

# S-Benzyl 3-[1-(6-methylpyridin-2-yl)ethylidene]-dithiocarbazate: crystal structure and Hirshfeld surface analysis

Siti Aminah Omar,<sup>a</sup> Chee Keong Chah,<sup>a</sup> Thahira B. S. A. Ravoof,<sup>a,‡</sup> Mukesh M. Jotani<sup>b</sup> and Edward R. T. Tiekink<sup>c\*</sup>

Received 20 January 2018

Accepted 22 January 2018

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

‡ Additional correspondence author, e-mail: thahira@upm.edu.my.

**Keywords:** crystal structure; dithiocarbazate ester; hydrogen bonding; Hirshfeld surface analysis.

**CCDC reference:** 1818384

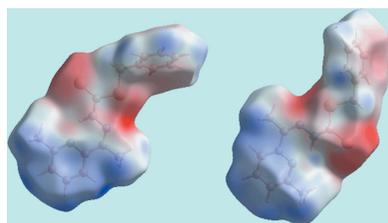
**Supporting information:** this article has supporting information at journals.iucr.org/e

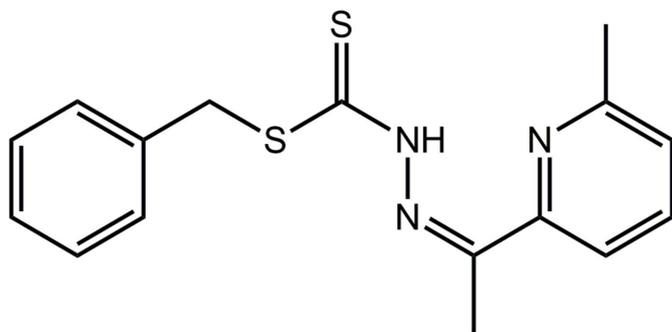
<sup>a</sup>Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia, <sup>b</sup>Department of Physics, Bhavan's Sheth R. A. College of Science, Ahmedabad, Gujarat 380 001, India, and <sup>c</sup>Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia. \*Correspondence e-mail: edwardt@sunway.edu.my

In the title dithiocarbazate ester, C<sub>16</sub>H<sub>17</sub>N<sub>3</sub>S<sub>2</sub> (systematic name: (*Z*)-{[(benzylsulfanyl)methanethioyl]amino}[1-(6-methylpyridin-2-yl)ethylidene]amine), the central methylidenehydrazinecarbodithioate (C<sub>2</sub>N<sub>2</sub>S<sub>2</sub>) core is almost planar (r.m.s. deviation = 0.0111 Å) and forms dihedral angles of 71.67 (3)° with the approximately orthogonally inclined thioester phenyl ring, and 7.16 (7)° with the approximately coplanar substituted pyridyl ring. The latter arrangement and the *Z* configuration about the imine-C=N bond allows for the formation of an intramolecular hydrazine-N—H···N(pyridyl) hydrogen bond that closes an *S*(6) loop. In the crystal, phenyl-C—H···S(thione), methylene-C—H···π(pyridyl), methylene- and phenyl-C—H···π(phenyl) contacts connect molecules into supramolecular layers propagating in the *bc* plane; the layers stack along the *a* axis with no directional interactions between them. The analysis of the Hirshfeld surface indicates the relative importance of an intralayer phenyl-H···H(pyridyl) contact upon the molecular packing.

## 1. Chemical context

Dithiocarbazates are compounds that contain both nitrogen and sulfur donor atoms, which can react with ketones or aldehydes, *via* condensation, to yield Schiff bases. Different ligands can be obtained by introducing different organic substituents, which causes variation in their biological properties, although they may differ only slightly in their molecular structures (Ali *et al.*, 1977; Tarafder *et al.*, 2001, 2002). Interest in this class of compound remains high as studies have shown that they possess anti-cancer (Mirza *et al.*, 2014), anti-bacterial (Bhat *et al.*, 2018), anti-fungal (Nithya *et al.*, 2017), anti-viral (Chew *et al.*, 2004) and anti-inflammatory (Zangrando *et al.*, 2015) properties. Pyridine derivatives have also been a subject of much interest since the 1930's with the discovery of niacin for the treatment of dermatitis and dementia (Henry, 2004). 3-Aminopyridinecarbaldehyde thiosemicarbazone is another pyridine-containing compound that has shown promising activity in advanced leukemia patients in a clinical phase I evaluation (Karp *et al.*, 2008). Although considerable work has been conducted on pyridine-derived Schiff bases and their biological activities, we report, as part of our research into the synthesis and characterization of pyridine-based Schiff bases and their metal complexes, the crystal structure and Hirshfeld surface analysis of a potentially tridentate Schiff base derived from the condensation of *S*-benzyl dithiocarbazate with 2-acetyl-6-methyl pyridine.



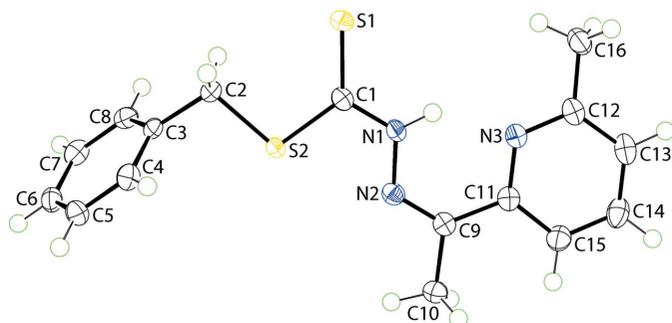


## 2. Structural commentary

The molecular structure of (I), Fig. 1, comprises three distinct almost planar residues with the central methylidenehydrazinecarbodithioate,  $C_2N_2S_2$ , chromophore [r.m.s. deviation = 0.0111 Å] being flanked by the thioester-phenyl ring and the substituted pyridyl ring, forming dihedral angles of 71.67 (3) and 7.16 (7)°, respectively, indicating nearly orthogonal and co-planar dispositions, respectively; the dihedral angle between the outer rings is 65.79 (4)°. The configuration about the imine-C9=N2 bond [1.2924 (18) Å] is *Z*, resulting in the hydrazine-N1—H hydrogen atom being directed towards the pyridyl-N3 atom, enabling the formation of an intermolecular amine-N1—H···N3(pyridyl) hydrogen bond that closes an *S*(6) loop, Table 1. The pyridyl-methyl group is *syn* with the thione-S1 atom and at the same time is orientated to the opposite side of the molecule to the imine-bound methyl group.

## 3. Supramolecular features

The participation of the hydrazine-N1—H hydrogen and pyridyl-N3 atoms in the intramolecular N—H···N hydrogen bond precludes their participation in intermolecular interactions. The molecular packing features weak phenyl-C8—H···S2(thione) interactions, leading to chains along the *b*-axis direction, and a number of C—H··· $\pi$  contacts, *i.e.* methylene-C2—H··· $\pi$ (pyridyl), phenyl-C7—H··· $\pi$ (phenyl) and methyl-C10—H··· $\pi$ (phenyl), as detailed in Table 1. The aforemen-



**Figure 1**  
The molecular structure of (I), showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level.

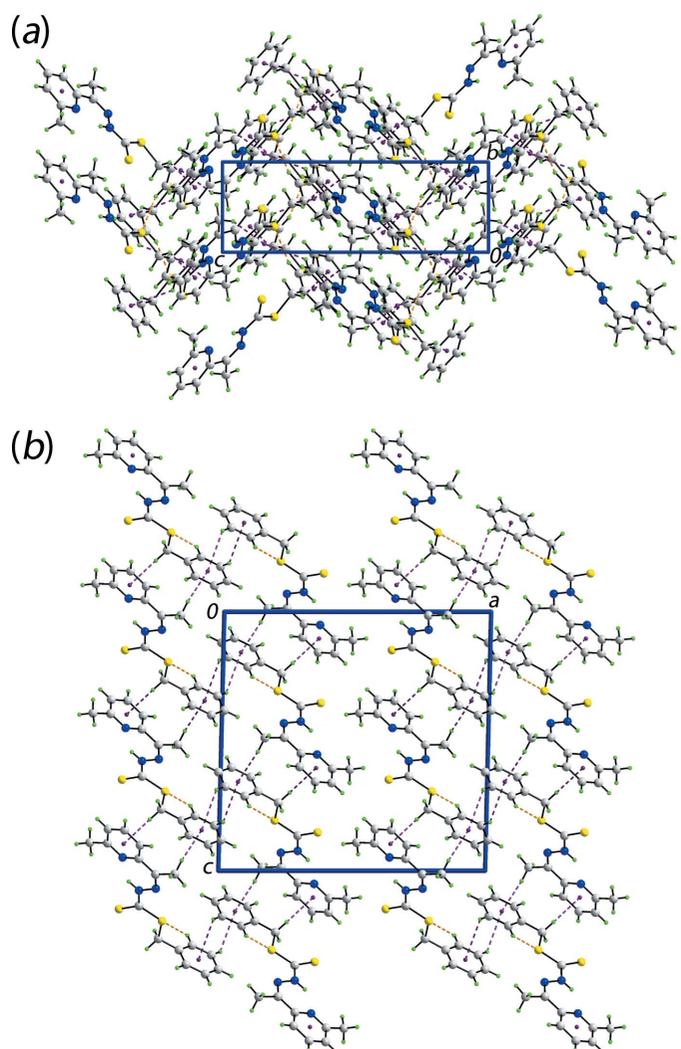
**Table 1**  
Hydrogen-bond geometry (Å, °).

$Cg1$  and  $Cg2$  are the centroids of the (N3,C11–C15) and (C3–C8) rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N···N3	0.87 (1)	1.91 (2)	2.6123 (16)	138 (1)
C8—H8···S2 <sup>i</sup>	0.95	2.90	3.6184 (16)	154
C2—H2A···Cg1 <sup>ii</sup>	0.99	2.76	3.5325 (15)	135
C7—H7···Cg2 <sup>iii</sup>	0.95	2.89	3.5760 (16)	130
C10—H10C···Cg2 <sup>iv</sup>	0.98	2.68	3.5842 (15)	153

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

tioned contacts link molecules into supramolecular layers in the *bc* plane, Fig. 2*a*. Layers stack along the *a* axis with no directional interactions between them, Fig. 2*b*.



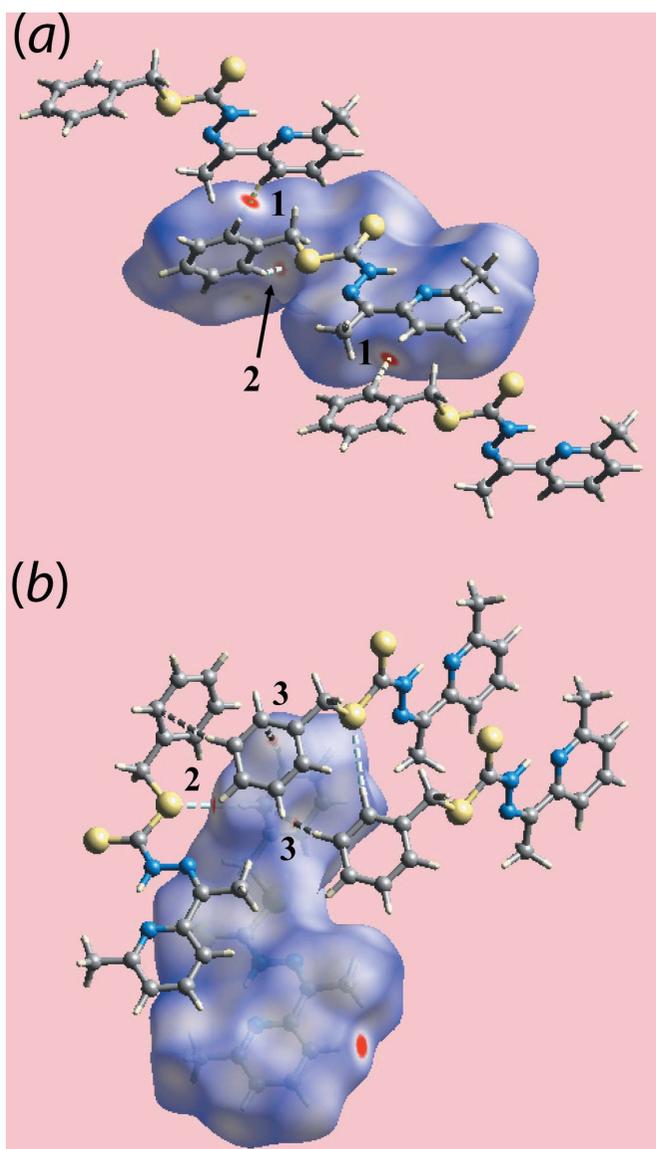
**Figure 2**  
Molecular packing in (I), showing (a) a view of the supramolecular layer sustained by C—H···S and C—H··· $\pi$  interactions and (b) a view of the unit-cell contents shown in projection down the *b* axis, highlighting the stacking of layers. The C—H···S and C—H··· $\pi$  interactions are shown as orange and purple dashed lines, respectively.

**Table 2**  
Summary of short surface contacts (Å) in (I).

Contact	Distance	Symmetry operation
H4...H15	1.98	$x, \frac{3}{2} - y, -\frac{1}{2} + z$
H7...C8	2.74	$-x, -\frac{1}{2} + y, \frac{1}{2} - z$
H2A...C11	2.85	$x, \frac{1}{2} - y, -\frac{1}{2} + z$
H10C...C3	2.86	$x, \frac{1}{2} - y, \frac{1}{2} + z$
H16C...S1	3.05	$-x, -y, -z$

#### 4. Analysis of the Hirshfeld surfaces

The Hirshfeld surfaces calculated for (I) were performed in accord with recent studies on an organic molecule (Tan *et al.*,



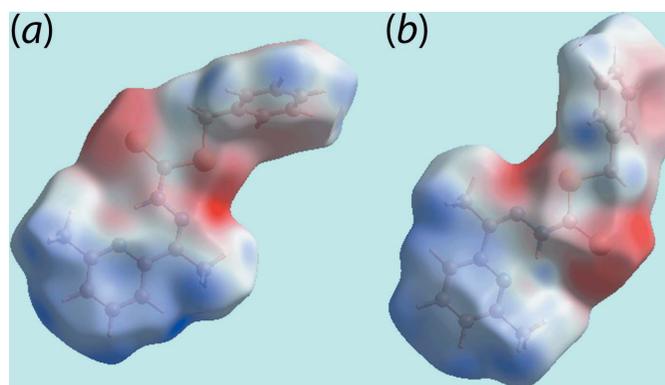
**Figure 3**  
Views of Hirshfeld surface mapped over  $d_{\text{norm}}$  for (I): (a) in the range  $-0.120$  to  $+1.541$  au highlighting short interatomic H...H contacts with yellow dashed lines and label '1' and (b) in the range  $-0.050$  to  $+1.541$  au highlighting short interatomic C...H/H...C contacts with black dashed lines and label '3'. Weak intermolecular C—H...S/S...H—C contacts are indicated by sky-blue dashed lines and label '2' in both (a) and (b).

**Table 3**  
Relative percentage contributions of close contacts to the Hirshfeld surface of (I).

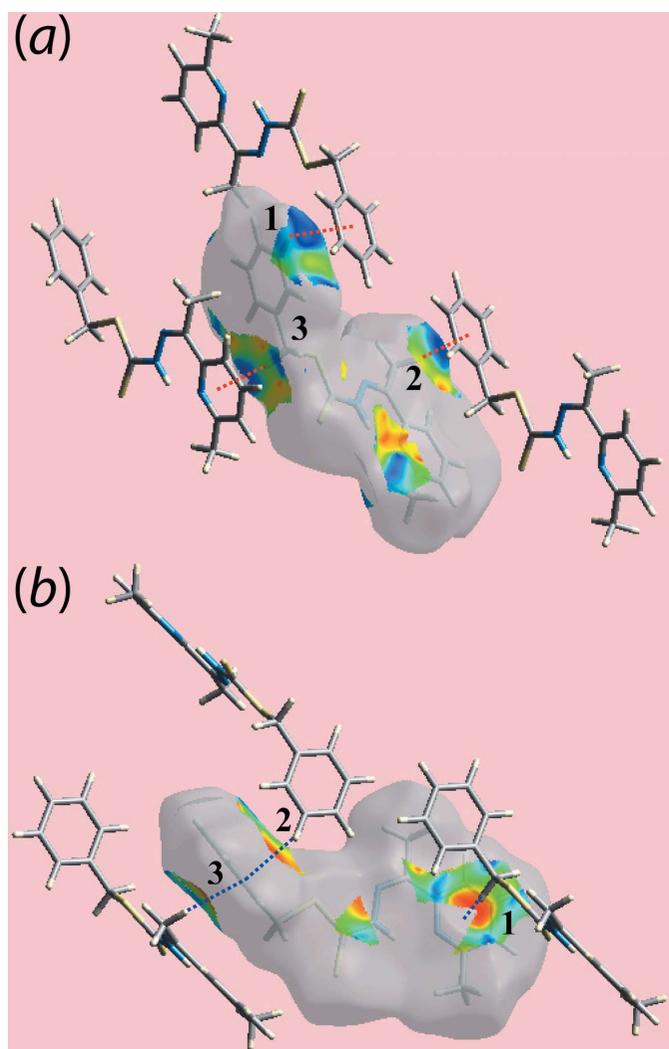
H...H	45.1
C...H/H...C	25.6
S...H/H...S	16.8
N...H/H...N	8.8
C...S/S...C	2.1
S...N/N...S	0.9
C...C	0.7

2017) and serve to provide insight into the influence of different intermolecular interactions in the crystal. A very short (2.23 Å) intra-layer H...H contact between the phenyl-H4 and pyridyl-H15 atoms (Table 2) is significant in the crystal of (I) and is viewed as the bright-red spots near these atoms on the Hirshfeld surface mapped over  $d_{\text{norm}}$  in Fig. 3a (labelled as '1'). The presence of the weak intermolecular C—H...S contact involving the phenyl-C8 and thione-S2 atoms is evident from the diminutive red spots near these atoms in Fig. 3 (labelled as '2'). The faint-red spots near the phenyl-H7 and -C8 atoms in Fig. 3b (labelled as '3') characterize the short surface C...H/H...C contacts and indicate the relative importance of this particular C—H... $\pi$  contact compared with the other two C—H... $\pi$  contacts summarized in Table 1. The most prominent interlayer contact appears to be a weak methyl-C16—H...S1(ester) interaction (Table 2). The donors and acceptors of intermolecular interactions are also represented with blue and red regions, respectively, corresponding to positive and negative electrostatic potentials on the Hirshfeld surface mapped over electrostatic potential in Fig. 4. The intermolecular C—H... $\pi$  contacts, involving donor atoms, and their reciprocal contacts, *i.e.*  $\pi$ ...H—C, containing  $\pi$ -bond acceptors, on the Hirshfeld surface mapped with the shape-index property are illustrated in Fig. 5.

The overall two-dimensional fingerprint plot for (I), Fig. 6a, and those delineated (McKinnon *et al.*, 2007) into H...H, C...H/H...C, S...H/H...S and N...H/H...N contacts are illustrated in Fig. 6b–e; the percentage contributions from the



**Figure 4**  
Two views of the Hirshfeld surface mapped over the electrostatic potential for (I) in the range  $\pm 0.055$  au. The red and blue regions represent negative and positive electrostatic potentials, respectively.



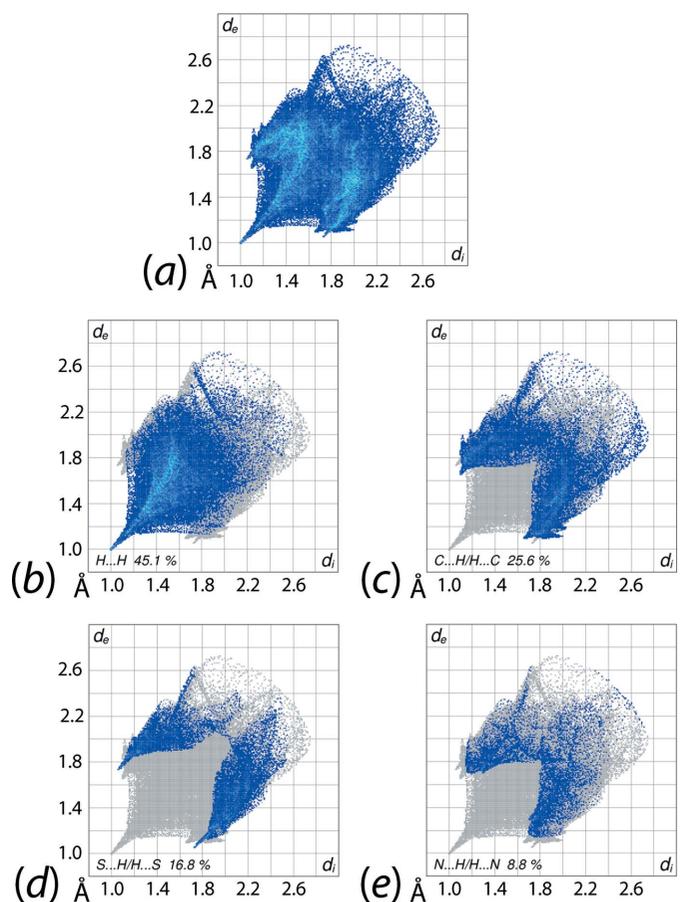
**Figure 5**  
Two views of Hirshfeld surface mapped with shape-index properties for (I) highlighting (a) C–H $\cdots$  $\pi$  contacts and (b) their reciprocal *i.e.*  $\pi\cdots$ H–C contacts, with red and blue dotted lines, respectively, and labels ‘1’–‘3’.

different interatomic contacts to the Hirshfeld surface are summarized in Table 3. The single tip at  $d_e + d_i \sim 2.0$  Å near the vertex of the cone-shaped distribution of points in the fingerprint plot delineated into H $\cdots$ H contacts (Fig. 6*b*) indicate the significant influence of the short interatomic phenyl–H $\cdots$ H(pyridyl) contacts in the crystal mentioned above. The intermolecular C–H $\cdots$  $\pi$  interactions discussed earlier are characterized by short interatomic C $\cdots$ H/H $\cdots$ C contacts (Table 2) and their presence are indicated by the distribution of points around a pair of peaks at  $d_e + d_i \sim 2.8$  Å in Fig. 6*c*, and by the concave surfaces around the phenyl (C3–C8) and pyridyl (N3, C11–C15) rings on the Hirshfeld surface mapped over the electrostatic potential in Fig. 4. The intermolecular C8–H8 $\cdots$ S2 contact in the crystal is characterized by the pair of forceps-like tips at  $d_e + d_i \sim 2.8$  Å in Fig. 6*d*. The interatomic N $\cdots$ H/H $\cdots$ N contacts do not represent directional interactions as the interatomic separations are greater than sum of their van der Waals radii as evident from Fig. 6*e*.

Similarly, the other surface contacts summarized in Table 3 have negligible effect on the packing.

## 5. Database survey

As mentioned in the *Chemical context*, there is sustained interest in this class of compound and this is reflected by the observation there are four closely related structures available for comparison, varying in the *S*-bound group and substitution in the 2-pyridyl ring. In common with (I), the derivative with the 4-methylbenzyl ester and with a methyl group in the 5-position of the pyridyl ring, a *Z*-configuration is noted about the imine bond allowing for the formation of an intramolecular hydrazine–N–H $\cdots$ N(pyridyl) hydrogen bond (Ravooft *et al.*, 2015). By contrast, the three remaining analogues, *i.e.* the methyl ester with no substitution in the pyridyl ring (Basha *et al.*, 2012), benzyl ester/4-methylpyridyl and 4-methylbenzyl ester/4-methylpyridyl (Omar *et al.*, 2014), an *E*-configuration is found about the imine bond, a disposition that allows for the formation of intermolecular thioamide–N–H $\cdots$ S(thione) hydrogen bonds and eight-membered  $\{\cdots$ HNCS $\}_2$  synthons.



**Figure 6**  
(a) The full two-dimensional fingerprint plot for (I) and fingerprint plots delineated into (b) H $\cdots$ H, (c) C $\cdots$ H/H $\cdots$ C, (d) S $\cdots$ H/H $\cdots$ S and (e) S $\cdots$ H/H $\cdots$ S contacts.

## 6. Synthesis and crystallization

All chemicals were of analytical grade and were used without any further purification. *S*-Benzylthiocarbamate (SBDTC) was prepared according to the method published by Ali & Tarafder (1977). Potassium hydroxide (11.4 g, 0.2 mol) was dissolved in absolute ethanol (70 ml) and to this solution hydrazine hydrate (10 g, 0.2 mol) was added. The mixture was then cooled in an ice bath followed by the dropwise addition of carbon disulfide (15.2 g, 0.2 mol) with constant stirring over 1 h. The two layers that formed were then separated using a separating funnel. The brown organic lower layer was dissolved in 40% ethanol. Benzyl chloride (25 ml, 0.2 mol) was then added dropwise into the mixture with vigorous stirring. The white product that formed was filtered off, washed with cold ethanol and dried in a desiccator over anhydrous silica gel. Pure SBDTC was obtained by recrystallization using absolute ethanol as the solvent. Yield: 75%, m.p. 397–399 K. SBDTC (1.98 g, 0.01 mol) was subsequently dissolved in hot acetonitrile (100 ml) and added to an equimolar solution of 2-acetyl-6-methyl pyridine (1.35 g, 0.01 mol) in ethanol (25 ml). The mixture was then heated on a water bath until the volume reduced to half. A yellow precipitate formed upon standing at room temperature for 1 h which was washed with cold ethanol. A small amount of product was dissolved in acetonitrile and left to stand for a week, after which yellow prisms suitable for single-crystal X-ray diffraction analysis formed. IR (cm<sup>-1</sup>): 2921  $\nu$ (N–H), 1560  $\nu$ (C=N), 1055  $\nu$ (N–N), 881  $\nu$ (CSS).

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The carbon-bound H atoms were placed in calculated positions (C–H = 0.95–0.99 Å) and were included in the refinement in the riding-model approximation, with  $U_{\text{iso}}(\text{H})$  set to 1.2–1.5 $U_{\text{eq}}(\text{C})$ . The nitrogen-bound H atom was located in a difference Fourier map, but was refined with a distance restraint of N–H = 0.88±0.01 Å, and with  $U_{\text{iso}}(\text{H})$  set to 1.2 $U_{\text{eq}}(\text{N})$ .

## Acknowledgements

We thank the Department of Chemistry (Universiti Putra Malaysia; UPM) for access to facilities.

## Funding information

This research was funded by UPM and the Malaysian Government under the Malaysian Fundamental Research Grant Scheme (FRGS No. 01-01-16-1833FR). CKC thanks the Malaysian government for the award of a MyBrain scholarship.

## References

- Agilent (2011). *CrysAlis PRO*. Agilent Technologies, Yarnton, England.  
 Ali, M. A. & Tarafder, M. T. H. (1977). *J. Inorg. Nucl. Chem.* **39**, 1785–1791.

Table 4

Experimental details.

Crystal data	
Chemical formula	C <sub>16</sub> H <sub>17</sub> N <sub>3</sub> S <sub>2</sub>
$M_r$	315.44
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
$a, b, c$ (Å)	17.0395 (3), 5.5354 (1), 16.4292 (2)
$\beta$ (°)	91.355 (1)
$V$ (Å <sup>3</sup> )	1549.18 (4)
$Z$	4
Radiation type	Cu $K\alpha$
$\mu$ (mm <sup>-1</sup> )	3.08
Crystal size (mm)	0.28 × 0.18 × 0.08
Data collection	
Diffractometer	Rigaku Oxford Diffraction Gemini E
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2011)
$T_{\text{min}}, T_{\text{max}}$	0.561, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	29598, 3000, 2888
$R_{\text{int}}$	0.034
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.032, 0.092, 1.04
No. of reflections	3000
No. of parameters	195
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.40, -0.26

Computer programs: *CrysAlis PRO* (Agilent, 2011), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Brandenburg, 2006) and *pubCIF* (Westrip, 2010).

- Basha, M. T., Chartres, J. D., Pantarat, N., Ali, M. A., Mirza, A. H., Kalinowski, D. S., Richardson, D. R. & Bernhardt, P. V. (2012). *Dalton Trans.* **41**, 6536–6548.  
 Bhat, R. A., Kumar, D., Malla, M. A., Bhat, S. U., Khan, Md. S., Manzoor, O., Srivastava, A., Naikoo, R. A., Mohsin, M. & Mir, M. A. (2018). *J. Mol. Struct.* **1156**, 280–289.  
 Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.  
 Chew, K.-B., Tarafder, M. T. H., Crouse, K. A., Ali, A. M., Yamin, B. M. & Fun, H.-K. (2004). *Polyhedron*, **23**, 1385–1392.  
 Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.  
 Henry, G. D. (2004). *Tetrahedron*, **60**, 6043–6061.  
 Karp, J. E., Giles, F. J., Gojo, I., Morris, L., Greer, J., Johnson, B., Thein, M., Sznol, M. & Low, J. (2008). *Leuk. Res.* **32**, 71–77.  
 McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.  
 Mirza, A. H., Hamid, M. H. S. A., Aripin, S., Karim, M. R., Arifuzzaman, Md., Ali, M. A. & Bernhardt, P. V. (2014). *Polyhedron*, **74**, 16–23.  
 Nithya, P., Simpson, J. & Govindarajan, S. (2017). *Inorg. Chim. Acta*, **467**, 180–193.  
 Omar, S. A., Ravooof, T. B. S. A., Tahir, M. I. M. & Crouse, K. A. (2014). *Transition Met. Chem.* **39**, 119–126.  
 Ravooof, T. B. S. A., Tiekink, E. R. T., Omar, S. A., Begum, S. Z. & Tahir, M. I. M. (2015). *Acta Cryst.* **E71**, o1071–o1072.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.  
 Tan, M. Y., Crouse, K. A., Ravooof, T. B. S. A., Jotani, M. M. & Tiekink, E. R. T. (2017). *Acta Cryst.* **E73**, o1001–o1008.  
 Tarafder, M. T. H., Kasbollah, A., Crouse, K. A., Ali, A. M., Yamin, B. M. & Fun, H.-K. (2001). *Polyhedron*, **20**, 2363–2370.

Tarafder, M. T. H., Khoo, T., Crouse, K. A., Ali, A. M., Yamin, B. M. & Fun, H.-K. (2002). *Polyhedron*, **21**, 2691–2698.  
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Zangrando, E., Islam, M. T., Islam, M. A. A. A., Sheikh, M. C., Tarafder, M. T. H., Miyatake, R., Zahan, R. & Hossain, M. A. (2015). *Inorg. Chim. Acta*, **427**, 278–284.

## supporting information

*Acta Cryst.* (2018). E74, 261-266 [https://doi.org/10.1107/S2056989018001330]

## S-Benzyl 3-[1-(6-methylpyridin-2-yl)ethylidene]dithiocarbazate: crystal structure and Hirshfeld surface analysis

**Siti Aminah Omar, Chee Keong Chah, Thahira B. S. A. Ravoof, Mukesh M. Jotani and Edward R. T. Tiekink**

### Computing details

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO* (Agilent, 2011); data reduction: *CrysAlis PRO* (Agilent, 2011); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### S-Benzyl 3-[1-(6-methylpyridin-2-yl)ethylidene]dithiocarbazate

#### Crystal data

$C_{16}H_{17}N_3S_2$

$M_r = 315.44$

Monoclinic,  $P2_1/c$

$a = 17.0395$  (3) Å

$b = 5.5354$  (1) Å

$c = 16.4292$  (2) Å

$\beta = 91.355$  (1)°

$V = 1549.18$  (4) Å<sup>3</sup>

$Z = 4$

$F(000) = 664$

$D_x = 1.352$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation,  $\lambda = 1.5418$  Å

Cell parameters from 16086 reflections

$\theta = 3.7\text{--}71.4^\circ$

$\mu = 3.08$  mm<sup>-1</sup>

$T = 100$  K

Prism, yellow

$0.28 \times 0.18 \times 0.08$  mm

#### Data collection

Rigaku Oxford Diffraction Gemini E diffractometer

Radiation source: Enhance X-ray source

Mirror monochromator

Detector resolution: 16.1952 pixels mm<sup>-1</sup>

$\omega$  scan

Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2011)

$T_{\min} = 0.561$ ,  $T_{\max} = 1.000$

29598 measured reflections

3000 independent reflections

2888 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 71.5^\circ$ ,  $\theta_{\min} = 5.2^\circ$

$h = -20 \rightarrow 20$

$k = -6 \rightarrow 6$

$l = -20 \rightarrow 20$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

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

$wR(F^2) = 0.092$

$S = 1.04$

3000 reflections

195 parameters

1 restraint

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 0.6508P]$

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

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

$\Delta\rho_{\max} = 0.40$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.26$  e Å<sup>-3</sup>

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.36900 (2)	0.02321 (6)	0.35206 (2)	0.01816 (12)
S2	0.20666 (2)	0.21559 (6)	0.30590 (2)	0.01465 (12)
N1	0.29576 (7)	0.3795 (2)	0.42370 (7)	0.0161 (3)
H1N	0.3346 (8)	0.396 (3)	0.4582 (9)	0.019*
N2	0.23272 (7)	0.5327 (2)	0.43063 (7)	0.0156 (3)
N3	0.35999 (7)	0.5890 (2)	0.55123 (7)	0.0151 (2)
C1	0.29438 (8)	0.2120 (2)	0.36453 (8)	0.0144 (3)
C2	0.21915 (8)	-0.0396 (3)	0.23758 (8)	0.0168 (3)
H2A	0.2609	-0.0060	0.1982	0.020*
H2B	0.2333	-0.1872	0.2686	0.020*
C3	0.14062 (8)	-0.0702 (3)	0.19410 (8)	0.0141 (3)
C4	0.11330 (8)	0.1021 (3)	0.13811 (8)	0.0166 (3)
H4	0.1456	0.2360	0.1253	0.020*
C5	0.03983 (8)	0.0805 (3)	0.10104 (8)	0.0182 (3)
H5	0.0221	0.1992	0.0631	0.022*
C6	-0.00811 (8)	-0.1147 (3)	0.11931 (8)	0.0178 (3)
H6	-0.0586	-0.1298	0.0940	0.021*
C7	0.01836 (9)	-0.2871 (3)	0.17477 (9)	0.0187 (3)
H7	-0.0140	-0.4211	0.1873	0.022*
C8	0.09226 (9)	-0.2646 (3)	0.21221 (9)	0.0166 (3)
H8	0.1097	-0.3829	0.2504	0.020*
C9	0.23507 (8)	0.6991 (2)	0.48580 (8)	0.0147 (3)
C10	0.16295 (8)	0.8567 (3)	0.48703 (8)	0.0175 (3)
H10A	0.1261	0.8058	0.4437	0.026*
H10B	0.1780	1.0254	0.4783	0.026*
H10C	0.1379	0.8411	0.5399	0.026*
C11	0.29926 (8)	0.7469 (3)	0.54680 (8)	0.0146 (3)
C12	0.41782 (8)	0.6242 (3)	0.60655 (8)	0.0167 (3)
C13	0.41666 (9)	0.8185 (3)	0.66067 (9)	0.0203 (3)
H13	0.4580	0.8395	0.6999	0.024*
C14	0.35505 (9)	0.9797 (3)	0.65674 (9)	0.0215 (3)
H14	0.3533	1.1126	0.6932	0.026*
C15	0.29548 (8)	0.9452 (3)	0.59868 (9)	0.0192 (3)
H15	0.2528	1.0553	0.5945	0.023*
C16	0.48418 (9)	0.4453 (3)	0.60873 (10)	0.0222 (3)
H16A	0.4773	0.3303	0.5638	0.033*
H16B	0.4844	0.3579	0.6606	0.033*
H16C	0.5341	0.5309	0.6032	0.033*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0127 (2)	0.0190 (2)	0.0227 (2)	0.00341 (12)	-0.00205 (14)	-0.00368 (13)
S2	0.01277 (19)	0.0172 (2)	0.01385 (19)	0.00289 (12)	-0.00273 (13)	-0.00297 (12)
N1	0.0123 (6)	0.0196 (6)	0.0162 (6)	0.0017 (5)	-0.0029 (4)	-0.0036 (5)
N2	0.0133 (6)	0.0174 (6)	0.0160 (6)	0.0005 (5)	0.0007 (4)	0.0005 (4)
N3	0.0150 (6)	0.0160 (6)	0.0141 (5)	-0.0020 (5)	-0.0001 (4)	0.0015 (4)
C1	0.0127 (7)	0.0164 (7)	0.0141 (6)	-0.0014 (5)	0.0004 (5)	0.0019 (5)
C2	0.0162 (7)	0.0172 (7)	0.0168 (6)	0.0032 (5)	-0.0014 (5)	-0.0054 (5)
C3	0.0140 (6)	0.0156 (6)	0.0125 (6)	0.0017 (5)	0.0005 (5)	-0.0042 (5)
C4	0.0175 (7)	0.0159 (7)	0.0165 (6)	-0.0040 (5)	0.0016 (5)	0.0003 (5)
C5	0.0197 (7)	0.0201 (7)	0.0146 (6)	0.0014 (6)	-0.0022 (5)	0.0012 (5)
C6	0.0140 (7)	0.0225 (7)	0.0168 (6)	-0.0006 (5)	-0.0001 (5)	-0.0053 (6)
C7	0.0184 (7)	0.0173 (7)	0.0206 (7)	-0.0036 (5)	0.0050 (6)	-0.0025 (5)
C8	0.0194 (7)	0.0150 (7)	0.0155 (6)	0.0025 (5)	0.0025 (5)	0.0004 (5)
C9	0.0140 (7)	0.0163 (7)	0.0137 (6)	-0.0017 (5)	0.0018 (5)	0.0020 (5)
C10	0.0161 (7)	0.0183 (7)	0.0181 (6)	0.0019 (6)	0.0009 (5)	0.0006 (5)
C11	0.0138 (7)	0.0170 (7)	0.0133 (6)	-0.0027 (5)	0.0031 (5)	0.0011 (5)
C12	0.0157 (7)	0.0199 (7)	0.0144 (6)	-0.0046 (5)	0.0000 (5)	0.0036 (5)
C13	0.0185 (7)	0.0269 (8)	0.0155 (7)	-0.0069 (6)	-0.0005 (5)	-0.0009 (6)
C14	0.0209 (8)	0.0251 (8)	0.0188 (7)	-0.0051 (6)	0.0039 (6)	-0.0074 (6)
C15	0.0160 (7)	0.0214 (7)	0.0203 (7)	-0.0004 (6)	0.0036 (5)	-0.0036 (6)
C16	0.0189 (7)	0.0225 (8)	0.0250 (7)	-0.0004 (6)	-0.0064 (6)	0.0010 (6)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

S1—C1	1.6624 (14)	C7—C8	1.394 (2)
S2—C1	1.7591 (14)	C7—H7	0.9500
S2—C2	1.8199 (14)	C8—H8	0.9500
N1—C1	1.3432 (18)	C9—C11	1.4895 (19)
N1—N2	1.3754 (16)	C9—C10	1.5074 (19)
N1—H1N	0.865 (9)	C10—H10A	0.9800
N2—C9	1.2924 (18)	C10—H10B	0.9800
N3—C12	1.3390 (18)	C10—H10C	0.9800
N3—C11	1.3554 (18)	C11—C15	1.392 (2)
C2—C3	1.5113 (19)	C12—C13	1.396 (2)
C2—H2A	0.9900	C12—C16	1.503 (2)
C2—H2B	0.9900	C13—C14	1.378 (2)
C3—C8	1.392 (2)	C13—H13	0.9500
C3—C4	1.397 (2)	C14—C15	1.389 (2)
C4—C5	1.384 (2)	C14—H14	0.9500
C4—H4	0.9500	C15—H15	0.9500
C5—C6	1.392 (2)	C16—H16A	0.9800
C5—H5	0.9500	C16—H16B	0.9800
C6—C7	1.387 (2)	C16—H16C	0.9800
C6—H6	0.9500		

C1—S2—C2	102.63 (7)	C7—C8—H8	119.7
C1—N1—N2	119.01 (11)	N2—C9—C11	127.48 (13)
C1—N1—H1N	123.2 (12)	N2—C9—C10	114.20 (12)
N2—N1—H1N	117.8 (12)	C11—C9—C10	118.31 (12)
C9—N2—N1	119.09 (12)	C9—C10—H10A	109.5
C12—N3—C11	119.42 (12)	C9—C10—H10B	109.5
N1—C1—S1	121.52 (10)	H10A—C10—H10B	109.5
N1—C1—S2	112.88 (10)	C9—C10—H10C	109.5
S1—C1—S2	125.60 (8)	H10A—C10—H10C	109.5
C3—C2—S2	105.26 (9)	H10B—C10—H10C	109.5
C3—C2—H2A	110.7	N3—C11—C15	121.47 (13)
S2—C2—H2A	110.7	N3—C11—C9	117.98 (12)
C3—C2—H2B	110.7	C15—C11—C9	120.54 (13)
S2—C2—H2B	110.7	N3—C12—C13	121.55 (14)
H2A—C2—H2B	108.8	N3—C12—C16	117.48 (13)
C8—C3—C4	118.60 (13)	C13—C12—C16	120.97 (13)
C8—C3—C2	120.51 (13)	C14—C13—C12	119.43 (13)
C4—C3—C2	120.81 (12)	C14—C13—H13	120.3
C5—C4—C3	120.98 (13)	C12—C13—H13	120.3
C5—C4—H4	119.5	C13—C14—C15	119.11 (14)
C3—C4—H4	119.5	C13—C14—H14	120.4
C4—C5—C6	120.09 (13)	C15—C14—H14	120.4
C4—C5—H5	120.0	C14—C15—C11	119.02 (14)
C6—C5—H5	120.0	C14—C15—H15	120.5
C7—C6—C5	119.49 (13)	C11—C15—H15	120.5
C7—C6—H6	120.3	C12—C16—H16A	109.5
C5—C6—H6	120.3	C12—C16—H16B	109.5
C6—C7—C8	120.32 (13)	H16A—C16—H16B	109.5
C6—C7—H7	119.8	C12—C16—H16C	109.5
C8—C7—H7	119.8	H16A—C16—H16C	109.5
C3—C8—C7	120.53 (13)	H16B—C16—H16C	109.5
C3—C8—H8	119.7		
C1—N1—N2—C9	-177.73 (12)	N1—N2—C9—C11	-1.3 (2)
N2—N1—C1—S1	179.30 (10)	N1—N2—C9—C10	179.55 (11)
N2—N1—C1—S2	-1.64 (16)	C12—N3—C11—C15	-0.14 (19)
C2—S2—C1—N1	-175.99 (10)	C12—N3—C11—C9	-178.65 (12)
C2—S2—C1—S1	3.02 (11)	N2—C9—C11—N3	-6.2 (2)
C1—S2—C2—C3	171.62 (9)	C10—C9—C11—N3	172.96 (12)
S2—C2—C3—C8	-107.95 (12)	N2—C9—C11—C15	175.28 (14)
S2—C2—C3—C4	68.72 (14)	C10—C9—C11—C15	-5.57 (19)
C8—C3—C4—C5	-0.2 (2)	C11—N3—C12—C13	0.81 (19)
C2—C3—C4—C5	-176.92 (12)	C11—N3—C12—C16	-179.56 (12)
C3—C4—C5—C6	0.0 (2)	N3—C12—C13—C14	-0.7 (2)
C4—C5—C6—C7	-0.1 (2)	C16—C12—C13—C14	179.73 (13)
C5—C6—C7—C8	0.3 (2)	C12—C13—C14—C15	-0.2 (2)
C4—C3—C8—C7	0.4 (2)	C13—C14—C15—C11	0.8 (2)
C2—C3—C8—C7	177.14 (12)	N3—C11—C15—C14	-0.7 (2)

---

C6—C7—C8—C3	-0.4 (2)	C9—C11—C15—C14	177.80 (13)
-------------	----------	----------------	-------------

---

*Hydrogen-bond geometry (Å, °)*

Cg1 and Cg2 are the centroids of the (N3,C11—C15) and (C3—C8) rings, respectively.

<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>
N1—H1N $\cdots$ N3	0.87 (1)	1.91 (2)	2.6123 (16)	138 (1)
C8—H8 $\cdots$ S2 <sup>i</sup>	0.95	2.90	3.6184 (16)	154
C2—H2A $\cdots$ Cg1 <sup>ii</sup>	0.99	2.76	3.5325 (15)	135
C7—H7 $\cdots$ Cg2 <sup>iii</sup>	0.95	2.89	3.5760 (16)	130
C10—H10C $\cdots$ Cg2 <sup>iv</sup>	0.98	2.68	3.5842 (15)	153

---

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