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2-Fluorobenzyl (*Z*)-2-(5-chloro-2-oxoindolin-3-ylidene)hydrazine-1-carbodithioate dimethyl sulfoxide monosolvate

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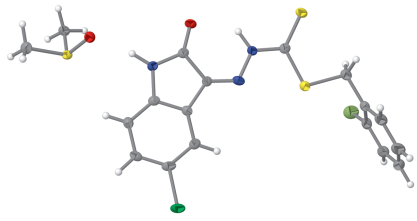
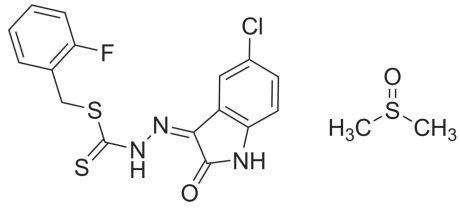
In the title solvate, $C_{16}H_{11}ClFN_3OS_2\cdot C_2H_6OS$, the C=N bond adopts a *Z*-configuration facilitating the formation of an intramolecular N—H···O hydrogen bond to the carbonyl O atom in an *S*(6) loop. The dimethylsulfoxide solvent molecule accepts a strong discrete N—H···O hydrogen bond from the γ-lactam grouping. In the extended structure, C_{ar}—H···S hydrogen bonds and quasi-Type I/II Cl···F halogen···halogen bonds are observed, while adjacent dimethyl sulfoxide molecules form S···O chalcogen-bonded chains.

3D view



Chemical scheme



Structure description

Halogen bonding is defined as a directional non-covalent attractive interaction between an electrophilic region of a halogen atom (the halogen-bond donor) and a Lewis base (the acceptor) (Desiraju *et al.*, 2013). The halogen···halogen subset of halogen bonding is divided into four major categories based on their geometry (Saha *et al.*, 2023) with the first two being Type I ($90 < \theta_1 \simeq \theta_2 < 180°$) and Type II ($\theta_1 \simeq 180°$, $\theta_2 \simeq 90°$), where θ_1 and θ_2 are the C—X···X' and C—X'···X angles, respectively (X, X' = F, Cl, Br, I; Desiraju & Parthasarathy, 1989; Nayak *et al.*, 2011). Organic molecules containing fluorine are of interest due to their prevalence in pharmaceuticals (Inoue *et al.* 2020; Du *et al.* 2025), with F atoms shown to act as the nucleophilic acceptors in a range of intermolecular interactions including halogen and chalcogen bonding (Cole & Taylor, 2022), as well as unusual short C—F···F—C interactions (Singla *et al.*, 2023), while having a van der Waals radii not much larger than that of hydrogen. As part of our studies in this area, we now report the synthesis and structure of the title solvate, $C_{16}H_{11}ClFN_3OS_2\cdot C_2H_6OS$ (**1**).

Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with one molecule and a dimethylsulfoxide (DMSO) solvent molecule in the asymmetric unit (Fig. 1). The C=N bond displays a *Z*-configuration, resulting in the hydrazine N4—H hydrogen atom being

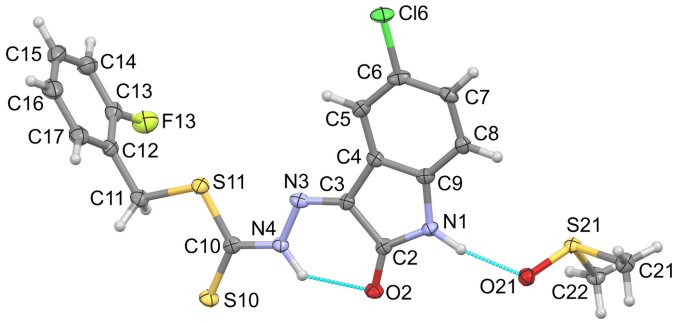


Figure 1
The molecular structure of **1** with displacement ellipsoids drawn at 50% probability and hydrogen bonds shown as blue dashed lines.

directed towards the isatin-O2 atom giving a intramolecular N—H···O hydrogen bond, generating an *S*(6) ring motif, while the N1—H amide of the γ-lactam forms a discrete N—H···O hydrogen bond to the DMSO solvate (Table 1). The isatin (O2) group is *syn* to the thione S10 atom with the *S*-2-fluorobenzyl moiety orientated in the opposite direction. The structure shows a small bow between the methylidenehydrazinecarbodithioate (MHT) grouping and the γ-lactam ring of 6.52 (12)° and the 2-fluorophenyl ring is twisted perpendicular to the MHT at 89.67 (11)°. Non-classical C_{ar}—H···S hydrogen bonds from the fused aromatic ring (C7) of the isatin moiety to S10 of the adjacent molecule related by the glide plane (x, $-y+\frac{3}{2}$, $z+\frac{1}{2}$) link molecules into pleated *C*(10) chains propagating along [001]. Alongside this hydrogen bond, there is a Cl···F halogen···halogen bond [Cl6···F13 = 2.936 (3) Å, C6—Cl6···F13 = 171.08 (15)°, C13—F13···Cl6 = 147.1 (2)°] between the same adjacent molecules, which adopts a quasi-Type I/II geometry [$\Delta\theta$ = 24.0 (4)°, where $\Delta\theta = |\theta_1 - \theta_2|$; Tothadi *et al.*, 2013] (Fig. 2). Hetero-halogen···halogen interactions ($X \neq X'$) have been found to generally favour Type II interactions ($30 < \Delta\theta < 90°$), which have attractive character, in the same electrophile···Lewis base manner as hydrogen bonding (Veluthaparambath *et al.*, 2023), although Cl···F halogen bonds generally show a spread of types more similar to homo-halogen···halogen interactions (Pedireddi *et al.*, 1994). The observed quasi-Type I/II Cl···F halogen bond is consistent with the general trend of Type II hetero-halogen···halogen interactions where θ for the heavier halogen is greater than θ at the lighter atom (Tothadi *et al.*, 2013). The pleated chains further pack together through weak, non-standard, π–π stacking [centroid$_{C4>C9}$···centroid$_{N3=C3}$ = 3.302 (4) Å] between the fused benzo ring (C4–C9), of the isatin moiety and the C3═N3 bond of a translation-related (x, y + 1, z) adjacent molecule. Concurrently, translation-related (x, $y\pm1$, z) DMSO solvent molecules form chalcogen-bonded [S21···O21 = 3.209 (3) Å, S21—O21···S21 = 173.82 (14)°] chains along [010], which, together with the C_{ar}—H···S hydrogen bonds and the π–π stacking, results in the formation of sheets parallel to (100). These sheets then pack together through a variety of weaker C—H···F [H···F = 2.865 (3) Å, C···F = 3.761 (5) Å] and C—H···Cl [H···Cl = 2.9968 (10)–3.3158 (10) Å, C···Cl 3.567 (4)–4.080 (4) Å] interactions.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O21	0.97 (2)	1.86 (2)	2.822 (4)	169 (5)
N4—H4···O2	0.96 (2)	1.98 (3)	2.749 (4)	135 (4)
C7—H7···S10^{i}	0.95	2.99	3.933 (4)	170

Symmetry code: (i) x, $-y+\frac{3}{2}$, $z+\frac{1}{2}$.

Hirshfeld analysis of **1** with the DMSO external to the surface, generated using *CrystalExplorer* (Spackman & Jayatilaka, 2009; Spackman *et al.*, 2021), shows sharp peaks in the fingerprint plots for both H···O and H···S contacts (5.6 and 16.1% of the overall surface, respectively) as would be expected from the observed classical and non-classical hydrogen bonding described above. The H···S fingerprint does show a broad tail indicating a diverse range of H···S contacts occurring beyond the discrete C—H···S hydrogen

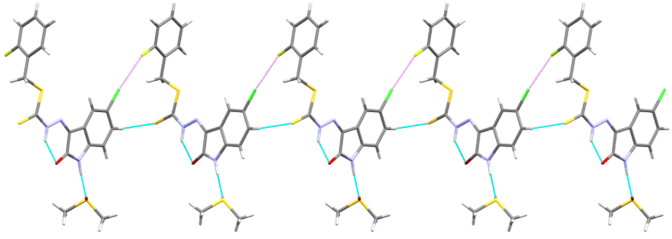


Figure 2
View along the *b* axis showing the packing of **1** into chains along [001] through a mixture of non-classical hydrogen bonding (blue dashed lines) and halogen bonding (violet dashed lines).

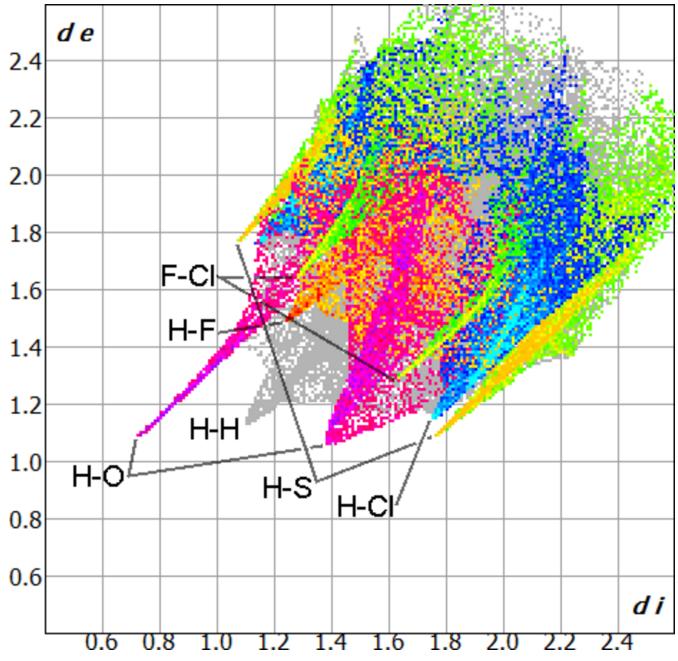


Figure 3
Hirshfeld fingerprint plot of **1** (with DMSO external to the surface) with H···O (pink/purple), H···F (red/orange), H···S (orange), H···Cl (blue), and F···Cl (yellow/green) contacts superimposed.

bonds. Similarly, sharp peaks are observed in the fingerprint plots for both H···Cl and H···F contacts (11.7 and 5.5% of the overall surface, respectively) consistent with the weaker C—H···*X* interactions noted above (Fig. 3). While the fingerprint plot for H···H contacts does show a sharp peak, this corresponds to a contact between hydrogen atoms on the DMSO methyl group and an aromatic C—H grouping with H···H > 2.3 Å, so it is considered unlikely to represent an attractive interaction.

Synthesis and crystallization

The 2-fluorobenzyl hydrazinecarbodithioate precursor **2**, was synthesized using our published methods for related compounds with minor modifications (Manan *et al.*, 2011) (Fig. 4). Potassium hydroxide (11.2 g, 0.2 mol, 1.0 eq) was dissolved in 70 ml of 90% ethanol and to this solution was added hydrazine hydrate (10.0 g, 0.2 mol, 99%, 1.0 eq) and stirred at 0 °C. To the resultant cooled solution, carbon disulfide (15.2 g, 0.2 mol, 1.0 eq) was added dropwise, whilst maintaining the solution below 0 °C with constant stirring. Upon addition of carbon disulfide, two layers were formed and the lower, brown, layer was collected. 40% ethanol (60 ml) was added to the brown solution and the resulting mixture was cooled in an ice bath while 2-fluorobenzyl chloride (28.9 g, 0.2 mol, 1.0 eq) was added dropwise with vigorous stirring. The white product formed was filtered and used directly for the next step without further purification.

A solution of 5-chloroisatin (1.82 g, 10.0 mmol) in hot ethanol (40 ml) was added to a solution of the dithiocarbazate precursor **2** (2.16 g, 10.0 mmol, 1.0 e.q) in hot ethanol (40 ml). The mixture was heated (80 °C) with continuous stirring for 15 min and later allowed to cool to room temperature and stand for about 20 min., until a precipitate formed, which was then collected by filtration and dried over silica gel. The crude solids were purified by recrystallization from ethanol solution to yield compound **1** as a light-yellow solid (yield: 3.23 g, 85%). m.p 227–228 °C. Elemental analysis calculated for $C_{16}H_{11}ClFN_3OS_2$: C, 50.59; H, 2.92; N, 11.06%. Found: C, 50.67; H, 2.89; N, 11.01%. FT–IR (KBr, ν, cm^{-1}): 3155 (NH), 1692 (C═O); 1613 (C═N); 1070 (C═S); 1141 (N—N); ^{1}H NMR (400 MHz, d_6-DMSO) δ: (p.p.m.): 4.56 (*s*, 2H), 6.96 (*d*, *J* = 8.3 Hz, 1H) 7.18–7.26 (*m*, 2H), 7.36–7.45 (*m*, 2H), 7.53–7.58 (*m*, 2H), 11.47 (*s*, 1H), 13.89 (*s*, 1H). Crystals suitable for X-ray diffraction were grown by slow evaporation of a dimethyl sulfoxide solution at room temperature.

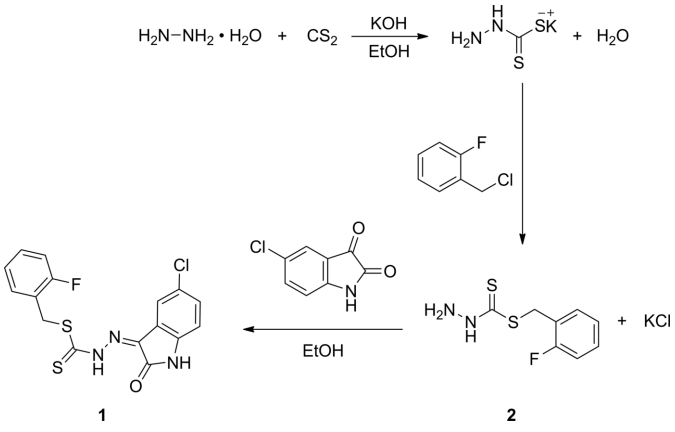


Figure 4
A synthetic scheme for the preparation of **1**.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{11}ClFN_3OS_2{\cdot}C_2H_6OS$
M_r	457.97
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, *b*, *c* (Å)	22.7322 (9), 4.72526 (18), 18.8781 (6)
β (°)	95.690 (3)
V (Å^3)	2017.81 (13)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.53
Crystal size (mm)	0.35 × 0.02 × 0.01
Data collection	
Diffractometer	Rigaku XtaLAB P200K
Absorption correction	Multi-scan (*CrysAlis PRO*; (Rigaku OD, 2023)
T_{min}, T_{max}	0.324, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	31534, 4903, 2962
R_{int}	0.132
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.687
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.072, 0.149, 1.02
No. of reflections	4903
No. of parameters	263
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})	0.67, −0.61

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2019/3* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2020), *enCIFer* (Allen *et al.*, 2004), *publCIF* (Westrip, 2010) and *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

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

Acknowledgements

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full crystallographic data

IUCrData (2025). **10**, x250849 [https://doi.org/10.1107/S2414314625008491]

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Crystal data

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$M_r = 457.97$
Monoclinic, $P2_1/c$
$a = 22.7322$ (9) Å
$b = 4.72526$ (18) Å
$c = 18.8781$ (6) Å
$\beta = 95.690$ (3)°
$V = 2017.81$ (13) Å^3
$Z = 4$
$F(000) = 944$
$D_x = 1.508$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8236 reflections
$\theta = 2.3$–$28.7°$
$\mu = 0.53$ mm^{-1}
$T = 100$ K
Needle, yellow
0.35 × 0.02 × 0.01 mm

Data collection

Rigaku XtaLAB P200K diffractometer
Radiation source: Rotating Anode, Rigaku FR-X
Rigaku Osmic Confocal Optical System monochromator
Detector resolution: 5.8140 pixels mm^{-1}
shutterless scans
Absorption correction: multi-scan (CrysAlis PRO; (Rigaku OD, 2023)
$T_{min} = 0.324$, $T_{max} = 1.000$
31534 measured reflections
4903 independent reflections
2962 reflections with $I > 2\sigma(I)$
$R_{int} = 0.132$
$\theta_{max} = 29.2°$, $\theta_{min} = 2.3°$
$h = -31 \rightarrow 30$
$k = -6 \rightarrow 6$
$l = -24 \rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.072$
$wR(F^2) = 0.149$
$S = 1.02$
4903 reflections
263 parameters
2 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 4.1991P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.67$ e Å^{-3}
$\Delta\rho_{min} = -0.61$ 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. Hydrogen atoms on N1 and N4 were located from the F_{map} and refined isotropically with N—H distance restrained. The DMSO solvate in the asymmetric unit is positioned outside the cell to clearly show discrete hydrogen bonding interaction between O21 and N1

The N-bound H atoms were located in a difference map and refined isotropically subject to a distance restraint. The C-bound H atoms were located geometrically (C—H = 0.95–0.99 Å) and refined as riding atoms. The constraint U_{iso}(H) = 1.2U_{eq}(phenyl or methylene C) or 1.5U_{eq}(methyl C) was applied in all cases.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl6	0.16950 (4)	1.1289 (2)	0.46870 (5)	0.0295 (3)
S10	0.27118 (4)	−0.1842 (2)	0.11690 (5)	0.0227 (2)
S11	0.17063 (4)	0.0822 (2)	0.18841 (5)	0.0221 (2)
F13	0.06348 (11)	0.2730 (6)	0.04236 (12)	0.0380 (6)
O2	0.39363 (11)	0.3792 (6)	0.26762 (12)	0.0207 (6)
N1	0.38425 (13)	0.7436 (7)	0.34837 (15)	0.0189 (7)
H1	0.4256 (11)	0.791 (12)	0.361 (3)	0.073 (18)*
N3	0.26014 (13)	0.3703 (7)	0.26647 (14)	0.0186 (7)
N4	0.28239 (13)	0.1886 (7)	0.22016 (15)	0.0178 (7)
H4	0.3246 (9)	0.180 (10)	0.218 (2)	0.043 (13)*
C2	0.36404 (15)	0.5343 (8)	0.30279 (18)	0.0169 (8)
C3	0.29790 (16)	0.5261 (8)	0.30428 (18)	0.0166 (8)
C5	0.23135 (16)	0.8183 (8)	0.38204 (18)	0.0202 (8)
H5	0.194712	0.734549	0.364798	0.024*
C6	0.23440 (16)	1.0262 (9)	0.43396 (18)	0.0228 (9)
C7	0.28730 (17)	1.1543 (8)	0.45932 (18)	0.0213 (9)
H7	0.287629	1.296018	0.495051	0.026*
C8	0.33970 (17)	1.0761 (8)	0.43270 (18)	0.0204 (8)
H8	0.376092	1.164404	0.449018	0.025*
C9	0.33718 (16)	0.8657 (8)	0.38168 (18)	0.0180 (8)
C4	0.28394 (16)	0.7369 (8)	0.35610 (17)	0.0174 (8)
C10	0.24498 (16)	0.0307 (8)	0.17534 (18)	0.0187 (8)
C11	0.13311 (17)	−0.1415 (9)	0.11935 (19)	0.0243 (9)
H11A	0.143520	−0.083799	0.071737	0.029*
H11B	0.144229	−0.342351	0.127333	0.029*
C12	0.06787 (16)	−0.0994 (9)	0.12501 (19)	0.0220 (9)
C13	0.03534 (17)	0.1027 (9)	0.08605 (19)	0.0258 (9)
C14	−0.02408 (18)	0.1457 (10)	0.0900 (2)	0.0325 (10)
H14	−0.045051	0.285628	0.061553	0.039*
C15	−0.05252 (19)	−0.0197 (10)	0.1365 (2)	0.0366 (11)
H15	−0.093438	0.007759	0.140623	0.044*
C16	−0.0218 (2)	−0.2235 (10)	0.1766 (2)	0.0368 (11)
H16	−0.041683	−0.337315	0.208217	0.044*
C17	0.03795 (18)	−0.2645 (9)	0.1714 (2)	0.0299 (10)

H17	0.058766	−0.405945	0.199507	0.036*
S21	0.50398 (4)	1.2715 (2)	0.39061 (4)	0.0183 (2)
O21	0.49915 (11)	0.9503 (6)	0.38890 (13)	0.0223 (6)
C21	0.56233 (17)	1.3495 (9)	0.45825 (18)	0.0247 (9)
H21A	0.550478	1.293115	0.504730	0.037*
H21B	0.570580	1.553093	0.458431	0.037*
H21C	0.597955	1.245142	0.448706	0.037*
C22	0.54195 (17)	1.3726 (9)	0.31624 (18)	0.0220 (9)
H22A	0.578537	1.262801	0.316345	0.033*
H22B	0.551476	1.574700	0.319444	0.033*
H22C	0.516682	1.335640	0.272074	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl6	0.0265 (5)	0.0366 (6)	0.0274 (5)	0.0067 (5)	0.0128 (4)	−0.0034 (5)
S10	0.0261 (5)	0.0255 (6)	0.0178 (4)	0.0005 (4)	0.0079 (4)	−0.0039 (4)
S11	0.0210 (5)	0.0266 (6)	0.0192 (4)	−0.0012 (4)	0.0048 (4)	−0.0054 (4)
F13	0.0392 (14)	0.0445 (16)	0.0311 (13)	0.0032 (13)	0.0083 (11)	0.0046 (12)
O2	0.0227 (14)	0.0226 (15)	0.0181 (12)	0.0011 (12)	0.0090 (11)	−0.0017 (11)
N1	0.0170 (16)	0.0208 (18)	0.0196 (15)	−0.0008 (14)	0.0050 (13)	−0.0001 (14)
N3	0.0243 (17)	0.0199 (18)	0.0127 (14)	0.0041 (14)	0.0070 (12)	0.0024 (13)
N4	0.0189 (16)	0.0200 (18)	0.0153 (14)	−0.0009 (14)	0.0051 (12)	−0.0022 (13)
C2	0.0185 (18)	0.019 (2)	0.0137 (16)	−0.0007 (16)	0.0042 (14)	0.0047 (15)
C3	0.0180 (18)	0.018 (2)	0.0138 (16)	−0.0020 (16)	0.0038 (14)	0.0029 (15)
C5	0.0192 (19)	0.025 (2)	0.0162 (17)	0.0000 (17)	0.0031 (14)	0.0034 (16)
C6	0.023 (2)	0.032 (2)	0.0154 (17)	0.0073 (18)	0.0087 (15)	0.0057 (17)
C7	0.029 (2)	0.019 (2)	0.0164 (17)	0.0038 (17)	0.0059 (16)	−0.0003 (16)
C8	0.023 (2)	0.020 (2)	0.0173 (17)	−0.0012 (17)	0.0002 (15)	−0.0002 (16)
C9	0.0196 (18)	0.020 (2)	0.0155 (16)	0.0027 (16)	0.0048 (14)	0.0047 (15)
C4	0.0219 (19)	0.019 (2)	0.0121 (16)	0.0009 (17)	0.0030 (14)	0.0009 (16)
C10	0.0205 (19)	0.021 (2)	0.0147 (17)	0.0006 (17)	0.0033 (15)	0.0039 (16)
C11	0.026 (2)	0.027 (2)	0.0210 (18)	−0.0011 (18)	0.0052 (16)	−0.0052 (18)
C12	0.0223 (19)	0.026 (2)	0.0174 (17)	−0.0011 (18)	0.0023 (15)	−0.0068 (17)
C13	0.027 (2)	0.031 (2)	0.0196 (18)	−0.0062 (19)	0.0051 (16)	−0.0062 (18)
C14	0.026 (2)	0.039 (3)	0.031 (2)	0.004 (2)	−0.0011 (18)	−0.012 (2)
C15	0.023 (2)	0.043 (3)	0.045 (3)	−0.005 (2)	0.009 (2)	−0.019 (2)
C16	0.037 (3)	0.034 (3)	0.043 (3)	−0.005 (2)	0.020 (2)	−0.010 (2)
C17	0.034 (2)	0.028 (2)	0.029 (2)	−0.003 (2)	0.0106 (18)	−0.0062 (19)
S21	0.0184 (5)	0.0213 (5)	0.0159 (4)	0.0001 (4)	0.0058 (4)	−0.0007 (4)
O21	0.0230 (14)	0.0213 (15)	0.0232 (13)	−0.0031 (12)	0.0057 (11)	−0.0011 (12)
C21	0.026 (2)	0.032 (3)	0.0156 (17)	−0.0019 (19)	0.0012 (16)	−0.0007 (17)
C22	0.026 (2)	0.027 (2)	0.0153 (17)	−0.0025 (18)	0.0092 (15)	−0.0015 (17)

Geometric parameters (Å, º)

Cl6—C6	1.742 (4)	C9—C4	1.397 (5)
S10—C10	1.653 (4)	C11—H11A	0.9900

S11—C10	1.749 (4)	C11—H11B	0.9900
S11—C11	1.823 (4)	C11—C12	1.511 (5)
F13—C13	1.357 (4)	C12—C13	1.376 (6)
O2—C2	1.232 (4)	C12—C17	1.398 (5)
N1—H1	0.974 (19)	C13—C14	1.375 (5)
N1—C2	1.360 (5)	C14—H14	0.9500
N1—C9	1.417 (4)	C14—C15	1.382 (6)
N3—N4	1.358 (4)	C15—H15	0.9500
N3—C3	1.291 (5)	C15—C16	1.373 (7)
N4—H4	0.964 (19)	C16—H16	0.9500
N4—C10	1.362 (5)	C16—C17	1.385 (6)
C2—C3	1.507 (5)	C17—H17	0.9500
C3—C4	1.453 (5)	S21—O21	1.522 (3)
C5—H5	0.9500	S21—C21	1.786 (4)
C5—C6	1.384 (5)	S21—C22	1.785 (3)
C5—C4	1.390 (5)	C21—H21A	0.9800
C6—C7	1.388 (5)	C21—H21B	0.9800
C7—H7	0.9500	C21—H21C	0.9800
C7—C8	1.388 (5)	C22—H22A	0.9800
C8—H8	0.9500	C22—H22B	0.9800
C8—C9	1.381 (5)	C22—H22C	0.9800

C10—S11—C11	102.02 (17)	H11A—C11—H11B	108.8
C2—N1—H1	126 (3)	C12—C11—S11	105.4 (3)
C2—N1—C9	110.8 (3)	C12—C11—H11A	110.7
C9—N1—H1	123 (3)	C12—C11—H11B	110.7
C3—N3—N4	116.5 (3)	C13—C12—C11	122.2 (4)
N3—N4—H4	119 (3)	C13—C12—C17	116.9 (4)
N3—N4—C10	119.8 (3)	C17—C12—C11	120.9 (4)
C10—N4—H4	121 (3)	F13—C13—C12	118.4 (3)
O2—C2—N1	127.2 (3)	F13—C13—C14	118.1 (4)
O2—C2—C3	126.4 (3)	C14—C13—C12	123.5 (4)
N1—C2—C3	106.4 (3)	C13—C14—H14	120.8
N3—C3—C2	127.9 (3)	C13—C14—C15	118.4 (4)
N3—C3—C4	125.8 (3)	C15—C14—H14	120.8
C4—C3—C2	106.3 (3)	C14—C15—H15	119.9
C6—C5—H5	121.3	C16—C15—C14	120.2 (4)
C6—C5—C4	117.5 (3)	C16—C15—H15	119.9
C4—C5—H5	121.3	C15—C16—H16	119.8
C5—C6—Cl6	118.6 (3)	C15—C16—C17	120.5 (4)
C5—C6—C7	122.3 (3)	C17—C16—H16	119.8
C7—C6—Cl6	119.1 (3)	C12—C17—H17	119.7
C6—C7—H7	119.9	C16—C17—C12	120.5 (4)
C8—C7—C6	120.3 (3)	C16—C17—H17	119.7
C8—C7—H7	119.9	O21—S21—C21	105.54 (18)
C7—C8—H8	121.1	O21—S21—C22	106.83 (17)
C9—C8—C7	117.8 (4)	C22—S21—C21	97.15 (18)
C9—C8—H8	121.1	S21—C21—H21A	109.5

C8—C9—N1	128.4 (3)	S21—C21—H21B	109.5
C8—C9—C4	122.0 (3)	S21—C21—H21C	109.5
C4—C9—N1	109.6 (3)	H21A—C21—H21B	109.5
C5—C4—C3	132.8 (3)	H21A—C21—H21C	109.5
C5—C4—C9	120.2 (3)	H21B—C21—H21C	109.5
C9—C4—C3	107.0 (3)	S21—C22—H22A	109.5
S10—C10—S11	126.6 (2)	S21—C22—H22B	109.5
N4—C10—S10	120.5 (3)	S21—C22—H22C	109.5
N4—C10—S11	112.9 (3)	H22A—C22—H22B	109.5
S11—C11—H11A	110.7	H22A—C22—H22C	109.5
S11—C11—H11B	110.7	H22B—C22—H22C	109.5

Cl6—C6—C7—C8	179.9 (3)	C6—C5—C4—C9	−0.8 (5)
S11—C11—C12—C13	91.9 (4)	C6—C7—C8—C9	−1.1 (5)
S11—C11—C12—C17	−87.3 (4)	C7—C8—C9—N1	−177.7 (3)
F13—C13—C14—C15	−177.5 (4)	C7—C8—C9—C4	1.2 (5)
O2—C2—C3—N3	−4.6 (6)	C8—C9—C4—C3	−179.4 (3)
O2—C2—C3—C4	176.9 (3)	C8—C9—C4—C5	−0.2 (5)
N1—C2—C3—N3	176.1 (3)	C9—N1—C2—O2	−177.0 (3)
N1—C2—C3—C4	−2.4 (4)	C9—N1—C2—C3	2.3 (4)
N1—C9—C4—C3	−0.3 (4)	C4—C5—C6—Cl6	−178.9 (3)
N1—C9—C4—C5	178.8 (3)	C4—C5—C6—C7	0.9 (5)
N3—N4—C10—S10	178.1 (3)	C10—S11—C11—C12	−177.7 (3)
N3—N4—C10—S11	−2.5 (4)	C11—S11—C10—S10	−3.0 (3)
N3—C3—C4—C5	4.1 (6)	C11—S11—C10—N4	177.6 (3)
N3—C3—C4—C9	−176.9 (3)	C11—C12—C13—F13	−1.4 (5)
N4—N3—C3—C2	0.8 (5)	C11—C12—C13—C14	179.9 (4)
N4—N3—C3—C4	179.0 (3)	C11—C12—C17—C16	179.6 (4)
C2—N1—C9—C8	177.7 (4)	C12—C13—C14—C15	1.1 (6)
C2—N1—C9—C4	−1.3 (4)	C13—C12—C17—C16	0.4 (6)
C2—C3—C4—C5	−177.4 (4)	C13—C14—C15—C16	−0.8 (6)
C2—C3—C4—C9	1.6 (4)	C14—C15—C16—C17	0.4 (7)
C3—N3—N4—C10	−175.8 (3)	C15—C16—C17—C12	−0.2 (6)
C5—C6—C7—C8	0.1 (6)	C17—C12—C13—F13	177.8 (3)
C6—C5—C4—C3	178.1 (4)	C17—C12—C13—C14	−0.8 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O21	0.97 (2)	1.86 (2)	2.822 (4)	169 (5)
N4—H4···O2	0.96 (2)	1.98 (3)	2.749 (4)	135 (4)
C7—H7···S10^{i}	0.95	2.99	3.933 (4)	170

Symmetry code: (i) x, $-y+3/2$, $z+1/2$.