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Crystal structure and Hirshfield surface analysis of 4-phenyl-3-(thiophen-3-ylmethyl)-1*H*-1,2,4-triazole-5(4*H*)-thione

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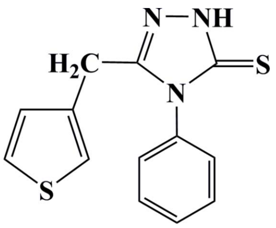
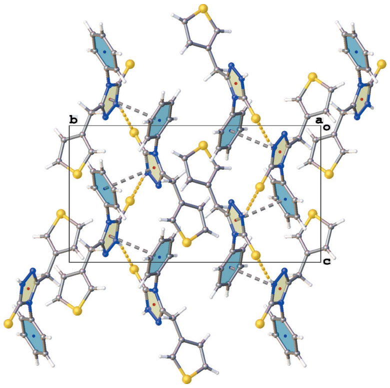
In the title compound, $C_{13}H_{11}N_3S_2$, the phenyl ring is twisted from the 1,2,4-triazole plane by 63.35 (9)° and by 47.35 (9)° from the thiophene plane. In the crystal, chains of molecules running along the *c*-axis direction are formed by N—H⋯S interactions [graph-set motif *C*(4)]. The 1,2,4-triazole and phenyl rings are involved in π–π stacking interactions [centroid–centroid distance = 3.4553 (10) Å]. The thiophene ring is involved in C—H⋯S and C—H⋯π interactions. The intermolecular interactions in the crystal packing were further analysed using Hirshfield surface analysis, which indicates that the most significant contacts are H⋯H (35.8%), followed by S⋯H/H⋯S (26.7%) and C⋯H/H⋯C (18.2%).

1. Chemical context

The triazole ring is an important component of bioactive heterocycles because of its effect in bactericides, pesticides and fungicides (Sengupta *et al.*, 1978; Singh *et al.*, 1979; Giri *et al.*, 1978). Many derivatives containing 1,2,4-triazoline-5-thione show a variety of biological activities: anti-inflamatory (Sahin *et al.*, 2001), antifungal (Knight *et al.*, 1978, 1979), analgesis (Mekuskiene *et al.*, 1998) and bacteriostatic (Eweiss *et al.*, 1986; Mazzone *et al.*, 1981). Thiophene-containing 1,2,4-triazole derivatives have been studied and these compounds have shown promising antimycotic activity (Wujec *et al.*, 2004). Combinations of the thiophene ring with other heterocyclic rings applied in conducting polymers have also been investigated (Ho *et al.*, 2002; Mohamed *et al.*, 2014; Bondarev *et al.*, 2010).



As part of our studies, we have synthesized a new thiophene monomer containing 1,2,4-triazole-5-thione. The polymer obtained from 4-phenyl-3-(thiophen-3-yl-methyl)-1*H*-1,2,4-triazole-5(4*H*)-thione was further characterized by IR spectroscopy and TGA. TG–TGA analysis shows that the polymer is thermally stable above 473 K, showing degradation beyond



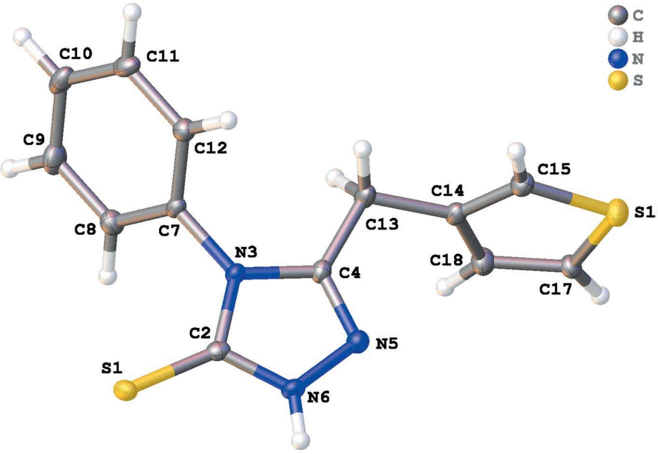


Figure 1
View of the asymmetric unit of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small circles of arbitrary radii.

773 K and exothermic maxima at 745 K. We present here the synthesis and crystal structure of the title compound.

2. Structural commentary

The title compound crystallizes in the monoclinic space group *P*2$_1$/*c* with one molecule in the asymmetric unit (Fig. 1). In the crystalline state, the central 1,2,4-triazole ring exists in its thione tautomeric state with a C2═S1 distance of 1.6845 (16) Å. The short C4═N5 distance [1.302 (2) Å] indicates its double-bond character. The 1,2,4-triazole ring is almost planar (r.m.s. deviation = 0.002 Å for ring C2/N3/C4/N5/N6), with the substituents S1, C7 and C13 deviating by −0.020 (1), −0.028 (2) and 0.061 (2) Å, respectively. The plane of the 1,2,4-triazole ring forms dihedral angles of 79.70 (9) and 63.35 (9)° with the best planes through the thiophene and phenyl rings, respectively. The thiophene and phenyl rings are inclined to each other by 47.35 (9)°. The thiophene ring does not show rotational disorder as observed in previous structure determinations of similar compounds (Vu Quoc *et al.*, 2017).

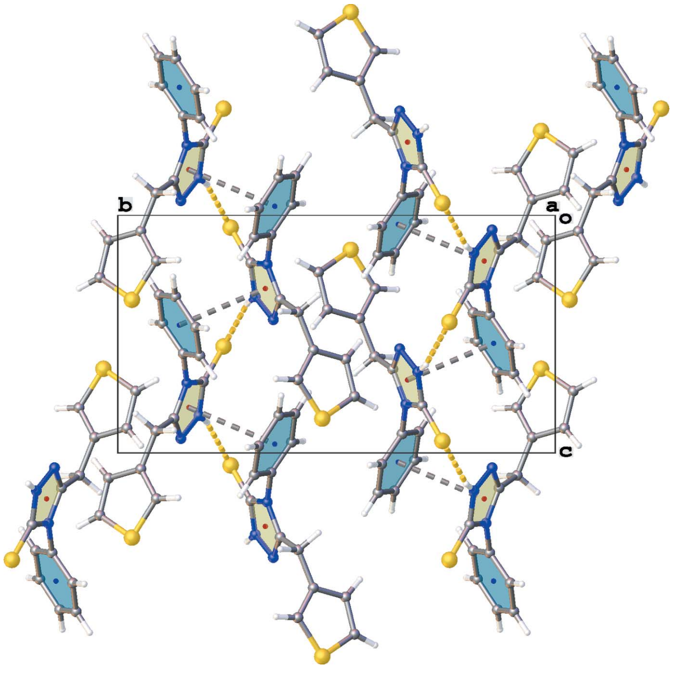


Figure 2
Crystal packing of the title compound shown in projection down the *a* axis illustrating chain formation along the *c*-axis direction by N—H⋯S hydrogen bonding (yellow dashed lines) and the π–π stacking interactions between the 1,2,4-triazole (yellow) and phenyl (blue) rings.

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

*Cg*1 is the centroid of the C14/C15/S16/C17/C18 thiophene ring.

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N6—H6⋯S1$^{\rm i}$	0.88	2.46	3.2866 (16)	156
C8—H8⋯S16$^{\rm ii}$	0.95	2.82	3.737 (2)	162
C10—H10⋯*Cg*1$^{\rm iii}$	0.95	2.83	3.566 (2)	135
C13—H13*B*⋯*Cg*1$^{\rm iv}$	0.99	2.76	3.409 (2)	123

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

3. Supramolecular features

The crystal packing of the title compound is shown in Fig. 2. The packing is dominated by N6—H6⋯S1 interactions (Table 1), resulting in the formation of chains of molecules with graph-set motif *C*(4) propagating along the *c*-axis direction. In addition, the 1,2,4-triazole and phenyl rings exhibit π–π stacking interactions [$Cg2\cdots Cg3^{\rm i}$ = 3.4553 (10) Å; angle of inclination = 9.98 (9)°; *Cg*2 and *Cg*3 are the centroids of the 1,2,4-triazole and phenyl rings, respectively; symmetry code: (i) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; Fig. 2].

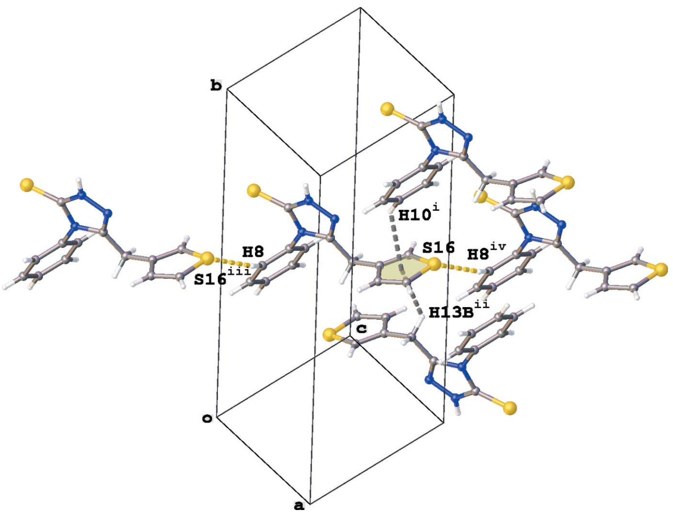


Figure 3
Partial crystal packing of the title compound, showing the C—H⋯π (gray dashed lines) and C—H⋯S interactions (yellow dashed lines) [see Table 1; symmetry codes: (i) $x, y, z+1$; (ii) $-x+2, -y+1, -z+1$; (iii) $x-1, y, z-1$; (iv) $x+1, y, z+1$].

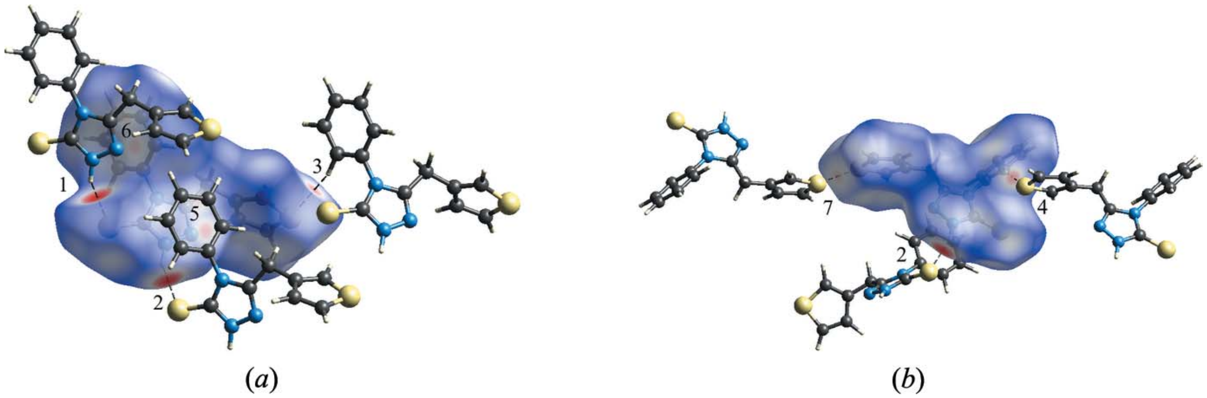


Figure 4
Two views of the Hirshfield surface for the title compound mapped over d_{norm} in the range −0.386 to +1.111 a.u., showing (*a*) the N—H⋯S and C—H⋯S hydrogen bonding and π–π interactions between the 1,2,4-triazole and phenyl rings, and (*b*) the N—H⋯S and C—H⋯S hydrogen bonding and S⋯S interactions.

The thiophene ring plays also a role in the crystal packing as illustrated by the weaker C8—H8⋯S16 interactions and C—H⋯π interactions involving H atoms H10 and H13*B* (Table 1, Fig. 3). The crystal packing contains no voids.

4. Hirshfield surface analysis

Hirshfield surface and two-dimensional fingerprint plot calculations were performed using *CrystalExplorer* (McKinnon *et al.*, 2007; Spackman & Jayatilaka, 2009). The larger bright-red spots near atoms S1, N6, S16 and H8 (labelled 1, 2, 3 and 4) on the Hirshfield surface mapped over d_{norm} in Fig. 4*a* and *b* represent the N—H⋯S and C—H⋯S hydrogen bonds present in the crystal packing. The pale-red spots in Fig. 4*a* near atom N5 and the phenyl ring (labelled 5 and 6) are the result of the π–π stacking between the 1,2,4-triazole and phenyl rings. In Fig. 4*b*, an additional pale-red spot is present near atom S16 (labelled 7), indicating a short S⋯S contact [S16⋯S16^{i} = 3.4688 (7) Å; symmetry code: (i) $-x + 2, -y + 1, -z + 2$]. The relative contributions of the different intermolecular interactions to the Hirshfield surface area, in descending order, are: H⋯H (35.8%), S⋯H/H⋯S (26.7%), C⋯H/H⋯C (18.2%), N⋯H/H⋯N (8.5%), C⋯N/N⋯C (3.7%), C⋯C (3.1%), S⋯C/C⋯S (2.8%) and S⋯S (1.2%). The latter value indicates that the S⋯S contact only makes a marginal contribution to the packing of the title compound.

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.39, last update November 2017; Groom *et al.*, 2016) for crystal structures containing a 1*H*-1,2,4-triazole-5(4*H*)-thione moiety results in 287 (only organics) or 375 structures (including organometallics). When considering only organics, the average C═S and C═N distances are, respectively, 1.676 (9) Å [ranging from 1.608 to 1.699 Å] and 1.302 (11) Å [ranging from 1.275 to 1.410 Å]. For the 66 structures with atom N3 bearing a phenyl subsituent (only organics), the dihedral angle between the 1,2,4-triazole and phenyl rings varies from 55.3 to 90° (the latter when bulky substituents are present at position C4). In the case of a –CH_2R group at position C4, 53 structures are retrieved from the CSD. In this case, the torsion angle N═C—CH_2—*R* shows three favoured regions: (1) *synperiplanar* for small subsituents (torsion angles between −23 and +32°, 28 hits), (2) +*anticlinal* (torsion angles between 67 and 115°, 15 hits) and (3) −*anticlinal* (torsion angles between −87 and −140°, 10 hits).

6. Synthesis and crystallization

The reaction scheme used to synthesize the title compound, **(3)**, is given in Fig. 5. Methyl 2-(thiophen-3-yl)acetate, **(1)**, and 2-(thiophen-3-yl)acetohydrazide, **(2)**, were synthesized as described in a previous study (Vu Quoc *et al.*, 2017).

A mixture of hydrazide **(2)** (0.01 mol), phenylisothiocyanate (0.01 mol) and 20 mL ethanol was refluxed at 353 K for 8h. The solid precipitate was filtered, washed and recrystallized from ethanol to give white crystals (m.p. 416 K). Then, the mixture of the resulting solid (0.411 g), 10 mL ethanol and NaOH 10% (1.25 mmol) was refluxed at 353 K for 3 h. The reaction mixture was cooled and neutralized with HCl 10% to pH = 1–2. The product was filtered, washed and recrystallized from ethanol to give 1.42 g (yield 52%) of **(3)** in the form of pale-yellow crystals (m.p. 451 K). IR (Nicolet Impact 410 FTIR, KBr, cm^{-1}): 3453 (NH), 3088, 2911 (CH), 1576 (C═C thiophene), 1278, 1207 (C═S). ^{1}H NMR [Bruker XL-500, 500 MHz, d_6-DMSO, δ (ppm), *J* (Hz)]: 6.96 (*m*, 1H, H^2), 6.75 (*d*, 1H, $^{5}J = 4.5$, H^4), 7.38 (*dd*, 1H, $^{2}J = 3.0$, $^{4}J = 5.0$, H^5), 3.85 (*s*, 2H, H^6), 13.77 (*s*, 1H, H^8), 7.26–7.28 (*m*, 2H, H^{11} and H^{15}), 7.48–7.50 (*m*, 3H, H^{12}, H^{13} and H^{14}). ^{13}C NMR [Bruker XL-500, 125 MHz, d_6-DMSO, δ (ppm)]: 123.86 (C2), 134.24 (C3),

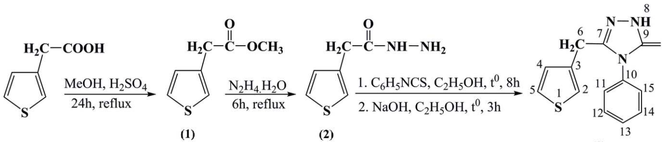


Figure 5
Reaction scheme for the title compound.

128.02 (C4), 126.14 (C5), 26.35 (C6), 150.83 (C7), 167.85 (C9), 133.55 (C10), 128.16 (C11 and C15), 129.20 (C12 and C14), 129.34 (C13). Calculation for $C_{13}H_{11}N_3S_2$: M = 273 a.u.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms were placed at calculated positions and refined in riding mode, with a N—H distance of 0.88 Å or C—H distances of 0.95 (aromatic) and 0.99 Å (CH_2), and isotropic displacement parameters equal to $1.2U_{eq}$ of the parent atoms.

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Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{13}H_{11}N_3S_2$
M_r	273.37
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	8.8257 (8), 16.0776 (16), 9.7437 (9)
β (°)	116.383 (3)
V (Å^3)	1238.6 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.41
Crystal size (mm)	0.31 × 0.21 × 0.09
Data collection	
Diffractometer	Bruker D8 Quest CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.700, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20908, 3082, 2697
R_{int}	0.038
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.668
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.035, 0.097, 1.06
No. of reflections	3082
No. of parameters	163
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.59, −0.38

Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

supporting information

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Crystal structure and Hirshfield surface analysis of 4-phenyl-3-(thiophen-3-ylmethyl)-1*H*-1,2,4-triazole-5(4*H*)-thione

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Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); 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).

4-Phenyl-3-(thiophen-3-ylmethyl)-1*H*-1,2,4-triazole-5(4*H*)-thione

Crystal data

$C_{13}H_{11}N_3S_2$
$M_r = 273.37$
Monoclinic, $P2_1/c$
$a = 8.8257\ (8)$ Å
$b = 16.0776\ (16)$ Å
$c = 9.7437\ (9)$ Å
$\beta = 116.383\ (3)°$
$V = 1238.6\ (2)$ Å^3
$Z = 4$

$F(000) = 568$
$D_x = 1.466$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9914 reflections
$\theta = 2.9–28.3°$
$\mu = 0.41$ mm^{-1}
$T = 100$ K
Block, yellow
0.31 × 0.21 × 0.09 mm

Data collection

Bruker D8 Quest CMOS diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
$T_{min} = 0.700$, $T_{max} = 0.746$
20908 measured reflections

3082 independent reflections
2697 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 28.4°$, $\theta_{min} = 2.9°$
$h = -11 \rightarrow 11$
$k = -21 \rightarrow 21$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.097$
$S = 1.06$
3082 reflections
163 parameters
0 restraints
Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0467P)^2 + 1.0177P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.59$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ 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.

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

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
S1	0.24329 (5)	0.74179 (3)	0.05131 (5)	0.01795 (11)
C2	0.40447 (19)	0.69570 (10)	0.19985 (17)	0.0138 (3)
N3	0.54765 (16)	0.65826 (8)	0.20563 (14)	0.0132 (3)
C4	0.64077 (19)	0.62860 (10)	0.35345 (17)	0.0141 (3)
N5	0.56488 (17)	0.64436 (8)	0.43857 (15)	0.0158 (3)
N6	0.42054 (16)	0.68568 (8)	0.34200 (15)	0.0151 (3)
H6	0.345269	0.703954	0.371018	0.018*
C7	0.59244 (19)	0.64996 (9)	0.08099 (17)	0.0130 (3)
C8	0.4894 (2)	0.60295 (10)	−0.04588 (18)	0.0184 (3)
H8	0.390920	0.576602	−0.050509	0.022*
C9	0.5328 (2)	0.59507 (11)	−0.16594 (19)	0.0235 (4)
H9	0.462216	0.563899	−0.254176	0.028*
C10	0.6780 (2)	0.63219 (11)	−0.1584 (2)	0.0225 (4)
H10	0.707029	0.626318	−0.240840	0.027*
C11	0.7808 (2)	0.67794 (11)	−0.02992 (19)	0.0201 (3)
H11	0.881215	0.702779	−0.023979	0.024*
C12	0.7379 (2)	0.68777 (10)	0.09068 (18)	0.0163 (3)
H12	0.807211	0.719883	0.178022	0.020*
C13	0.8089 (2)	0.58721 (11)	0.40650 (18)	0.0183 (3)
H13A	0.891635	0.627925	0.403638	0.022*
H13B	0.799421	0.541364	0.335289	0.022*
C14	0.87343 (19)	0.55283 (10)	0.56653 (18)	0.0154 (3)
C15	1.0020 (2)	0.58833 (10)	0.69147 (18)	0.0174 (3)
H15	1.058440	0.638022	0.687921	0.021*
S16	1.04926 (5)	0.53259 (3)	0.85492 (5)	0.02086 (12)
C17	0.89607 (19)	0.45897 (10)	0.76090 (17)	0.0150 (3)
H17	0.872539	0.412045	0.807510	0.018*
C18	0.8116 (2)	0.47912 (11)	0.60493 (19)	0.0196 (3)
H18	0.721852	0.446760	0.532024	0.024*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01244 (19)	0.0249 (2)	0.0173 (2)	0.00407 (14)	0.00726 (15)	0.00491 (15)
C2	0.0135 (7)	0.0139 (7)	0.0161 (7)	−0.0021 (5)	0.0084 (6)	−0.0012 (5)
N3	0.0134 (6)	0.0155 (6)	0.0117 (6)	0.0015 (5)	0.0066 (5)	0.0012 (5)
C4	0.0159 (7)	0.0148 (7)	0.0115 (7)	−0.0002 (5)	0.0061 (6)	0.0009 (5)
N5	0.0159 (6)	0.0175 (6)	0.0146 (6)	0.0017 (5)	0.0073 (5)	0.0016 (5)
N6	0.0147 (6)	0.0178 (6)	0.0154 (6)	0.0019 (5)	0.0091 (5)	0.0001 (5)

C7	0.0141 (7)	0.0147 (7)	0.0120 (6)	0.0038 (5)	0.0073 (5)	0.0024 (5)
C8	0.0163 (7)	0.0208 (8)	0.0164 (7)	0.0002 (6)	0.0058 (6)	−0.0006 (6)
C9	0.0274 (9)	0.0267 (9)	0.0145 (7)	0.0019 (7)	0.0075 (7)	−0.0030 (6)
C10	0.0284 (9)	0.0267 (9)	0.0176 (8)	0.0108 (7)	0.0150 (7)	0.0061 (7)
C11	0.0185 (7)	0.0235 (8)	0.0226 (8)	0.0049 (6)	0.0132 (7)	0.0083 (6)
C12	0.0154 (7)	0.0182 (8)	0.0151 (7)	0.0013 (6)	0.0067 (6)	0.0021 (6)
C13	0.0184 (7)	0.0238 (8)	0.0143 (7)	0.0070 (6)	0.0087 (6)	0.0053 (6)
C14	0.0157 (7)	0.0178 (7)	0.0137 (7)	0.0046 (6)	0.0073 (6)	0.0028 (6)
C15	0.0179 (7)	0.0183 (8)	0.0165 (7)	0.0007 (6)	0.0080 (6)	0.0023 (6)
S16	0.0193 (2)	0.0267 (2)	0.0146 (2)	−0.00099 (16)	0.00573 (16)	0.00087 (15)
C17	0.0129 (7)	0.0168 (7)	0.0132 (7)	−0.0010 (5)	0.0038 (6)	−0.0004 (5)
C18	0.0194 (8)	0.0213 (8)	0.0159 (7)	−0.0015 (6)	0.0058 (6)	0.0007 (6)

Geometric parameters (Å, º)

S1—C2	1.6845 (16)	C10—C11	1.386 (3)
C2—N3	1.378 (2)	C11—H11	0.9500
C2—N6	1.338 (2)	C11—C12	1.395 (2)
N3—C4	1.3876 (19)	C12—H12	0.9500
N3—C7	1.4407 (19)	C13—H13A	0.9900
C4—N5	1.302 (2)	C13—H13B	0.9900
C4—C13	1.494 (2)	C13—C14	1.507 (2)
N5—N6	1.3727 (18)	C14—C15	1.367 (2)
N6—H6	0.8800	C14—C18	1.423 (2)
C7—C8	1.388 (2)	C15—H15	0.9500
C7—C12	1.385 (2)	C15—S16	1.7098 (16)
C8—H8	0.9500	S16—C17	1.7226 (16)
C8—C9	1.389 (2)	C17—H17	0.9500
C9—H9	0.9500	C17—C18	1.401 (2)
C9—C10	1.386 (3)	C18—H18	0.9500
C10—H10	0.9500		

N3—C2—S1	129.51 (12)	C10—C11—H11	119.8
N6—C2—S1	127.09 (12)	C10—C11—C12	120.48 (16)
N6—C2—N3	103.39 (13)	C12—C11—H11	119.8
C2—N3—C4	107.58 (13)	C7—C12—C11	118.91 (15)
C2—N3—C7	126.59 (13)	C7—C12—H12	120.5
C4—N3—C7	125.83 (13)	C11—C12—H12	120.5
N3—C4—C13	123.47 (14)	C4—C13—H13A	109.1
N5—C4—N3	111.06 (14)	C4—C13—H13B	109.1
N5—C4—C13	125.43 (14)	C4—C13—C14	112.45 (13)
C4—N5—N6	103.95 (12)	H13A—C13—H13B	107.8
C2—N6—N5	114.02 (13)	C14—C13—H13A	109.1
C2—N6—H6	123.0	C14—C13—H13B	109.1
N5—N6—H6	123.0	C15—C14—C13	123.41 (15)
C8—C7—N3	118.99 (14)	C15—C14—C18	112.18 (14)
C12—C7—N3	119.67 (14)	C18—C14—C13	124.39 (15)
C12—C7—C8	121.33 (15)	C14—C15—H15	124.1

C7—C8—H8	120.6	C14—C15—S16	111.90 (12)
C7—C8—C9	118.88 (16)	S16—C15—H15	124.1
C9—C8—H8	120.6	C15—S16—C17	93.21 (8)
C8—C9—H9	119.6	S16—C17—H17	125.3
C10—C9—C8	120.70 (16)	C18—C17—S16	109.37 (12)
C10—C9—H9	119.6	C18—C17—H17	125.3
C9—C10—H10	120.2	C14—C18—H18	123.3
C9—C10—C11	119.68 (16)	C17—C18—C14	113.35 (14)
C11—C10—H10	120.2	C17—C18—H18	123.3

S1—C2—N3—C4	−179.20 (12)	N6—C2—N3—C4	−0.37 (16)
S1—C2—N3—C7	−0.1 (2)	N6—C2—N3—C7	178.76 (14)
S1—C2—N6—N5	178.97 (11)	C7—N3—C4—N5	−178.60 (14)
C2—N3—C4—N5	0.55 (18)	C7—N3—C4—C13	3.6 (2)
C2—N3—C4—C13	−177.23 (15)	C7—C8—C9—C10	1.1 (3)
C2—N3—C7—C8	−63.5 (2)	C8—C7—C12—C11	−0.1 (2)
C2—N3—C7—C12	117.40 (17)	C8—C9—C10—C11	−0.2 (3)
N3—C2—N6—N5	0.10 (17)	C9—C10—C11—C12	−0.9 (3)
N3—C4—N5—N6	−0.46 (17)	C10—C11—C12—C7	1.0 (2)
N3—C4—C13—C14	−173.79 (14)	C12—C7—C8—C9	−1.0 (2)
N3—C7—C8—C9	179.97 (15)	C13—C4—N5—N6	177.26 (15)
N3—C7—C12—C11	178.94 (14)	C13—C14—C15—S16	−178.12 (12)
C4—N3—C7—C8	115.47 (17)	C13—C14—C18—C17	178.09 (15)
C4—N3—C7—C12	−63.6 (2)	C14—C15—S16—C17	−0.21 (13)
C4—N5—N6—C2	0.22 (18)	C15—C14—C18—C17	−0.4 (2)
C4—C13—C14—C15	−106.27 (18)	C15—S16—C17—C18	−0.01 (13)
C4—C13—C14—C18	75.4 (2)	S16—C17—C18—C14	0.22 (18)
N5—C4—C13—C14	8.8 (2)	C18—C14—C15—S16	0.37 (18)

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the C14/C15/S16/C17/C18 thiophene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6···S1^{i}	0.88	2.46	3.2866 (16)	156
C8—H8···S16^{ii}	0.95	2.82	3.737 (2)	162
C10—H10···*Cg*1^{iii}	0.95	2.83	3.566 (2)	135
C13—H13*B*···*Cg*1^{iv}	0.99	2.76	3.409 (2)	123

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