



Crystal structure, Hirshfeld surface analysis and computational studies of 5-[(prop-2-en-1-yl)sulfanyl]-1-[2-(trifluoromethyl)phenyl]-1*H*-tetrazole

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The title compound, C₁₁H₉F₃N₄S, was synthesized from 2-(trifluoromethyl)aniline by a multi-step reaction. It crystallizes in the non-centrosymmetric space group *Pna*2₁, with one molecule in the asymmetric unit, and is constructed from a pair of aromatic rings [2-(trifluoromethyl)phenyl and tetrazole], which are twisted by 76.8 (1)° relative to each other because of significant steric hindrance of the trifluoromethyl group at the *ortho* position of the benzene ring. In the crystal, very weak C—H···N and C—H···F hydrogen bonds and aromatic π–π stacking interactions link the molecules into a three-dimensional network. To further analyse the intermolecular interactions, a Hirshfeld surface analysis, as well as interaction energy calculations, were performed.

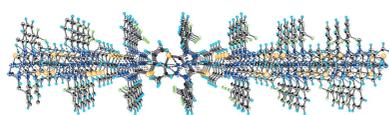
1. Chemical context

Tetrazoles are a well-known class of aromatic five-membered heterocycles, which have been investigated since the end of the 19th century. Their biological properties, including antiviral, anticancer, anti-tuberculosis, antifungal and antioxidant activities have been shown by numerous studies (see, for example, Ostrovskii *et al.*, 2017). They also are increasingly regarded as efficient and selective inhibitors of enzymes governing the metabolic processes in the human body (Pegklidou *et al.*, 2010; Al-Hourani *et al.*, 2012; Aggarwal *et al.*, 2016).

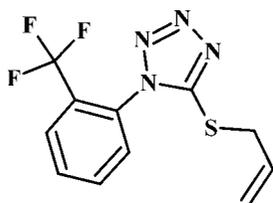
Tetrazoles are well established as suitable precursors for the construction of other nitrogen-containing heterocycles such as pyrimidines (Shyyka *et al.*, 2018; Pokhodylo *et al.*, 2015), as well as being widely used as ligands in their own right to generate coordination compounds (Gaponik *et al.*, 2006; Aromí *et al.*, 2011). For example, allyl derivatives of 1*H*-tetrazole-5-thiols have been used for the preparation of copper(I) π,σ-complexes possessing non-linear optical properties (Slyvka *et al.*, 2018, 2019). Among these, three copper(I) π,σ-coordination compounds, [Cu₂(C₁₁H₉F₃N₄S)₂(CF₃SO₃)₂] (Slyvka, 2015), [Cu(C₁₁H₉F₃N₄S)₂]BF₄ and [Cu(C₁₁H₉F₃N₄S)(NH₂SO₃)(MeOH)] based on 5-[(prop-2-en-1-yl)sulfanyl]-1-[2-(trifluoromethyl)phenyl]-1*H*-tetrazole (I) (C₁₁H₉F₃N₄S) have been reported recently (Slyvka *et al.*, 2019). As part of our ongoing studies in this area, the synthesis and structure of the title compound, (I), are reported here.

2. Structural commentary

The title compound crystallizes in the non-centrosymmetric space group *Pna*2₁, with one molecule in the asymmetric unit.



As shown in Fig. 1, it is constructed from two aromatic rings [2-(trifluoromethyl)phenyl and tetrazole rings], which are twisted relative to each other by 76.8 (1)° because of the significant steric hindrance of the trifluoromethyl group attached to C10. This dihedral angle is comparable with the analogous parameter in the same ligand when it is π,σ -coordinated to a copper atom in [Cu(C₁₁H₉F₃N₄S)₂]BF₄ [dihedral angle = 78.0 (1)°] and [Cu(C₁₁H₉F₃N₄S)(NH₂SO₃)(MeOH)] [85.5 (1)°] (Slyvka *et al.*, 2019). The (prop-2-en-1-yl)sulfanyl group in (I) has an anticlinal conformation relative to the C2–C3 bond and a synclinal conformation relative to the S1–C2 bond. The S1–C2–C3–C4 and C1–S1–C2–C3 torsion angles are 117.0 (3) and 75.0 (2)°, respectively.



3. Supramolecular features

As shown in Fig. 2 and listed in Table 1, the crystal structure of (I) features several weak intermolecular interactions. The hydrogen atoms of the (prop-2-en-1-yl)sulfanyl group are involved in C–H···N bonding with the tetrazole ring of an adjacent molecule; these bonds link independent molecules into layers (Fig. 3). The layers are interconnected by C–H···F contacts into a three-dimensional network (Fig. 4).

4. Hirshfeld surface analysis and computational study

To further analyse the intermolecular interactions between the molecules of (I), Hirshfeld surface analysis through the mapping of the normalized contact distance (d_{norm}) as well as

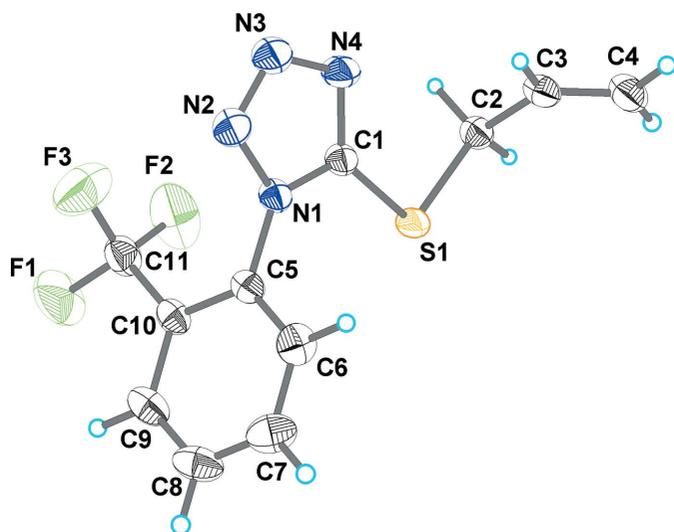


Figure 1
The molecular structure of (I) with displacement ellipsoids drawn at the 50% probability level.

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

D–H···A	D–H	H···A	D···A	D–H···A
C2–H2A···N3 ⁱ	0.99	2.58	3.464 (3)	148
C2–H2B···N2 ⁱⁱ	0.99	2.69	3.666 (4)	169
C3–H3···F3 ⁱⁱⁱ	0.95	2.71	3.351 (3)	125
C4–H4A···N3 ⁱ	0.95	2.67	3.491 (3)	145
C4–H4B···F1 ^{iv}	0.95	2.47	3.355 (3)	155
C6–H6···N4 ⁱⁱⁱ	0.95	2.76	3.601 (3)	148

Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 1, -y + 1, z - \frac{1}{2}$; (iii) $-x + 1, -y + 1, z + \frac{1}{2}$; (iv) $-x + \frac{3}{2}, y + \frac{1}{2}, z + \frac{1}{2}$.

calculation of the interaction energies were performed using *CrystalExplorer* (Turner *et al.*, 2017; Spackman & Jayatilaka, 2009). The most prominent interactions among the allyl group H atoms and tetrazole N atoms as well as among allylic H atoms and F atoms of neighbouring molecules can be seen in the Hirshfeld surface plot as the red areas (Fig. 5a). Fingerprint plots were produced to show the intermolecular surface bond distances with the regions highlighted for C–H···F

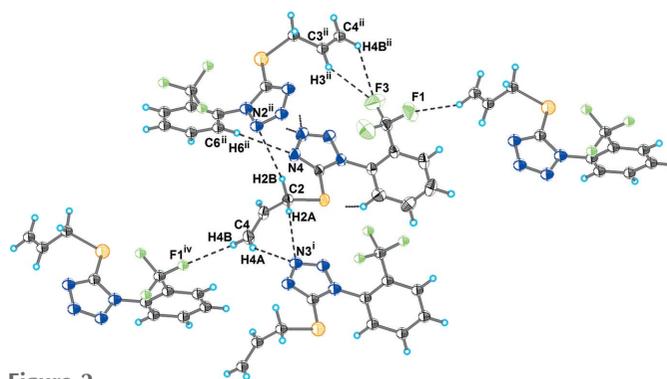


Figure 2
The hydrogen-bonding of molecules in (I). Hydrogen bonds are shown as dashed lines. The symmetry codes are as in Table 1.

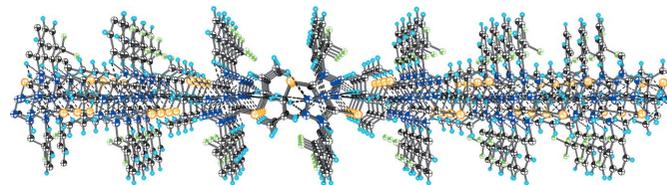


Figure 3
A C–H···N-bonded layer in the structure of compound (I).

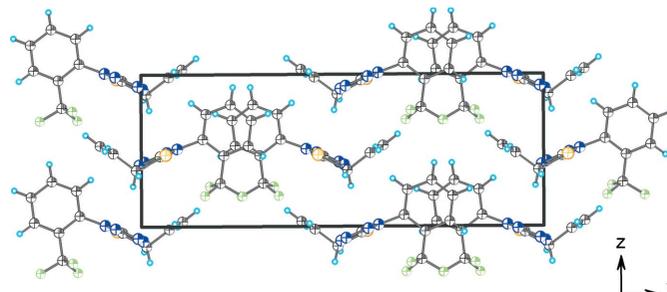


Figure 4
A view along the *a* axis of the crystal packing of the title compound.

Table 2
Interaction energies (kJ mol⁻¹) for selected close contacts in the crystal of (I).

Contact	$E_{\text{electrostatic}}$	$E_{\text{polarization}}$	$E_{\text{dispersion}}$	$E_{\text{exchange-repulsion}}$	E_{total}	Symmetry operation
C4—H4B···F1	-1.4	-0.3	-5.2	5.7	-2.6	$-x + \frac{3}{2}, y + \frac{1}{2}, z + \frac{1}{2}$
C4—H4A···N3/C2—H2A···N3	-12.0	-4.1	-13.4	16.6	-17.1	$x + 1, y, z$
C2—H2B···N2/C3—H3···F3/C4—H4B···F3	-14.6	-5.3	-31.0	16.4	-36.2	$-x + 1, -y + 1, z - \frac{1}{2}$
(CF ₃ C ₆ H ₄ -)···(CF ₃ C ₆ H ₄ -)	-5.0	-1.9	-31.8	14.1	-25.7	$x - \frac{1}{2}, -y + \frac{1}{2}, z$

(Fig. 5*b*) and C—H···N (Fig. 5*c*) interactions. The contribution to the surface area for H···H contacts is 19.8%.

The interaction energies in (I) were calculated using a dispersion-corrected CE-B3LYP/6-31G(d,p) quantum level of theory, as available in *CrystalExplorer*. The total intermolecular energy is the sum of energies of four main components, *viz.* electrostatic, polarization, dispersion and exchange-repulsion factors of 1.057, 0.740, 0.871 and 0.618, respectively (Mackenzie *et al.*, 2017). The total calculated energy of the intermolecular interactions of (I) is -115.9 kJ mol⁻¹. From Table 2, one can see the highest energy value (-36.2 kJ mol⁻¹) covers C—H···N and C—H···F interactions with the neighbouring molecule generated by the symmetry code $-x + 1, -y + 1, z - \frac{1}{2}$. The interactions between the neighbouring 2-(trifluoromethyl)phenyl rings stacked along [100] cover -25.7 kJ mol⁻¹ and are mainly dispersive in nature.

5. Database survey

A survey of the Cambridge Structural Database (CSD version 5.39, last update August 2018; Groom *et al.*, 2016) confirmed that 1-aryl substituted 5-[(prop-2-en-1-yl)sulfanyl]-1*H*-tetrazoles are known only as ligands in the structures of copper(I) and silver(I) π -complexes. In the crystal structures of bis[μ^2 - η^2 -5-(allylsulfanyl)-1-phenyl-1*H*-tetrazole]diaquadisilver bis(tetrafluoroborate) (refcode HAHTIV; Slyvka *et al.*, 2011), bis[μ - η^2 -1-phenyl-5-[(prop-2-en-1-yl)sulfanyl]-1*H*-tetrazole]diaquadicopper bis(tetrafluoroborate) (JAHCON; Slyvka *et*

al., 2010), bis[μ - η^2 -1-(4-chlorophenyl)-5-[(prop-2-en-1-yl)sulfanyl]-1*H*-tetrazole]diaquadicopper bis(tetrafluoroborate) ethanol solvate (JAH CUT; Slyvka *et al.*, 2010) and bis[μ -5-[(prop-2-en-1-yl)sulfanyl]-1-[2-(trifluoromethyl)phenyl]-1*H*-tetrazole]bis(trifluoromethanesulfonato)dicopper (JADHII; Slyvka, 2015), the tetrazole moieties are bonded to the metal ions through two heterocyclic nitrogen atoms and the allylic C=C bond in the chelate-bridging mode. In *catena*-{[μ -sulfamato}{ η^2 -1-(3,5-dimethylphenyl)-5-[(prop-2-en-1-yl)sulfanyl]-1*H*-tetrazole}copper(I)} (ZEYRUT; Slyvka *et al.*, 2018) (VI), the organic molecule is coordinated to the copper atom by the allylic C=C bond and the only tetrazole nitrogen atom. As a result of the presence of back-donation from an occupied 3*d* metal orbital to a low-lying empty π^* orbital of the olefin, in all these compounds the double bond of the (prop-2-en-1-yl)sulfanyl group is slightly elongated to 1.35–1.38 Å, in comparison with noncoordinated olefin bond value. The other S-substituted 1-phenyl-1*H*-tetrazole-5-thiol structures in the Cambridge Structural Database have different alkyl substituents, such as 2-naphthyl (TICRAY; Alves *et al.*, 1996), 1,7,7-trimethylbicyclo[2.2.1]hept-2-yl (GIJRAU; Bodrov *et al.*, 2013) and benzoyl (BAZVAA; Kim *et al.*, 2003).

6. Synthesis and crystallization

The title compound was synthesized from 2-(trifluoromethyl)aniline by a multi-step reaction. Commercially available 2-(trifluoromethyl)aniline (1.611 g, 0.010 mol) was dissolved in the minimum amount of benzene and treated with carbon

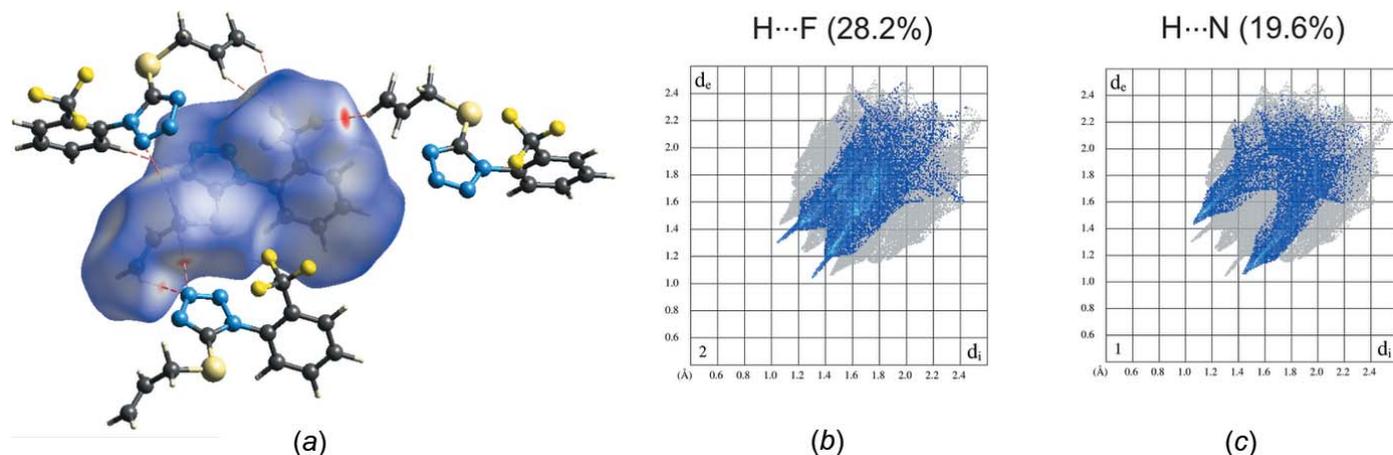


Figure 5
(a) Hirshfeld surface for molecule of (I) mapped with d_{norm} over the range -0.15 to 1.2 showing C—H···N and C—H···F hydrogen-bonded contacts. Fingerprint plots for molecule resolved into (b) F···H/H···F and (c) N···H/H···N contacts. Neighbouring molecules associated with close contacts are also shown.

disulfide (0.7 ml, 0.01 mol) and triethylamine (1.4 ml, 0.010 mol). The solution was cooled to 273 K and left for 5 d. After complete precipitation of the triethylammonium dithiocarbamate salt, the solution was filtered. The solid was washed with anhydrous ether and air-dried for about 10 min. The salt was then dissolved in about 7.5 ml of chloroform, treated with 1.4 ml of triethylamine and cooled to 273 K. To this solution was added ethyl chloroformate (1.02 ml, 0.01 mol) dropwise over a 15 min period under intensive stirring. The resulting solution was stirred at 273 K for 10 min and allowed to warm to room temperature over 1 h. The chloroform solution was washed with 3 M HCl and twice with water and dried over Na₂SO₄. The chloroform was evaporated and the 1-isothiocyanato-2-(trifluoromethyl)benzene was distilled *in vacuo*.

The obtained isothiocyanate (1.016 g, 5.0 mmol) was mixed with water (10 ml) and NaN₃ (0.71 g, 0.011 mol) and refluxed under intensive stirring until the suspension disappeared. The solution was cooled to room temperature and washed with TBME. The water fraction was separated and acidified with 3 M HCl (Caution! During the acidification beware of toxic HN₃ gas). The sediment of 1-[2-(trifluoromethyl)phenyl]-1H-tetrazole-5-thiol was separated by filtration and used for alkylation without further purification.

1-[2-(Trifluoromethyl)phenyl]-1H-tetrazole-5-thiol (0.985 g, 0.004 mol) was dissolved in a solution of KOH (0.22 g, 0.004 mol) in ethanol (10 ml). To the solution allyl bromide (0.43 ml, 0.005 mole) was added and the mixture was heated at 323 K for 1 h. The solvent was removed *in vacuo* and to the residue was added water (5 ml) and dichloromethane (10 ml). The dichloromethane was separated and removed to give the title compound. Colourless blocks of (I) were obtained by recrystallization from an ethanol solution, m.p. 336 K.

NMR ¹H (400 MHz, DMSO-*d*₆), δ, p.p.m. 8.03 (*d*, *J* = 7.3 Hz, 1H, H_{Ph-3}), 7.98–7.88 (*m*, 2H, H_{Ph-4,5}), 7.71 (*d*, *J* = 7.3 Hz, 1H, H_{Ph-6}), 5.94 (*td*, *J* = 16.8, 7.2 Hz, 1H, =CH), 5.36 (*d*, *J* = 16.8 Hz, 1H, =CH₂), 5.18 (*d*, *J* = 9.9 Hz, 1H, =CH₂), 3.98 (*d*, *J* = 6.9 Hz, 2H, CH₂). Analysis calculated for C₁₁H₉F₃N₄S: C, 46.15; H, 3.17; N, 19.57; S, 11.20; found: C, 45.97; H, 3.04; N, 19.49; S, 11.27.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms were positioned geometrically and refined using riding model, with C–H = 0.95 or 0.99 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C).

Funding information

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Table 3

Experimental details.

Crystal data	
Chemical formula	C ₁₁ H ₉ F ₃ N ₄ S
<i>M</i> _r	286.28
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 ₁
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.6595 (3), 20.9841 (7), 7.8641 (3)
<i>V</i> (Å ³)	1263.98 (8)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.28
Crystal size (mm)	0.35 × 0.24 × 0.15
Data collection	
Diffractometer	Rigaku Oxford Diffraction New Gemini, Dual, Cu at home/near, Atlas
Absorption correction	Analytical (<i>CrysAlis PRO</i> ; Rigaku OD, 2018)
<i>T</i> _{min} , <i>T</i> _{max}	0.929, 0.969
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	28170, 3094, 2730
<i>R</i> _{int}	0.059
(sin θ/λ) _{max} (Å ⁻¹)	0.680
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.035, 0.079, 1.07
No. of reflections	3094
No. of parameters	172
No. of restraints	1
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.23, -0.22
Absolute structure	Flack <i>x</i> determined using 1094 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons et al., 2013)
Absolute structure parameter	0.07 (4)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov et al., 2009).

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supporting information

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Crystal structure, Hirshfeld surface analysis and computational studies of 5-[(prop-2-en-1-yl)sulfanyl]-1-[2-(trifluoromethyl)phenyl]-1*H*-tetrazole

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* (Rigaku OD, 2018); data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

5-[(Prop-2-en-1-yl)sulfanyl]-1-[2-(trifluoromethyl)phenyl]-1*H*-tetrazole

Crystal data

$C_{11}H_9F_3N_4S$

$M_r = 286.28$

Orthorhombic, *Pna*2₁

$a = 7.6595$ (3) Å

$b = 20.9841$ (7) Å

$c = 7.8641$ (3) Å

$V = 1263.98$ (8) Å³

$Z = 4$

$F(000) = 584$

$D_x = 1.504$ Mg m⁻³

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

Cell parameters from 9726 reflections

$\theta = 3.9$ – 28.4°

$\mu = 0.28$ mm⁻¹

$T = 150$ K

Block, colourless

$0.35 \times 0.24 \times 0.15$ mm

Data collection

Rigaku Oxford Diffraction New Gemini, Dual,
Cu at home/near, Atlas
diffractometer

Detector resolution: 10.6426 pixels mm⁻¹

ω scans

Absorption correction: analytical
(*CrysAlis PRO*; Rigaku OD, 2018)

$T_{\min} = 0.929$, $T_{\max} = 0.969$

28170 measured reflections

3094 independent reflections

2730 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.059$

$\theta_{\max} = 28.9^\circ$, $\theta_{\min} = 2.8^\circ$

$h = -10 \rightarrow 10$

$k = -28 \rightarrow 28$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.079$

$S = 1.07$

3094 reflections

172 parameters

1 restraint

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0298P)^2 + 0.4395P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.23$ e Å⁻³

$\Delta\rho_{\min} = -0.22$ e Å⁻³

Absolute structure: Flack x determined using
1094 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: 0.07 (4)

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. 1. Fixed Uiso At 1.2 times of: All C(H) groups, All C(H,H) groups 2.a Secondary CH2 refined with riding coordinates: C2(H2A,H2B) 2.b Aromatic/amide H refined with riding coordinates: C3(H3), C6(H6), C7(H7), C8(H8), C9(H9) 2.c X=CH2 refined with riding coordinates: C4(H4A,H4B)

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.82933 (7)	0.43951 (3)	0.47114 (11)	0.02848 (15)
F1	0.4353 (3)	0.24877 (9)	0.1989 (3)	0.0619 (6)
F2	0.5490 (3)	0.34169 (11)	0.2020 (2)	0.0590 (6)
F3	0.2811 (3)	0.32951 (12)	0.2643 (3)	0.0614 (6)
N1	0.4878 (3)	0.41022 (10)	0.5110 (3)	0.0263 (5)
N2	0.3257 (3)	0.43591 (10)	0.4866 (5)	0.0357 (6)
N3	0.3518 (3)	0.49149 (11)	0.4245 (4)	0.0406 (7)
N4	0.5253 (3)	0.50465 (11)	0.4058 (3)	0.0348 (6)
C1	0.6066 (3)	0.45334 (10)	0.4616 (4)	0.0252 (5)
C2	0.9068 (3)	0.51253 (12)	0.3701 (3)	0.0264 (5)
H2A	1.030061	0.506647	0.335573	0.032*
H2B	0.837482	0.520356	0.265975	0.032*
C3	0.8943 (3)	0.56925 (10)	0.4825 (5)	0.0301 (5)
H3	0.781849	0.582487	0.519235	0.036*
C4	1.0299 (4)	0.60194 (13)	0.5336 (4)	0.0378 (7)
H4A	1.143885	0.589750	0.498837	0.045*
H4B	1.014415	0.637872	0.605561	0.045*
C5	0.5129 (3)	0.34687 (11)	0.5739 (3)	0.0253 (5)
C6	0.5647 (4)	0.33874 (16)	0.7405 (4)	0.0363 (7)
H6	0.580710	0.374616	0.812478	0.044*
C7	0.5933 (5)	0.27776 (17)	0.8017 (4)	0.0436 (8)
H7	0.631875	0.271828	0.915363	0.052*
C8	0.5662 (4)	0.22597 (15)	0.6992 (5)	0.0427 (8)
H8	0.583610	0.184288	0.743224	0.051*
C9	0.5136 (4)	0.23375 (13)	0.5317 (4)	0.0370 (7)
H9	0.495146	0.197514	0.461602	0.044*
C10	0.4879 (3)	0.29472 (11)	0.4665 (4)	0.0278 (5)
C11	0.4394 (4)	0.30342 (14)	0.2845 (4)	0.0373 (7)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0220 (3)	0.0207 (2)	0.0428 (3)	0.0028 (2)	-0.0018 (3)	0.0025 (4)
F1	0.1032 (19)	0.0361 (10)	0.0464 (12)	-0.0050 (11)	-0.0153 (12)	-0.0163 (10)
F2	0.0844 (16)	0.0638 (14)	0.0287 (10)	-0.0314 (12)	0.0085 (10)	0.0003 (10)
F3	0.0620 (13)	0.0750 (15)	0.0472 (11)	0.0155 (11)	-0.0163 (10)	-0.0005 (11)

N1	0.0222 (10)	0.0226 (10)	0.0341 (14)	0.0019 (8)	0.0027 (9)	-0.0039 (9)
N2	0.0222 (9)	0.0327 (11)	0.0522 (16)	0.0065 (8)	0.0027 (12)	-0.0053 (13)
N3	0.0282 (12)	0.0328 (13)	0.0607 (19)	0.0074 (9)	-0.0022 (11)	-0.0004 (11)
N4	0.0269 (12)	0.0265 (11)	0.0511 (15)	0.0058 (9)	-0.0015 (11)	0.0045 (11)
C1	0.0223 (10)	0.0218 (10)	0.0317 (13)	0.0029 (8)	0.0014 (14)	-0.0030 (13)
C2	0.0260 (13)	0.0243 (13)	0.0290 (14)	-0.0003 (10)	0.0015 (11)	0.0011 (10)
C3	0.0306 (12)	0.0228 (11)	0.0368 (14)	0.0022 (9)	0.0041 (15)	0.0025 (14)
C4	0.0427 (16)	0.0251 (13)	0.0456 (18)	-0.0011 (12)	0.0008 (13)	-0.0017 (12)
C5	0.0232 (12)	0.0229 (12)	0.0297 (14)	-0.0001 (10)	0.0053 (11)	0.0001 (11)
C6	0.0404 (17)	0.0397 (17)	0.0288 (16)	0.0005 (14)	0.0036 (13)	-0.0043 (13)
C7	0.049 (2)	0.051 (2)	0.0311 (16)	0.0076 (15)	0.0049 (14)	0.0108 (14)
C8	0.0466 (18)	0.0338 (15)	0.0477 (19)	0.0052 (13)	0.0142 (15)	0.0146 (15)
C9	0.0415 (16)	0.0257 (13)	0.0440 (17)	-0.0033 (12)	0.0099 (13)	0.0025 (12)
C10	0.0279 (11)	0.0237 (11)	0.0318 (13)	-0.0034 (9)	0.0055 (14)	-0.0005 (13)
C11	0.0489 (19)	0.0294 (15)	0.0337 (16)	-0.0053 (13)	-0.0017 (13)	-0.0046 (12)

Geometric parameters (Å, °)

S1—C1	1.732 (2)	C3—C4	1.308 (4)
S1—C2	1.825 (3)	C4—H4A	0.9500
F1—C11	1.330 (3)	C4—H4B	0.9500
F2—C11	1.331 (4)	C5—C6	1.380 (4)
F3—C11	1.340 (4)	C5—C10	1.396 (4)
N1—N2	1.367 (3)	C6—H6	0.9500
N1—C1	1.341 (3)	C6—C7	1.384 (5)
N1—C5	1.431 (3)	C7—H7	0.9500
N2—N3	1.280 (3)	C7—C8	1.369 (5)
N3—N4	1.365 (3)	C8—H8	0.9500
N4—C1	1.319 (3)	C8—C9	1.387 (5)
C2—H2A	0.9900	C9—H9	0.9500
C2—H2B	0.9900	C9—C10	1.392 (4)
C2—C3	1.486 (4)	C10—C11	1.490 (4)
C3—H3	0.9500		
C1—S1—C2	99.24 (12)	C6—C5—C10	121.1 (2)
N2—N1—C5	122.5 (2)	C10—C5—N1	120.0 (2)
C1—N1—N2	108.0 (2)	C5—C6—H6	120.3
C1—N1—C5	129.5 (2)	C5—C6—C7	119.3 (3)
N3—N2—N1	105.7 (2)	C7—C6—H6	120.3
N2—N3—N4	112.2 (2)	C6—C7—H7	119.8
C1—N4—N3	105.0 (2)	C8—C7—C6	120.4 (3)
N1—C1—S1	122.86 (17)	C8—C7—H7	119.8
N4—C1—S1	128.06 (19)	C7—C8—H8	119.7
N4—C1—N1	109.1 (2)	C7—C8—C9	120.6 (3)
S1—C2—H2A	109.0	C9—C8—H8	119.7
S1—C2—H2B	109.0	C8—C9—H9	120.0
H2A—C2—H2B	107.8	C8—C9—C10	120.0 (3)
C3—C2—S1	113.13 (19)	C10—C9—H9	120.0

C3—C2—H2A	109.0	C5—C10—C11	121.3 (2)
C3—C2—H2B	109.0	C9—C10—C5	118.5 (3)
C2—C3—H3	118.3	C9—C10—C11	120.1 (3)
C4—C3—C2	123.5 (2)	F1—C11—F2	106.8 (3)
C4—C3—H3	118.3	F1—C11—F3	105.7 (3)
C3—C4—H4A	120.0	F1—C11—C10	112.7 (2)
C3—C4—H4B	120.0	F2—C11—F3	105.5 (3)
H4A—C4—H4B	120.0	F2—C11—C10	112.6 (2)
C6—C5—N1	118.8 (2)	F3—C11—C10	112.9 (2)
S1—C2—C3—C4	117.0 (3)	C5—N1—N2—N3	-177.7 (2)
N1—N2—N3—N4	0.0 (4)	C5—N1—C1—S1	-1.9 (4)
N1—C5—C6—C7	-178.5 (3)	C5—N1—C1—N4	177.3 (2)
N1—C5—C10—C9	179.9 (2)	C5—C6—C7—C8	-1.6 (5)
N1—C5—C10—C11	1.5 (4)	C5—C10—C11—F1	174.8 (2)
N2—N1—C1—S1	-179.8 (3)	C5—C10—C11—F2	53.9 (4)
N2—N1—C1—N4	-0.6 (3)	C5—C10—C11—F3	-65.4 (3)
N2—N1—C5—C6	-104.5 (3)	C6—C5—C10—C9	1.1 (4)
N2—N1—C5—C10	76.6 (3)	C6—C5—C10—C11	-177.3 (3)
N2—N3—N4—C1	-0.3 (4)	C6—C7—C8—C9	1.4 (5)
N3—N4—C1—S1	179.7 (2)	C7—C8—C9—C10	0.0 (5)
N3—N4—C1—N1	0.6 (3)	C8—C9—C10—C5	-1.2 (4)
C1—S1—C2—C3	75.0 (2)	C8—C9—C10—C11	177.2 (3)
C1—N1—N2—N3	0.4 (4)	C9—C10—C11—F1	-3.6 (4)
C1—N1—C5—C6	77.8 (4)	C9—C10—C11—F2	-124.5 (3)
C1—N1—C5—C10	-101.1 (3)	C9—C10—C11—F3	116.2 (3)
C2—S1—C1—N1	175.3 (2)	C10—C5—C6—C7	0.3 (4)
C2—S1—C1—N4	-3.8 (3)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2A \cdots N3 ⁱ	0.99	2.58	3.464 (3)	148
C2—H2B \cdots N2 ⁱⁱ	0.99	2.69	3.666 (4)	169
C3—H3 \cdots F3 ⁱⁱⁱ	0.95	2.71	3.351 (3)	125
C4—H4A \cdots N3 ⁱ	0.95	2.67	3.491 (3)	145
C4—H4B \cdots F1 ^{iv}	0.95	2.47	3.355 (3)	155
C6—H6 \cdots N4 ⁱⁱⁱ	0.95	2.76	3.601 (3)	148

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1, -y+1, z-1/2$; (iii) $-x+1, -y+1, z+1/2$; (iv) $-x+3/2, y+1/2, z+1/2$.