0.98	2.63	3.486 (14)	146
C17A—H17E···N1^{iv}	0.97	2.56	3.47 (2)	156

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{17}N_3O_3S$
M_r	367.41
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	225
a, b, c (Å)	7.2713 (2), 11.3575 (3), 12.7769 (4)
α, β, γ (°)	67.004 (1), 79.649 (1), 72.217 (1)
V (Å^3)	922.71 (5)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	1.76
Crystal size (mm)	0.22 × 0.15 × 0.07
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*TWINABS*; Sheldrick, 2009)
T_{min}, T_{max}	0.70, 0.89
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13203, 13203, 8440
R_{int}	0.039
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.067, 0.210, 1.05
No. of reflections	13203
No. of parameters	250
No. of restraints	31
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.72, −0.75

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014/7* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

associated along the *a*-axis direction by pairwise N2—H2B···N1^{i} [symmetry code: (i) $-x, -y+2, -z+2$] hydrogen bonds and along the *c*-axis direction by pairwise C10—H10···O1^{ii} [symmetry code: (ii) $-x+1, -y+2, -z+1$] hydrogen bonds (Table 1 and Fig. 3).

Synthesis and crystallization

The title compound was prepared by heating equimolar quantities of 5-ethoxycarbonyl-3-cyano-6-methyl-4-(4-methoxyphenyl)pyridine-2(1*H*)-thione (3.284 g; 10 mmol) and chloroacetonitrile (0.76 g; 10 mmol) in absolute ethanol (30 ml) containing dissolved sodium (0.50 g) under reflux for 20 min. The solid that formed on cooling was collected by filtration and recrystallized from ethanol solution as yellow crystals of the title compound. Yield: 90%, m.p.: 457–458 K.

IR (KBr) cm^{-1}: 3476, 3342 (NH_2); 2976 (C—H, aliphatic); 2199 (C≡N); 1729 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) p.p.m.: 7.27–7.30 (*dd*, *J* = 2.4 Hz, 2H, Ar—H), 7.00–7.03 (*dd*, *J* = 2.4 Hz, 2H, Ar—H), 4.32 (*s*, 2H, NH_2), 4.01–4.06 (*q*, *J* = 7.0 Hz, 2H, OCH_2), 3.88 (*s*, 3H, OCH_3), 2.67 (*s*, 3H, CH_3), 0.99–1.03 (*t*, *J* = 7.2 Hz, 3H, CH_3 of ester); ^{13}C NMR (100 MHz, $CDCl_3$) p.p.m.: 167.5, 161.3, 160.6, 156.3, 149.3, 143.8, 130.0 (CH), 127.6, 125.4, 118.5, 114.7, 114.1 (CH),61.6 (OCH_2), 55.4 (OCH_3), 23.1 (CH_3 at C-6), 13.8 (CH_3 of ester group). MS: *m*/*z* 367 (*M*+, 100%), 339 (*M*±CO, 10%), 322 (*M*±OEt, 15%), 321 (*M*± EtOH, 15%). Analysis calculated for $C_{19}H_{17}N_3O_3S$ (367.1): C, 62.11; H, 4.66; N, 11.44; S, 8.73%. Found: C, 62.00; H, 4.70; N, 11.83; S, 9.02%.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The carboethoxy substituent is disordered over several closely spaced sites and was modeled as having two-component disorder with the disordered atoms lightly restrained with ISOR instructions [occupancy ratio 0.548 (16):0.452 (16)]. Geometrical restraints were also imposed to make the geometries of the two components comparable. The final refinement was as a two-component twin with a 0.945 (7):0.055 (7) domain ratio.

Acknowledgements

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full crystallographic data

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Crystal data

$C_{19}H_{17}N_3O_3S$
M_r = 367.41
Triclinic, $P\overline{1}$
a = 7.2713 (2) Å
b = 11.3575 (3) Å
c = 12.7769 (4) Å
α = 67.004 (1)°
β = 79.649 (1)°
γ = 72.217 (1)°
V = 922.71 (5) Å^3
Z = 2
$F(000)$ = 384
D_x = 1.322 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 7181 reflections
θ = 6.7–72.3°
μ = 1.76 mm^{-1}
T = 225 K
Plate, yellow
0.22 × 0.15 × 0.07 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 (*TWINABS*; Sheldrick, 2009)
T_{min} = 0.70, T_{max} = 0.89
13203 measured reflections
13203 independent reflections
8440 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 72.3°, θ_{min} = 3.8°
h = −8→8
k = −14→14
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.210
S = 1.05
13203 reflections
250 parameters
31 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0917P)^2 + 0.306P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.72 e Å^{-3}
$\Delta\rho_{min}$ = −0.75 e Å^{-3}

Special details

Experimental. Analysis of 887 reflections having I/σ(I) > 12 and chosen from the full data set with *CELL_NOW* (Sheldrick, 2008) showed the crystal to belong to the triclinic system and to be twinned by a 180° rotation about the *b** axis. The raw data were processed using the multi- component version of *SAINT* under control of the two-component orientation file generated by *CELL_NOW*.

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. The carboethoxy substituent is disordered over several closely spaced sites and was modeled as a 2-component disorder with the disordered atoms lightly restrained with ISOR instructions. Geometrical restraints were also imposed to make the geometries of the two components comparable. The final refinement was as a 2-component twin.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.17612 (11)	0.52232 (7)	1.16443 (7)	0.0422 (3)	
O1	0.3137 (5)	0.9605 (3)	0.4124 (2)	0.0686 (8)	
O2	0.5748 (13)	0.391 (2)	0.7012 (18)	0.063 (4)	0.452 (16)
O3	0.280 (3)	0.367 (5)	0.708 (2)	0.0726 (11)	0.452 (16)
O2A	0.5864 (11)	0.3522 (19)	0.7172 (15)	0.063 (4)	0.548 (16)
O3A	0.276 (2)	0.364 (4)	0.714 (2)	0.0726 (11)	0.548 (16)
N1	0.0048 (6)	0.8833 (3)	1.1436 (3)	0.0732 (10)	
N2	0.1236 (5)	0.8287 (3)	0.8772 (3)	0.0589 (8)	
H2A	0.1775	0.8439	0.8046	0.071*	
H2B	0.0903	0.9056	0.8909	0.071*	
N3	0.3041 (4)	0.3476 (2)	1.0592 (2)	0.0395 (6)	
C1	0.2904 (4)	0.5543 (3)	0.8421 (3)	0.0364 (6)	
C2	0.3499 (4)	0.4209 (3)	0.8549 (3)	0.0383 (7)	
C3	0.3555 (4)	0.3206 (3)	0.9638 (3)	0.0398 (7)	
C4	0.2451 (4)	0.4757 (3)	1.0464 (3)	0.0355 (6)	
C5	0.1273 (4)	0.6884 (3)	1.0750 (3)	0.0411 (7)	
C6	0.1604 (4)	0.7082 (3)	0.9608 (3)	0.0391 (7)	
C7	0.2347 (4)	0.5831 (3)	0.9426 (2)	0.0346 (6)	
C8	0.2925 (4)	0.6600 (3)	0.7277 (3)	0.0391 (7)	
C9	0.4199 (5)	0.7398 (3)	0.6993 (3)	0.0471 (8)	
H9	0.5054	0.7255	0.7527	0.056*	
C10	0.4226 (6)	0.8388 (3)	0.5946 (3)	0.0520 (8)	
H10	0.5085	0.8922	0.5773	0.062*	
C11	0.2981 (6)	0.8604 (3)	0.5139 (3)	0.0510 (8)	
C12	0.1734 (6)	0.7819 (4)	0.5398 (3)	0.0537 (9)	
H12	0.0896	0.7955	0.4857	0.064*	
C13	0.1712 (5)	0.6822 (3)	0.6461 (3)	0.0481 (8)	
H13	0.0856	0.6287	0.6630	0.058*	
C14	0.1925 (8)	0.9851 (6)	0.3254 (4)	0.0799 (13)	

H14A	0.2187	0.9060	0.3071	0.120*	
H14B	0.2190	1.0574	0.2578	0.120*	
H14C	0.0577	1.0085	0.3524	0.120*	
C15	0.4197 (5)	0.3826 (3)	0.7514 (3)	0.0453 (7)	
C16	0.319 (2)	0.3661 (19)	0.5911 (15)	0.075 (3)	0.452 (16)
H16A	0.3679	0.4421	0.5406	0.090*	0.452 (16)
H16B	0.4162	0.2849	0.5901	0.090*	0.452 (16)
C17	0.154 (3)	0.372 (3)	0.5549 (19)	0.122 (5)	0.452 (16)
H17A	0.1770	0.3714	0.4779	0.183*	0.452 (16)
H17B	0.1063	0.2963	0.6049	0.183*	0.452 (16)
H17C	0.0583	0.4530	0.5555	0.183*	0.452 (16)
C16A	0.3287 (18)	0.3101 (15)	0.6216 (13)	0.075 (3)	0.548 (16)
H16C	0.3799	0.3740	0.5548	0.090*	0.548 (16)
H16D	0.4338	0.2290	0.6459	0.090*	0.548 (16)
C17A	0.188 (2)	0.282 (2)	0.5890 (16)	0.122 (5)	0.548 (16)
H17D	0.2394	0.2471	0.5283	0.183*	0.548 (16)
H17E	0.1385	0.2159	0.6533	0.183*	0.548 (16)
H17F	0.0844	0.3615	0.5619	0.183*	0.548 (16)
C18	0.4230 (6)	0.1760 (3)	0.9794 (3)	0.0541 (9)	
H18A	0.4865	0.1265	1.0501	0.081*	
H18B	0.5135	0.1645	0.9162	0.081*	
H18C	0.3126	0.1437	0.9819	0.081*	
C19	0.0588 (5)	0.7929 (3)	1.1170 (3)	0.0493 (8)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0488 (5)	0.0409 (4)	0.0407 (5)	−0.0131 (3)	−0.0006 (3)	−0.0187 (3)
O1	0.097 (2)	0.0602 (15)	0.0456 (15)	−0.0313 (14)	−0.0267 (14)	0.0022 (12)
O2	0.0553 (18)	0.080 (11)	0.073 (5)	−0.018 (3)	0.004 (2)	−0.052 (7)
O3	0.0555 (16)	0.114 (3)	0.085 (3)	−0.0209 (15)	−0.0008 (14)	−0.076 (3)
O2A	0.0553 (18)	0.080 (11)	0.073 (5)	−0.018 (3)	0.004 (2)	−0.052 (7)
O3A	0.0555 (16)	0.114 (3)	0.085 (3)	−0.0209 (15)	−0.0008 (14)	−0.076 (3)
N1	0.104 (3)	0.0515 (18)	0.070 (2)	−0.0031 (17)	−0.0112 (19)	−0.0381 (17)
N2	0.092 (2)	0.0312 (13)	0.0486 (17)	0.0031 (13)	−0.0180 (15)	−0.0174 (12)
N3	0.0427 (13)	0.0327 (12)	0.0458 (15)	−0.0105 (9)	−0.0064 (11)	−0.0148 (11)
C1	0.0378 (14)	0.0341 (14)	0.0409 (17)	−0.0071 (10)	−0.0095 (12)	−0.0161 (12)
C2	0.0399 (14)	0.0359 (14)	0.0456 (18)	−0.0081 (11)	−0.0073 (12)	−0.0209 (13)
C3	0.0403 (15)	0.0334 (14)	0.0505 (19)	−0.0090 (11)	−0.0072 (13)	−0.0189 (13)
C4	0.0323 (13)	0.0362 (14)	0.0431 (17)	−0.0094 (10)	−0.0061 (11)	−0.0177 (13)
C5	0.0417 (15)	0.0393 (15)	0.0480 (18)	−0.0065 (11)	−0.0056 (13)	−0.0236 (14)
C6	0.0410 (15)	0.0334 (14)	0.0467 (18)	−0.0035 (11)	−0.0113 (12)	−0.0193 (13)
C7	0.0354 (14)	0.0307 (13)	0.0409 (16)	−0.0055 (10)	−0.0093 (12)	−0.0156 (12)
C8	0.0476 (16)	0.0341 (14)	0.0388 (17)	−0.0078 (11)	−0.0084 (12)	−0.0163 (13)
C9	0.0596 (19)	0.0383 (15)	0.0479 (19)	−0.0138 (13)	−0.0211 (15)	−0.0121 (14)
C10	0.067 (2)	0.0438 (17)	0.049 (2)	−0.0234 (15)	−0.0174 (16)	−0.0078 (15)
C11	0.068 (2)	0.0427 (16)	0.043 (2)	−0.0153 (14)	−0.0152 (16)	−0.0105 (15)
C12	0.062 (2)	0.060 (2)	0.0431 (19)	−0.0180 (16)	−0.0187 (16)	−0.0156 (16)

C13	0.0539 (18)	0.0524 (18)	0.0455 (19)	−0.0200 (14)	−0.0100 (14)	−0.0181 (16)
C14	0.093 (3)	0.091 (3)	0.047 (2)	−0.025 (3)	−0.028 (2)	−0.005 (2)
C15	0.0479 (18)	0.0439 (16)	0.053 (2)	−0.0080 (12)	−0.0068 (14)	−0.0283 (15)
C16	0.082 (3)	0.095 (7)	0.077 (6)	−0.019 (5)	−0.007 (3)	−0.063 (6)
C17	0.131 (7)	0.178 (12)	0.111 (8)	−0.054 (9)	−0.007 (5)	−0.098 (10)
C16A	0.082 (3)	0.095 (7)	0.077 (6)	−0.019 (5)	−0.007 (3)	−0.063 (6)
C17A	0.131 (7)	0.178 (12)	0.111 (8)	−0.054 (9)	−0.007 (5)	−0.098 (10)
C18	0.070 (2)	0.0325 (15)	0.060 (2)	−0.0087 (14)	−0.0082 (17)	−0.0188 (15)
C19	0.0590 (19)	0.0446 (17)	0.048 (2)	−0.0074 (14)	−0.0069 (15)	−0.0242 (15)

Geometric parameters (Å, º)

S1—C4	1.731 (3)	C8—C9	1.395 (5)
S1—C5	1.744 (3)	C9—C10	1.372 (5)
O1—C11	1.364 (4)	C9—H9	0.9400
O1—C14	1.431 (5)	C10—C11	1.395 (5)
O2—C15	1.204 (6)	C10—H10	0.9400
O3—C15	1.321 (5)	C11—C12	1.372 (5)
O3—C16	1.479 (10)	C12—C13	1.388 (5)
O2A—C15	1.204 (6)	C12—H12	0.9400
O3A—C15	1.320 (5)	C13—H13	0.9400
O3A—C16A	1.479 (10)	C14—H14A	0.9700
N1—C19	1.142 (5)	C14—H14B	0.9700
N2—C6	1.350 (4)	C14—H14C	0.9700
N2—H2A	0.9099	C16—C17	1.333 (11)
N2—H2B	0.9100	C16—H16A	0.9800
N3—C3	1.333 (4)	C16—H16B	0.9800
N3—C4	1.336 (4)	C17—H17A	0.9700
C1—C2	1.393 (4)	C17—H17B	0.9700
C1—C7	1.407 (4)	C17—H17C	0.9700
C1—C8	1.487 (4)	C16A—C17A	1.334 (11)
C2—C3	1.410 (5)	C16A—H16C	0.9800
C2—C15	1.506 (4)	C16A—H16D	0.9800
C3—C18	1.505 (4)	C17A—H17D	0.9700
C4—C7	1.403 (4)	C17A—H17E	0.9700
C5—C6	1.373 (5)	C17A—H17F	0.9700
C5—C19	1.409 (4)	C18—H18A	0.9700
C6—C7	1.453 (4)	C18—H18B	0.9700
C8—C13	1.385 (4)	C18—H18C	0.9700
C4—S1—C5	89.80 (14)	C8—C13—H13	119.3
C11—O1—C14	117.8 (3)	C12—C13—H13	119.3
C15—O3—C16	116.9 (13)	O1—C14—H14A	109.5
C15—O3A—C16A	116.4 (11)	O1—C14—H14B	109.5
C6—N2—H2A	123.3	H14A—C14—H14B	109.5
C6—N2—H2B	122.9	O1—C14—H14C	109.5
H2A—N2—H2B	108.8	H14A—C14—H14C	109.5
C3—N3—C4	116.4 (3)	H14B—C14—H14C	109.5

C2—C1—C7	116.7 (3)	O2A—C15—O3A	123.2 (7)
C2—C1—C8	121.1 (3)	O2—C15—O3	123.0 (8)
C7—C1—C8	122.1 (2)	O2—C15—C2	122.7 (10)
C1—C2—C3	121.1 (3)	O2A—C15—C2	125.5 (8)
C1—C2—C15	119.6 (3)	O3A—C15—C2	110.3 (7)
C3—C2—C15	119.2 (3)	O3—C15—C2	112.8 (8)
N3—C3—C2	122.3 (3)	C17—C16—O3	108.6 (13)
N3—C3—C18	115.9 (3)	C17—C16—H16A	110.0
C2—C3—C18	121.8 (3)	O3—C16—H16A	110.0
N3—C4—C7	126.0 (3)	C17—C16—H16B	110.0
N3—C4—S1	120.4 (2)	O3—C16—H16B	110.0
C7—C4—S1	113.6 (2)	H16A—C16—H16B	108.3
C6—C5—C19	123.1 (3)	C16—C17—H17A	109.5
C6—C5—S1	114.4 (2)	C16—C17—H17B	109.5
C19—C5—S1	122.5 (3)	H17A—C17—H17B	109.5
N2—C6—C5	124.0 (3)	C16—C17—H17C	109.5
N2—C6—C7	124.9 (3)	H17A—C17—H17C	109.5
C5—C6—C7	111.2 (3)	H17B—C17—H17C	109.5
C4—C7—C1	117.5 (2)	C17A—C16A—O3A	117.0 (11)
C4—C7—C6	111.0 (3)	C17A—C16A—H16C	108.1
C1—C7—C6	131.5 (3)	O3A—C16A—H16C	108.1
C13—C8—C9	117.9 (3)	C17A—C16A—H16D	108.1
C13—C8—C1	121.9 (3)	O3A—C16A—H16D	108.1
C9—C8—C1	120.2 (3)	H16C—C16A—H16D	107.3
C10—C9—C8	121.2 (3)	C16A—C17A—H17D	109.5
C10—C9—H9	119.4	C16A—C17A—H17E	109.5
C8—C9—H9	119.4	H17D—C17A—H17E	109.5
C9—C10—C11	120.1 (3)	C16A—C17A—H17F	109.5
C9—C10—H10	119.9	H17D—C17A—H17F	109.5
C11—C10—H10	119.9	H17E—C17A—H17F	109.5
O1—C11—C12	125.0 (3)	C3—C18—H18A	109.5
O1—C11—C10	115.4 (3)	C3—C18—H18B	109.5
C12—C11—C10	119.6 (3)	H18A—C18—H18B	109.5
C11—C12—C13	119.9 (3)	C3—C18—H18C	109.5
C11—C12—H12	120.0	H18A—C18—H18C	109.5
C13—C12—H12	120.0	H18B—C18—H18C	109.5
C8—C13—C12	121.4 (3)	N1—C19—C5	175.4 (4)

C7—C1—C2—C3	−0.7 (4)	C5—C6—C7—C1	−179.3 (3)
C8—C1—C2—C3	177.3 (3)	C2—C1—C8—C13	66.5 (4)
C7—C1—C2—C15	−177.4 (3)	C7—C1—C8—C13	−115.6 (3)
C8—C1—C2—C15	0.7 (4)	C2—C1—C8—C9	−113.1 (3)
C4—N3—C3—C2	0.5 (4)	C7—C1—C8—C9	64.9 (4)
C4—N3—C3—C18	179.6 (3)	C13—C8—C9—C10	1.2 (5)
C1—C2—C3—N3	0.3 (5)	C1—C8—C9—C10	−179.3 (3)
C15—C2—C3—N3	176.9 (3)	C8—C9—C10—C11	−0.7 (6)
C1—C2—C3—C18	−178.8 (3)	C14—O1—C11—C12	−0.7 (6)
C15—C2—C3—C18	−2.1 (4)	C14—O1—C11—C10	178.6 (4)

C3—N3—C4—C7	−0.8 (4)	C9—C10—C11—O1	−179.4 (3)
C3—N3—C4—S1	−179.6 (2)	C9—C10—C11—C12	−0.1 (6)
C5—S1—C4—N3	−179.9 (3)	O1—C11—C12—C13	179.6 (4)
C5—S1—C4—C7	1.1 (2)	C10—C11—C12—C13	0.4 (6)
C4—S1—C5—C6	0.3 (2)	C9—C8—C13—C12	−1.0 (5)
C4—S1—C5—C19	−179.9 (3)	C1—C8—C13—C12	179.5 (3)
C19—C5—C6—N2	−2.9 (5)	C11—C12—C13—C8	0.2 (6)
S1—C5—C6—N2	176.9 (3)	C16A—O3A—C15—O2A	−3 (4)
C19—C5—C6—C7	178.6 (3)	C16A—O3A—C15—C2	−173 (2)
S1—C5—C6—C7	−1.6 (3)	C16—O3—C15—O2	−2 (4)
N3—C4—C7—C1	0.4 (4)	C16—O3—C15—C2	164 (2)
S1—C4—C7—C1	179.3 (2)	C1—C2—C15—O2	73.6 (15)
N3—C4—C7—C6	178.9 (3)	C3—C2—C15—O2	−103.2 (15)
S1—C4—C7—C6	−2.2 (3)	C1—C2—C15—O2A	96.1 (12)
C2—C1—C7—C4	0.4 (4)	C3—C2—C15—O2A	−80.6 (12)
C8—C1—C7—C4	−177.6 (3)	C1—C2—C15—O3A	−94.9 (19)
C2—C1—C7—C6	−177.7 (3)	C3—C2—C15—O3A	88.4 (19)
C8—C1—C7—C6	4.2 (5)	C1—C2—C15—O3	−93 (2)
N2—C6—C7—C4	−176.0 (3)	C3—C2—C15—O3	91 (2)
C5—C6—C7—C4	2.4 (4)	C15—O3—C16—C17	−170 (3)
N2—C6—C7—C1	2.2 (5)	C15—O3A—C16A—C17A	175 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*B*···N1^{i}	0.91	2.17	3.030 (4)	159
C10—H10···O1^{ii}	0.94	2.46	3.366 (4)	162
C16*A*—H16*D*···O1^{iii}	0.98	2.63	3.486 (14)	146
C17*A*—H17*E*···N1^{iv}	0.97	2.56	3.47 (2)	156

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