organic compounds

2-Phenyl-4H-thiazolo[3,2-a][1,3,5]-triazine-4-thione

Uzma Yunus,[a]* **Mohammad Kalim Tahir,**[a] **Moazzam Hussain Bhatti,**[a] **Saqib Ali**[b] **and Madeleine Helliwell**[c]

[a]Department of Chemistry, Allama Iqbal Open University, Islamabad, Pakistan, [b]Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan, and [c]School of Chemistry, University of Manchester, Manchester M30 9PL, England
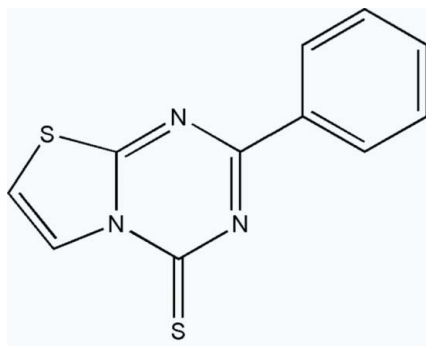Correspondence e-mail: uzma_yunus@yahoo.com

The title compound, $C_{11}H_7N_3S_2$, was synthesized from benzoyl chloride, ammonium thiocyanate and 2-aminothiazole in dry acetone. The whole molecule is essentially planar. The structure was determined using data from a non-merohedrally twinned crystal with a refined twin fraction of 0.523 (1). The structure is stabilized by short intermolecular S···S [3.491 (1) Å] and π–π stacking interactions, as well as weak C—H···N and C—H···S hydrogen bonds.

Related literature

For related literature, see: Lakomska *et al.* (2005); Lee & Chui (1999); Leroux *et al.* (1999); Pauling (1960); Senga *et al.* (1982); Vicentini *et al.* (2004).

Experimental

Crystal data

$C_{11}H_7N_3S_2$	$V = 1025.6$ (7) Å^3
$M_r = 245.32$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 6.847$ (3) Å	$\mu = 0.49$ mm^{-1}
$b = 10.839$ (4) Å	$T = 100$ (2) K
$c = 14.110$ (6) Å	$0.40 \times 0.25 \times 0.08$ mm
$\beta = 101.622$ (6)°	

Data collection

Bruker SMART CCD area-detector diffractometer	10242 measured reflections
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 2007)	2777 independent reflections
$T_{min} = 0.814$, $T_{max} = 0.96$	2486 reflections with $I > 2\sigma(I)$
	R_{int} not defined due to twin pairing errors

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	146 parameters
$wR(F^2) = 0.088$	H-atom parameters constrained
$S = 1.15$	$\Delta\rho_{max} = 0.49$ e Å^{-3}
2777 reflections	$\Delta\rho_{min} = -0.25$ e Å^{-3}

Table 1
Hydrogen bonding and π–π stacking interactions.

$Cg1$, $Cg2$ and $Cg3$ are the centroids of the S1/C1/C2/N1/C3, N1/C3/N2/C4/N3/C5 and C6—C11 rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···N3^i	0.95	2.48	3.280 (3)	142
C2—H2···S1^{ii}	0.95	2.85	3.631 (3)	141
$Cg1$···$Cg3^{iii}$			3.509 (2)	
$Cg2$···$Cg3^{iv}$			3.719 (2)	
$Cg1$···$Cg3^{iv}$			3.619 (2)	
$Cg2$···$Cg3^{iv}$			3.554 (2)	

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *CELL_NOW* (Sheldrick, 2005); data reduction: *SAINT* (Bruker, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001) and *PLATON* (Spek 2003); software used to prepare material for publication: *SHELXTL* and *PLATON*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2050).

References

Bruker (2001). *SMART* (Version 5.625) and *SHELXTL* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2002). *SAINT*. Version 6.36a. Bruker AXS Inc., Madison, Wisconsin, USA.

Lakomska, I., Golankiewicz, B., Wietrzyk, J., Pelczynska, M., Nasulewicz, A., Opolski, A., Sitkowski, J., Kozerski, L. & Szlyk, E. (2005). *Inorg. Chim. Acta*, **358**, 1911–1917.

Lee, H. K. & Chui, W. K. (1999). *Bioorg. Med. Chem.* **7**, 1255-1262.

Leroux, F., van Keulen, B. J., Daliers, J., Pommery, N. & Hénichart, J. P. (1999). *Bioorg. Med. Chem.* **7**, 509–516.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell University Press.

Senga, K., O'Brien, D. E., Scholten, M. B., Novinson, T. & Miller, J. P. (1982). *J. Med. Chem.* **25**, 243–249.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (2005). *CELL_NOW*. University of Göttingen, Germany.

Sheldrick, G. M. (2007). *TWINABS*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Vicentini, C. B., Mares, D., Tartari, A., Manfrini, M. & Forlani, G. (2004). *J. Agric. Food Chem.* **52**, 1898–1906.

supplementary materials

2-Phenyl-4*H*-thiazolo[3,2-*a*][1,3,5]triazine-4-thione

U. Yunus, M. K. Tahir, M. H. Bhatti, S. Ali and M. Helliwell

Comment

Fused heterocyclic 1,3,5-triazines possess a wide array of biological activities such as herbicidal activity (Vicentini *et al.*, 2004), antitumor activity (Lakomska *et al.*, 2005), and inhibitory activity against the enzymes phosphodiesterase (PED) (Senga *et al.*, 1982; Leroux *et al.*, 1999), which is expected to be the target for the treatment of diseases like asthma, diabetes mellitus, and thrombosis. They are also able to block dihydrofolate reductase (DHFR), the inhibition of which leads to cell death (Lee & Chui, 1999). The title compound (I) is an example of a such a fused heterocyclic 1,3,5-triazine.

The whole of molecule (I) is essentially planar. The CN bond distances of the triazine ring are in the range of 1.310 (2)–1.417 (2) Å, in which the N1—C5 bond length is slightly longer than that of N3—C5. These values are intermediate between those expected for single and double C—N bonds (1.47 and 1.27 Å, respectively). The C=S bond length of 1.661 (2) Å is slightly longer than the pure double bond distance (1.61 Å) (Pauling 1960). The bond angles and bond lengths in the thiazole ring attached to the triazine ring are within the normal ranges. The crystal structure is stabilized by intermolecular S···S interactions with atom S1 of the thiazole ring linking to S2 of of the 1,3,5-triazine ring] (with a distance of 3.491 (1) Å; symmetry code $x - 1/2$, $-y + 3/2$, $+z - 1/2$). There are also weak C—H···N and C—H···S hydrogen bonding interactions (Table 1). Finally, the molecules are stacked one above the other in a head-to-tail fashion, linked by π-π stacking interactions (see Table 1 and Figure 2).

Experimental

A mixture of ammonium thiocyanate (26 mmol) and benzoyl chloride (26 mmol) in dry acetone (60 ml) was stirred for 30 min. Then 2-aminothiazole (26 mmol) was added and the reaction mixture was heated to reflux for 2 h. After cooling, the reaction mixture was poured in acidified cold water. The resulting yellow solid was filtered and washed with cold acetone. The title compound (I) was obtained as single crystals suitable for X-ray analysis after recrystallization of the yellow solid from an ethanol-dichloromethane mixture.

Refinement

H atoms were included in calculated positions using the riding method with C—H distances of 0.95 Å and U_{iso}(H) being equal to 1.2 times U_{eq} of their respective parent atoms.

The crystal under investigation was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell_Now (Sheldrick, 2005), and the data were processed using both orientation matrices with *SAINT* (Bruker 2002), resulting in a total of 10242 reflections. 2489 reflections (983 unique ones) involved component 1 only (mean I/sigma = 14.8), 2468 reflections (976 unique ones) involved component 2 only (mean I/sigma = 15.3), and 5285 reflections (1891 unique ones) involved both components (mean I/sigma = 18.2). The exact twin matrix identified by the integration program was found to be (−1.000 − 0.001 − 0.001 / 0.003 − 1.000 − 0.001 / 0.838 0.003 1.000). The second domain is rotated from first domain by 180 ° about the reciprocal lattice *c* axis. The absorption correction was

supplementary materials

carried out using TWINABS (Sheldrick 2007) to create an hklf5 file which was used in all refinements; the structure was solved using direct methods with only the non-overlapping reflections of component 1. The twin fraction refined to a value of 0.523 (1). When the twinning was not accounted for, the conventional R1 value was around 18%.
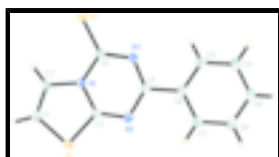
Figures

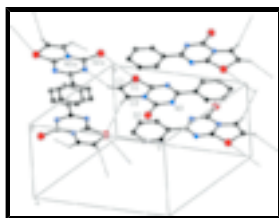Fig. 1. The molecular structure of (I) with ellipsoids drawn at the 50% probability level.

Fig. 2. showing S1···S2, π-π stacking and hydrogen bonding interactions with dashed lines; the symmetry code a is $-1/2 + x, 3/2 - y, -1/2 + z$.

2-phenyl-4H-thiazolo[3,2-a][1,3,5]triazine-4-thione

Crystal data

$C_{11}H_7N_3S_2$	$F_{000} = 504$
$M_r = 245.32$	$D_x = 1.589$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P2yn	Cell parameters from 4033 reflections
$a = 6.847$ (3) Å	$\theta = 2.4–26.8°$
$b = 10.839$ (4) Å	$\mu = 0.49$ mm^{-1}
$c = 14.110$ (6) Å	$T = 100$ (2) K
$\beta = 101.622$ (6)°	Plate, yellow
$V = 1025.6$ (7) Å^3	$0.40 \times 0.25 \times 0.08$ mm
$Z = 4$	

Data collection

Bruker SMART CCD area-detector diffractometer	2777 independent reflections
Radiation source: fine-focus sealed tube	2486 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = not defined due to twin pairing errors
$T = 100(2)$ K	$\theta_{max} = 26.5°$
φ and ω scans	$\theta_{min} = 2.4°$
Absorption correction: multi-scan (TWINABS; Sheldrick, 2007)	$h = -8 \rightarrow 8$
$T_{min} = 0.814$, $T_{max} = 0.96$	$k = 0 \rightarrow 13$
10242 measured reflections	$l = 0 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.031$	H-atom parameters constrained
$wR(F^2) = 0.088$	$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.056P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.15$	$(\Delta/\sigma)_{max} = 0.001$
2777 reflections	$\Delta\rho_{max} = 0.49$ e Å^{-3}
146 parameters	$\Delta\rho_{min} = -0.25$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

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

	x	y	z	$U_{iso}*/U_{eq}$
S1	0.08047 (7)	0.93115 (4)	0.21369 (3)	0.01678 (13)
S2	0.25020 (9)	0.61499 (4)	0.49345 (3)	0.02268 (15)
N1	0.1783 (2)	0.79541 (14)	0.36309 (10)	0.0135 (3)
N2	0.1877 (2)	1.00925 (14)	0.39873 (11)	0.0147 (3)
N3	0.2645 (2)	0.85785 (14)	0.52456 (11)	0.0151 (3)
C1	0.0830 (3)	0.77317 (18)	0.20055 (14)	0.0177 (4)
H1	0.0498	0.7322	0.1399	0.021*
C2	0.1368 (3)	0.71478 (18)	0.28516 (14)	0.0172 (4)
H2	0.1457	0.6276	0.2913	0.021*
C3	0.1563 (3)	0.91697 (17)	0.33755 (14)	0.0142 (4)
C4	0.2431 (3)	0.97366 (16)	0.49194 (13)	0.0129 (4)
C5	0.2320 (3)	0.76289 (17)	0.46220 (13)	0.0146 (4)
C6	0.2830 (3)	1.07262 (17)	0.56603 (13)	0.0146 (4)
C7	0.2579 (3)	1.19652 (18)	0.53972 (14)	0.0182 (4)
H7	0.2133	1.2184	0.4737	0.022*
C8	0.2981 (3)	1.28779 (19)	0.60983 (15)	0.0221 (4)
H8	0.2813	1.3721	0.5915	0.027*
C9	0.3625 (3)	1.25680 (19)	0.70655 (15)	0.0211 (4)

H9	0.3906	1.3198	0.7542	0.025*
C10	0.3858 (3)	1.13343 (18)	0.73370 (14)	0.0194 (4)
H10	0.4288	1.1117	0.7999	0.023*
C11	0.3459 (3)	1.04248 (18)	0.66347 (14)	0.0173 (4)
H11	0.3616	0.9582	0.6820	0.021*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0206 (2)	0.0167 (2)	0.0122 (2)	−0.0003 (2)	0.0012 (2)	0.00127 (18)
S2	0.0368 (3)	0.0119 (2)	0.0165 (2)	0.0001 (2)	−0.0015 (2)	0.00132 (18)
N1	0.0147 (8)	0.0124 (7)	0.0128 (8)	0.0006 (6)	0.0013 (6)	−0.0007 (6)
N2	0.0143 (8)	0.0134 (8)	0.0160 (8)	−0.0012 (7)	0.0026 (7)	−0.0009 (6)
N3	0.0155 (8)	0.0150 (8)	0.0140 (8)	−0.0003 (7)	0.0012 (6)	−0.0016 (6)
C1	0.0176 (10)	0.0185 (10)	0.0167 (10)	0.0002 (8)	0.0026 (8)	−0.0036 (7)
C2	0.0179 (10)	0.0163 (9)	0.0164 (10)	−0.0006 (8)	0.0008 (8)	−0.0059 (7)
C3	0.0121 (9)	0.0162 (9)	0.0144 (9)	−0.0004 (8)	0.0028 (7)	0.0013 (7)
C4	0.0103 (9)	0.0134 (10)	0.0154 (9)	−0.0002 (7)	0.0031 (7)	0.0000 (7)
C5	0.0137 (10)	0.0151 (10)	0.0142 (9)	−0.0003 (8)	0.0007 (7)	0.0026 (7)
C6	0.0115 (9)	0.0158 (9)	0.0172 (9)	−0.0017 (8)	0.0049 (7)	−0.0016 (7)
C7	0.0171 (10)	0.0177 (10)	0.0197 (10)	−0.0006 (8)	0.0037 (8)	−0.0001 (8)
C8	0.0222 (11)	0.0146 (10)	0.0301 (11)	−0.0006 (9)	0.0062 (9)	−0.0035 (8)
C9	0.0193 (10)	0.0193 (10)	0.0258 (11)	−0.0034 (8)	0.0068 (9)	−0.0090 (8)
C10	0.0173 (10)	0.0250 (11)	0.0162 (9)	−0.0014 (8)	0.0037 (8)	−0.0043 (8)
C11	0.0148 (10)	0.0177 (10)	0.0194 (10)	−0.0009 (8)	0.0034 (8)	−0.0002 (8)

Geometric parameters (Å, °)

S1—C1	1.723 (2)	C4—C6	1.484 (3)
S1—C3	1.727 (2)	C6—C11	1.394 (3)
S2—C5	1.661 (2)	C6—C7	1.395 (3)
N1—C3	1.366 (2)	C7—C8	1.387 (3)
N1—C2	1.388 (2)	C7—H7	0.9500
N1—C5	1.417 (2)	C8—C9	1.388 (3)
N2—C3	1.310 (2)	C8—H8	0.9500
N2—C4	1.350 (2)	C9—C10	1.391 (3)
N3—C4	1.335 (2)	C9—H9	0.9500
N3—C5	1.343 (2)	C10—C11	1.385 (3)
C1—C2	1.336 (3)	C10—H10	0.9500
C1—H1	0.9500	C11—H11	0.9500
C2—H2	0.9500		
C1—S1—C3	90.74 (9)	N1—C5—S2	119.53 (14)
C3—N1—C2	113.83 (15)	C11—C6—C7	119.02 (18)
C3—N1—C5	119.54 (15)	C11—C6—C4	120.11 (17)
C2—N1—C5	126.58 (16)	C7—C6—C4	120.87 (17)
C3—N2—C4	113.60 (16)	C8—C7—C6	120.06 (19)
C4—N3—C5	120.16 (16)	C8—C7—H7	120.0
C2—C1—S1	112.43 (15)	C6—C7—H7	120.0

C2—C1—H1	123.8	C7—C8—C9	120.45 (19)
S1—C1—H1	123.8	C7—C8—H8	119.8
C1—C2—N1	112.65 (17)	C9—C8—H8	119.8
C1—C2—H2	123.7	C8—C9—C10	119.96 (19)
N1—C2—H2	123.7	C8—C9—H9	120.0
N2—C3—N1	124.59 (17)	C10—C9—H9	120.0
N2—C3—S1	125.08 (15)	C11—C10—C9	119.45 (19)
N1—C3—S1	110.33 (13)	C11—C10—H10	120.3
N3—C4—N2	126.49 (17)	C9—C10—H10	120.3
N3—C4—C6	116.41 (17)	C10—C11—C6	121.06 (18)
N2—C4—C6	117.10 (15)	C10—C11—H11	119.5
N3—C5—N1	115.57 (16)	C6—C11—H11	119.5
N3—C5—S2	124.90 (15)		
C3—S1—C1—C2	0.37 (16)	C4—N3—C5—S2	−179.04 (15)
S1—C1—C2—N1	−0.2 (2)	C3—N1—C5—N3	−2.3 (3)
C3—N1—C2—C1	−0.2 (2)	C2—N1—C5—N3	−179.84 (18)
C5—N1—C2—C1	177.56 (18)	C3—N1—C5—S2	177.64 (14)
C4—N2—C3—N1	−0.7 (3)	C2—N1—C5—S2	0.1 (3)
C4—N2—C3—S1	179.01 (14)	N3—C4—C6—C11	2.1 (3)
C2—N1—C3—N2	−179.82 (18)	N2—C4—C6—C11	−178.31 (17)
C5—N1—C3—N2	2.3 (3)	N3—C4—C6—C7	−177.70 (17)
C2—N1—C3—S1	0.4 (2)	N2—C4—C6—C7	1.9 (3)
C5—N1—C3—S1	−177.46 (13)	C11—C6—C7—C8	0.9 (3)
C1—S1—C3—N2	179.80 (18)	C4—C6—C7—C8	−179.29 (18)
C1—S1—C3—N1	−0.44 (15)	C6—C7—C8—C9	−0.3 (3)
C5—N3—C4—N2	0.8 (3)	C7—C8—C9—C10	−0.5 (3)
C5—N3—C4—C6	−179.72 (16)	C8—C9—C10—C11	0.5 (3)
C3—N2—C4—N3	−0.9 (3)	C9—C10—C11—C6	0.1 (3)
C3—N2—C4—C6	179.61 (16)	C7—C6—C11—C10	−0.8 (3)
C4—N3—C5—N1	0.9 (3)	C4—C6—C11—C10	179.37 (18)

Hydrogen bonding and π–π stacking interactions

D—H···A	D—H	H···A	D···A	D—H···A
C1–H1···N3[i]	0.95	2.48	3.280 (3)	142
C2—H2···S1[ii]	0.95	2.85	3.631 (3)	141
*Cg*1···*Cg*3[iii]			3.509 (2)	
*Cg*2···*Cg*3[iv]			3.719 (2)	
*Cg*1···*Cg*3[iv]			3.619 (2)	
*Cg*2···*Cg*3[iv]			3.554 (2)	

*Cg*1, *Cg*2 and *Cg*3 are the centroids of the S1/C1/C2/N1/C3, N1/C3/N2/C4/N3/C5 and C6–C11 rings, respectively.
Symmetry codes: (i) $x − 1/2, −y + 3/2, z − 1/2$, (ii) $−x + 1/2, y − 1/2, -z + 1/2$, (iii) $−x, -y + 2, -z + 1$, (iv) $−x + 1, -y + 2, -z + 1$.
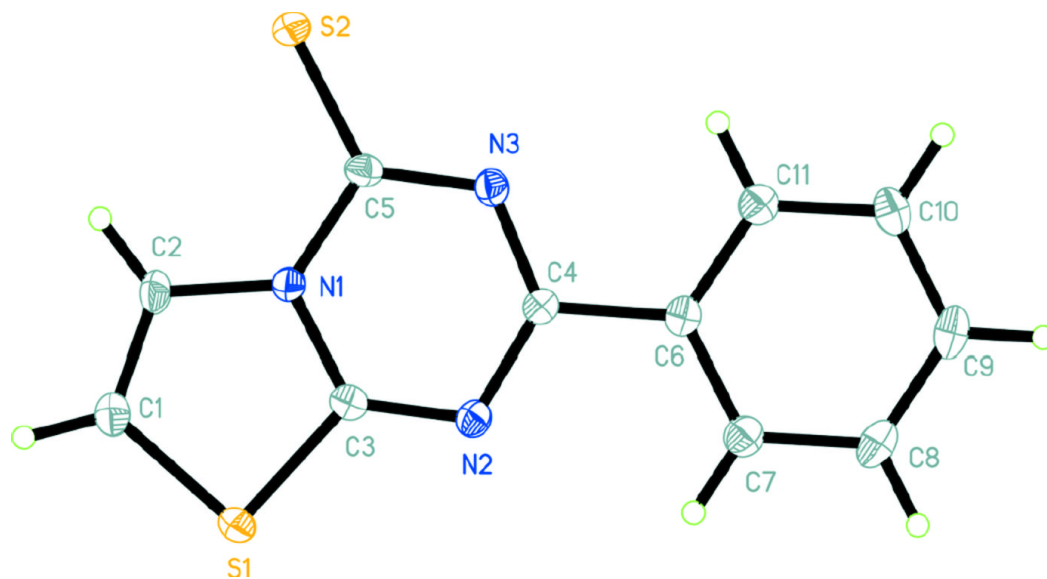
Fig. 1

Fig. 2