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Ethyl 3-amino-2-carbamoyl-4-(4-methoxyphenyl)-6-methylthieno[2,3-*b*]pyridine-5-carboxylate dimethyl sulfoxide monosolvate

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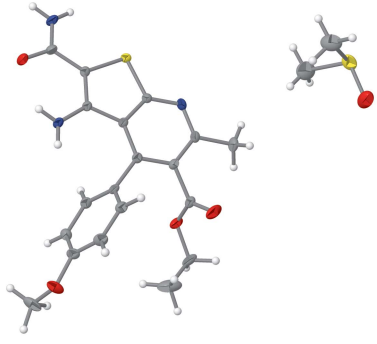
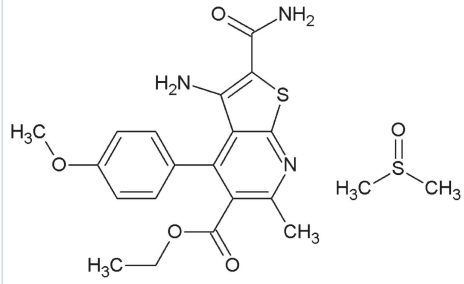
Structural data: full structural data are available from iucrdata.iucr.org

The conformation of the title molecule, $C_{19}H_{19}N_3O_4S\cdot C_2H_6OS$, which crystallized as a DMSO solvate, is partially determined by an intramolecular N—H···O hydrogen bond, forming an $S(6)$ loop. The thienopyridine bicyclic system is almost planar, with an r.m.s. deviation of 0.002 Å. The benzene ring makes a dihedral angle of 65.44 (8)° with the mean plane of the thienopyridine bicyclic system. In the crystal, molecules are linked by pairs of N—H···O hydrogen bonds, forming inversion dimers with an $R_2^2(8)$ ring motif. Within the dimers, which stack along the *a*-axis direction, there is a weak π–π interaction [centroid-to-centroid distance = 3.5428 (11) Å] involving inversion-related thiophene rings. In addition, N—H···O and C—H···O hydrogen bonds help to consolidate the packing, *via* the solvent molecules.

3D view



Chemical scheme



Structure description

Nowadays, after a lapse of more than one century, the chemistry of thieno[2,3-*b*]pyridines is well known. This is associated primarily with the great practical importance of many derivatives of thieno[2,3-*b*]pyridine (Litvinov *et al.*, 2005). The spectrum of biological activities of this class of compounds is rather broad and includes antiviral (Attaby *et al.*, 2007), antidiabetic (Bahekar *et al.* 2007) and antimicrobial (Abdel-Rahman *et al.*, 2003). As part of our studies in this area, we undertook the synthesis of the title compound in order to establish its crystal structure.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···O1^{i}	0.87 (2)	2.07 (2)	2.916 (2)	165 (2)
N1—H1A···O1S^{ii}	0.88 (2)	2.08 (2)	2.918 (3)	158 (2)
N2—H2A···O1	0.86 (2)	2.10 (2)	2.719 (2)	129 (2)
C14—H14···O3^{iii}	0.95	2.50	3.381 (2)	155
C16—H16A···O2^{iv}	0.99	2.48	3.254 (3)	134
C19—H19C···O1^{v}	0.98	2.75	3.474 (3)	131
C19—H19A···O1S^{vi}	0.98	2.84	3.483 (3)	124

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

The conformation of the title molecule (Fig. 1) is partially determined by an intramolecular N2—H2A···O1 hydrogen bond, forming an S(6) loop (Table 1). The thienopyridine bicyclic system (S1/N3/C2–C8) is almost planar, with an r.m.s. deviation of 0.002 Å. The benzene ring (C9–C14) makes a dihedral angle of 65.44 (8)° with the mean plane of the thienopyridine bicyclic system.

In the crystal, molecules are linked by pairs of N1—H1A···O1 hydrogen bonds, forming inversion dimers with an $R_2^2(8)$ ring motif (Table 1). Within the dimers, which stack along the a-axis direction, there is a weak π–π interaction [centroid-to-centroid distance = 3.5428 (11) Å] involving inversion-related thiophene rings. In addition, N1—H1A···O1S($x, y, z-1$) and C19—H19A···O1S($-x, -y+1, -z+2$) hydrogen bonds help to establish the packin (Fig. 2 and Table 1).

Synthesis and crystallization

The title compound was prepared by heating equimolar quantities of ethyl 3-cyano-6-methyl-4-(4-methoxyphenyl)-2-thioxo-1,2-dihydropyridine-5-carboxylate (10 mmol) and chloroacetamide (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 DMSO solution to give yellow crystals of the title compound (yield 75%; m.p. 487–488 K). IR (KBr, cm^{-1}) ν = 3490, 3450, 3300, 3200 (2 NH$_2$), 1720(C═O, ester), 1650 (C═O, amide). ^{1}H NMR (DMSO-d_6): δ7.0–7.3 (m, 6H,

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{19}N_3O_4S\cdot C_2H_6OS$
M_r	463.56
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	173
a, b, c (Å)	9.9950 (7), 10.1492 (5), 11.2620 (8)
α, β, γ (°)	90.656 (5), 92.291 (5), 101.925 (5)
V (Å^3)	1116.66 (13)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	2.49
Crystal size (mm)	0.34 × 0.18 × 0.12
Data collection	
Diffractometer	Rigaku Oxford Diffraction
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2014)
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6959, 4247, 3706
R_{int}	0.041
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.615
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.139, 1.06
No. of reflections	4247
No. of parameters	298
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.40, −0.45

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

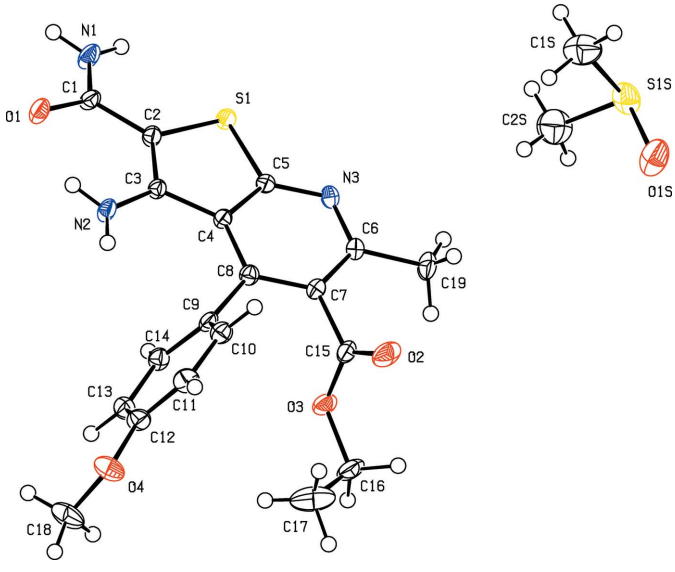


Figure 1
The molecular structure of the title molecule, shown with 50% probability displacement ellipsoids.

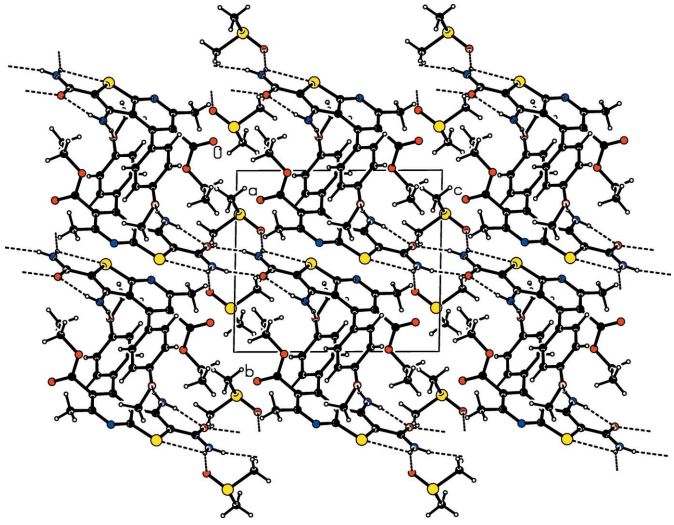


Figure 2
The packing of the title molecule, viewed down the a axis, with the hydrogen bonds shown by dotted lines.

NH_2 and ArH's), 5.6 (*s*, 2H, NH_2), 3.5–4.2 (*m*, 5H, OCH_2 and OCH_3), 2.6 (*s*, 3H, CH_3), 0.9–1.1 (*t*, 3H, CH_3 of ester).

Refinement

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

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full crystallographic data

IUCrData (2016). **1**, x161474 [doi:10.1107/S2414314616014747]

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Crystal data

$C_{19}H_{19}N_3O_4S\cdot C_2H_6OS$
M_r = 463.56
Triclinic, $P\overline{1}$
a = 9.9950 (7) Å
b = 10.1492 (5) Å
c = 11.2620 (8) Å
α = 90.656 (5)°
β = 92.291 (5)°
γ = 101.925 (5)°
V = 1116.66 (13) Å^3
Z = 2
$F(000)$ = 488
D_x = 1.379 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 3206 reflections
θ = 3.9–71.4°
μ = 2.49 mm^{-1}
T = 173 K
Prism, yellow
0.34 × 0.18 × 0.12 mm

Data collection

Rigaku Oxford Diffraction diffractometer
Radiation source: Enhance (Cu) X-ray Source
Graphite monochromator
Detector resolution: 16.0416 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)
6959 measured reflections
4247 independent reflections
3706 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 71.4°, θ_{min} = 3.9°
h = −11→12
k = −12→8
l = −11→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.139
S = 1.06
4247 reflections
298 parameters
4 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0879P)^2 + 0.1101P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0058 (7)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.4772 (2)	0.54248 (19)	0.17912 (17)	0.0186 (4)
C1S	0.1585 (3)	0.1551 (3)	0.9746 (3)	0.0492 (7)
H1S1	0.241592	0.221202	0.957889	0.074*
H1S2	0.126523	0.099851	0.903084	0.074*
H1S3	0.178572	0.097249	1.039111	0.074*
C2	0.45367 (19)	0.57636 (18)	0.30206 (17)	0.0174 (4)
C2S	0.0347 (3)	0.3450 (3)	0.8908 (3)	0.0513 (7)
H2S1	−0.027459	0.407176	0.899931	0.077*
H2S2	0.006674	0.288510	0.819296	0.077*
H2S3	0.128268	0.396611	0.883296	0.077*
C3	0.54673 (19)	0.66430 (18)	0.37518 (16)	0.0154 (4)
C4	0.49047 (18)	0.68700 (18)	0.48843 (16)	0.0149 (4)
C5	0.35832 (19)	0.60709 (18)	0.49757 (17)	0.0165 (4)
C6	0.3323 (2)	0.68041 (18)	0.68476 (17)	0.0187 (4)
C7	0.4619 (2)	0.76783 (18)	0.68325 (16)	0.0181 (4)
C8	0.54318 (19)	0.77362 (18)	0.58518 (17)	0.0164 (4)
C9	0.67405 (19)	0.87524 (18)	0.58362 (16)	0.0169 (4)
C10	0.7836 (2)	0.87283 (19)	0.66376 (17)	0.0210 (4)
H10	0.778935	0.800126	0.716865	0.025*
C11	0.8990 (2)	0.9754 (2)	0.66657 (18)	0.0234 (4)
H11	0.973988	0.971543	0.720067	0.028*
C12	0.9058 (2)	1.08446 (19)	0.59123 (18)	0.0219 (4)
C13	0.7987 (2)	1.08628 (19)	0.50918 (18)	0.0214 (4)
H13	0.803726	1.158816	0.455849	0.026*
C14	0.6846 (2)	0.98204 (19)	0.50535 (17)	0.0194 (4)
H14	0.612227	0.983306	0.448360	0.023*
C15	0.5046 (2)	0.8659 (2)	0.78571 (17)	0.0205 (4)
C16	0.5193 (3)	1.0959 (2)	0.84395 (19)	0.0306 (5)
H16A	0.492045	1.059334	0.922553	0.037*
H16B	0.466229	1.165710	0.824692	0.037*
C17	0.6686 (3)	1.1581 (3)	0.8497 (3)	0.0513 (8)
H17A	0.720710	1.091136	0.876167	0.077*
H17B	0.686200	1.234740	0.905894	0.077*
H17C	0.696878	1.189203	0.770682	0.077*
C18	1.0181 (2)	1.3070 (2)	0.5402 (3)	0.0349 (6)
H18A	1.019823	1.288610	0.454779	0.052*
H18B	1.098354	1.376174	0.565212	0.052*
H18C	0.934616	1.339043	0.557130	0.052*
C19	0.2440 (2)	0.6782 (2)	0.7903 (2)	0.0295 (5)

H19A	0.151364	0.627493	0.769318	0.044*
H19B	0.240061	0.770723	0.813381	0.044*
H19C	0.282981	0.635101	0.856858	0.044*
N1	0.37300 (19)	0.47179 (19)	0.11272 (16)	0.0261 (4)
H1A	0.2873 (19)	0.443 (2)	0.132 (2)	0.031*
H1B	0.392 (3)	0.445 (2)	0.0427 (17)	0.031*
N2	0.67459 (17)	0.72257 (17)	0.34414 (15)	0.0209 (4)
H2A	0.704 (2)	0.691 (2)	0.2818 (17)	0.025*
H2B	0.734 (2)	0.778 (2)	0.385 (2)	0.025*
N3	0.27964 (16)	0.60146 (16)	0.59184 (15)	0.0195 (4)
O1	0.59216 (15)	0.58235 (15)	0.13776 (12)	0.0248 (3)
O1S	0.08790 (18)	0.3310 (2)	1.12153 (16)	0.0446 (5)
O2	0.54367 (19)	0.83839 (15)	0.88281 (13)	0.0336 (4)
O3	0.48721 (16)	0.98795 (14)	0.75431 (12)	0.0252 (3)
O4	1.02006 (15)	1.18517 (14)	0.60450 (15)	0.0291 (4)
S1	0.29893 (5)	0.51409 (4)	0.36893 (4)	0.01890 (17)
S1S	0.02868 (6)	0.24091 (6)	1.01773 (6)	0.0356 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0185 (9)	0.0198 (9)	0.0166 (9)	0.0024 (7)	0.0007 (7)	−0.0055 (7)
C1S	0.0440 (16)	0.0411 (14)	0.0611 (19)	0.0072 (12)	−0.0024 (14)	−0.0080 (13)
C2	0.0158 (9)	0.0199 (9)	0.0153 (9)	0.0008 (7)	0.0021 (7)	−0.0017 (7)
C2S	0.063 (2)	0.0492 (16)	0.0415 (16)	0.0117 (14)	−0.0065 (14)	0.0055 (13)
C3	0.0137 (9)	0.0175 (8)	0.0143 (9)	0.0015 (7)	0.0015 (7)	−0.0015 (7)
C4	0.0129 (9)	0.0171 (8)	0.0140 (9)	0.0016 (7)	0.0010 (7)	−0.0018 (7)
C5	0.0163 (9)	0.0155 (8)	0.0163 (9)	0.0004 (7)	0.0021 (7)	−0.0015 (7)
C6	0.0204 (10)	0.0191 (9)	0.0166 (9)	0.0030 (8)	0.0053 (7)	0.0011 (7)
C7	0.0216 (10)	0.0188 (9)	0.0135 (9)	0.0033 (8)	0.0019 (7)	−0.0014 (7)
C8	0.0163 (9)	0.0177 (9)	0.0153 (9)	0.0034 (7)	0.0003 (7)	0.0001 (7)
C9	0.0165 (9)	0.0199 (9)	0.0133 (9)	0.0014 (7)	0.0019 (7)	−0.0057 (7)
C10	0.0241 (10)	0.0213 (9)	0.0170 (9)	0.0035 (8)	−0.0009 (8)	−0.0016 (7)
C11	0.0193 (10)	0.0267 (10)	0.0226 (10)	0.0023 (8)	−0.0060 (8)	−0.0029 (8)
C12	0.0154 (9)	0.0217 (9)	0.0264 (11)	−0.0014 (8)	0.0019 (8)	−0.0053 (8)
C13	0.0203 (10)	0.0210 (9)	0.0214 (10)	0.0005 (8)	0.0026 (8)	0.0004 (8)
C14	0.0171 (9)	0.0229 (9)	0.0168 (9)	0.0014 (8)	−0.0003 (7)	−0.0018 (7)
C15	0.0224 (10)	0.0233 (10)	0.0154 (9)	0.0037 (8)	0.0043 (8)	−0.0030 (7)
C16	0.0520 (15)	0.0245 (10)	0.0171 (10)	0.0133 (10)	−0.0010 (10)	−0.0077 (8)
C17	0.0543 (18)	0.0345 (13)	0.0632 (19)	0.0106 (13)	−0.0226 (15)	−0.0208 (13)
C18	0.0190 (11)	0.0234 (10)	0.0582 (16)	−0.0056 (9)	0.0013 (10)	0.0043 (10)
C19	0.0282 (11)	0.0350 (11)	0.0244 (11)	0.0024 (9)	0.0139 (9)	−0.0012 (9)
N1	0.0212 (9)	0.0340 (10)	0.0186 (9)	−0.0044 (7)	0.0027 (7)	−0.0124 (7)
N2	0.0147 (8)	0.0279 (9)	0.0166 (8)	−0.0038 (7)	0.0044 (6)	−0.0081 (7)
N3	0.0165 (8)	0.0206 (8)	0.0208 (8)	0.0010 (6)	0.0070 (6)	0.0015 (6)
O1	0.0205 (7)	0.0330 (8)	0.0176 (7)	−0.0025 (6)	0.0041 (6)	−0.0084 (6)
O1S	0.0257 (9)	0.0666 (12)	0.0361 (10)	−0.0024 (8)	0.0035 (7)	−0.0127 (9)
O2	0.0574 (11)	0.0298 (8)	0.0155 (7)	0.0153 (8)	−0.0053 (7)	−0.0035 (6)

O3	0.0395 (9)	0.0218 (7)	0.0146 (7)	0.0076 (6)	−0.0019 (6)	−0.0039 (5)
O4	0.0172 (7)	0.0231 (7)	0.0427 (9)	−0.0050 (6)	−0.0038 (6)	0.0015 (6)
S1	0.0145 (3)	0.0207 (3)	0.0183 (3)	−0.00379 (18)	0.00207 (18)	−0.00517 (18)
S1S	0.0216 (3)	0.0423 (4)	0.0372 (4)	−0.0064 (2)	−0.0002 (2)	0.0015 (3)

Geometric parameters (Å, º)

C1—O1	1.247 (2)	C11—C12	1.394 (3)
C1—N1	1.332 (3)	C11—H11	0.9500
C1—C2	1.463 (3)	C12—O4	1.368 (2)
C1S—S1S	1.784 (3)	C12—C13	1.389 (3)
C1S—H1S1	0.9800	C13—C14	1.385 (3)
C1S—H1S2	0.9800	C13—H13	0.9500
C1S—H1S3	0.9800	C14—H14	0.9500
C2—C3	1.385 (3)	C15—O2	1.202 (2)
C2—S1	1.7489 (19)	C15—O3	1.335 (2)
C2S—S1S	1.783 (3)	C16—O3	1.458 (2)
C2S—H2S1	0.9800	C16—C17	1.494 (4)
C2S—H2S2	0.9800	C16—H16A	0.9900
C2S—H2S3	0.9800	C16—H16B	0.9900
C3—N2	1.354 (2)	C17—H17A	0.9800
C3—C4	1.449 (2)	C17—H17B	0.9800
C4—C8	1.407 (2)	C17—H17C	0.9800
C4—C5	1.408 (3)	C18—O4	1.443 (3)
C5—N3	1.341 (2)	C18—H18A	0.9800
C5—S1	1.7351 (19)	C18—H18B	0.9800
C6—N3	1.333 (3)	C18—H18C	0.9800
C6—C7	1.412 (3)	C19—H19A	0.9800
C6—C19	1.507 (3)	C19—H19B	0.9800
C7—C8	1.391 (3)	C19—H19C	0.9800
C7—C15	1.505 (3)	N1—H1A	0.883 (17)
C8—C9	1.490 (3)	N1—H1B	0.872 (17)
C9—C14	1.395 (3)	N2—H2A	0.856 (16)
C9—C10	1.395 (3)	N2—H2B	0.849 (17)
C10—C11	1.384 (3)	O1S—S1S	1.4997 (19)
C10—H10	0.9500		

O1—C1—N1	121.43 (18)	C13—C12—C11	119.54 (18)
O1—C1—C2	119.93 (17)	C14—C13—C12	119.80 (18)
N1—C1—C2	118.62 (18)	C14—C13—H13	120.1
S1S—C1S—H1S1	109.5	C12—C13—H13	120.1
S1S—C1S—H1S2	109.5	C13—C14—C9	121.21 (18)
H1S1—C1S—H1S2	109.5	C13—C14—H14	119.4
S1S—C1S—H1S3	109.5	C9—C14—H14	119.4
H1S1—C1S—H1S3	109.5	O2—C15—O3	124.74 (18)
H1S2—C1S—H1S3	109.5	O2—C15—C7	125.44 (18)
C3—C2—C1	124.40 (17)	O3—C15—C7	109.77 (16)
C3—C2—S1	113.21 (14)	O3—C16—C17	111.1 (2)

C1—C2—S1	122.33 (14)	O3—C16—H16A	109.4
S1S—C2S—H2S1	109.5	C17—C16—H16A	109.4
S1S—C2S—H2S2	109.5	O3—C16—H16B	109.4
H2S1—C2S—H2S2	109.5	C17—C16—H16B	109.4
S1S—C2S—H2S3	109.5	H16A—C16—H16B	108.0
H2S1—C2S—H2S3	109.5	C16—C17—H17A	109.5
H2S2—C2S—H2S3	109.5	C16—C17—H17B	109.5
N2—C3—C2	123.98 (17)	H17A—C17—H17B	109.5
N2—C3—C4	124.14 (17)	C16—C17—H17C	109.5
C2—C3—C4	111.89 (16)	H17A—C17—H17C	109.5
C8—C4—C5	117.15 (17)	H17B—C17—H17C	109.5
C8—C4—C3	131.66 (17)	O4—C18—H18A	109.5
C5—C4—C3	111.17 (16)	O4—C18—H18B	109.5
N3—C5—C4	126.23 (18)	H18A—C18—H18B	109.5
N3—C5—S1	120.69 (15)	O4—C18—H18C	109.5
C4—C5—S1	113.06 (14)	H18A—C18—H18C	109.5
N3—C6—C7	122.10 (17)	H18B—C18—H18C	109.5
N3—C6—C19	116.99 (18)	C6—C19—H19A	109.5
C7—C6—C19	120.84 (18)	C6—C19—H19B	109.5
C8—C7—C6	121.53 (18)	H19A—C19—H19B	109.5
C8—C7—C15	120.07 (17)	C6—C19—H19C	109.5
C6—C7—C15	118.10 (17)	H19A—C19—H19C	109.5
C7—C8—C4	116.71 (17)	H19B—C19—H19C	109.5
C7—C8—C9	119.62 (17)	C1—N1—H1A	128.2 (17)
C4—C8—C9	123.53 (17)	C1—N1—H1B	116.7 (18)
C14—C9—C10	118.48 (18)	H1A—N1—H1B	115 (2)
C14—C9—C8	119.18 (17)	C3—N2—H2A	116.7 (17)
C10—C9—C8	122.19 (17)	C3—N2—H2B	127.3 (17)
C11—C10—C9	120.59 (18)	H2A—N2—H2B	115 (2)
C11—C10—H10	119.7	C6—N3—C5	116.20 (16)
C9—C10—H10	119.7	C15—O3—C16	117.63 (15)
C10—C11—C12	120.30 (18)	C12—O4—C18	116.62 (16)
C10—C11—H11	119.9	C5—S1—C2	90.56 (9)
C12—C11—H11	119.9	O1S—S1S—C2S	106.93 (13)
O4—C12—C13	123.92 (18)	O1S—S1S—C1S	106.65 (12)
O4—C12—C11	116.53 (18)	C2S—S1S—C1S	96.36 (15)

O1—C1—C2—C3	7.7 (3)	C7—C8—C9—C10	64.7 (2)
N1—C1—C2—C3	−170.64 (18)	C4—C8—C9—C10	−119.9 (2)
O1—C1—C2—S1	−175.41 (14)	C14—C9—C10—C11	1.1 (3)
N1—C1—C2—S1	6.2 (3)	C8—C9—C10—C11	−174.31 (18)
C1—C2—C3—N2	−4.7 (3)	C9—C10—C11—C12	1.7 (3)
S1—C2—C3—N2	178.22 (15)	C10—C11—C12—O4	176.32 (18)
C1—C2—C3—C4	174.97 (17)	C10—C11—C12—C13	−3.2 (3)
S1—C2—C3—C4	−2.1 (2)	O4—C12—C13—C14	−177.50 (18)
N2—C3—C4—C8	4.5 (3)	C11—C12—C13—C14	1.9 (3)
C2—C3—C4—C8	−175.14 (18)	C12—C13—C14—C9	0.8 (3)
N2—C3—C4—C5	−176.73 (17)	C10—C9—C14—C13	−2.3 (3)

C2—C3—C4—C5	3.6 (2)	C8—C9—C14—C13	173.22 (17)
C8—C4—C5—N3	−2.9 (3)	C8—C7—C15—O2	−109.9 (2)
C3—C4—C5—N3	178.15 (17)	C6—C7—C15—O2	76.3 (3)
C8—C4—C5—S1	175.38 (13)	C8—C7—C15—O3	72.7 (2)
C3—C4—C5—S1	−3.6 (2)	C6—C7—C15—O3	−101.1 (2)
N3—C6—C7—C8	−1.6 (3)	C7—C6—N3—C5	1.7 (3)
C19—C6—C7—C8	−178.25 (18)	C19—C6—N3—C5	178.43 (17)
N3—C6—C7—C15	172.07 (17)	C4—C5—N3—C6	0.6 (3)
C19—C6—C7—C15	−4.6 (3)	S1—C5—N3—C6	−177.53 (13)
C6—C7—C8—C4	−0.8 (3)	O2—C15—O3—C16	0.6 (3)
C15—C7—C8—C4	−174.30 (16)	C7—C15—O3—C16	178.10 (17)
C6—C7—C8—C9	175.02 (16)	C17—C16—O3—C15	84.1 (2)
C15—C7—C8—C9	1.5 (3)	C13—C12—O4—C18	8.8 (3)
C5—C4—C8—C7	2.7 (2)	C11—C12—O4—C18	−170.63 (19)
C3—C4—C8—C7	−178.55 (18)	N3—C5—S1—C2	−179.58 (16)
C5—C4—C8—C9	−172.84 (16)	C4—C5—S1—C2	2.04 (14)
C3—C4—C8—C9	5.9 (3)	C3—C2—S1—C5	0.10 (15)
C7—C8—C9—C14	−110.7 (2)	C1—C2—S1—C5	−177.08 (16)
C4—C8—C9—C14	64.8 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···O1^{i}	0.87 (2)	2.07 (2)	2.916 (2)	165 (2)
N1—H1*A*···O1*S*^{ii}	0.88 (2)	2.08 (2)	2.918 (3)	158 (2)
N2—H2*A*···O1	0.86 (2)	2.10 (2)	2.719 (2)	129 (2)
C14—H14···O3^{iii}	0.95	2.50	3.381 (2)	155
C16—H16*A*···O2^{iv}	0.99	2.48	3.254 (3)	134
C19—H19*C*···O1^{v}	0.98	2.75	3.474 (3)	131
C19—H19*A*···O1*S*^{vi}	0.98	2.84	3.483 (3)	124

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