

5-Chloro-*N*-{4-oxo-2-[4-(trifluoromethyl)-phenyl]-1,3-thiazolidin-3-yl}-3-phenyl-1*H*-indole-2-carboxamide

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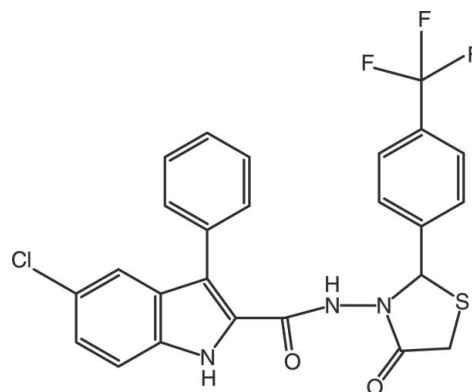
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; disorder in main residue; R factor = 0.073; wR factor = 0.210; data-to-parameter ratio = 14.4.

In the title compound, $\text{C}_{25}\text{H}_{17}\text{ClF}_3\text{N}_3\text{O}_2\text{S}$, the five-membered 1,3-thiazolidine ring adopts a twist conformation. The three F atoms of the CF_3 group are disordered over two sets of sites with refined occupancies of 0.542 (18) and 0.458 (18). In the nine-membered 1*H*-indoline ring system, the 1*H*-pyrrole ring forms a dihedral angle of 4.7 (2)° with the benzene ring, while it is twisted at an angle of 46.5 (2)° with respect to the attached phenyl ring. The dihedral angle between the phenyl and trifluoromethyl-substituted benzene rings is 56.0 (2)°. In the crystal, $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds connect the molecules into a three-dimensional network. In addition, weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds and weak $\text{C}-\text{H}\cdots\pi$ interactions are observed.

Related literature

For medicinal applications of indole derivatives, see: Beale (2011); Brancale & Silvestri (2007); Cihan-Ustundag & Capan (2012); Oudard *et al.* (2011); Verma & Saraf (2008). For the definition of ring-puckering parameters, see: Cremer & Pople (1975). For related structures, see: Akkurt *et al.* (2010, 2011*a,b,c*). For standard values of bond lengths, see: Allen *et al.* (1987).



Experimental

Crystal data

$\text{C}_{25}\text{H}_{17}\text{ClF}_3\text{N}_3\text{O}_2\text{S}$
 $M_r = 515.94$
 Tetragonal, $I4_1/a$
 $a = 22.9020$ (6) Å
 $c = 18.3260$ (6) Å
 $V = 9612.0$ (6) Å³

$Z = 16$
 Mo $K\alpha$ radiation
 $\mu = 0.30$ mm⁻¹
 $T = 296$ K
 $0.57 \times 0.43 \times 0.29$ mm

Data collection

Stoe IPDS 2 diffractometer
 Absorption correction: integration
 (*X-RED32*; Stoe & Cie, 2002)
 $T_{\min} = 0.849$, $T_{\max} = 0.919$

71781 measured reflections
 4968 independent reflections
 3054 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.076$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.073$
 $wR(F^2) = 0.210$
 $S = 1.05$
 4968 reflections
 345 parameters

14 restraints
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.53$ e Å⁻³
 $\Delta\rho_{\min} = -0.30$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$Cg1$ and $Cg2$ are the centroids of the $\text{N1}/\text{C1}/\text{C6}-\text{C8}$ and $\text{C9}-\text{C14}$ rings, respectively.

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{N1}-\text{H1}\cdots\text{O1}^{\text{i}}$ | 0.86 | 2.08 | 2.864 (4) | 151 |
| $\text{N2}-\text{H2A}\cdots\text{O2}^{\text{ii}}$ | 0.86 | 2.34 | 2.851 (4) | 118 |
| $\text{C18}-\text{H18}\cdots\text{O2}^{\text{ii}}$ | 0.98 | 2.53 | 3.145 (5) | 121 |
| $\text{C24}-\text{H24}\cdots\text{Cg1}^{\text{iii}}$ | 0.93 | 2.77 | 3.438 (5) | 129 |
| $\text{C17}-\text{H17B}\cdots\text{Cg2}^{\text{iv}}$ | 0.97 | 2.95 | 3.799 (5) | 147 |

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $y - \frac{1}{4}, -x + \frac{3}{4}, -z + \frac{3}{4}$; (iii) $-y + \frac{3}{4}, x + \frac{1}{4}, z + \frac{3}{4}$; (iv) $-y + \frac{5}{4}, x + \frac{1}{4}, -z + \frac{3}{4}$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5532).

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supporting information

Acta Cryst. (2012). E68, o2969–o2970 [https://doi.org/10.1107/S1600536812039347]

5-Chloro-*N*-{4-oxo-2-[4-(trifluoromethyl)phenyl]-1,3-thiazolidin-3-yl}-3-phenyl-1*H*-indole-2-carboxamide

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S1. Comment

The indole ring system is one of the most encountered heterocycles in natural and synthetic drug compounds (Brancale & Silvestri, 2007). Several indole derivatives, such as sunitinib as tyrosine kinase inhibitor (Oudard *et al.*, 2011) or delavirdine as nonnucleoside reverse transcriptase inhibitor (Beale, 2011), are in clinical use. Here, we aimed to combine this basic scaffold with 4-thiazolidinones, which have been shown to have anticancer (Cihan-Ustundag & Capan, 2012), antifungal, antibacterial and antiviral properties (Verma & Saraf, 2008), to obtain leads toward the design of anticancer compounds.

The molecular structure of the title compound is shown in Fig. 1. The 1,3-thiazolidine ring (S1/N3/C16–C18) has a twist conformation as indicated by the puckering parameters (Cremer & Pople, 1975) of $Q(2) = 0.354(4) \text{ \AA}$, $\varphi(2) = 342.0(6)^\circ$. In the nine-membered 1*H*-indoline ring system (N1/C1–C8), the 1*H*-pyrrole ring (N1C1/C6–C8) makes a dihedral angle of $4.7(2)^\circ$ with the benzene ring (C1–C6), while it is twisted an angle of $46.5(2)^\circ$ with respect to the attached phenyl ring (C9–C14). The dihedral angle between the C9–C14 phenyl and C19–C24 benzene rings which are attached to the *H*-pyrrole and 1,3-thiazolidine rings, respectively, is $56.0(2)^\circ$.

All bond lengths and bond angles in (I) are within normal ranges (Allen *et al.*, 1987) and are comparable to those reported for the related structures (Akkurt *et al.*, 2010, 2011*a,b,c*). The C7–C15–N2–N3, N1–C7–C15–O1 and O1–C15–N2–N3 torsion angles are $176.4(3)$, $-19.5(5)$ and $-2.6(5)^\circ$, respectively.

In the crystal, N—H \cdots O and weak C—H \cdots O hydrogen bonds, and C—H $\cdots\pi$ interactions stabilize the crystal structure, forming a three-dimensional network (Table 1).

S2. Experimental

0.002 mol of *N'*-(4-(trifluoromethyl)benzylidene-5-chloro-3-phenyl-1*H*-indole-2-carbohydrazide) was reacted with 3 ml of mercaptoacetic acid in anhydrous benzene for 6 h using a Dean–Stark trap. Excess benzene was removed under reduced pressure. The residue was triturated with saturated sodium bicarbonate solution. The separated solid was filtered, washed with water and crystallized from ethanol. Orange crystalline solid. m.p. 510 K. IR (KBr) ν 3303 (indol N—H and amide N—H); 1717 (C=O), 1655, (C=O) cm^{-1} ; Analysis calculated for $\text{C}_{25}\text{H}_{17}\text{ClF}_3\text{N}_3\text{O}_2\text{S}$: C: 58.20; H: 3.32; N: 8.14%. Found: C: 57.18; H: 3.59; N: 7.87%.

S3. Refinement

H atoms were positioned geometrically, with N—H = 0.86 Å, C—H = 0.93 Å (aromatic), 0.97 Å (methylene) and 0.98 Å (methine) H atoms, respectively, and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{N})$. The three fluorine atoms of the CF_3 group are disordered over two sets of sites in a 0.542(18):0.458(18) ratio. The carbon atom of the CF_3 group was refined

as two atoms (C25 and C25') sharing the same site [their xyz and U^{ij} parameters were equated by dummy atom constraints using the EXYZ and EADP commands]. Thirteen poorly fitted reflections (-4 6 0), (-2 4 2), (2 8 2), (-3 6 1), (0 6 2), (2 9 5), (-1 3 6), (1 1 2), (-1 2 3), (1 2 3), (2 2 2), (-7 10 7) and (3 4 3) were omitted from the refinement. These reflections have Fobs much greater than Fcalc and this might be attributed to the poor quality of the available crystal and the presence of disorder in the structure.

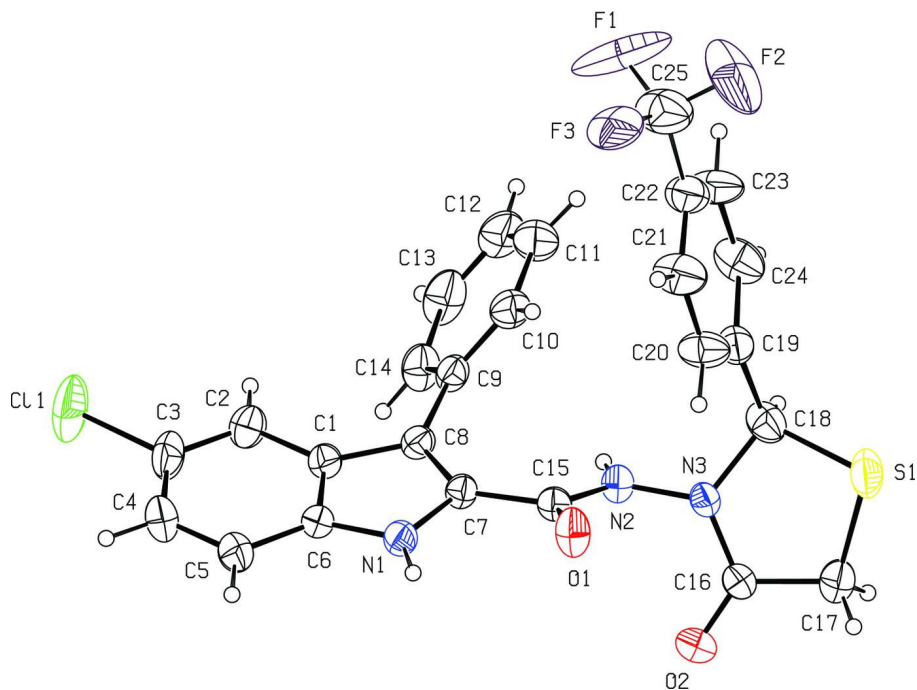


Figure 1

The molecular structure of the title compound with displacement ellipsoids for non-H atoms drawn at the 30% probability level. The disorder is not shown.

5-Chloro-*N*-{4-oxo-2-[4-(trifluoromethyl)phenyl]-1,3-thiazolidin-3-yl}-3-phenyl-1*H*-indole-2-carboxamide

Crystal data

$C_{25}H_{17}ClF_3N_3O_2S$

$M_r = 515.94$

Tetragonal, $I4_1/a$

Hall symbol: -I 4ad

$a = 22.9020$ (6) Å

$c = 18.3260$ (6) Å

$V = 9612.0$ (6) Å³

$Z = 16$

$F(000) = 4224$

$D_x = 1.426$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 45035 reflections

$\theta = 1.4$ – 27.8°

$\mu = 0.30$ mm⁻¹

$T = 296$ K

Prism, orange

$0.57 \times 0.43 \times 0.29$ mm

Data collection

Stoe IPDS 2

diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4

mm long-fine focus

Plane graphite monochromator

Detector resolution: 6.67 pixels mm⁻¹

ω scans

Absorption correction: integration

(*X-RED32*; Stoe & Cie, 2002)

$T_{\min} = 0.849$, $T_{\max} = 0.919$

71781 measured reflections

4968 independent reflections

3054 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.076$

$$\theta_{\max} = 26.5^\circ, \theta_{\min} = 1.8^\circ$$

$$h = -28 \rightarrow 28$$

$$k = -28 \rightarrow 28$$

$$l = -22 \rightarrow 22$$

*Refinement*Refinement on F^2

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.073$$

$$wR(F^2) = 0.210$$

$$S = 1.05$$

4968 reflections

345 parameters

14 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.1132P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.53 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$$

Special details

Experimental. $^1\text{H-NMR}$ (400 MHz) (DMSO d_6 /TMS) δ 3.80 (1H, d, J = 15.90 Hz, H5-thia.), 3.96 (1H, dd, J1 = 15.87 Hz, J2 = 1.71 Hz, H5-thia.), 5.97 (1H, s, H2-thia.), 7.19–7.21 (3H, m, 3-C₆H₅-ind.), 7.25–7.29 (3H, m, H6-ind, 3-C₆H₅-ind.) 7.43–7.51 (2H, m H4-, H7-ind.), 7.67 (2H, d, J = 8.23 Hz, 2-C₆H₄-(H2,6)-thia), 7.75 (2H, d, J = 8.31 Hz, 2-C₆H₄-(H3,5)-thia.), 10.19 (1H, s, CONH), 12.04 (1H, s, NH) p.p.m.; $^{13}\text{C-NMR}$ (HMBC) (125 MHz) (DMSO- d_6) δ 29.91 (C5-thia.), 61.66 (C2-thia.), 114.92 (C7-ind.), 119.24 (C3-ind.), 119.68 (C4-ind.) 125.13 (C6-ind.), 125.84 (C3a-ind), 126.25 (2-C₆H₄-(C3,5)-thia.), 127.18 (C5-ind.), 127.93 (C2-ind.), 128.92 (2-C₆H₄-(C2,6)-thia.), 133.06 (3-C₆H₅-(C1)-ind), 134.99 (C7a-ind), 144.17 (2-C₆H₄-(C1)-thia.), 161.21 (CONH), 169.66 (C=O) p.p.m.; APCI+ m/z (%) = 516.1/518.2 (MH⁺, 29.4/12.7), 79.5 (100).

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 e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|--------------|--------------|--------------|----------------------------------|-----------|
| C11 | 0.52469 (9) | 0.62509 (8) | 0.11058 (7) | 0.1214 (8) | |
| S1 | 0.33741 (6) | 0.62264 (6) | 0.73456 (6) | 0.0809 (5) | |
| O1 | 0.44994 (13) | 0.54850 (11) | 0.54646 (14) | 0.0633 (10) | |
| O2 | 0.49070 (12) | 0.64975 (16) | 0.66104 (17) | 0.0816 (13) | |
| N1 | 0.50355 (13) | 0.56361 (13) | 0.41587 (15) | 0.0493 (9) | |
| N2 | 0.41564 (12) | 0.64048 (12) | 0.54712 (15) | 0.0455 (9) | |
| N3 | 0.39991 (12) | 0.63564 (12) | 0.61935 (14) | 0.0439 (9) | |
| C1 | 0.48360 (15) | 0.62222 (16) | 0.32162 (18) | 0.0495 (11) | |
| C2 | 0.48633 (19) | 0.63894 (18) | 0.2484 (2) | 0.0623 (14) | |
| C3 | 0.5236 (2) | 0.6087 (2) | 0.2038 (2) | 0.0733 (16) | |
| C4 | 0.5597 (2) | 0.5641 (2) | 0.2289 (2) | 0.0763 (19) | |
| C5 | 0.55736 (18) | 0.5467 (2) | 0.2994 (2) | 0.0647 (14) | |
| C6 | 0.51797 (15) | 0.57519 (16) | 0.34551 (18) | 0.0481 (11) | |
| C7 | 0.46139 (15) | 0.60221 (14) | 0.43855 (17) | 0.0439 (11) | |
| C8 | 0.44742 (15) | 0.63943 (15) | 0.38228 (18) | 0.0464 (11) | |
| C9 | 0.39990 (17) | 0.68331 (16) | 0.37637 (18) | 0.0512 (11) | |

| | | | | | |
|------|--------------|--------------|--------------|-------------|------------|
| C10 | 0.34426 (19) | 0.6712 (2) | 0.3996 (2) | 0.0657 (16) | |
| C11 | 0.2991 (2) | 0.7108 (3) | 0.3882 (3) | 0.0867 (19) | |
| C12 | 0.3093 (3) | 0.7615 (3) | 0.3509 (3) | 0.092 (2) | |
| C13 | 0.3642 (3) | 0.7747 (2) | 0.3279 (2) | 0.087 (2) | |
| C14 | 0.4097 (2) | 0.73647 (18) | 0.3411 (2) | 0.0683 (14) | |
| C15 | 0.44188 (15) | 0.59419 (14) | 0.51464 (18) | 0.0446 (11) | |
| C16 | 0.43981 (16) | 0.64471 (17) | 0.6722 (2) | 0.0523 (12) | |
| C17 | 0.41203 (19) | 0.6458 (2) | 0.7458 (2) | 0.0737 (16) | |
| C18 | 0.33692 (18) | 0.64343 (19) | 0.6371 (2) | 0.0647 (14) | |
| C19 | 0.29649 (17) | 0.60608 (18) | 0.5938 (2) | 0.0587 (14) | |
| C20 | 0.3035 (2) | 0.54741 (18) | 0.5819 (3) | 0.0733 (17) | |
| C21 | 0.2629 (2) | 0.5169 (2) | 0.5429 (3) | 0.0863 (19) | |
| C22 | 0.21510 (19) | 0.5420 (2) | 0.5160 (3) | 0.0747 (17) | |
| C23 | 0.2074 (2) | 0.5992 (3) | 0.5246 (3) | 0.092 (2) | |
| C24 | 0.2472 (2) | 0.6329 (2) | 0.5623 (3) | 0.0813 (18) | |
| C25 | 0.1692 (3) | 0.5063 (3) | 0.4760 (4) | 0.111 (3) | 0.500 |
| C25' | 0.1692 (3) | 0.5063 (3) | 0.4760 (4) | 0.111 (3) | 0.500 |
| F1 | 0.1487 (8) | 0.5287 (4) | 0.4197 (9) | 0.197 (8) | 0.542 (18) |
| F2 | 0.1278 (6) | 0.4936 (8) | 0.5184 (9) | 0.252 (12) | 0.542 (18) |
| F3 | 0.1890 (4) | 0.4577 (4) | 0.4534 (5) | 0.108 (4) | 0.542 (18) |
| F1' | 0.1752 (7) | 0.5149 (15) | 0.4092 (6) | 0.37 (2) | 0.458 (18) |
| F2' | 0.1190 (6) | 0.5316 (11) | 0.4860 (11) | 0.227 (12) | 0.458 (18) |
| F3' | 0.1645 (14) | 0.4561 (7) | 0.494 (2) | 0.42 (2) | 0.458 (18) |
| H1 | 0.51850 | 0.53630 | 0.44220 | 0.0590* | |
| H2 | 0.46370 | 0.66950 | 0.23060 | 0.0750* | |
| H2A | 0.40900 | 0.67210 | 0.52320 | 0.0550* | |
| H4 | 0.58570 | 0.54610 | 0.19690 | 0.0920* | |
| H5 | 0.58120 | 0.51680 | 0.31660 | 0.0780* | |
| H10 | 0.33660 | 0.63610 | 0.42340 | 0.0790* | |
| H11 | 0.26190 | 0.70280 | 0.40590 | 0.1040* | |
| H12 | 0.27870 | 0.78700 | 0.34120 | 0.1100* | |
| H13 | 0.37110 | 0.80950 | 0.30330 | 0.1040* | |
| H14 | 0.44730 | 0.74630 | 0.32620 | 0.0820* | |
| H17A | 0.41340 | 0.68490 | 0.76600 | 0.0880* | |
| H17B | 0.43240 | 0.61960 | 0.77870 | 0.0880* | |
| H18 | 0.32600 | 0.68460 | 0.63200 | 0.0770* | |
| H20 | 0.33610 | 0.52830 | 0.60040 | 0.0880* | |
| H21 | 0.26890 | 0.47720 | 0.53490 | 0.1030* | |
| H23 | 0.17450 | 0.61690 | 0.50470 | 0.1100* | |
| H24 | 0.24160 | 0.67300 | 0.56690 | 0.0970* | |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|-------------|--------------|--------------|
| Cl1 | 0.1764 (17) | 0.1380 (14) | 0.0499 (6) | 0.0150 (11) | 0.0362 (8) | 0.0157 (7) |
| S1 | 0.0795 (8) | 0.1053 (10) | 0.0579 (6) | -0.0299 (7) | 0.0263 (5) | -0.0225 (6) |
| O1 | 0.091 (2) | 0.0421 (14) | 0.0567 (15) | 0.0209 (13) | 0.0195 (14) | 0.0083 (12) |
| O2 | 0.0434 (17) | 0.129 (3) | 0.0724 (19) | 0.0023 (17) | -0.0013 (14) | -0.0113 (18) |

| | | | | | | |
|------|-------------|-------------|-------------|--------------|--------------|--------------|
| N1 | 0.0518 (17) | 0.0503 (17) | 0.0459 (15) | 0.0110 (14) | 0.0002 (13) | -0.0016 (13) |
| N2 | 0.0564 (17) | 0.0372 (15) | 0.0430 (14) | 0.0060 (13) | 0.0052 (13) | 0.0036 (12) |
| N3 | 0.0420 (16) | 0.0464 (16) | 0.0434 (15) | 0.0043 (12) | 0.0070 (12) | -0.0025 (12) |
| C1 | 0.047 (2) | 0.057 (2) | 0.0446 (18) | -0.0042 (17) | 0.0022 (15) | 0.0004 (16) |
| C2 | 0.075 (3) | 0.062 (2) | 0.050 (2) | -0.001 (2) | 0.0029 (19) | 0.0076 (18) |
| C3 | 0.090 (3) | 0.088 (3) | 0.042 (2) | -0.008 (3) | 0.017 (2) | 0.004 (2) |
| C4 | 0.072 (3) | 0.097 (4) | 0.060 (3) | 0.006 (3) | 0.021 (2) | -0.011 (2) |
| C5 | 0.059 (2) | 0.078 (3) | 0.057 (2) | 0.013 (2) | 0.0061 (19) | -0.007 (2) |
| C6 | 0.0431 (19) | 0.059 (2) | 0.0422 (17) | 0.0002 (16) | 0.0001 (14) | -0.0034 (16) |
| C7 | 0.049 (2) | 0.0433 (18) | 0.0395 (17) | 0.0042 (15) | 0.0011 (14) | -0.0007 (14) |
| C8 | 0.049 (2) | 0.048 (2) | 0.0423 (17) | 0.0019 (16) | -0.0036 (15) | 0.0008 (15) |
| C9 | 0.060 (2) | 0.055 (2) | 0.0385 (17) | 0.0102 (18) | -0.0020 (16) | 0.0012 (16) |
| C10 | 0.068 (3) | 0.072 (3) | 0.057 (2) | 0.014 (2) | -0.007 (2) | 0.007 (2) |
| C11 | 0.072 (3) | 0.110 (4) | 0.078 (3) | 0.034 (3) | -0.007 (2) | 0.009 (3) |
| C12 | 0.110 (4) | 0.097 (4) | 0.068 (3) | 0.057 (3) | -0.018 (3) | 0.005 (3) |
| C13 | 0.138 (5) | 0.062 (3) | 0.061 (3) | 0.038 (3) | 0.000 (3) | 0.014 (2) |
| C14 | 0.090 (3) | 0.059 (2) | 0.056 (2) | 0.017 (2) | 0.008 (2) | 0.0124 (19) |
| C15 | 0.0468 (19) | 0.0401 (19) | 0.0469 (18) | 0.0047 (15) | 0.0000 (15) | 0.0019 (15) |
| C16 | 0.045 (2) | 0.060 (2) | 0.052 (2) | 0.0065 (17) | 0.0041 (17) | -0.0046 (17) |
| C17 | 0.074 (3) | 0.094 (3) | 0.053 (2) | -0.003 (2) | 0.006 (2) | -0.013 (2) |
| C18 | 0.056 (2) | 0.059 (2) | 0.079 (3) | -0.0005 (19) | 0.010 (2) | -0.011 (2) |
| C19 | 0.053 (2) | 0.064 (3) | 0.059 (2) | -0.016 (2) | 0.0066 (18) | -0.0145 (18) |
| C20 | 0.062 (3) | 0.056 (3) | 0.102 (3) | 0.012 (2) | -0.022 (2) | -0.004 (2) |
| C21 | 0.071 (3) | 0.062 (3) | 0.126 (4) | 0.003 (2) | -0.016 (3) | -0.032 (3) |
| C22 | 0.058 (3) | 0.083 (3) | 0.083 (3) | 0.009 (2) | -0.009 (2) | -0.023 (2) |
| C23 | 0.061 (3) | 0.094 (4) | 0.120 (4) | 0.015 (3) | -0.034 (3) | -0.004 (3) |
| C24 | 0.071 (3) | 0.052 (2) | 0.121 (4) | 0.017 (2) | 0.006 (3) | -0.007 (3) |
| C25 | 0.085 (4) | 0.106 (5) | 0.141 (6) | 0.004 (4) | -0.020 (4) | -0.041 (5) |
| C25' | 0.085 (4) | 0.106 (5) | 0.141 (6) | 0.004 (4) | -0.020 (4) | -0.041 (5) |
| F1 | 0.231 (16) | 0.109 (7) | 0.252 (17) | 0.000 (6) | -0.205 (15) | -0.005 (7) |
| F2 | 0.110 (9) | 0.37 (3) | 0.275 (18) | -0.148 (12) | 0.098 (11) | -0.244 (19) |
| F3 | 0.098 (5) | 0.106 (7) | 0.120 (7) | -0.009 (4) | -0.037 (5) | -0.063 (5) |
| F1' | 0.112 (11) | 0.88 (7) | 0.105 (11) | -0.010 (19) | -0.014 (8) | -0.20 (2) |
| F2' | 0.070 (7) | 0.40 (3) | 0.210 (18) | 0.013 (12) | -0.056 (10) | -0.102 (18) |
| F3' | 0.54 (5) | 0.151 (18) | 0.57 (5) | -0.16 (2) | -0.42 (4) | 0.14 (3) |

Geometric parameters (Å, °)

| | | | |
|--------|-----------|---------|-----------|
| C11—C3 | 1.749 (4) | C12—C13 | 1.360 (9) |
| S1—C17 | 1.801 (5) | C13—C14 | 1.382 (7) |
| S1—C18 | 1.849 (4) | C16—C17 | 1.492 (5) |
| O1—C15 | 1.212 (4) | C18—C19 | 1.490 (6) |
| O2—C16 | 1.189 (5) | C19—C20 | 1.371 (6) |
| N1—C6 | 1.357 (4) | C19—C24 | 1.409 (6) |
| N1—C7 | 1.374 (4) | C20—C21 | 1.365 (7) |
| N2—N3 | 1.376 (4) | C21—C22 | 1.331 (7) |
| N2—C15 | 1.356 (4) | C22—C23 | 1.331 (8) |
| N3—C16 | 1.348 (5) | C22—C25 | 1.520 (8) |

| | | | |
|------------|------------|--------------|-----------|
| N3—C18 | 1.490 (5) | C22—C25' | 1.520 (8) |
| N1—H1 | 0.8600 | C23—C24 | 1.380 (7) |
| N2—H2A | 0.8600 | C2—H2 | 0.9300 |
| C1—C2 | 1.397 (5) | C4—H4 | 0.9300 |
| C1—C6 | 1.404 (5) | C5—H5 | 0.9300 |
| C1—C8 | 1.441 (5) | C10—H10 | 0.9300 |
| C2—C3 | 1.370 (6) | C11—H11 | 0.9300 |
| C3—C4 | 1.392 (6) | C12—H12 | 0.9300 |
| C4—C5 | 1.353 (5) | C13—H13 | 0.9300 |
| C5—C6 | 1.398 (5) | C14—H14 | 0.9300 |
| C7—C8 | 1.376 (5) | C17—H17A | 0.9700 |
| C7—C15 | 1.476 (5) | C17—H17B | 0.9700 |
| C8—C9 | 1.485 (5) | C18—H18 | 0.9800 |
| C9—C10 | 1.372 (6) | C20—H20 | 0.9300 |
| C9—C14 | 1.397 (5) | C21—H21 | 0.9300 |
| C10—C11 | 1.391 (7) | C23—H23 | 0.9300 |
| C11—C12 | 1.368 (9) | C24—H24 | 0.9300 |
| | | | |
| C17—S1—C18 | 92.32 (18) | S1—C18—C19 | 111.8 (3) |
| C6—N1—C7 | 109.4 (3) | C18—C19—C24 | 117.8 (4) |
| N3—N2—C15 | 118.4 (3) | C20—C19—C24 | 117.1 (4) |
| N2—N3—C16 | 120.1 (3) | C18—C19—C20 | 125.1 (4) |
| N2—N3—C18 | 117.0 (3) | C19—C20—C21 | 120.4 (4) |
| C16—N3—C18 | 118.8 (3) | C20—C21—C22 | 122.2 (4) |
| C7—N1—H1 | 125.00 | C23—C22—C25' | 119.7 (5) |
| C6—N1—H1 | 125.00 | C21—C22—C25 | 121.0 (5) |
| N3—N2—H2A | 121.00 | C21—C22—C25' | 121.0 (5) |
| C15—N2—H2A | 121.00 | C21—C22—C23 | 119.4 (5) |
| C2—C1—C6 | 119.0 (3) | C23—C22—C25 | 119.7 (5) |
| C2—C1—C8 | 133.8 (3) | C22—C23—C24 | 121.5 (5) |
| C6—C1—C8 | 107.0 (3) | C19—C24—C23 | 119.4 (4) |
| C1—C2—C3 | 117.6 (4) | C1—C2—H2 | 121.00 |
| C2—C3—C4 | 122.9 (4) | C3—C2—H2 | 121.00 |
| C11—C3—C2 | 118.9 (3) | C3—C4—H4 | 120.00 |
| C11—C3—C4 | 118.1 (3) | C5—C4—H4 | 120.00 |
| C3—C4—C5 | 120.5 (4) | C4—C5—H5 | 121.00 |
| C4—C5—C6 | 117.7 (4) | C6—C5—H5 | 121.00 |
| N1—C6—C1 | 108.0 (3) | C9—C10—H10 | 120.00 |
| N1—C6—C5 | 129.8 (3) | C11—C10—H10 | 120.00 |
| C1—C6—C5 | 122.1 (3) | C10—C11—H11 | 120.00 |
| N1—C7—C8 | 109.6 (3) | C12—C11—H11 | 120.00 |
| C8—C7—C15 | 135.7 (3) | C11—C12—H12 | 120.00 |
| N1—C7—C15 | 114.8 (3) | C13—C12—H12 | 120.00 |
| C1—C8—C7 | 106.0 (3) | C12—C13—H13 | 120.00 |
| C1—C8—C9 | 123.4 (3) | C14—C13—H13 | 120.00 |
| C7—C8—C9 | 130.1 (3) | C9—C14—H14 | 120.00 |
| C10—C9—C14 | 118.0 (4) | C13—C14—H14 | 120.00 |
| C8—C9—C14 | 120.4 (3) | S1—C17—H17A | 110.00 |

| | | | |
|----------------|------------|-----------------|------------|
| C8—C9—C10 | 121.4 (3) | S1—C17—H17B | 110.00 |
| C9—C10—C11 | 120.8 (4) | C16—C17—H17A | 110.00 |
| C10—C11—C12 | 120.1 (5) | C16—C17—H17B | 110.00 |
| C11—C12—C13 | 120.1 (6) | H17A—C17—H17B | 109.00 |
| C12—C13—C14 | 120.1 (5) | S1—C18—H18 | 110.00 |
| C9—C14—C13 | 120.8 (4) | N3—C18—H18 | 110.00 |
| O1—C15—N2 | 122.1 (3) | C19—C18—H18 | 110.00 |
| O1—C15—C7 | 121.1 (3) | C19—C20—H20 | 120.00 |
| N2—C15—C7 | 116.9 (3) | C21—C20—H20 | 120.00 |
| O2—C16—C17 | 124.9 (4) | C20—C21—H21 | 119.00 |
| N3—C16—C17 | 111.3 (3) | C22—C21—H21 | 119.00 |
| O2—C16—N3 | 123.8 (3) | C22—C23—H23 | 119.00 |
| S1—C17—C16 | 107.2 (3) | C24—C23—H23 | 119.00 |
| N3—C18—C19 | 114.6 (3) | C19—C24—H24 | 120.00 |
| S1—C18—N3 | 100.0 (2) | C23—C24—H24 | 120.00 |
| | | | |
| C17—S1—C18—C19 | 150.1 (3) | C15—C7—C8—C1 | -179.5 (4) |
| C18—S1—C17—C16 | -22.9 (3) | C15—C7—C8—C9 | -8.0 (7) |
| C17—S1—C18—N3 | 28.4 (3) | N1—C7—C8—C1 | -0.1 (4) |
| C6—N1—C7—C15 | -180.0 (3) | N1—C7—C8—C9 | 171.4 (3) |
| C7—N1—C6—C1 | -0.8 (4) | C8—C7—C15—O1 | 159.8 (4) |
| C6—N1—C7—C8 | 0.5 (4) | C8—C7—C15—N2 | -21.3 (6) |
| C7—N1—C6—C5 | -178.2 (4) | N1—C7—C15—N2 | 159.4 (3) |
| N3—N2—C15—O1 | 2.6 (5) | C7—C8—C9—C14 | 142.6 (4) |
| C15—N2—N3—C16 | 82.3 (4) | C7—C8—C9—C10 | -43.0 (6) |
| C15—N2—N3—C18 | -120.9 (3) | C1—C8—C9—C10 | 127.2 (4) |
| N3—N2—C15—C7 | -176.4 (3) | C1—C8—C9—C14 | -47.2 (5) |
| C18—N3—C16—C17 | 15.4 (5) | C8—C9—C10—C11 | -174.6 (4) |
| N2—N3—C18—C19 | 52.5 (4) | C8—C9—C14—C13 | 172.5 (3) |
| N2—N3—C16—C17 | 171.8 (3) | C10—C9—C14—C13 | -2.2 (5) |
| C16—N3—C18—C19 | -150.3 (3) | C14—C9—C10—C11 | 0.0 (6) |
| C16—N3—C18—S1 | -30.6 (4) | C9—C10—C11—C12 | 2.6 (7) |
| C18—N3—C16—O2 | -166.3 (4) | C10—C11—C12—C13 | -3.2 (8) |
| N2—N3—C18—S1 | 172.2 (2) | C11—C12—C13—C14 | 1.1 (8) |
| N2—N3—C16—O2 | -9.8 (6) | C12—C13—C14—C9 | 1.7 (6) |
| C8—C1—C2—C3 | -173.9 (4) | O2—C16—C17—S1 | -169.2 (4) |
| C6—C1—C2—C3 | -1.1 (6) | N3—C16—C17—S1 | 9.1 (4) |
| C6—C1—C8—C7 | -0.4 (4) | S1—C18—C19—C20 | -65.7 (5) |
| C2—C1—C6—N1 | -173.9 (3) | S1—C18—C19—C24 | 114.5 (4) |
| C2—C1—C6—C5 | 3.8 (6) | N3—C18—C19—C20 | 47.2 (5) |
| C2—C1—C8—C9 | 0.9 (6) | N3—C18—C19—C24 | -132.6 (4) |
| C2—C1—C8—C7 | 173.1 (4) | C18—C19—C20—C21 | 178.2 (4) |
| C6—C1—C8—C9 | -172.6 (3) | C24—C19—C20—C21 | -2.0 (7) |
| C8—C1—C6—C5 | 178.4 (3) | C18—C19—C24—C23 | -177.1 (4) |
| C8—C1—C6—N1 | 0.7 (4) | C20—C19—C24—C23 | 3.1 (7) |
| C1—C2—C3—C11 | 175.8 (3) | C19—C20—C21—C22 | -1.0 (8) |
| C1—C2—C3—C4 | -2.3 (7) | C20—C21—C22—C23 | 2.8 (8) |
| C11—C3—C4—C5 | -175.0 (4) | C20—C21—C22—C25 | -177.0 (5) |

| | | | |
|--------------|-----------|------------------|------------|
| C2—C3—C4—C5 | 3.1 (7) | C20—C21—C22—C25' | -177.0 (5) |
| C3—C4—C5—C6 | -0.4 (6) | C21—C22—C23—C24 | -1.6 (8) |
| C4—C5—C6—N1 | 174.1 (4) | C25—C22—C23—C24 | 178.2 (5) |
| C4—C5—C6—C1 | -3.0 (6) | C25'—C22—C23—C24 | 178.2 (5) |
| N1—C7—C15—O1 | -19.5 (5) | C22—C23—C24—C19 | -1.4 (8) |

Hydrogen-bond geometry (Å, °)

Cg1 and Cg2 are the centroids of the N1/C1/C6—C8 and C9—C14 rings, respectively.

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|-------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N1—H1 \cdots O1 ⁱ | 0.86 | 2.08 | 2.864 (4) | 151 |
| N2—H2A \cdots O2 ⁱⁱ | 0.86 | 2.34 | 2.851 (4) | 118 |
| C18—H18 \cdots O2 ⁱⁱ | 0.98 | 2.53 | 3.145 (5) | 121 |
| C21—H21 \cdots F3 | 0.93 | 2.40 | 2.719 (10) | 100 |
| C24—H24 \cdots Cg1 ⁱⁱⁱ | 0.93 | 2.77 | 3.438 (5) | 129 |
| C17—H17B \cdots Cg2 ^{iv} | 0.97 | 2.95 | 3.799 (5) | 147 |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $y-1/4, -x+5/4, -z+5/4$; (iii) $-y+3/4, x+1/4, z+1/4$; (iv) $-y+5/4, x+1/4, -z+5/4$.