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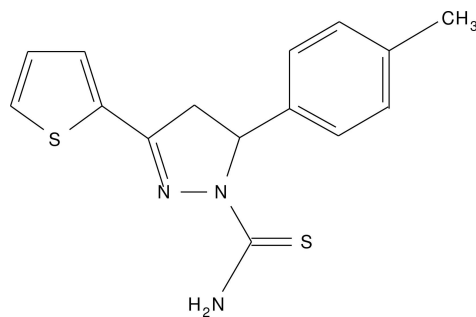
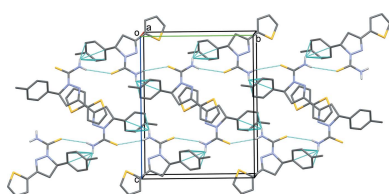
# Crystal structure of 3-(thiophen-2-yl)-5-*p*-tolyl-4,5-dihydro-1*H*-pyrazole-1-carbothioamide

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In the title compound, C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>S<sub>2</sub>, the central pyrazole ring adopts a twisted conformation on the —CH—CH<sub>2</sub>— bond. Its mean plane makes dihedral angles of 7.19 (12) and 71.13 (11)° with those of the thiophene and toluene rings, respectively. The carbothioamide group [C(=S)—N] is inclined to the pyrazole ring mean plane by 16.8 (2)°. In the crystal, molecules are linked by N—H...S hydrogen bonds, forming chains propagating along [010]. Within the chains, there are N—H... $\pi$  interactions present. Between the chains there are weak parallel slipped  $\pi$ — $\pi$  interactions involving inversion-related thiophene and pyrazole rings [inter-centroid distance = 3.7516 (14) Å; inter-planar distance = 3.5987 (10) Å; slippage = 1.06 Å].

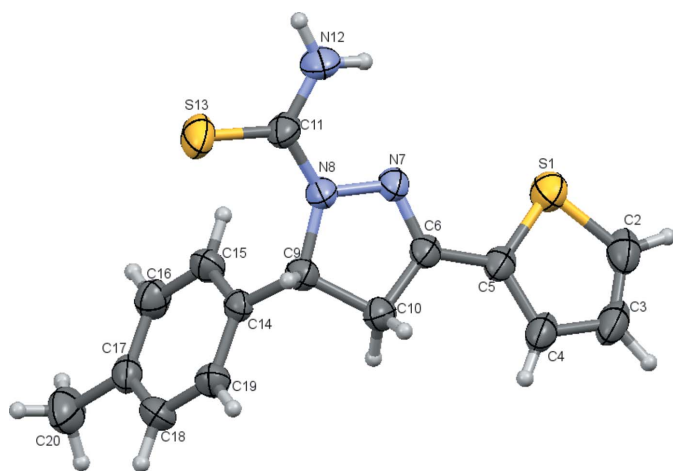
## 1. Chemical context

Five-membered heterocyclic pyrazole analogues have been used extensively as building blocks in organic synthesis. They have been transformed efficiently into molecules of potential medicinal and pharmaceutical important. Pyrazole derivatives have known to exhibit diverse biological applications such as antidiabetic, anaesthetic, antimicrobial and antioxidant. In addition, they have also shown potential anticancer and antiameobic activity and to be potent and selective inhibitors of tissue-nonspecific alkaline phosphatase (Sidique *et al.* 2009). Earlier we synthesized  $\alpha$  and  $\beta$ -unsaturated compounds which served as useful intermediates for the synthesis of pyrazolines (Manjula *et al.*, 2013) and thiazepines (Manjunath *et al.*, 2014). As part of our ongoing research on pyrazole analogues, the title compound was synthesized and we report herein on its crystal structure. Studies of the biological activity of the title compound are underway and will be reported elsewhere.



## 2. Structural commentary

The molecular structure of the title compound is illustrated in Fig. 1. The central pyrazole ring (N7/N8/C8—C10) adopts a

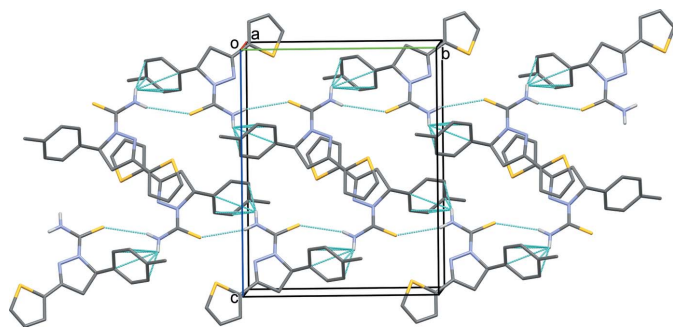


**Figure 1**  
View of the molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

twisted conformation with respect to the C9–C10 bond and its mean plane makes dihedral angles of 7.19 (12) and 71.13 (11)° with the thiophene (S1/C2–C5) and toluene (C14–C19) rings, respectively. The carbothiamide group [C11(=S13)N12] lies in the plane of the pyrazole ring, as indicated by the torsion angles N12–C11–N8–N7 = 0.6 (3) and S13–C11–N8–N7 = 179.96 (16)°, and adopts +*syn*-periplanar and +*anti*-periplanar conformations, respectively. The title compound possess a chiral center at atom C9 but crystallized as a racemate.

### 3. Supramolecular features

In the crystal, molecules are linked by N–H···S hydrogen bonds, forming chains propagating along [010]. Within the chains there are N–H··· $\pi$  interactions involving the toluene ring (Fig. 2 and Table 1). Between the chains there are weak parallel slipped  $\pi$ – $\pi$  interactions involving inversion-related thiophene and pyrazole rings [ $Cg1 \cdots Cg2^i = 3.7516$  (14) Å; inter-planar distance = 3.5987 (10) Å; slippage = 1.06 Å;  $Cg1$



**Figure 2**  
A view along the *a* axis of the crystal packing of the title compound. The hydrogen bonds and C–H··· $\pi$  interactions are shown as dashed lines (see Table 1 for details). C-bound H atoms have been omitted for clarity.

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

$Cg3$  is the centroid of the benzene ring C14–C19.

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N12–H12A···S13 <sup>i</sup>	0.86	2.83	3.620 (2)	154
N12–H12B···Cg3 <sup>i</sup>	0.86	2.81	3.443 (2)	132

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

and  $Cg2$  are the centroids of rings S1/C2–C5 and N7/N8/C8–C10, respectively; symmetry code: (i)  $-x + 2, -y + 1, -z + 1$ ].

### 4. Database survey

A search of the Cambridge Structural Database (Version 5.36, May 2015; Groom & Allen, 2014) revealed seven structures containing the 3-(thiophen-2-yl)-pyrazole unit. Amongst these are two thioamides; the phenyl derivative of the title compound, 5-phenyl-3-(2-thienyl)-2-pyrazoline-1-thioamide (HEFXEW; Işık *et al.*, 2006), and 1-(*N*-ethylthiocarbamoyl)-3,5-bis(2-thienyl)-2-pyrazoline (YINFUX; Köysal *et al.*, 2007). In these two compounds, the pyrazole rings have envelope conformations with the methine C atom as the flap, and the mean planes of the two rings are inclined to one another by 11.98 and 10.13°, respectively. This is in contrast to the situation in the title compound where the pyrazole ring has a twisted conformation on the –CH–CH<sub>2</sub>– bond and its mean plane is inclined to the thiophene ring by 7.19 (12)°. In the crystal of the phenyl derivative (HEFXEW), molecules are also linked by N–H···S hydrogen bonds, forming chains.

### 5. Synthesis and crystallization

A mixture of 3-(4-methylphenyl)-1-(thiophen-2-yl)prop-2-en-1-one (0.001 mol) and thiosemicarbazine hydrochloride (0.01 mol) and potassium hydroxide (0.02 mol) in ethyl alcohol (20 ml) was refluxed on a water bath for 6–8 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was poured into ice-cold water and stirred. The solid that separated was filtered, and washed with ice-cold water. The product was recrystallized from ethyl alcohol to give the title compound as rectangular yellow crystals. Analysis calculated for C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>S<sub>2</sub>: C, 59.77; H, 5.02; N, 13.94%; found: C, 59.74; H, 5.06; N, 13.88%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.297 (s, 3H, CH<sub>3</sub>), (dd, 1H, C4–Hb: *J* = 18.0, 8.5 Hz), (dd, 1H, C4–Hb: *J* = 18.0, 8.5 Hz), 5.976–6.013 (dd, 1H, C–Ha: *J* = 18.0, 12.0 Hz), 6.163–7.169 (*m*, 7H, Ar–H and thiophene ring-H), 7.330 (s, 2H, –NH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  43.77, 1 C, C-4), 63.34 (1 C, C-5), 125.35 (2C, Ar–C), 127.88 (1C, 5 m ring-C), 129.57 (1C, Ar–C), 129.67 (1C, Ar–C), 129.72 (1C, 5 m ring-C), 130.01 (1C, 5 m ring-C), 134.12, (1C, 5 m ring-C), 137.31 (1C, Ar–C), 138.67 (1C, Ar–C), 151.38 (1C, C-3), 176.36 (1C, C=S). MS (*m/z*): 303 (*M*+2, 10) 302 (*M*+1, 18), 301 (*M*+, 100), 284 (40), 161 (15).

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>15</sub> H <sub>15</sub> N <sub>3</sub> S <sub>2</sub>
<i>M<sub>r</sub></i>	301.44
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.1035 (4), 12.0193 (5), 15.1312 (7)
$\beta$ (°)	94.347 (2)
<i>V</i> (Å <sup>3</sup> )	1469.52 (12)
<i>Z</i>	4
Radiation type	Cu <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	3.22
Crystal size (mm)	0.27 × 0.25 × 0.24
Data collection	
Diffractometer	Bruker X8 Proteum
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2013)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.477, 0.512
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	11926, 2397, 2262
<i>R<sub>int</sub></i>	0.044
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.583
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.046, 0.127, 1.07
No. of reflections	2397
No. of parameters	183
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.37, -0.44

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009).

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were fixed geometrically

and allowed to ride on their parent atoms: C–H = 0.93–0.98 Å with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl H atoms and  $1.2U_{\text{eq}}(\text{C})$  for other H atoms.

## Acknowledgements

The authors are thankful to the IOE, Vijnana Bhavana, University of Mysore, Mysore, for providing the single-crystal X-ray diffraction facility. IW is grateful to An-Najah National University and Zamala (fellowship program for the development of university education) for financial support.

## References

- Bruker (2013). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
- Işık, S., Köysal, Y., Özdemir, Z. & Bilgin, A. A. (2006). *Acta Cryst.* **E62**, o491–o493.
- Köysal, Y., Işık, S., Özdemir, Z. & Bilgin, A. A. (2007). *Anal. Sci.* **23**, x193–x194.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Manjula, M., Jayaroopa, P., Manjunath, B. C., Ajay kumar, K. & Lokanath, N. K. (2013). *Acta Cryst.* **E69**, o602.
- Manjunath, B. C., Manjula, M., Raghavendra, K. R., Shashikanth, S., Ajay Kumar, K. & Lokanath, N. K. (2014). *Acta Cryst.* **E70**, o121.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sidique, S., Ardecky, R., Su, Y., Narisawa, S., Brown, B., Millán, J. L., Sergienko, E. & Cosford, N. D. P. (2009). *Bioorg. Med. Chem. Lett.* **19**, 222–225.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

## supporting information

*Acta Cryst.* (2015). E71, 763-765 [doi:10.1107/S2056989015010774]

## Crystal structure of 3-(thiophen-2-yl)-5-*p*-tolyl-4,5-dihydro-1*H*-pyrazole-1-carbothioamide

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### Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINTE* (Bruker, 2013); data reduction: *SAINTE* (Bruker, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

### 5-(4-Methylphenyl)-3-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide

#### Crystal data

C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>S<sub>2</sub>

*M<sub>r</sub>* = 301.44

Monoclinic, *P2<sub>1</sub>/c*

Hall symbol: -*P* 2ybc

*a* = 8.1035 (4) Å

*b* = 12.0193 (5) Å

*c* = 15.1312 (7) Å

$\beta$  = 94.347 (2)°

*V* = 1469.52 (12) Å<sup>3</sup>

*Z* = 4

*F*(000) = 632

*D<sub>x</sub>* = 1.362 Mg m<sup>-3</sup>

Cu *K* $\alpha$  radiation,  $\lambda$  = 1.54178 Å

Cell parameters from 2262 reflections

$\theta$  = 5.5–64.1°

$\mu$  = 3.22 mm<sup>-1</sup>

*T* = 296 K

Rectangle, yellow

0.27 × 0.25 × 0.24 mm

#### Data collection

Bruker X8 Proteum  
diffractometer

Radiation source: Bruker MicroStar microfocus  
rotating anode

Graphite monochromator

Detector resolution: 18.4 pixels mm<sup>-1</sup>

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2013)

*T<sub>min</sub>* = 0.477, *T<sub>max</sub>* = 0.512

11926 measured reflections

2397 independent reflections

2262 reflections with *I* > 2 $\sigma$ (*I*)

*R<sub>int</sub>* = 0.044

$\theta_{\max}$  = 64.1°,  $\theta_{\min}$  = 5.5°

*h* = -9→9

*k* = -13→13

*l* = -16→17

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.046

*wR*(*F*<sup>2</sup>) = 0.127

*S* = 1.07

2397 reflections

183 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

H-atom parameters constrained

*w* = 1/[ $\sigma^2(F_o^2) + (0.074P)^2 + 0.626P$ ]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

$(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.44 \text{ e } \text{\AA}^{-3}$

Extinction correction: *SHELXL*,  
 $\text{FC}^* = \text{KFC}[1 + 0.001 \text{XFC}^2 \Lambda^3 / \text{SIN}(2\Theta)]^{-1/4}$   
 Extinction coefficient: 0.0160 (12)

*Special details*

**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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.83886 (8)	0.35843 (5)	0.55113 (4)	0.0527 (2)
S13	0.41488 (9)	0.76951 (5)	0.77019 (4)	0.0611 (3)
N7	0.6560 (2)	0.55350 (14)	0.63166 (11)	0.0396 (5)
N8	0.5837 (2)	0.65224 (14)	0.65865 (11)	0.0418 (6)
N12	0.5024 (3)	0.55813 (17)	0.77851 (13)	0.0572 (7)
C2	0.9012 (3)	0.3098 (2)	0.45389 (18)	0.0561 (8)
C3	0.8661 (3)	0.3801 (2)	0.38623 (17)	0.0613 (9)
C4	0.7858 (3)	0.4794 (2)	0.41081 (15)	0.0494 (8)
C5	0.7627 (3)	0.47817 (18)	0.50124 (13)	0.0400 (6)
C6	0.6841 (2)	0.56438 (17)	0.54966 (13)	0.0368 (6)
C9	0.5786 (3)	0.73914 (17)	0.58990 (13)	0.0381 (6)
C10	0.6257 (3)	0.67214 (18)	0.50885 (13)	0.0417 (6)
C11	0.5039 (3)	0.65429 (18)	0.73411 (14)	0.0438 (7)
C14	0.6974 (2)	0.83434 (15)	0.61077 (13)	0.0326 (5)
C15	0.8130 (3)	0.83437 (18)	0.68204 (14)	0.0421 (7)
C16	0.9258 (3)	0.92083 (19)	0.69439 (15)	0.0469 (7)
C17	0.9243 (3)	1.00979 (18)	0.63663 (14)	0.0437 (7)
C18	0.8065 (3)	1.00989 (18)	0.56564 (15)	0.0470 (7)
C19	0.6951 (3)	0.92360 (18)	0.55243 (14)	0.0419 (6)
C20	1.0453 (4)	1.1050 (2)	0.65103 (19)	0.0688 (10)
H2	0.95400	0.24170	0.44810	0.0670*
H3	0.89180	0.36530	0.32850	0.0740*
H4	0.75340	0.53690	0.37220	0.0590*
H9	0.46560	0.76780	0.57940	0.0460*
H10A	0.53080	0.66110	0.46670	0.0500*
H10B	0.71300	0.70870	0.47930	0.0500*
H12A	0.55020	0.50040	0.75860	0.0690*
H12B	0.45370	0.55400	0.82700	0.0690*
H15	0.81560	0.77590	0.72240	0.0500*
H16	1.00410	0.91880	0.74260	0.0560*
H18	0.80230	1.06920	0.52610	0.0560*
H19	0.61750	0.92520	0.50390	0.0500*

H20A	0.98990	1.16790	0.67420	0.1030*
H20B	1.08790	1.12470	0.59560	0.1030*
H20C	1.13490	1.08270	0.69240	0.1030*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0578 (4)	0.0494 (4)	0.0530 (4)	−0.0001 (3)	0.0172 (3)	−0.0061 (2)
S13	0.0750 (5)	0.0495 (4)	0.0628 (4)	−0.0051 (3)	0.0306 (3)	−0.0180 (3)
N7	0.0483 (10)	0.0317 (9)	0.0408 (9)	−0.0044 (7)	0.0164 (7)	−0.0045 (7)
N8	0.0561 (11)	0.0321 (9)	0.0395 (9)	−0.0044 (8)	0.0188 (8)	−0.0026 (7)
N12	0.0786 (14)	0.0492 (12)	0.0478 (11)	−0.0064 (10)	0.0304 (10)	0.0030 (9)
C2	0.0557 (14)	0.0474 (14)	0.0681 (16)	−0.0092 (11)	0.0240 (12)	−0.0190 (12)
C3	0.0728 (17)	0.0637 (16)	0.0506 (14)	−0.0182 (13)	0.0258 (12)	−0.0257 (13)
C4	0.0583 (14)	0.0489 (13)	0.0429 (12)	−0.0148 (11)	0.0156 (10)	−0.0163 (10)
C5	0.0403 (11)	0.0424 (12)	0.0386 (10)	−0.0145 (9)	0.0112 (8)	−0.0087 (9)
C6	0.0377 (10)	0.0362 (11)	0.0372 (10)	−0.0118 (8)	0.0084 (8)	−0.0055 (8)
C9	0.0409 (11)	0.0348 (11)	0.0391 (11)	−0.0036 (8)	0.0070 (8)	−0.0004 (8)
C10	0.0509 (12)	0.0387 (11)	0.0357 (10)	−0.0121 (9)	0.0050 (9)	−0.0036 (9)
C11	0.0491 (12)	0.0444 (12)	0.0398 (11)	−0.0122 (10)	0.0157 (9)	−0.0080 (9)
C14	0.0362 (10)	0.0275 (9)	0.0349 (9)	0.0015 (8)	0.0087 (8)	−0.0029 (7)
C15	0.0504 (12)	0.0342 (11)	0.0410 (11)	0.0016 (9)	−0.0004 (9)	0.0053 (8)
C16	0.0491 (12)	0.0474 (13)	0.0430 (11)	−0.0019 (10)	−0.0040 (9)	−0.0065 (10)
C17	0.0495 (12)	0.0371 (12)	0.0459 (11)	−0.0077 (9)	0.0137 (9)	−0.0128 (9)
C18	0.0642 (14)	0.0324 (11)	0.0451 (11)	−0.0070 (10)	0.0090 (10)	0.0057 (9)
C19	0.0508 (12)	0.0375 (11)	0.0366 (10)	−0.0002 (9)	−0.0010 (9)	0.0022 (8)
C20	0.0790 (19)	0.0592 (17)	0.0697 (17)	−0.0309 (15)	0.0151 (14)	−0.0182 (14)

*Geometric parameters (Å, °)*

S1—C2	1.695 (3)	C15—C16	1.387 (3)
S1—C5	1.718 (2)	C16—C17	1.381 (3)
S13—C11	1.672 (2)	C17—C18	1.382 (3)
N7—N8	1.398 (2)	C17—C20	1.512 (4)
N7—C6	1.285 (3)	C18—C19	1.380 (3)
N8—C9	1.473 (3)	C2—H2	0.9300
N8—C11	1.354 (3)	C3—H3	0.9300
N12—C11	1.337 (3)	C4—H4	0.9300
N12—H12B	0.8600	C9—H9	0.9800
N12—H12A	0.8600	C10—H10A	0.9700
C2—C3	1.341 (4)	C10—H10B	0.9700
C3—C4	1.422 (3)	C15—H15	0.9300
C4—C5	1.395 (3)	C16—H16	0.9300
C5—C6	1.445 (3)	C18—H18	0.9300
C6—C10	1.496 (3)	C19—H19	0.9300
C9—C14	1.513 (3)	C20—H20A	0.9600
C9—C10	1.539 (3)	C20—H20B	0.9600
C14—C19	1.389 (3)	C20—H20C	0.9600

C14—C15	1.374 (3)		
C2—S1—C5	91.62 (11)	C18—C17—C20	120.9 (2)
N8—N7—C6	107.73 (16)	C17—C18—C19	121.2 (2)
N7—N8—C9	112.69 (15)	C14—C19—C18	120.8 (2)
N7—N8—C11	119.94 (17)	S1—C2—H2	124.00
C9—N8—C11	126.37 (17)	C3—C2—H2	124.00
H12A—N12—H12B	120.00	C2—C3—H3	123.00
C11—N12—H12A	120.00	C4—C3—H3	123.00
C11—N12—H12B	120.00	C3—C4—H4	125.00
S1—C2—C3	112.67 (19)	C5—C4—H4	125.00
C2—C3—C4	113.8 (2)	N8—C9—H9	110.00
C3—C4—C5	110.2 (2)	C10—C9—H9	110.00
S1—C5—C4	111.68 (17)	C14—C9—H9	110.00
S1—C5—C6	122.38 (15)	C6—C10—H10A	111.00
C4—C5—C6	125.9 (2)	C6—C10—H10B	111.00
N7—C6—C10	114.39 (17)	C9—C10—H10A	111.00
N7—C6—C5	122.27 (18)	C9—C10—H10B	111.00
C5—C6—C10	123.33 (17)	H10A—C10—H10B	109.00
N8—C9—C10	101.33 (16)	C14—C15—H15	120.00
N8—C9—C14	113.93 (17)	C16—C15—H15	120.00
C10—C9—C14	111.69 (18)	C15—C16—H16	119.00
C6—C10—C9	102.35 (16)	C17—C16—H16	119.00
N8—C11—N12	115.5 (2)	C17—C18—H18	119.00
S13—C11—N12	122.08 (18)	C19—C18—H18	119.00
S13—C11—N8	122.39 (16)	C14—C19—H19	120.00
C9—C14—C15	123.31 (18)	C18—C19—H19	120.00
C9—C14—C19	118.29 (18)	C17—C20—H20A	109.00
C15—C14—C19	118.32 (18)	C17—C20—H20B	109.00
C14—C15—C16	120.6 (2)	C17—C20—H20C	109.00
C15—C16—C17	121.4 (2)	H20A—C20—H20B	110.00
C16—C17—C20	121.4 (2)	H20A—C20—H20C	109.00
C16—C17—C18	117.7 (2)	H20B—C20—H20C	110.00
C5—S1—C2—C3	-0.2 (2)	C4—C5—C6—N7	174.6 (2)
C2—S1—C5—C4	0.1 (2)	C4—C5—C6—C10	-4.2 (3)
C2—S1—C5—C6	179.6 (2)	C5—C6—C10—C9	-171.56 (19)
C6—N7—N8—C9	-5.9 (2)	N7—C6—C10—C9	9.6 (2)
C6—N7—N8—C11	163.41 (18)	C10—C9—C14—C15	-107.0 (2)
N8—N7—C6—C5	178.34 (17)	C10—C9—C14—C19	69.6 (2)
N8—N7—C6—C10	-2.8 (2)	N8—C9—C14—C19	-176.34 (18)
C11—N8—C9—C14	82.7 (3)	N8—C9—C10—C6	-11.5 (2)
C9—N8—C11—N12	168.3 (2)	C14—C9—C10—C6	110.18 (18)
N7—N8—C11—S13	179.96 (16)	N8—C9—C14—C15	7.1 (3)
N7—N8—C9—C10	11.3 (2)	C9—C14—C15—C16	175.7 (2)
C11—N8—C9—C10	-157.2 (2)	C19—C14—C15—C16	-0.9 (3)
N7—N8—C11—N12	0.6 (3)	C9—C14—C19—C18	-176.6 (2)
N7—N8—C9—C14	-108.84 (18)	C15—C14—C19—C18	0.2 (3)

C9—N8—C11—S13	-12.4 (3)	C14—C15—C16—C17	0.9 (4)
S1—C2—C3—C4	0.3 (3)	C15—C16—C17—C18	-0.1 (4)
C2—C3—C4—C5	-0.3 (3)	C15—C16—C17—C20	178.9 (2)
C3—C4—C5—S1	0.1 (3)	C16—C17—C18—C19	-0.6 (3)
C3—C4—C5—C6	-179.4 (2)	C20—C17—C18—C19	-179.6 (2)
S1—C5—C6—N7	-4.9 (3)	C17—C18—C19—C14	0.6 (3)
S1—C5—C6—C10	176.33 (17)		

*Hydrogen-bond geometry (Å, °)*

Cg3 is the centroid of the benzene ring C14—C19.

<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>
N12—H12 <i>A</i> $\cdots$ S13 <sup>i</sup>	0.86	2.83	3.620 (2)	154
N12—H12 <i>B</i> $\cdots$ Cg3 <sup>i</sup>	0.86	2.81	3.443 (2)	132

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