

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Ethyl 6-methyl-2-sulfanylidene-4-[4-(trifluoromethyl)phenyl]-1,2,3,4-tetrahydropyrimidine-5-carboxylate

 Susanta K. Nayak,^{a*} K. N. Venugopala,^{b*} Thavendran Govender,^c Hendrik G. Kruger,^b Glenn E. M. Maguire^b and T. N. Guru Row^a

^aSolid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India, ^bSchool of Chemistry, University of KwaZulu-Natal, Durban 4000, South Africa, and ^cSchool of Pharmacy and Pharmacology, University of Kwazulu-Natal, Durban 4000, South Africa

Correspondence e-mail: nksusa@gmail.com, venugopala@ukzn.ac.za

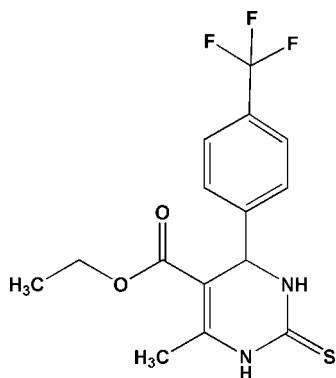
Received 13 May 2011; accepted 23 May 2011

Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.032; wR factor = 0.085; data-to-parameter ratio = 11.1.

The title compound, $\text{C}_{15}\text{H}_{15}\text{F}_3\text{N}_2\text{O}_2\text{S}$, adopts a conformation with an intramolecular $\text{C}-\text{H}\cdots\pi$ interaction. The dihedral angles between the planes of the 4-(trifluoromethyl)phenyl and ester groups with the plane of the six-membered tetrahydropyrimidine ring are 81.8 (1) and 16.0 (1)°, respectively. In the crystal structure, intermolecular $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds link pairs of molecules into dimers and $\text{N}-\text{H}\cdots\text{O}$ interactions generate hydrogen-bonded molecular chains along the crystallographic a axis.

Related literature

For applications of multi-functionalized dihydropyrimidines, see: Jauk *et al.* (2000); Kappe (2000); Mayer *et al.* (1999). For structural analysis, see: Nayak *et al.* (2009, 2010).



Experimental

Crystal data

$\text{C}_{15}\text{H}_{15}\text{F}_3\text{N}_2\text{O}_2\text{S}$
 $M_r = 344.36$
 Triclinic, $P\bar{1}$
 $a = 7.2682$ (3) Å
 $b = 9.3205$ (2) Å
 $c = 12.4779$ (3) Å
 $\alpha = 74.199$ (2)°
 $\beta = 88.092$ (3)°
 $\gamma = 69.377$ (3)°
 $V = 759.39$ (5) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.26$ mm⁻¹
 $T = 120$ K
 $0.28 \times 0.22 \times 0.17$ mm

Data collection

Oxford Diffraction Xcalibur diffractometer with an Eos (Nova) detector
 Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
 $T_{\min} = 0.932$, $T_{\max} = 0.958$
 16986 measured reflections
 2982 independent reflections
 2670 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.085$
 $S = 1.05$
 2982 reflections
 268 parameters
 All H-atom parameters refined
 $\Delta\rho_{\text{max}} = 0.33$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1N}\cdots\text{O1}^i$	0.80 (2)	2.20 (2)	2.9868 (19)	169.8 (18)
$\text{N2}-\text{H2N}\cdots\text{S1}^{ii}$	0.830 (19)	2.462 (19)	3.2830 (14)	170 (2)
$\text{C14}-\text{H14}\cdots\text{Cg1}$	0.94 (2)	2.655 (2)	3.129 (2)	112

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *PLATON* (Spek, 2009) and *PARST* (Nardelli, 1995).

We acknowledge funding under the DST-FIST program (Level II) for the Oxford Diffraction facility at SSCU, IISc. SKN thanks the DST, India, for a research associate fellowship and KNV is grateful to the University of KwaZulu-Natal, South Africa, for a post-doctoral fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2356).

References

- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Jauk, B., Pernet, T. & Kappe, C. O. (2000). *Molecules*, **5**, 227–239.
 Kappe, C. O. (2000). *Eur. J. Med. Chem.* **35**, 1043–1052.
 Mayer, T. U., Kapoor, T. M., Haggarty, S. J., King, R. W., Schreiber, S. I. & Mitchison, T. J. (1999). *Science*, **286**, 971–974.
 Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
 Nayak, S. K., Venugopala, K. N., Chopra, D., Govender, T., Kruger, H. G., Maguire, G. E. M. & Guru Row, T. N. (2009). *Acta Cryst.* **E65**, o2518.
 Nayak, S. K., Venugopala, K. N., Chopra, D., Vasu & Guru Row, T. N. (2010). *CrystEngComm*, **12**, 1205–1216.

Oxford Diffraction (2009). *CrysAlis CCD* and *CrysAlis PRO RED*. Oxford Diffraction Ltd, Yarnton, England.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
Watkin, D. M., Pearce, L. & Prout, C. K. (1993). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.

supporting information

Acta Cryst. (2011). E67, o1559–o1560 [doi:10.1107/S1600536811019441]

Ethyl 6-methyl-2-sulfanylidene-4-[4-(trifluoromethyl)phenyl]-1,2,3,4-tetrahydropyrimidine-5-carboxylate

Susanta K. Nayak, K. N. Venugopala, Thavendran Govender, Hendrik G. Kruger, Glenn E. M. Maguire and T. N. Guru Row

S1. Comment

The synthesis of multifunctionalized dihydropyrimidone (DHPM) compounds was first reported by the Italian chemist Pietro Biginelli in 1893 (Kappe, 2000 and references therein). DHPMs have emerged as important target molecules because of their therapeutic and pharmacological properties such as anticarcinogenic (Kappe, 2000; Mayer *et al.*, 1999) and calcium channel modulators (Jauk *et al.*, 2000 and references therein). We have been working on this DHPMS system in view of the immense range of applications (Nayak *et al.*, 2009; 2010). Here, we are reporting the single-crystal structure of the title compound.

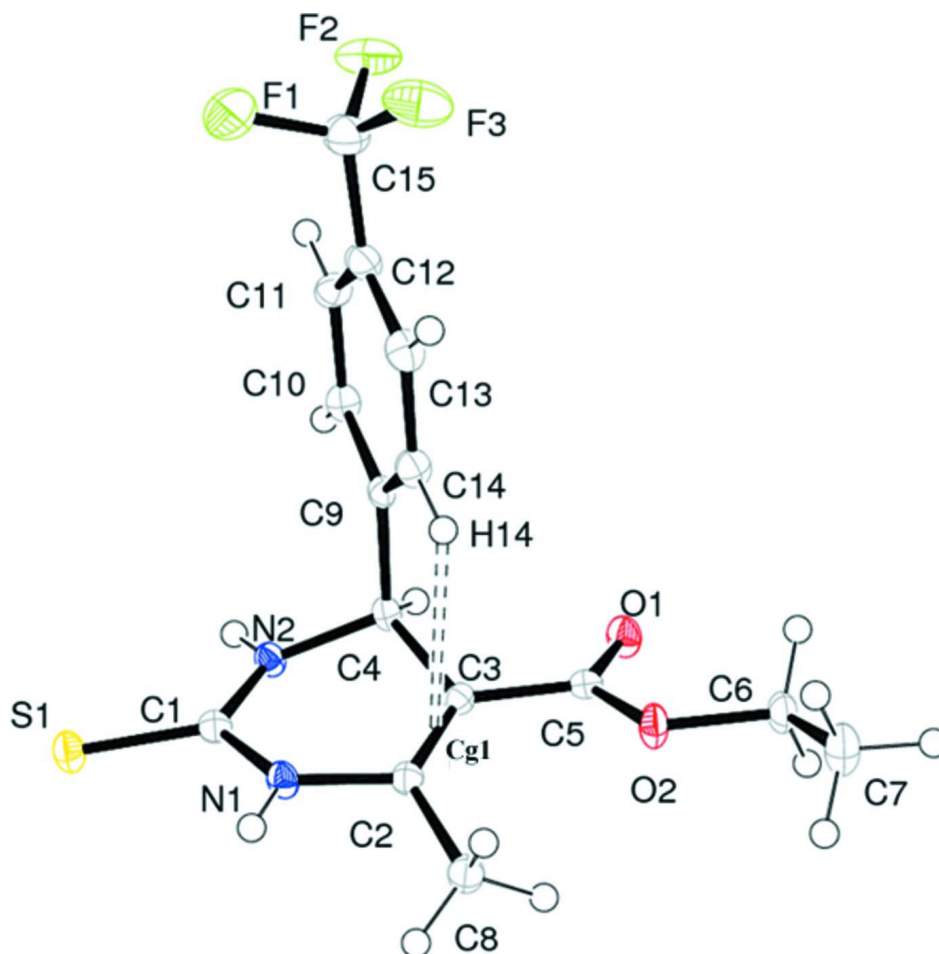
The conformation of the molecule is controlled by an intra-molecular C—H \cdots π interaction (2.655 (2) Å, Table 1) wherein the aryl hydrogen H14 is oriented towards the π electrons corresponding to the C2=C3 double bond (Fig. 1). The dihedral angles between the planes of 4-trifluoromethylphenyl and ester groups (O1/C5/O2/C6/C7) with the plane of the six-membered tetrahydropyrimidine ring are 81.8 (1)° and 16.0 (1)°, respectively. The crystal structure is mainly stabilized by hydrogen bonds of centrosymmetric N—H \cdots S dimers and N—H \cdots O molecular chains along the crystallographic *a* axis (Fig. 2). The molecules are arranged as polar and hydrophobic sheets with the spacer distances of 4.673 (2) Å and 8.359 (2) Å, respectively as briefly explained in literature (Fig. 3, Nayak *et al.*, 2009; 2010).

S2. Experimental

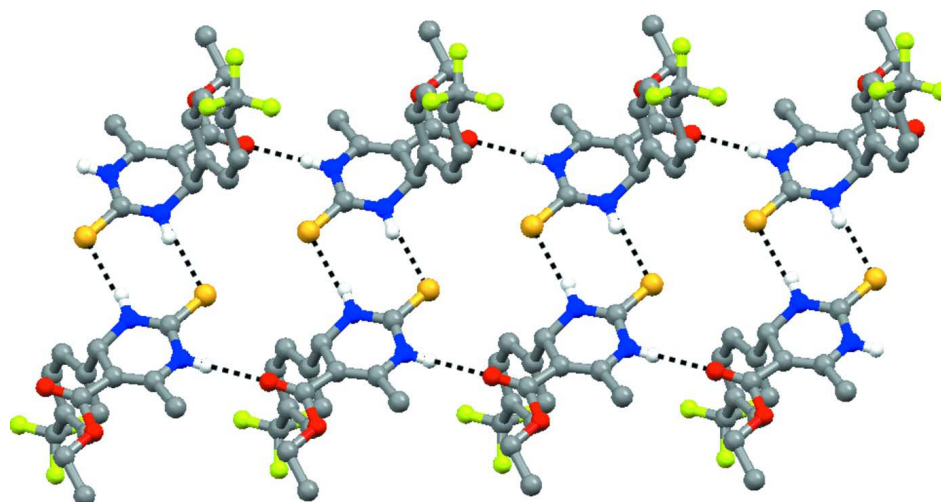
A mixture of ethylacetoacetate (0.1 mol), 4-trifluoromethylbenzaldehyde (0.1 mol) and thiourea (0.11 mol) was refluxed in 50 ml of ethanol for 2 h in the presence of concentrated hydrochloric acid as a catalyst. The reaction was monitored with thin layer chromatography and the reaction medium was quenched in ice cold water. The precipitate obtained was filtered, dried and crystallized from ethanol at room temperature to obtain the title compound.

S3. Refinement

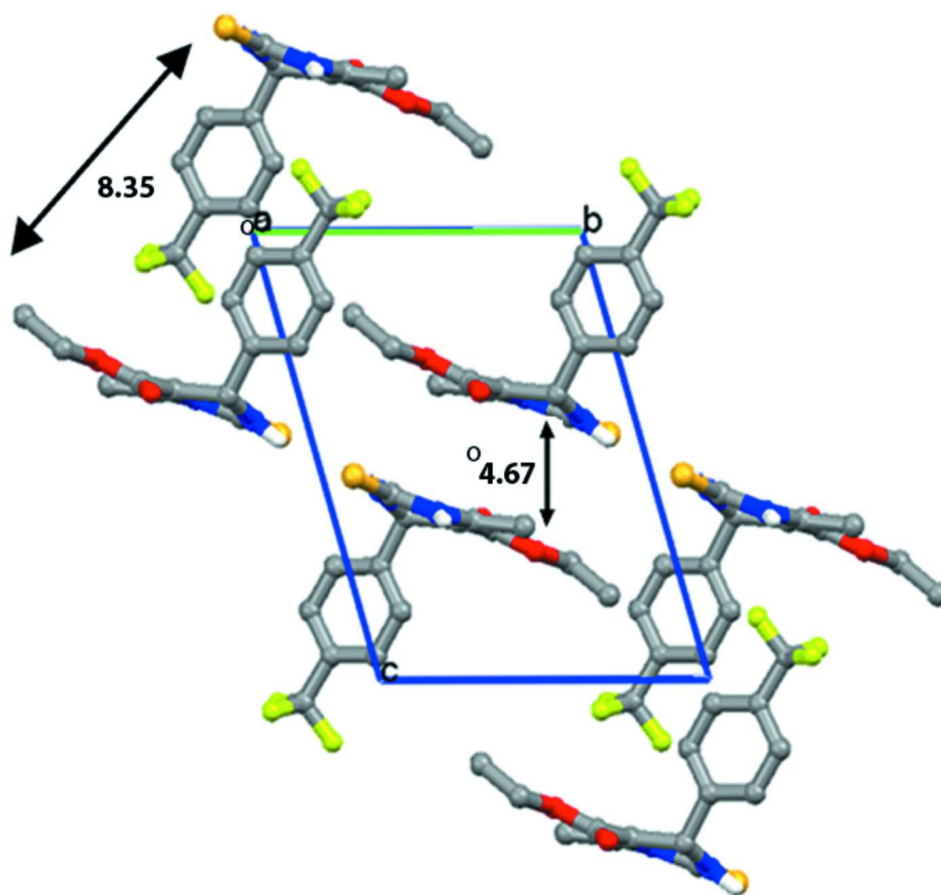
All H atoms were located from difference Fourier map and refined freely with C—H and N—H distances in the range between 0.80 Å and 1.0 Å.

**Figure 1**

Molecular structure shows the atom labelling scheme with displacement ellipsoids for non-H atoms at 50% probability level, hydrogen atoms are arbitrary circle. The dotted line shows the C—H \cdots π intramolecular interactions. Cg1 denotes the center of gravity of the C2=C3 bond.

**Figure 2**

The molecular packing shows the molecular chain of N—H \cdots O hydrogen bonds and N—H \cdots S intermolecular dimers.

**Figure 3**

The molecular packing along the *a* axis with their polar and hydrophobic spacer distance (open circle represents centre of inversion).

Ethyl 6-methyl-2-sulfanylidene-4-[4-(trifluoromethyl)phenyl]-1,2,3,4-tetrahydropyrimidine-5-carboxylate

Crystal data

$C_{15}H_{15}F_3N_2O_2S$
 $M_r = 344.36$
 Triclinic, $P\bar{1}$
 Hall symbol: -P 1
 $a = 7.2682$ (3) Å
 $b = 9.3205$ (2) Å
 $c = 12.4779$ (3) Å
 $\alpha = 74.199$ (2)°
 $\beta = 88.092$ (3)°
 $\gamma = 69.377$ (3)°
 $V = 759.39$ (5) Å³

$Z = 2$
 $F(000) = 356$
 $D_x = 1.506$ Mg m⁻³
 Melting point: 471(2) K
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 467 reflections
 $\theta = 1.0$ – 27.9 °
 $\mu = 0.26$ mm⁻¹
 $T = 120$ K
 Block, colorless
 $0.28 \times 0.22 \times 0.17$ mm

Data collection

Oxford Diffraction Xcalibur
 diffractometer with an Eos (Nova) detector
 Radiation source: Enhance (Mo) X-ray Source
 Graphite monochromator
 Detector resolution: 16.0839 pixels mm⁻¹
 ω scans
 Absorption correction: multi-scan
 (CrysAlis PRO; Oxford Diffraction, 2009)
 $T_{\min} = 0.932$, $T_{\max} = 0.958$

16986 measured reflections
 2982 independent reflections
 2670 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$
 $\theta_{\max} = 26.0$ °, $\theta_{\min} = 2.4$ °
 $h = -8 \rightarrow 8$
 $k = -11 \rightarrow 11$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.085$
 $S = 1.05$
 2982 reflections
 268 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0385P)^2 + 0.4675P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.33$ e Å⁻³
 $\Delta\rho_{\min} = -0.26$ e Å⁻³

Special details

Experimental. CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.34d Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s 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 $F^2 > 2\sigma(F^2)$ 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.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.30321 (6)	0.90692 (5)	0.45283 (3)	0.01866 (12)

O2	-0.02059 (15)	0.41096 (13)	0.28311 (9)	0.0192 (2)
N2	-0.01311 (19)	0.83739 (15)	0.42302 (10)	0.0152 (3)
N1	0.2762 (2)	0.67834 (15)	0.37360 (10)	0.0152 (3)
C3	-0.0065 (2)	0.61577 (17)	0.35436 (12)	0.0137 (3)
O1	-0.28789 (15)	0.54256 (13)	0.35999 (9)	0.0202 (2)
C9	-0.2190 (2)	0.89964 (17)	0.25202 (12)	0.0142 (3)
C4	-0.1317 (2)	0.77821 (17)	0.36488 (12)	0.0139 (3)
C5	-0.1193 (2)	0.52013 (17)	0.33520 (12)	0.0146 (3)
C14	-0.1469 (2)	0.87476 (19)	0.15166 (13)	0.0179 (3)
C1	0.1797 (2)	0.80426 (17)	0.41397 (12)	0.0144 (3)
C2	0.1916 (2)	0.57285 (17)	0.35621 (12)	0.0139 (3)
F3	-0.42949 (18)	1.20109 (14)	-0.14515 (8)	0.0412 (3)
C6	-0.1217 (2)	0.31314 (19)	0.25754 (14)	0.0189 (3)
C10	-0.3740 (2)	1.04101 (18)	0.25052 (13)	0.0170 (3)
F2	-0.64945 (16)	1.33939 (13)	-0.05806 (9)	0.0389 (3)
C11	-0.4529 (2)	1.15589 (19)	0.15063 (13)	0.0199 (3)
C13	-0.2264 (2)	0.98893 (19)	0.05111 (13)	0.0202 (3)
C8	0.3400 (2)	0.42067 (19)	0.34389 (15)	0.0196 (3)
C12	-0.3786 (2)	1.12940 (19)	0.05093 (13)	0.0198 (3)
C7	0.0075 (3)	0.2226 (2)	0.18351 (16)	0.0249 (4)
F1	-0.3667 (2)	1.36503 (15)	-0.07403 (10)	0.0514 (4)
C15	-0.4567 (3)	1.2573 (2)	-0.05606 (14)	0.0280 (4)
H4	-0.246 (2)	0.7766 (19)	0.4098 (13)	0.010 (4)*
H2N	-0.075 (3)	0.907 (2)	0.4538 (15)	0.016 (4)*
H1N	0.393 (3)	0.652 (2)	0.3721 (16)	0.024 (5)*
H10	-0.424 (3)	1.059 (2)	0.3189 (15)	0.016 (4)*
H6B	-0.139 (3)	0.241 (2)	0.3277 (15)	0.016 (4)*
H14	-0.045 (3)	0.779 (2)	0.1506 (15)	0.023 (5)*
H13	-0.179 (3)	0.971 (2)	-0.0173 (16)	0.024 (5)*
H6A	-0.251 (3)	0.384 (2)	0.2200 (16)	0.025 (5)*
H11	-0.557 (3)	1.253 (2)	0.1503 (16)	0.026 (5)*
H7A	0.021 (3)	0.296 (3)	0.1166 (18)	0.034 (5)*
H7B	-0.054 (3)	0.152 (2)	0.1647 (17)	0.035 (5)*
H7C	0.132 (3)	0.156 (3)	0.2222 (18)	0.037 (6)*
H8B	0.292 (3)	0.332 (3)	0.3678 (17)	0.037 (6)*
H8C	0.456 (3)	0.395 (3)	0.3874 (19)	0.042 (6)*
H8A	0.367 (3)	0.431 (3)	0.265 (2)	0.049 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0165 (2)	0.0207 (2)	0.0237 (2)	-0.00844 (16)	0.00304 (15)	-0.01173 (16)
O2	0.0148 (5)	0.0196 (6)	0.0303 (6)	-0.0092 (5)	0.0051 (4)	-0.0143 (5)
N2	0.0131 (6)	0.0161 (6)	0.0180 (6)	-0.0042 (5)	0.0007 (5)	-0.0088 (5)
N1	0.0104 (7)	0.0178 (6)	0.0199 (6)	-0.0062 (5)	0.0035 (5)	-0.0080 (5)
C3	0.0144 (7)	0.0134 (7)	0.0133 (7)	-0.0049 (6)	0.0012 (5)	-0.0038 (5)
O1	0.0127 (6)	0.0223 (6)	0.0293 (6)	-0.0079 (5)	0.0048 (4)	-0.0114 (5)
C9	0.0124 (7)	0.0151 (7)	0.0175 (7)	-0.0074 (6)	0.0006 (6)	-0.0052 (6)

C4	0.0125 (7)	0.0162 (7)	0.0154 (7)	-0.0061 (6)	0.0027 (6)	-0.0072 (6)
C5	0.0141 (7)	0.0128 (7)	0.0147 (7)	-0.0032 (6)	-0.0009 (6)	-0.0023 (5)
C14	0.0161 (8)	0.0186 (8)	0.0205 (8)	-0.0053 (6)	0.0023 (6)	-0.0089 (6)
C1	0.0162 (7)	0.0156 (7)	0.0113 (7)	-0.0061 (6)	0.0016 (5)	-0.0030 (5)
C2	0.0156 (7)	0.0141 (7)	0.0124 (7)	-0.0061 (6)	0.0011 (5)	-0.0032 (5)
F3	0.0453 (7)	0.0503 (7)	0.0175 (5)	-0.0100 (6)	-0.0023 (5)	-0.0018 (5)
C6	0.0178 (8)	0.0185 (8)	0.0255 (8)	-0.0103 (7)	0.0016 (6)	-0.0089 (7)
C10	0.0144 (7)	0.0193 (8)	0.0193 (8)	-0.0063 (6)	0.0044 (6)	-0.0084 (6)
F2	0.0303 (6)	0.0363 (6)	0.0314 (6)	0.0008 (5)	-0.0071 (5)	0.0045 (5)
C11	0.0156 (8)	0.0165 (8)	0.0253 (8)	-0.0040 (6)	0.0003 (6)	-0.0043 (6)
C13	0.0219 (8)	0.0254 (8)	0.0166 (7)	-0.0109 (7)	0.0042 (6)	-0.0081 (6)
C8	0.0135 (8)	0.0174 (8)	0.0287 (9)	-0.0043 (6)	0.0014 (7)	-0.0092 (7)
C12	0.0176 (8)	0.0220 (8)	0.0201 (8)	-0.0092 (6)	-0.0020 (6)	-0.0031 (6)
C7	0.0233 (9)	0.0267 (9)	0.0333 (10)	-0.0137 (8)	0.0069 (7)	-0.0166 (8)
F1	0.0618 (9)	0.0444 (7)	0.0454 (7)	-0.0363 (7)	-0.0147 (6)	0.0168 (6)
C15	0.0277 (9)	0.0293 (9)	0.0243 (9)	-0.0120 (8)	-0.0022 (7)	-0.0005 (7)

Geometric parameters (Å, °)

S1—C1	1.6863 (15)	F3—C15	1.334 (2)
O2—C5	1.3369 (18)	C6—C7	1.502 (2)
O2—C6	1.4557 (18)	C6—H6B	0.982 (18)
N2—C1	1.3323 (19)	C6—H6A	0.98 (2)
N2—C4	1.4725 (18)	C10—C11	1.385 (2)
N2—H2N	0.829 (19)	C10—H10	0.949 (18)
N1—C1	1.3572 (19)	F2—C15	1.336 (2)
N1—C2	1.3940 (19)	C11—C12	1.389 (2)
N1—H1N	0.80 (2)	C11—H11	0.95 (2)
C3—C2	1.351 (2)	C13—C12	1.384 (2)
C3—C5	1.472 (2)	C13—H13	0.946 (19)
C3—C4	1.506 (2)	C8—H8B	0.98 (2)
O1—C5	1.2128 (18)	C8—H8C	0.94 (2)
C9—C14	1.388 (2)	C8—H8A	0.99 (2)
C9—C10	1.396 (2)	C12—C15	1.494 (2)
C9—C4	1.534 (2)	C7—H7A	0.95 (2)
C4—H4	0.988 (17)	C7—H7B	1.00 (2)
C14—C13	1.389 (2)	C7—H7C	0.95 (2)
C14—H14	0.941 (19)	F1—C15	1.348 (2)
C2—C8	1.493 (2)		
C5—O2—C6	117.51 (12)	O2—C6—H6A	108.1 (11)
C1—N2—C4	123.64 (13)	C7—C6—H6A	112.1 (11)
C1—N2—H2N	119.0 (13)	H6B—C6—H6A	109.9 (15)
C4—N2—H2N	116.5 (13)	C11—C10—C9	120.59 (14)
C1—N1—C2	123.78 (13)	C11—C10—H10	120.0 (10)
C1—N1—H1N	118.1 (14)	C9—C10—H10	119.4 (10)
C2—N1—H1N	116.8 (14)	C10—C11—C12	119.70 (15)
C2—C3—C5	125.59 (13)	C10—C11—H11	120.2 (12)

C2—C3—C4	119.99 (13)	C12—C11—H11	120.1 (11)
C5—C3—C4	114.30 (12)	C12—C13—C14	119.71 (15)
C14—C9—C10	118.99 (14)	C12—C13—H13	119.8 (11)
C14—C9—C4	122.22 (13)	C14—C13—H13	120.5 (11)
C10—C9—C4	118.79 (13)	C2—C8—H8B	111.7 (12)
N2—C4—C3	109.18 (12)	C2—C8—H8C	109.6 (13)
N2—C4—C9	109.86 (11)	H8B—C8—H8C	108.3 (18)
C3—C4—C9	113.06 (12)	C2—C8—H8A	110.1 (14)
N2—C4—H4	106.2 (9)	H8B—C8—H8A	106.3 (18)
C3—C4—H4	112.9 (9)	H8C—C8—H8A	110.7 (19)
C9—C4—H4	105.4 (9)	C13—C12—C11	120.31 (15)
O1—C5—O2	123.28 (13)	C13—C12—C15	120.14 (15)
O1—C5—C3	123.34 (13)	C11—C12—C15	119.47 (15)
O2—C5—C3	113.31 (12)	C6—C7—H7A	109.3 (12)
C9—C14—C13	120.70 (15)	C6—C7—H7B	109.3 (12)
C9—C14—H14	120.4 (11)	H7A—C7—H7B	109.4 (17)
C13—C14—H14	118.9 (11)	C6—C7—H7C	109.8 (13)
N2—C1—N1	116.24 (13)	H7A—C7—H7C	111.7 (18)
N2—C1—S1	123.24 (11)	H7B—C7—H7C	107.3 (17)
N1—C1—S1	120.50 (11)	F3—C15—F2	106.80 (14)
C3—C2—N1	118.64 (13)	F3—C15—F1	106.00 (15)
C3—C2—C8	128.19 (14)	F2—C15—F1	106.29 (15)
N1—C2—C8	113.16 (13)	F3—C15—C12	112.93 (15)
O2—C6—C7	106.10 (12)	F2—C15—C12	112.89 (14)
O2—C6—H6B	108.8 (10)	F1—C15—C12	111.43 (14)
C7—C6—H6B	111.6 (10)		
C1—N2—C4—C3	32.85 (18)	C5—C3—C2—N1	178.91 (13)
C1—N2—C4—C9	-91.67 (16)	C4—C3—C2—N1	3.2 (2)
C2—C3—C4—N2	-24.38 (18)	C5—C3—C2—C8	-2.4 (2)
C5—C3—C4—N2	159.44 (12)	C4—C3—C2—C8	-178.11 (14)
C2—C3—C4—C9	98.24 (16)	C1—N1—C2—C3	15.8 (2)
C5—C3—C4—C9	-77.94 (15)	C1—N1—C2—C8	-163.11 (14)
C14—C9—C4—N2	105.73 (15)	C5—O2—C6—C7	170.73 (13)
C10—C9—C4—N2	-73.24 (16)	C14—C9—C10—C11	-1.0 (2)
C14—C9—C4—C3	-16.51 (19)	C4—C9—C10—C11	177.99 (13)
C10—C9—C4—C3	164.51 (13)	C9—C10—C11—C12	0.8 (2)
C6—O2—C5—O1	-1.3 (2)	C9—C14—C13—C12	0.3 (2)
C6—O2—C5—C3	-178.35 (12)	C14—C13—C12—C11	-0.5 (2)
C2—C3—C5—O1	161.70 (15)	C14—C13—C12—C15	176.18 (15)
C4—C3—C5—O1	-22.4 (2)	C10—C11—C12—C13	0.0 (2)
C2—C3—C5—O2	-21.2 (2)	C10—C11—C12—C15	-176.74 (15)
C4—C3—C5—O2	154.72 (12)	C13—C12—C15—F3	25.8 (2)
C10—C9—C14—C13	0.5 (2)	C11—C12—C15—F3	-157.42 (15)
C4—C9—C14—C13	-178.50 (13)	C13—C12—C15—F2	147.12 (15)
C4—N2—C1—N1	-17.6 (2)	C11—C12—C15—F2	-36.1 (2)
C4—N2—C1—S1	163.99 (11)	C13—C12—C15—F1	-93.35 (19)
C2—N1—C1—N2	-8.8 (2)	C11—C12—C15—F1	83.40 (19)

C2—N1—C1—S1 169.61 (11)

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1N...O1 ⁱ	0.80 (2)	2.20 (2)	2.9868 (19)	169.8 (18)
N2—H2N...S1 ⁱⁱ	0.830 (19)	2.462 (19)	3.2830 (14)	170 (2)
C14—H14...Cg1	0.94 (2)	2.655 (2)	3.129 (2)	112

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