

5,6-Di-2-thienyl-2,3-dihydropyrazine

 Madhukar Hemamalini[‡] and Hoong-Kun Fun*[§]

X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

Correspondence e-mail: hkfun@usm.my

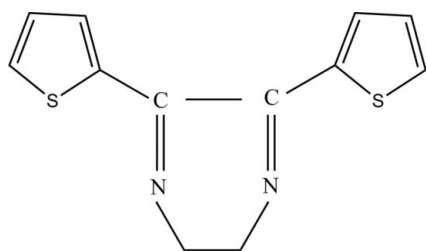
Received 5 April 2010; accepted 6 April 2010

 Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.032; wR factor = 0.115; data-to-parameter ratio = 31.7.

In the title compound, $\text{C}_{12}\text{H}_{10}\text{N}_2\text{S}_2$, which was synthesized by the reaction of 2,2'-thienyl and ethylenediamine, the dihedral angle between the two thiophene rings is $66.33(9)^\circ$. In the crystal structure, intermolecular $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonds link the molecules into infinite chains along the b axis and weak $\text{C}-\text{H}\cdots\pi$ interactions may further stabilize the structure.

Related literature

For background to thienyls, see: Shimon *et al.* (1993). For related structures, see: Crundwell *et al.* (2002*a,b*, 2003); Linehan *et al.* (2003); Stacy *et al.* (2003). For bond-length data, see: Allen *et al.* (1987). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

 $\text{C}_{12}\text{H}_{10}\text{N}_2\text{S}_2$
 $M_r = 246.34$

 Monoclinic, $P2_1$
 $a = 5.5006(9)$ Å

 $b = 7.5246(12)$ Å

 $c = 14.116(2)$ Å

 $\beta = 97.902(5)^\circ$
 $V = 578.73(16)$ Å³
 $Z = 2$

 Mo $K\alpha$ radiation

 $\mu = 0.43$ mm⁻¹
 $T = 100$ K

 $0.32 \times 0.26 \times 0.08$ mm

Data collection

 Bruker APEX DUO CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2009)
 $T_{\min} = 0.875$, $T_{\max} = 0.965$

 9583 measured reflections
 4603 independent reflections
 4295 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.115$
 $S = 1.20$

4603 reflections

145 parameters

1 restraint

 All H-atom parameters refined
 $\Delta\rho_{\max} = 0.62$ e Å⁻³
 $\Delta\rho_{\min} = -0.47$ e Å⁻³
 Absolute structure: Flack (1983), with 1899 Friedel pairs
 Flack parameter: 0.07 (6)

Table 1

Hydrogen-bond geometry (Å, °).

Cg2 is the centroid of the S2/C9–C12 ring.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C1}-\text{H1A}\cdots\text{N1}^i$	0.93	2.33	3.235 (3)	163
$\text{C2}-\text{H2A}\cdots\text{Cg2}^{ii}$	0.93	2.85	3.7737 (18)	171

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

The authors thank the Malaysian Government and Universiti Sains Malaysia for Research University Golden Goose grant No. 1001/PFIZIK/811012. MH thanks Universiti Sains Malaysia for a postdoctoral research fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5396).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Bruker (2009). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
- Crundwell, G., Meskill, T., Sayers, D. & Kantardjieff, K. (2002*a*). *Acta Cryst.* **E58**, o666–o667.
- Crundwell, G., Meskill, T., Sayers, D. & Kantardjieff, K. (2002*b*). *Acta Cryst.* **E58**, o668–o670.
- Crundwell, G., Sayers, D., Herron, S. R. & Kantardjieff, K. A. (2003). *Acta Cryst.* **E59**, o314–o315.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Linehan, J., Crundwell, G., Herron, S. R. & Kantardjieff, K. A. (2003). *Acta Cryst.* **E59**, o466–o468.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Shimon, L. J. W., Vaida, M., Frolow, F., Lahav, M., Leiserowitz, L., Weissinger-Lewin, Y. & McMullan, R. K. (1993). *Faraday Discuss.* **95**, 307–327.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Stacy, V. L., Crundwell, G., Updegraff, J. B. III, Zeller, M. & Hunter, A. D. (2003). *Acta Cryst.* **E59**, o1812–o1813.

[‡] Additional correspondence author, e-mail: mhemamalini2k3@yahoo.co.in.

[§] Thomson Reuters ResearcherID: A-3561-2009.

supplementary materials

Acta Cryst. (2010). E66, o1062 [doi:10.1107/S1600536810012705]

5,6-Di-2-thienyl-2,3-dihydropyrazine

M. Hemamalini and H.-K. Fun

Comment

Thienyl-based guests have shown preferential inclusion into the host by keeping thienyl ring *S* atoms pointed away from the face of growing crystals, possibly to avoid unfavorable electrostatic interactions between sulfur lone pairs coplanar with the thiophene ring and molecules already incorporated into the growing crystal face (Shimon *et al.*, 1993). The structural studies on thenoins (Crundwell *et al.*, 2002*a,b*) and thenils (Crundwell *et al.*, 2003), and other thiophene-containing molecules such as 2,5-diphenyl-3,4-dithien-3-ylcyclopentadien-1-one (Linehan *et al.*, 2003) and 4-bromo-2-thiophenecarboxaldehyde (Stacy *et al.*, 2003) have been reported in the literature. In continuation of this area of study, the crystal structure of the title compound, (I), is reported here.

In the molecule of the title compound (Fig. 1), the bond lengths (Allen *et al.*, 1987) and angles are within normal ranges. The dihedral angle between the two thiophene rings S1/C1–C4 and S2/C9–C12 is 66.33 (9)°. In the crystal structure, intermolecular C—H···N hydrogen bonds (Table 1) link the molecules (Fig. 2) into infinite chains along the *b* axis, in which they may be effective in the stabilization of the structure. The crystal structure is further stabilized by C—H··· π interactions (Table 1), involving the S2/C9–C12 (centroid Cg2) ring.

Experimental

2,2'-thenil (55 mg) and ethylenediamine (15 mg) in ethanol/water (40 ml) were heated under reflux for 2 h with stirring. The resulting solution was then cooled to room temperature. After a few days of slow evaporation of the solvent, brown plates of (I) were obtained.

Refinement

All H atoms were positioned geometrically (C—H = 0.93 or 0.97 Å) and were refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5U_{\text{eq}}(\text{C})$. In the absence of significant anomalous scattering effects, 1899 Friedel pairs were merged.

Figures

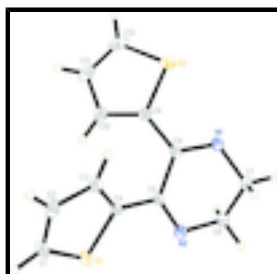


Fig. 1. The asymmetric unit of (I) with displacement ellipsoids drawn at the 50% probability level.

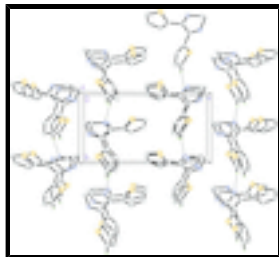


Fig. 2. The crystal packing of (I), showing hydrogen-bonded (dashed lines) networks. H atoms not involving the hydrogen bond interactions are omitted for clarity.

5,6-Di-2-thienyl-2,3-dihydropyrazine

Crystal data

$C_{12}H_{10}N_2S_2$

$M_r = 246.34$

Monoclinic, $P2_1$

Hall symbol: $P\ 2yb$

$a = 5.5006\ (9)\ \text{\AA}$

$b = 7.5246\ (12)\ \text{\AA}$

$c = 14.116\ (2)\ \text{\AA}$

$\beta = 97.902\ (5)^\circ$

$V = 578.73\ (16)\ \text{\AA}^3$

$Z = 2$

$F(000) = 256$

$D_x = 1.414\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 5014 reflections

$\theta = 2.9\text{--}34.8^\circ$

$\mu = 0.43\ \text{mm}^{-1}$

$T = 100\ \text{K}$

Plate, brown

$0.32 \times 0.26 \times 0.08\ \text{mm}$

Data collection

Bruker APEX DUO CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

φ and ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2009)

$T_{\min} = 0.875$, $T_{\max} = 0.965$

9583 measured reflections

4603 independent reflections

4295 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 35.1^\circ$, $\theta_{\min} = 1.5^\circ$

$h = -8 \rightarrow 8$

$k = -12 \rightarrow 12$

$l = -22 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.115$

$S = 1.20$

4603 reflections

145 parameters

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0632P)^2 + 0.0559P]$

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

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

$\Delta\rho_{\max} = 0.62\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.47\ \text{e \AA}^{-3}$

1 restraint Absolute structure: Flack (1983), with 1899 Friedel pairs
 Primary atom site location: structure-invariant direct methods Flack parameter: 0.07 (6)

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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 (\AA^2)

	x	y	z	U_{iso}^*/U_{eq}
S1	0.53730 (6)	0.88379 (6)	0.15567 (3)	0.02249 (9)
S2	-0.08370 (7)	0.37500 (7)	0.39261 (3)	0.02435 (10)
N1	-0.1511 (2)	0.42753 (19)	0.18646 (9)	0.0176 (2)
N2	0.2016 (2)	0.58341 (19)	0.08083 (8)	0.0167 (2)
C1	0.5372 (3)	1.0745 (3)	0.22117 (12)	0.0256 (3)
H1A	0.6518	1.1651	0.2206	0.031*
C2	0.3468 (3)	1.0777 (2)	0.27490 (12)	0.0225 (3)
H2A	0.3166	1.1719	0.3143	0.027*
C3	0.2025 (3)	0.9222 (2)	0.26367 (10)	0.0176 (2)
H3A	0.0665	0.9026	0.2948	0.021*
C4	0.2854 (2)	0.8021 (2)	0.20133 (9)	0.0141 (2)
C5	0.1765 (2)	0.6334 (2)	0.16622 (10)	0.0141 (2)
C6	0.0602 (3)	0.4259 (2)	0.04601 (10)	0.0199 (3)
H6A	0.1494	0.3194	0.0686	0.024*
H6B	0.0373	0.4245	-0.0234	0.024*
C7	-0.1875 (3)	0.4280 (2)	0.08163 (10)	0.0192 (3)
H7A	-0.2783	0.5333	0.0582	0.023*
H7B	-0.2817	0.3244	0.0579	0.023*
C8	0.0286 (2)	0.5231 (2)	0.22635 (9)	0.0136 (2)
C9	0.0980 (3)	0.5061 (2)	0.32993 (9)	0.0148 (2)
C10	0.3080 (3)	0.5582 (2)	0.38767 (10)	0.0199 (3)
H10A	0.4286	0.6292	0.3670	0.024*
C11	0.3203 (4)	0.4914 (3)	0.48252 (11)	0.0272 (3)
H11A	0.4496	0.5144	0.5307	0.033*
C12	0.1220 (4)	0.3904 (3)	0.49497 (11)	0.0296 (4)
H12A	0.1007	0.3360	0.5524	0.036*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02124 (15)	0.02353 (19)	0.02375 (16)	-0.01080 (15)	0.00690 (12)	-0.00227 (15)
S2	0.02570 (17)	0.0293 (2)	0.01976 (15)	-0.00416 (17)	0.00917 (12)	0.00490 (16)
N1	0.0195 (5)	0.0164 (5)	0.0168 (4)	-0.0061 (4)	0.0022 (4)	-0.0014 (4)
N2	0.0188 (5)	0.0166 (5)	0.0151 (5)	-0.0038 (4)	0.0037 (4)	-0.0023 (4)
C1	0.0311 (8)	0.0176 (7)	0.0264 (7)	-0.0130 (6)	-0.0022 (6)	0.0022 (6)
C2	0.0283 (7)	0.0127 (6)	0.0246 (6)	-0.0012 (6)	-0.0030 (5)	-0.0006 (5)
C3	0.0178 (5)	0.0161 (6)	0.0186 (5)	-0.0030 (5)	0.0010 (4)	-0.0018 (5)
C4	0.0142 (5)	0.0126 (6)	0.0151 (5)	-0.0027 (4)	0.0007 (4)	0.0008 (4)
C5	0.0138 (5)	0.0131 (6)	0.0154 (5)	-0.0023 (4)	0.0019 (4)	0.0006 (4)
C6	0.0256 (6)	0.0162 (6)	0.0181 (5)	-0.0039 (5)	0.0042 (5)	-0.0054 (5)
C7	0.0203 (6)	0.0200 (7)	0.0164 (5)	-0.0066 (5)	0.0001 (4)	-0.0024 (5)
C8	0.0154 (5)	0.0113 (5)	0.0141 (5)	-0.0022 (4)	0.0027 (4)	0.0000 (4)
C9	0.0180 (5)	0.0129 (6)	0.0140 (5)	-0.0001 (5)	0.0036 (4)	0.0004 (4)
C10	0.0205 (6)	0.0206 (7)	0.0173 (5)	-0.0006 (5)	-0.0017 (5)	0.0012 (5)
C11	0.0331 (8)	0.0304 (9)	0.0163 (6)	0.0034 (7)	-0.0030 (5)	0.0006 (6)
C12	0.0399 (8)	0.0353 (10)	0.0151 (5)	0.0070 (9)	0.0087 (5)	0.0054 (7)

Geometric parameters (\AA , $^\circ$)

S1—C1	1.707 (2)	C4—C5	1.461 (2)
S1—C4	1.7201 (14)	C5—C8	1.5040 (19)
S2—C12	1.7124 (19)	C6—C7	1.516 (2)
S2—C9	1.7317 (14)	C6—H6A	0.9700
N1—C8	1.2874 (18)	C6—H6B	0.9700
N1—C7	1.4658 (19)	C7—H7A	0.9700
N2—C5	1.2880 (18)	C7—H7B	0.9700
N2—C6	1.465 (2)	C8—C9	1.4652 (19)
C1—C2	1.375 (3)	C9—C10	1.376 (2)
C1—H1A	0.9300	C10—C11	1.423 (2)
C2—C3	1.411 (2)	C10—H10A	0.9300
C2—H2A	0.9300	C11—C12	1.361 (3)
C3—C4	1.382 (2)	C11—H11A	0.9300
C3—H3A	0.9300	C12—H12A	0.9300
C1—S1—C4	92.13 (8)	C7—C6—H6B	109.7
C12—S2—C9	91.82 (8)	H6A—C6—H6B	108.2
C8—N1—C7	115.50 (12)	N1—C7—C6	109.29 (12)
C5—N2—C6	115.48 (12)	N1—C7—H7A	109.8
C2—C1—S1	111.76 (12)	C6—C7—H7A	109.8
C2—C1—H1A	124.1	N1—C7—H7B	109.8
S1—C1—H1A	124.1	C6—C7—H7B	109.8
C1—C2—C3	112.51 (15)	H7A—C7—H7B	108.3
C1—C2—H2A	123.7	N1—C8—C9	117.84 (12)
C3—C2—H2A	123.7	N1—C8—C5	120.25 (12)
C4—C3—C2	112.59 (13)	C9—C8—C5	121.61 (12)

C4—C3—H3A	123.7	C10—C9—C8	130.47 (13)
C2—C3—H3A	123.7	C10—C9—S2	110.85 (10)
C3—C4—C5	128.94 (12)	C8—C9—S2	118.02 (10)
C3—C4—S1	110.99 (11)	C9—C10—C11	112.61 (15)
C5—C4—S1	119.83 (10)	C9—C10—H10A	123.7
N2—C5—C4	118.67 (13)	C11—C10—H10A	123.7
N2—C5—C8	120.18 (13)	C12—C11—C10	112.55 (15)
C4—C5—C8	121.10 (11)	C12—C11—H11A	123.7
N2—C6—C7	109.89 (12)	C10—C11—H11A	123.7
N2—C6—H6A	109.7	C11—C12—S2	112.16 (12)
C7—C6—H6A	109.7	C11—C12—H12A	123.9
N2—C6—H6B	109.7	S2—C12—H12A	123.9
C4—S1—C1—C2	-1.31 (14)	C7—N1—C8—C5	3.3 (2)
S1—C1—C2—C3	0.95 (19)	N2—C5—C8—N1	-29.3 (2)
C1—C2—C3—C4	0.1 (2)	C4—C5—C8—N1	148.07 (15)
C2—C3—C4—C5	-175.19 (14)	N2—C5—C8—C9	144.36 (15)
C2—C3—C4—S1	-1.03 (16)	C4—C5—C8—C9	-38.3 (2)
C1—S1—C4—C3	1.33 (12)	N1—C8—C9—C10	163.90 (16)
C1—S1—C4—C5	176.10 (12)	C5—C8—C9—C10	-9.9 (2)
C6—N2—C5—C4	-172.06 (13)	N1—C8—C9—S2	-5.87 (19)
C6—N2—C5—C8	5.4 (2)	C5—C8—C9—S2	-179.66 (11)
C3—C4—C5—N2	147.03 (16)	C12—S2—C9—C10	-0.12 (14)
S1—C4—C5—N2	-26.69 (19)	C12—S2—C9—C8	171.56 (13)
C3—C4—C5—C8	-30.4 (2)	C8—C9—C10—C11	-170.37 (16)
S1—C4—C5—C8	155.92 (11)	S2—C9—C10—C11	-0.03 (18)
C5—N2—C6—C7	37.17 (19)	C9—C10—C11—C12	0.2 (2)
C8—N1—C7—C6	38.97 (19)	C10—C11—C12—S2	-0.3 (2)
N2—C6—C7—N1	-60.13 (17)	C9—S2—C12—C11	0.26 (17)
C7—N1—C8—C9	-170.61 (13)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1A \cdots N1 ⁱ	0.93	2.33	3.235 (3)	163
C2—H2A \cdots Cg2 ⁱⁱ	0.93	2.85	3.7737 (18)	171

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

Fig. 1

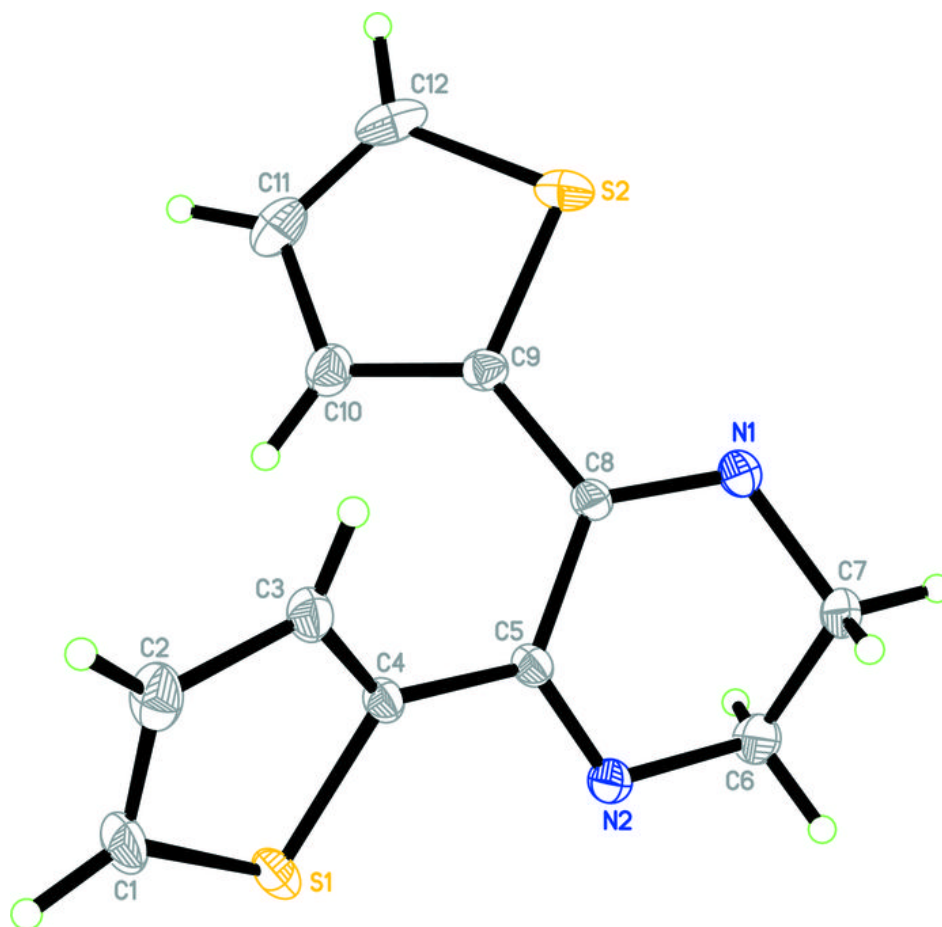


Fig. 2

