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2-(5-Fluoro-1-methyl-2-oxoindolin-3-ylidene)-*N*-[4-(methylsulfanyl)phenyl]hydrazine-1-carbothioamide

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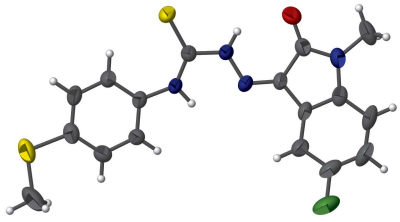
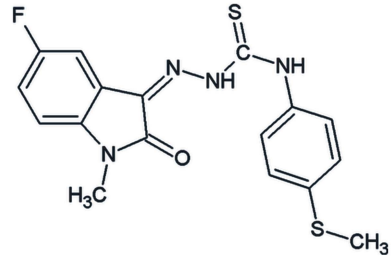
Structural data: full structural data are available from iucrdata.iucr.org

The title molecule, $C_{17}H_{15}FN_4OS_2$, obtained from 5-fluoro-1-methyl-1*H*-indol-2,3-dione, and 3-[4-(methylsulfanyl)phenyl]thiosemicarbazide, has an essentially planar conformation (r.m.s deviation for all non-H atoms = 0.116 Å). Intramolecular N—H···N and N—H···O hydrogen bonds generate *S*(5) and *S*(6) ring motifs, respectively. In the crystal, C—H···S hydrogen bonds occur between layers of molecules parallel to the $(10\bar{1})$ plane. Face-to-face π–π stacking interactions are also observed.

3D view



Chemical scheme



Structure description

The indole ring system is an important structural component in many pharmaceutical agents, including compounds with antiviral, anti-inflammatory and antitumor properties (Ma *et al.*, 2015). 1*H*-Indole-2,3-dione (isatin) has a wide spectrum of biological properties, such as cytotoxic and antineoplastic effects. Isatin derivatives with halogens and *N*-alkylhaloisatins have been reported to exhibit anticancer activity (Podichetty *et al.*, 2009). The biological activities of thiosemicarbazones, such as anticancer, antiviral, antimicrobial *etc*, have been known for a long time. Isatin 3-thiosemicarbazone derivatives, which have anti-HIV effects, are used as prophylaxes against smallpox and vaccinia viruses (Bal *et al.*, 2005; Hall *et al.*, 2009). Isatin 3-[N^4-(phenyl substituted) thiosemicarbazone] derivatives have been shown to be have significantly more multidrug

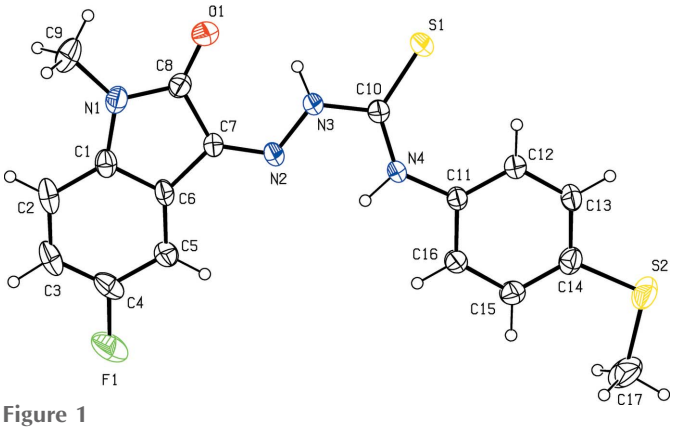


Figure 1
View of the molecular structure of the title compound, with the atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

resistant-selective activity than N^4-alkyl and N^4-cycloalkyl thiosemicarbazone derivatives (Hall *et al.*, 2009, 2011).

In the title compound (Fig. 1), the N—N—C═S and N—N—C(═S)—N torsion angles are 170.0 (3) and −9.6 (6)°, respectively. Intramolecular N—H···N and N—H···O hydrogen bonds (Table 1) generate $S(5)$ and $S(6)$ ring motifs, respectively (Fig. 2). All bond lengths and angles are within normal ranges and agree with those reported for (3*E*)-3-[(4-butylphenyl)imino]-1,3-dihydro-2*H*-indol-2-one (Akkurt *et al.*, 2003), *N*′-[(2*Z*)-3-allyl-4-oxo-1,3-thiazolidin-2-ylidene]-5-fluoro-3-phenyl-1*H*-indole-2-carbohydrazide (Akkurt *et al.*, 2009), 2-(4-isobutylphenyl)-*N*′-[(3*Z*)-2-oxoindolin-3-ylidene]-

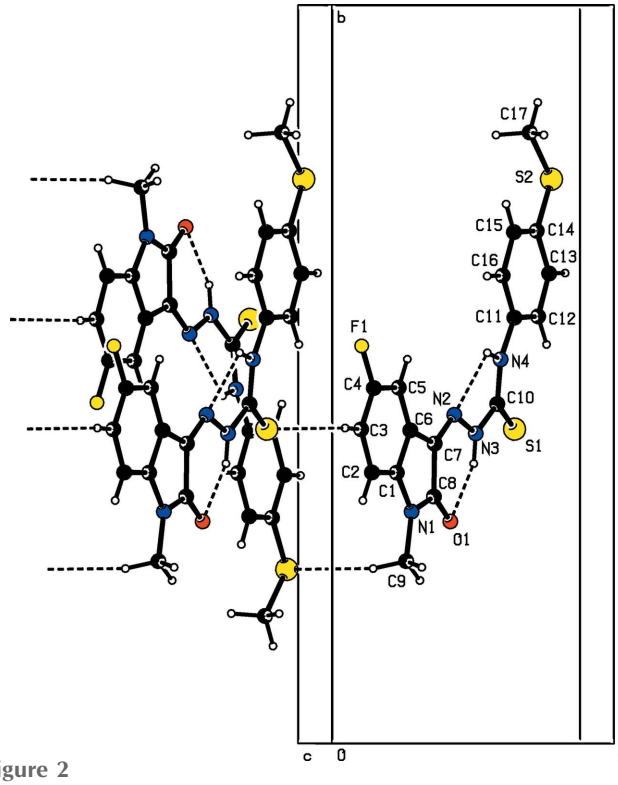


Figure 2
A partial view along the *c* axis of the N—H···N, N—H···O and C—H···S hydrogen bonding (Table 1) in the crystal packing of the title compound.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*N*···O1	0.87 (4)	2.09 (5)	2.757 (5)	133 (5)
N4—H4*N*···N2	0.90 (5)	2.14 (5)	2.598 (5)	110 (3)
C3—H3···S1^{i}	0.93	2.84	3.712 (5)	158
C9—H9*B*···S2^{ii}	0.96	2.84	3.652 (7)	142
C12—H12···S1	0.93	2.61	3.256 (4)	128

Symmetry codes: (i) $x-1, y, z-1$; (ii) $x-1, -y+1, z-\frac{1}{2}$.

propanohydrazide (Mohamed *et al.*, 2012), 5-fluoro-1*H*-indole-2,3-dione 3-thiosemicarbazone derivatives (Özbey *et al.*, 2006; Karayel *et al.*, 2015) and 5-trifluoromethoxy-1*H*-indole-2,3-dione 3-thiosemicarbazone derivatives (Kaynak *et al.*, 2013).

In the crystal, C—H···S hydrogen bonds (Table 1) occur between layers of molecules located parallel to the $(10\bar{1})$ plane (Fig. 3). Face-to-face π–π stacking interactions [$Cg1\cdots Cg3(x, 1-y, -\frac{1}{2}+z)$ = 3.615 (3) Å and $Cg2\cdots Cg3(-1+x, 1-y, -\frac{1}{2}+z)$ = 3.835 (3) Å, where *Cg*1, *Cg*2 and *Cg*3 are the centroids of the N1/C1/C6–C8, C1–C6 and C11–C16 rings, respectively] are also observed.

Synthesis and crystallization

Steps in the synthesis of the title compound (**5**) are shown in Fig. 4.

3-[4-(Methylsulfanyl)phenyl]thiosemicarbazide (2)

To a solution of hydrazine hydrate (5 mmol) in ethanol (10 ml), a suspension of 4-(methylsulfanyl)phenylisothiocyanate (**1**) (5 mmol) in ethanol (10 ml) was added dropwise with vigorous stirring and cooling in an ice bath. The mixture was allowed to stand overnight. The crystals formed were recrystallized from ethanol solution.

5-Fluoro-1-methyl-1*H*-indole-2,3-dione (4)

A suspension of 5-fluoro-1*H*-indole-2,3-dione (**3**) (5 mmol), K_2CO_3 (7 mmol) and KI (1 mmol) in anhydrous DMF (5 ml)

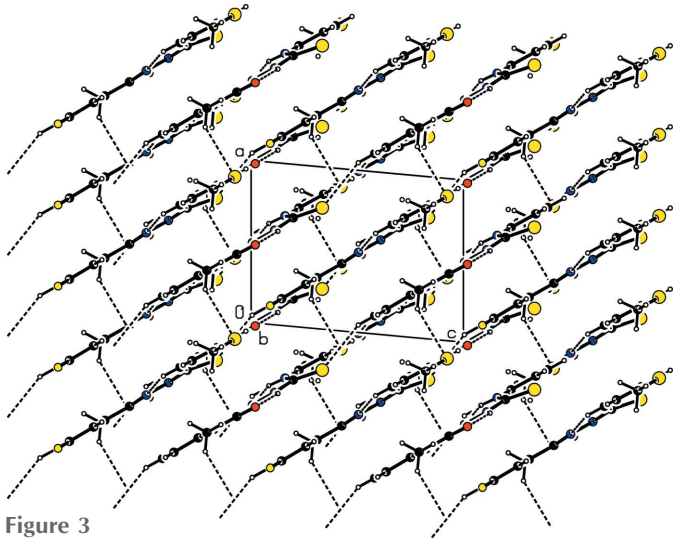


Figure 3
A view along the *b* axis of the crystal packing of the title compound.

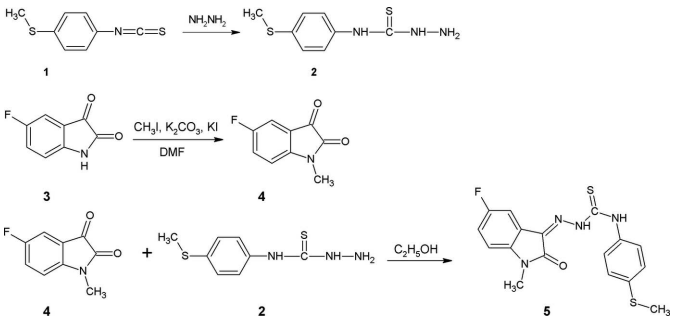


Figure 4
The synthesis of the title compound **5**.

was stirred for 30 min at room temperature. After addition of iodomethane (15 mmol), the mixture was refluxed for 4 h. The product was poured onto ice–water then filtered.

5-Fluoro-1-methyl-1*H*-indole-2,3-dione 3-[4-(methylsulfanyl)phenyl] thiosemicarbazone (5)

A solution of *N*-[(4-methylsulfanyl)phenyl]thiosemicarbazide (**2**) (2.5 mmol) in ethanol (10 ml) was added to a solution of 5-fluoro-1-methyl-1*H*-indole-2,3-dione (**4**) (2.5 mmol) in ethanol (20 ml). The mixture was refluxed on a water bath for 10 h. The product formed after cooling was filtered and washed with ethanol or recrystallized from ethanol. Orange crystals were obtained in 94% yield, m.p. 508–511 K.

IR (KBr): ν 3269, 3226 (NH), 1681 (C═O), 1274 (C═S); ^{1}H NMR (DMSO-d_6; 400 MHz): δ 2.49 (*s*, 3H, SCH_3), 3.21 (*s*, 3H, ind. N—CH_3), 7.15 (*dd*, *J* = 8.60, 4.00 Hz, 1H, ind. C7—H), 7.26–7.32 (*m*, 1H, ind. C6—H), 7.30 (*d*, *J* = 8.60 Hz, 2H, fen. C3,5-H), 7.55 (*d*, *J* = 8.60 Hz, 2H, fen. C2,6-H), 7.64 (*dd*, *J* = 8.00, 2.66 Hz, 1H, ind. C4—H), 10.81 (*s*, 1H, N4—H), 12.56 (*s*, 1H, N2—H). Analysis calculated for $C_{17}H_{15}FN_4OS_2$ (374.45): C, 54.53; H, 4.04; N, 14.96. Found: C, 54.24; H, 4.09; N, 14.99. 3.

Refinement

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{15}FN_4OS_2$
M_r	374.45
Crystal system, space group	Monoclinic, *Cc*
Temperature (K)	296
a, *b*, *c* (Å)	7.9661 (6), 20.8680 (17), 10.4774 (9)
β (°)	95.257 (3)
V (Å^3)	1734.4 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.33
Crystal size (mm)	0.19 × 0.15 × 0.14
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2007)
T_{min}, T_{max}	0.663, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18078, 3245, 2910
R_{int}	0.036
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.626
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.096, 1.10
No. of reflections	3245
No. of parameters	236
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, −0.23
Absolute structure	Flack (1983)
Absolute structure parameter	0.09 (12)

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

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full crystallographic data

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2-(5-Fluoro-1-methyl-2-oxoindolin-3-ylidene)-*N*-[4-(methylsulfanyl)phenyl]-hydrazine-1-carbothioamide

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2-(5-Fluoro-1-methyl-2-oxoindolin-3-ylidene)-*N*-[4-(methylsulfanyl)phenyl]hydrazine-1-carbothioamide

Crystal data

$C_{17}H_{15}FN_4OS_2$
M_r = 374.45
Monoclinic, *Cc*
Hall symbol: C -2yc
a = 7.9661 (6) Å
b = 20.8680 (17) Å
c = 10.4774 (9) Å
β = 95.257 (3)°
V = 1734.4 (2) Å^3
Z = 4
F(000) = 776
D_x = 1.434 Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å
Cell parameters from 9917 reflections
θ = 3.2–26.4°
μ = 0.33 mm^{-1}
T = 296 K
Block, orange
0.19 × 0.15 × 0.14 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2007)
T_{min} = 0.663, T_{max} = 0.745
18078 measured reflections
3245 independent reflections
2910 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 26.4°, θ_{min} = 3.2°
h = −9→8
k = −26→26
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.096
S = 1.10
3245 reflections
236 parameters
2 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0199P)^2 + 2.3048P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Extinction correction: SHELXL-2014 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.016 (2)
Absolute structure: Flack (1983)
Absolute structure parameter: 0.09 (12)

Special details

Experimental. The melting point was estimated with a Buchi 540 melting-point apparatus in an open capillary and is uncorrected. Elemental analysis was performed on a Thermo Finnigan Flash EA 1112 elemental analyzer. IR spectra was recorded on a KBr disc using a Perkin– Elmer Model 1600 FT–IR spectrometer. The ^{1}H NMR spectra were obtained on Bruker Avance DPX 400 spectrophotometer using DMSO-d_6. All chemicals and solvents were purchased from Merck–Schuchardt and Aldrich.

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses 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 observed criterion of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating -R-factor-obs 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.
C-bound H atoms were placed in calculated positions (C—H = 0.93 Å and 0.96 Å) and N-bound H atoms were found from a difference Fourier map. All H atoms were refined using the riding-model approximation with U_{iso}(H) = 1.2 or 1.5 U_{eq}(C,*N*). The coordinates of the H atoms bonded to N were refined.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.7480 (2)	0.42568 (6)	0.83501 (13)	0.0655 (5)
S2	0.8897 (2)	0.76426 (7)	0.92299 (15)	0.0745 (6)
F1	0.1155 (5)	0.53841 (19)	0.0901 (3)	0.0908 (16)
O1	0.4820 (5)	0.30064 (15)	0.5192 (3)	0.0583 (13)
N1	0.3211 (5)	0.31394 (17)	0.3247 (3)	0.0492 (14)
N2	0.4943 (5)	0.44513 (16)	0.5056 (3)	0.0428 (11)
N3	0.5831 (5)	0.41981 (18)	0.6103 (3)	0.0459 (11)
N4	0.6774 (5)	0.52015 (16)	0.6595 (3)	0.0428 (10)
C1	0.2595 (6)	0.3667 (2)	0.2503 (4)	0.0452 (16)
C2	0.1575 (6)	0.3670 (3)	0.1361 (4)	0.0603 (18)
C3	0.1126 (6)	0.4254 (3)	0.0825 (4)	0.0639 (18)
C4	0.1651 (6)	0.4813 (3)	0.1437 (4)	0.0591 (19)
C5	0.2671 (6)	0.4819 (2)	0.2571 (4)	0.0503 (17)
C6	0.3147 (5)	0.4240 (2)	0.3100 (4)	0.0426 (12)
C7	0.4150 (5)	0.40606 (19)	0.4266 (4)	0.0407 (11)
C8	0.4131 (6)	0.33431 (19)	0.4325 (4)	0.0450 (14)
C9	0.2977 (8)	0.2468 (2)	0.2914 (6)	0.072 (2)
C10	0.6701 (6)	0.45967 (19)	0.6982 (4)	0.0432 (14)
C11	0.7340 (5)	0.57666 (19)	0.7249 (3)	0.0379 (11)
C12	0.8323 (6)	0.5784 (2)	0.8413 (4)	0.0467 (14)
C13	0.8783 (6)	0.6365 (2)	0.8973 (4)	0.0502 (16)
C14	0.8271 (6)	0.6943 (2)	0.8390 (4)	0.0497 (16)
C15	0.7321 (6)	0.6925 (2)	0.7212 (4)	0.0498 (14)
C16	0.6853 (6)	0.63372 (19)	0.6650 (4)	0.0448 (14)
C17	0.8004 (10)	0.8275 (3)	0.8227 (7)	0.090 (3)
H2	0.12060	0.32900	0.09680	0.0720*
H3	0.04650	0.42720	0.00470	0.0760*
H3N	0.578 (7)	0.379 (2)	0.626 (5)	0.0550*

H4N	0.621 (6)	0.529 (2)	0.583 (5)	0.0520*
H5	0.30230	0.52030	0.29620	0.0600*
H9A	0.34370	0.23840	0.21150	0.1080*
H9B	0.17950	0.23680	0.28330	0.1080*
H9C	0.35430	0.22070	0.35740	0.1080*
H12	0.86720	0.54040	0.88170	0.0560*
H13	0.94450	0.63710	0.97510	0.0600*
H15	0.69950	0.73050	0.67970	0.0600*
H16	0.62070	0.63290	0.58650	0.0540*
H17A	0.84050	0.82420	0.73930	0.1350*
H17B	0.83330	0.86820	0.86000	0.1350*
H17C	0.67980	0.82410	0.81520	0.1350*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0947 (11)	0.0465 (6)	0.0489 (6)	−0.0041 (7)	−0.0286 (6)	0.0070 (6)
S2	0.0981 (12)	0.0552 (8)	0.0695 (9)	−0.0178 (8)	0.0044 (8)	−0.0215 (7)
F1	0.086 (3)	0.104 (3)	0.078 (2)	0.023 (2)	−0.0169 (19)	0.031 (2)
O1	0.076 (3)	0.0428 (17)	0.055 (2)	−0.0027 (16)	−0.0003 (17)	0.0041 (14)
N1	0.052 (3)	0.047 (2)	0.048 (2)	−0.0094 (17)	0.0018 (18)	−0.0098 (16)
N2	0.047 (2)	0.0440 (19)	0.0349 (17)	−0.0005 (16)	−0.0093 (15)	−0.0005 (14)
N3	0.058 (2)	0.0360 (18)	0.0401 (19)	−0.0043 (16)	−0.0151 (16)	0.0027 (15)
N4	0.055 (2)	0.0383 (18)	0.0321 (16)	−0.0053 (16)	−0.0123 (15)	0.0016 (13)
C1	0.040 (3)	0.058 (3)	0.038 (2)	−0.0052 (19)	0.0055 (19)	−0.0100 (18)
C2	0.043 (3)	0.094 (4)	0.042 (2)	−0.006 (3)	−0.006 (2)	−0.021 (3)
C3	0.044 (3)	0.104 (4)	0.041 (2)	0.002 (3)	−0.011 (2)	−0.008 (3)
C4	0.046 (3)	0.083 (4)	0.047 (3)	0.012 (2)	−0.003 (2)	0.018 (2)
C5	0.047 (3)	0.054 (3)	0.048 (3)	−0.003 (2)	−0.006 (2)	0.0053 (19)
C6	0.037 (2)	0.054 (2)	0.035 (2)	−0.0059 (19)	−0.0065 (17)	−0.0047 (17)
C7	0.043 (2)	0.042 (2)	0.0356 (19)	−0.0073 (18)	−0.0044 (17)	−0.0022 (17)
C8	0.050 (3)	0.040 (2)	0.045 (2)	−0.0059 (19)	0.0037 (19)	−0.0038 (19)
C9	0.082 (4)	0.052 (3)	0.083 (4)	−0.014 (3)	0.009 (3)	−0.028 (3)
C10	0.051 (3)	0.038 (2)	0.039 (2)	−0.0008 (19)	−0.0039 (18)	−0.0011 (17)
C11	0.038 (2)	0.043 (2)	0.0323 (19)	−0.0045 (17)	0.0010 (16)	−0.0023 (16)
C12	0.051 (3)	0.043 (2)	0.044 (2)	−0.0045 (19)	−0.007 (2)	0.0008 (18)
C13	0.057 (3)	0.056 (3)	0.036 (2)	−0.010 (2)	−0.005 (2)	−0.0051 (19)
C14	0.055 (3)	0.050 (3)	0.045 (2)	−0.011 (2)	0.010 (2)	−0.0097 (19)
C15	0.059 (3)	0.041 (2)	0.049 (2)	0.0017 (19)	0.003 (2)	0.0015 (18)
C16	0.055 (3)	0.039 (2)	0.039 (2)	0.0029 (19)	−0.0030 (19)	−0.0009 (16)
C17	0.137 (7)	0.044 (3)	0.092 (4)	−0.012 (3)	0.022 (4)	−0.013 (3)

Geometric parameters (Å, º)

S1—C10	1.667 (4)	C6—C7	1.446 (6)
S2—C14	1.753 (4)	C7—C8	1.499 (6)
S2—C17	1.793 (7)	C11—C16	1.385 (6)
F1—C4	1.361 (7)	C11—C12	1.388 (5)

O1—C8	1.236 (5)	C12—C13	1.382 (6)
N1—C1	1.411 (5)	C13—C14	1.396 (6)
N1—C8	1.357 (5)	C14—C15	1.388 (6)
N1—C9	1.452 (6)	C15—C16	1.397 (6)
N2—N3	1.357 (5)	C2—H2	0.9300
N2—C7	1.286 (5)	C3—H3	0.9300
N3—C10	1.380 (6)	C5—H5	0.9300
N4—C10	1.329 (5)	C9—H9A	0.9600
N4—C11	1.417 (5)	C9—H9B	0.9600
C1—C2	1.383 (6)	C9—H9C	0.9600
C1—C6	1.401 (6)	C12—H12	0.9300
C2—C3	1.375 (8)	C13—H13	0.9300
C3—C4	1.378 (8)	C15—H15	0.9300
N3—H3N	0.87 (4)	C16—H16	0.9300
N4—H4N	0.90 (5)	C17—H17A	0.9600
C4—C5	1.377 (6)	C17—H17B	0.9600
C5—C6	1.368 (6)	C17—H17C	0.9600

C14—S2—C17	103.9 (3)	N4—C11—C12	125.2 (4)
C1—N1—C8	110.5 (3)	C11—C12—C13	120.2 (4)
C1—N1—C9	126.2 (4)	C12—C13—C14	121.1 (4)
C8—N1—C9	123.4 (4)	S2—C14—C13	116.2 (3)
N3—N2—C7	117.6 (3)	C13—C14—C15	118.7 (4)
N2—N3—C10	119.9 (4)	S2—C14—C15	125.2 (3)
C10—N4—C11	131.6 (3)	C14—C15—C16	120.1 (4)
N1—C1—C2	128.9 (4)	C11—C16—C15	120.8 (4)
N1—C1—C6	109.9 (4)	C1—C2—H2	121.00
C2—C1—C6	121.2 (4)	C3—C2—H2	121.00
C1—C2—C3	117.9 (5)	C2—C3—H3	120.00
C2—C3—C4	120.3 (4)	C4—C3—H3	120.00
N2—N3—H3N	120 (3)	C4—C5—H5	121.00
C10—N3—H3N	120 (4)	C6—C5—H5	121.00
F1—C4—C3	119.0 (4)	N1—C9—H9A	110.00
C10—N4—H4N	116 (3)	N1—C9—H9B	110.00
F1—C4—C5	118.3 (5)	N1—C9—H9C	109.00
C3—C4—C5	122.7 (5)	H9A—C9—H9B	109.00
C11—N4—H4N	112 (3)	H9A—C9—H9C	109.00
C4—C5—C6	117.5 (4)	H9B—C9—H9C	109.00
C1—C6—C5	120.6 (4)	C11—C12—H12	120.00
C1—C6—C7	106.4 (4)	C13—C12—H12	120.00
C5—C6—C7	133.0 (4)	C12—C13—H13	119.00
N2—C7—C8	127.8 (4)	C14—C13—H13	119.00
C6—C7—C8	106.7 (3)	C14—C15—H15	120.00
N2—C7—C6	125.5 (4)	C16—C15—H15	120.00
O1—C8—N1	127.1 (4)	C11—C16—H16	120.00
O1—C8—C7	126.3 (4)	C15—C16—H16	120.00
N1—C8—C7	106.6 (3)	S2—C17—H17A	109.00
N3—C10—N4	113.7 (4)	S2—C17—H17B	109.00

S1—C10—N3	116.2 (3)	S2—C17—H17C	110.00
S1—C10—N4	130.0 (3)	H17A—C17—H17B	109.00
N4—C11—C16	115.7 (3)	H17A—C17—H17C	110.00
C12—C11—C16	119.2 (4)	H17B—C17—H17C	109.00
C17—S2—C14—C15	0.8 (5)	C1—C2—C3—C4	−1.7 (7)
C17—S2—C14—C13	−179.1 (4)	C2—C3—C4—F1	−178.4 (4)
C9—N1—C1—C2	4.2 (8)	C2—C3—C4—C5	2.0 (7)
C8—N1—C1—C6	0.9 (5)	C3—C4—C5—C6	−0.9 (7)
C8—N1—C1—C2	−178.1 (5)	F1—C4—C5—C6	179.6 (4)
C9—N1—C8—C7	176.4 (4)	C4—C5—C6—C1	−0.5 (7)
C1—N1—C8—O1	178.5 (5)	C4—C5—C6—C7	−178.3 (4)
C9—N1—C1—C6	−176.8 (5)	C1—C6—C7—C8	−0.8 (5)
C1—N1—C8—C7	−1.4 (5)	C1—C6—C7—N2	176.8 (4)
C9—N1—C8—O1	−3.7 (8)	C5—C6—C7—C8	177.2 (5)
N3—N2—C7—C6	−179.8 (4)	C5—C6—C7—N2	−5.1 (8)
C7—N2—N3—C10	−179.8 (4)	C6—C7—C8—O1	−178.5 (5)
N3—N2—C7—C8	−2.6 (7)	C6—C7—C8—N1	1.3 (5)
N2—N3—C10—N4	−9.6 (6)	N2—C7—C8—O1	3.9 (8)
N2—N3—C10—S1	170.0 (3)	N2—C7—C8—N1	−176.2 (4)
C10—N4—C11—C12	15.7 (7)	N4—C11—C16—C15	179.3 (4)
C11—N4—C10—S1	−8.7 (8)	C12—C11—C16—C15	−0.9 (7)
C11—N4—C10—N3	170.8 (4)	N4—C11—C12—C13	−179.1 (4)
C10—N4—C11—C16	−164.5 (5)	C16—C11—C12—C13	1.1 (7)
N1—C1—C2—C3	179.2 (4)	C11—C12—C13—C14	0.2 (7)
C2—C1—C6—C7	179.1 (4)	C12—C13—C14—C15	−1.7 (7)
N1—C1—C6—C7	0.0 (5)	C12—C13—C14—S2	178.3 (4)
C6—C1—C2—C3	0.4 (7)	S2—C14—C15—C16	−178.1 (4)
C2—C1—C6—C5	0.8 (7)	C13—C14—C15—C16	1.9 (7)
N1—C1—C6—C5	−178.3 (4)	C14—C15—C16—C11	−0.6 (7)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*N*···O1	0.87 (4)	2.09 (5)	2.757 (5)	133 (5)
N4—H4*N*···N2	0.90 (5)	2.14 (5)	2.598 (5)	110 (3)
C3—H3···S1^{i}	0.93	2.84	3.712 (5)	158
C9—H9*B*···S2^{ii}	0.96	2.84	3.652 (7)	142
C9—H9*C*···O1	0.96	2.52	2.911 (7)	104
C12—H12···S1	0.93	2.61	3.256 (4)	128

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