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# 2-[(1*E*)-({[(Benzylsulfanyl)methanethioyl]amino}-imino)methyl]-6-methoxyphenol: crystal structure and Hirshfeld surface analysis

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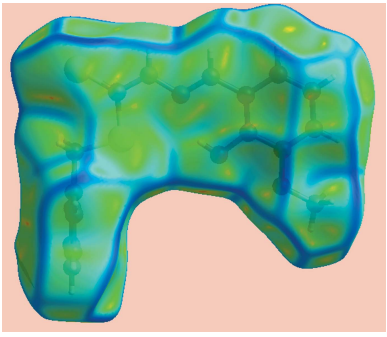
The title dithiocarbazate ester, $C_{16}H_{16}N_2O_2S_2$, comprises two almost planar residues, *i.e.* the phenyl ring and the remaining 14 non-H atoms (r.m.s. deviation = 0.0410 Å). These are orientated perpendicularly, forming a dihedral angle of 82.72 (5)°. An intramolecular hydroxy-O—H···N(imine) hydrogen bond, leading to an *S*(6) loop, is noted. An analysis of the geometric parameters is consistent with the molecule existing as the thione tautomer, and the conformation about the C=N bond is *E*. The thione S and imine H atoms lie to the same side of the molecule, facilitating the formation of intermolecular N—H···S hydrogen bonds leading to eight-membered $\{\cdots HNCS\}_2$ synthons in the crystal. These aggregates are connected by phenyl-C—H···O(hydroxy) interactions into a supramolecular layer in the *bc* plane; these stack with no directional interactions between them. An analysis of the Hirshfeld surface confirms the nature of the intermolecular interactions.

## 1. Chemical context

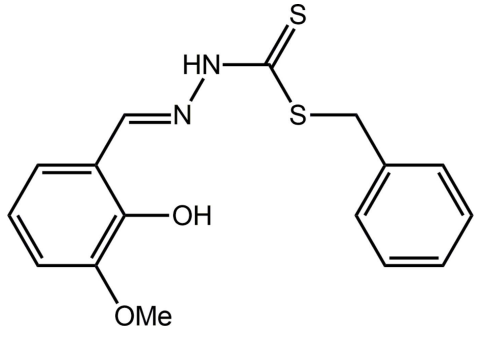
Dithiocarbazate, $NH_2NHC(=S)S^-$, and more specifically substituted derivatives, have attracted the attention of researchers for decades (Ali & Livingstone, 1974). While a common motivation for investigating transition metal complexes of these anions relates to potential biological activity (Basha *et al.*, 2012; Vijayan *et al.*, 2015), including our own recent work (Yusof, Ravoof, Jamsari *et al.*, 2015; Yusof, Ravoof, Tiekink *et al.*, 2015), other motivations exist. Thus, recent studies have described the photo-catalytic production of hydrogen mediated by a conjugated nickel(II) bis-dithiocarbazate complex (Wise *et al.*, 2015). The use of a coumarin-based dithiocarbazate as a ratiometric and colormetric chemosensor for cobalt(II) is another recent development (Liu *et al.*, 2015). In rationalizing the electronic structures of metal dithiocarbazates, a knowledge of the uncomplexed or 'free ligand' structure is most useful. In keeping with this notion and as a part of an on-going study of the structural chemistry of metal dithiocarbazates and their ligands, the title compound was prepared and characterized both crystallographically and by a Hirshfeld surface analysis.



## 2. Structural commentary

The title compound, Fig. 1, comprises two almost planar regions, one being the phenyl ring, the other being the

remaining 14 non-hydrogen atoms. The maximum deviations from the least-squares plane through the latter plane, with a r.m.s. deviation = 0.0410 Å, are 0.0715 (15) for the O1 atom and −0.0796 (18) for atom C16. To a first approximation, the molecule can be described as having mirror symmetry with the 1,4-atoms of the terminal ring being bisected by the plane. Substantiating this description is the dihedral angle between the planes of 82.72 (5)°, indicating a very close to perpendicular relationship. The observed planarity in the larger fragment may be ascribed, in part, to the presence of an intramolecular hydroxy-O—H···N(imine) hydrogen bond (Table 1), which leads to the formation of an *S*(6) loop. The molecule exists in the thione tautomeric form. Consistent with this assignment, the thione C1═S2 bond length, *i.e.* 1.670 (2) Å, is considerably shorter than the thiol C1—S1 and, especially, C2—S1 bonds of 1.749 (2) and 1.817 (2) Å, respectively. The conformation about the C═N bond is *E*, and the amine-N—H atom is flanked on either side by the thione-S and imine-H atoms.




## 3. Supramolecular features

The most prominent feature of the packing of the title compound is the formation of centrosymmetric, eight-membered $\{\cdots$HNCS$\}_2$ synthons through the agency of thioamide-N—H···S(thione) hydrogen bonds, Table 1. The dimeric aggregates are connected by phenyl-C—H···O(hydroxy) interactions to form a supramolecular layer in the *bc*-plane, Fig. 2*a*. The layers stack along the *a* axis with no directional interactions between them, Fig. 2*b*.

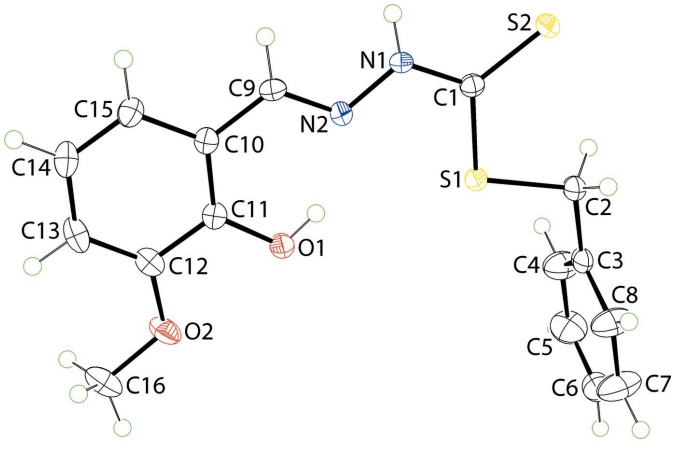



**Figure 1**
The molecular structure of the title compound, showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1*O*···N2 | 0.84 (2) | 1.90 (2) | 2.639 (2) | 146 (2) |
| N1—H1*N*···S2$^{i}$ | 0.88 (2) | 2.47 (2) | 3.3351 (18) | 168 (2) |
| C6—H6···O1$^{ii}$ | 0.95 | 2.51 | 3.453 (3) | 170 |

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

## 4. Analysis of the Hirshfeld surfaces

*Crystal Explorer 3.1* (Wolff *et al.*, 2012) was used to generate Hirshfeld surfaces mapped over $d_{norm}$, $d_e$, curvedness and electrostatic potential. The latter was calculated using *TONTO* (Spackman *et al.*, 2008; Jayatilaka *et al.*, 2005) which was integrated into *Crystal Explorer*; the experimental geometry was used as the input. Further, the electrostatic

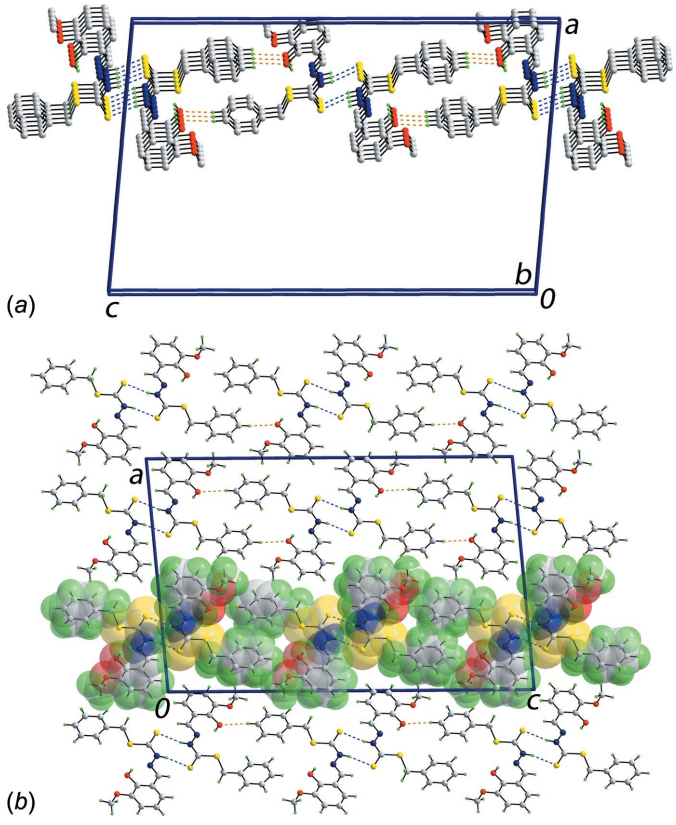



**Figure 2**
Molecular packing in the title compound: (*a*) a perspective view of the supramolecular layer sustained by thioamide-N—H···S(thione) and phenyl-C—H···O(hydroxy) interactions and, (*b*) a view of the unit-cell contents shown in projection down the *b* axis, highlighting one layer in space-filling mode. The N—H···S and C—H···O interactions are shown as blue and orange dashed lines, respectively. For (*a*), non-interacting H atoms have been omitted.

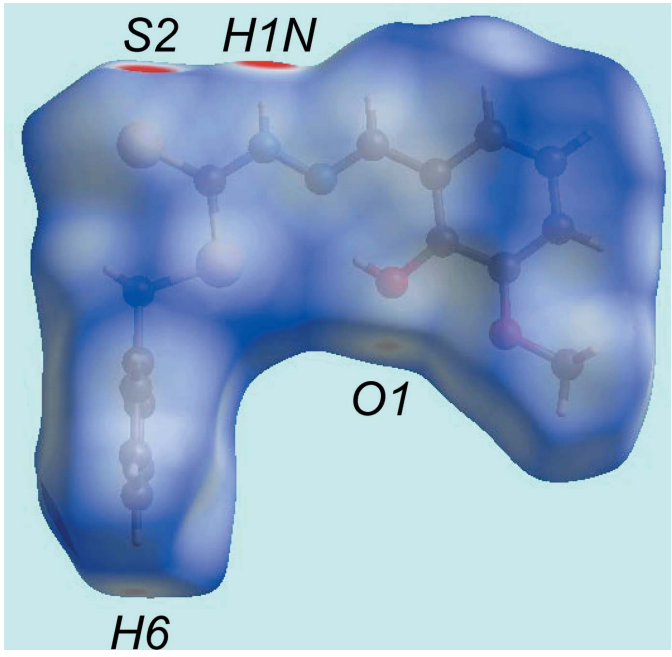



**Figure 3**
View of the Hirshfeld surface mapped over $d_{norm}$.

potentials were mapped on the Hirshfeld surface using the STO-3G basis set at the Hartree–Fock level of theory over the range ±0.1 au. The contact distances $d_i$ and $d_e$ from the Hirshfeld surface to the nearest atom inside and outside, respectively, enable the analysis of the intermolecular interactions through the mapping of $d_{norm}$. The combination of $d_e$ and $d_i$ in the form of a two-dimensional fingerprint plot (Rohl *et al.*, 2008) provides a summary of the intermolecular contacts in the crystal.

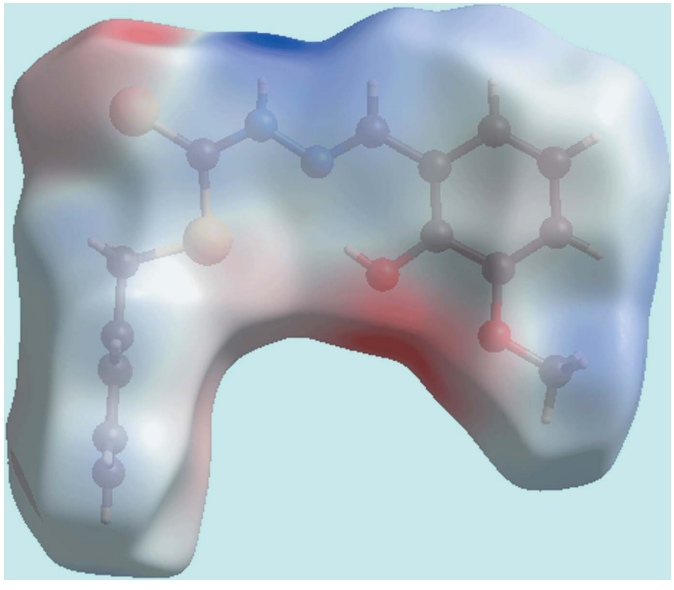


**Figure 4**
View of the Hirshfeld surface mapped over the electrostatic potential.

**Table 2**
Major percentage contribution of the different intermolecular interactions to the Hirshfeld surface of the title compound.

| Contact | % |
|---|---|
| H···H | 43.4 |
| O···H/H···O | 10.3 |
| S···H/H···S | 14.4 |
| C···H/H···C | 21.3 |
| N···H/H···N | 0.8 |
| C···C | 2.5 |
| S···S | 0.4 |
| C···N/N···C | 2.9 |
| S···O/O···S | 1.4 |
| S···N/N···S | 1.4 |
| C···S/S···C | 0.9 |

From the view of the Hirshfeld surface mapped over $d_{norm}$, Fig. 3, the deep-red depressions at atoms H1*N* and S2 confirm their role as the N—H···S hydrogen-bond donor and acceptor, respectively. On the surface mapped over the electrostatic potential, Fig. 4, these atoms appear as the respective blue and red regions. The light-red spots near the phenyl-hydrogen atom, H6, and hydroxyl oxygen, O1, on the $d_{norm}$-mapped surface indicate the intermolecular C—H···O interaction between them. The immediate environment about the molecule within $d_{norm}$-mapped Hirshfeld surface mediated by the above interactions is illustrated in Fig. 5.

The overall two-dimensional fingerprint (FP) plot, Fig. 6*a*, and those delineated into H···H, O···H/H···O, S···H/H···S, C···H/H···C and C···C interactions are illustrated in Fig. 6*b*–*f*; the relative contributions are summarized in Table 2. The H···H contacts appear as the scattered points in nearly the entire plot, Fig. 6*b*, and make a significant contribution, *i.e.* 43.4%, to the Hirshfeld surface. The round single peak at $d_e + d_i \sim 2.3$ Å results from a short interatomic H···H contact, Table 3. The FP delineated into O···H/H···O contacts show a pair of short spikes at $d_e + d_i \sim 2.5$ Å and the small arcs linked to them are identified with labels 1 and 2 in Fig. 6*c*. These features correspond to a 10.3% contribution to the Hirshfeld

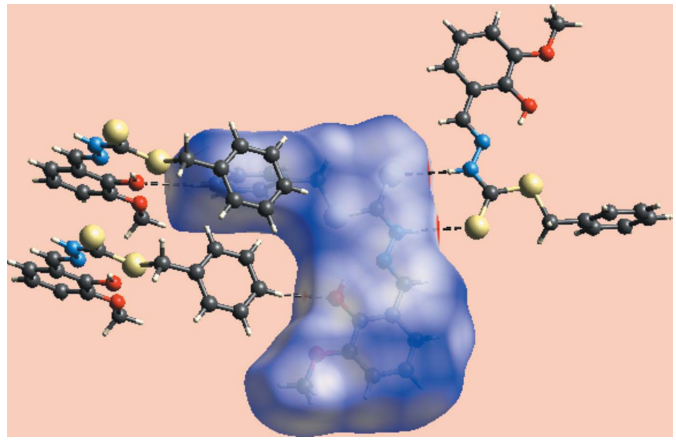


**Figure 5**
Hirshfeld surface mapped over $d_{norm}$ showing hydrogen-bonding interactions with neighbouring molecules.

**Table 3**
Additional short interatomic contacts (Å) for the title compound.

| Interaction | distance | symmetry operation |
|---|---|---|
| H8···H16*C* | 2.25 | $-\frac{1}{2}+x, \frac{1}{2}+y, z$ |
| C6···H16*B* | 2.86 | $\frac{1}{2}-x, \frac{3}{2}+y, \frac{3}{2}-z$ |
| O1···H16*A* | 2.70 | $x, 1+y, z$ |
| C11···H16*A* | 2.78 | $x, 1+y, z$ |
| C12···H16*A* | 2.89 | $x, 1+y, z$ |

surfaces and reflect the presence of intermolecular C—H···O interactions as well as interatomic O···H contacts only slightly shorter than their van der Waals separation, *i.e.* around $d_e + d_i \sim 2.7$ Å, Table 3. The presence of intermolecular N—H···S hydrogen bonds in the crystal is evident from a prominent pair of sharp spikes in the outer region of the FP plot shown in Fig. 6*d*, *i.e.* at $d_e + d_i \sim 2.45$ Å, with a 14.4% contribution to the Hirshfeld surface. The distinct pair of wings corresponding to C···H/H···C contacts, Fig. 6*e*, have 'forceps-like' tips at $d_e + d_i \sim 2.8$ Å due to short interatomic C···H/H···C contacts, Table 3, although C—H···$\pi$ interactions are not evident in the structure within the sum of their van der Waals radii. The 2.5%

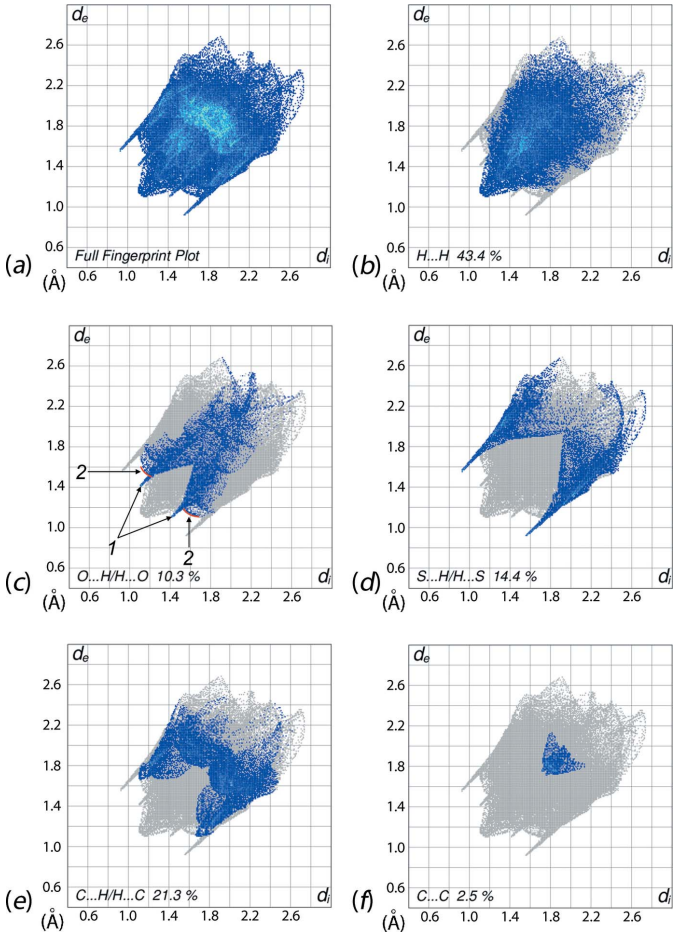



**Figure 6**
The two-dimensional fingerprint plots for (*a*) all interactions, and delineated into (*b*) H···H, (*c*) O···H/H···O, (*d*) S···H/H···S, (*e*) C···H/H···C and (*f*) C···C interactions.

**Table 4**
Enrichment ratios (ER) for the title compound..

| Interaction | ER |
|---|---|
| H···H | 0.97 |
| O···H/H···O | 1.28 |
| S···H/H···S | 1.14 |
| C···C | 1.09 |
| C···H/H···C | 1.05 |
| S···O/O···S | 1.24 |
| S···S | 0.45 |
| C···S/S···C | 0.31 |

contribution from C···C contacts to the Hirshfeld surface features two overlapping triangles, Fig. 6*f*, but the minimum ($d_e + d_i$) distance is greater than van der Waals separation, confirming the absence of $\pi$–$\pi$ stacking interactions. This is also evident from the small segments delineated by blue outlines in the Hirshfeld surface mapped over curvedness, Fig. 7.

The enrichment ratio (ER), based on Hirshfeld surface analysis, gives further description of intermolecular interactions operating in a crystal (Jelsch *et al.*, 2014). The ER values are summarized in Table 4. The ER value close to but slightly less than unity, *i.e.* 0.97, for H···H contacts is in accord with expectation (Jelsch *et al.*, 2014). The sulfur atoms comprise 9.5% of Hirshfeld surface and the overall 14.4% contribution by S···H/H···S contacts results in an ER value of 1.14, which is in the expected range for N—H···S interactions, *i.e.* 1.0–1.5 (Jelsch *et al.*, 2014). The ER value of 1.28 corresponding to O···H/H···O contacts show a high propensity to form even though the percentage relative contribution to the overall surface, *i.e.* 10.3%, is small as is the 6.0% exposure provided by hydroxyl- and methoxy-oxygen atoms. The low ER value of 1.09 corresponding to C···C contacts is consistent with a low propensity for $\pi$–$\pi$ stacking interactions in the

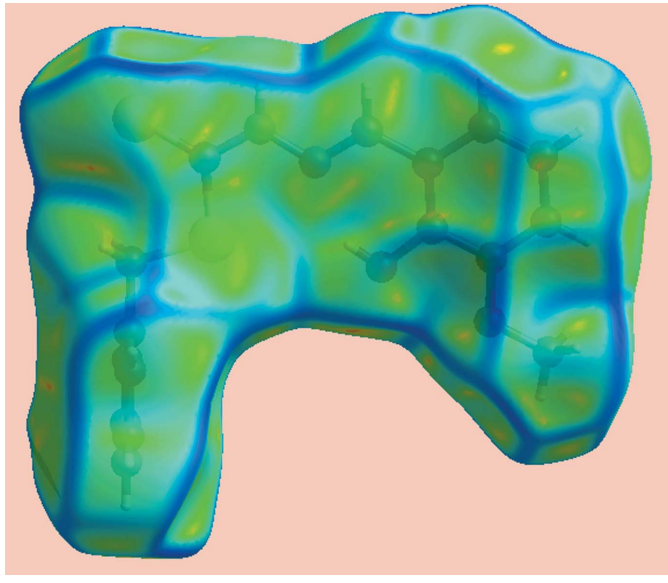
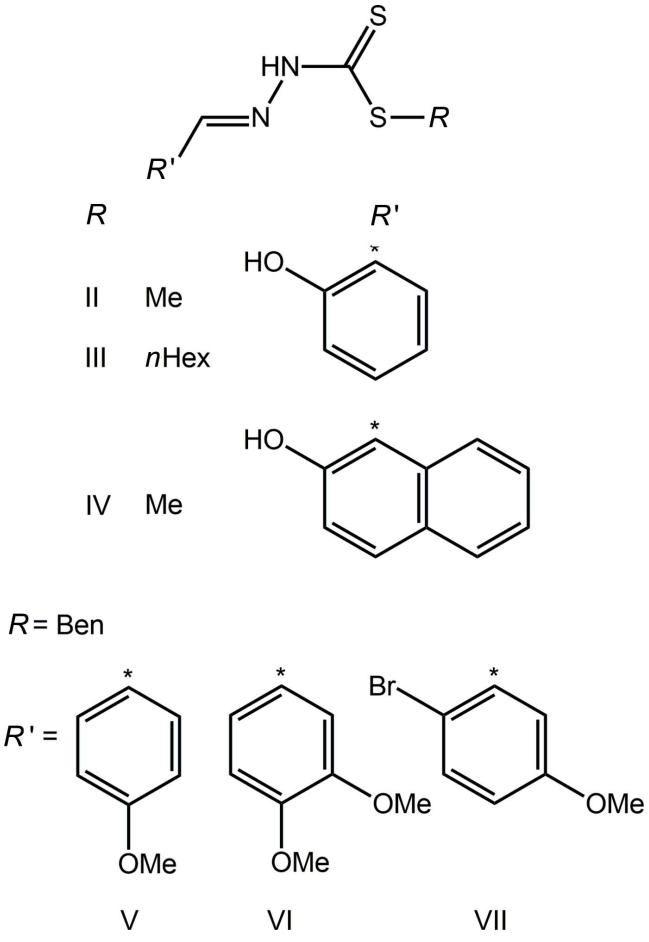


**Figure 7**
View of the Hirshfeld surface mapped over curvedness.

structure. The presence of short interatomic non-bonded C···H/H···C contacts result in an ER value close to unity, Table 4, as there is little influence of C—H···$\pi$ interactions on the molecular packing. The other contributions to the surface *i.e.* N···H/H···N, S···S, S···O/O···S, C···S/S···C, *etc.* are very small and therefore, the ER values are not particularly informative although being > 1 for some interactions.

## 5. Database survey

Dithiocarbazate *S*-esters are well studied with many examples included in the Cambridge Structural Database (Groom & Allen, 2014).




There are three examples, II–IV, of derivatives with a hydroxy group in the 2-position of the ring connected to the imine-C atom (Madanhire *et al.*, 2015; Sethuraman *et al.*, 2002; Begum *et al.*, 2016), with their chemical diagrams shown in Scheme 2. Interestingly, there are four virtually identical molecules comprising the asymmetric unit in IV (Begum *et al.*, 2016). A common feature of each of I–IV, is the formation of an intramolecular hydroxy-O—H···N(imine) hydrogen bond. By contrast to I, each of the molecules in II–IV is effectively planar. Reflecting the interest in the structural chemistry of this class of compound, there are several structures of *S*-benzyl esters with methoxy-substituted terminal rings (Fan *et al.*, 2011*a*; Fan *et al.*, 2011*b*; Tan *et al.*, 2015), see Scheme 2 for chemical structures. In each of V–VII, each methoxy group is co-planar with the benzene ring to which it is connected. To a first approximation, the molecules in V and VII adopt approximately the same conformation as in I, *i.e.* with all but the benzyl rings lying in a plane. The dihedral angles between the two residues are 85.23 (12)° in V and 63.01 (8)° in VII. By contrast, a somewhat twisted conformation is observed for each of the two independent molecules in VI.

**Table 5**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{16}H_{16}N_2O_2S_2$ |
| $M_r$ | 332.43 |
| Crystal system, space group | Monoclinic, *C*2/*c* |
| Temperature (K) | 100 |
| *a*, *b*, *c* (Å) | 20.7896 (10), 4.6965 (2), 32.5217 (13) |
| $\beta$ (°) | 95.004 (4) |
| $V$ (Å$^3$) | 3163.3 (2) |
| $Z$ | 8 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.35 |
| Crystal size (mm) | 0.25 × 0.15 × 0.07 |
| Data collection | |
| Diffractometer | Agilent Xcalibur Eos Gemini |
| Absorption correction | Multi-scan (*CrysAlis PRO*; Agilent, 2011) |
| $T_{min}$, $T_{max}$ | 0.87, 0.98 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 6979, 3270, 2595 |
| $R_{int}$ | 0.033 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.628 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.041, 0.097, 1.06 |
| No. of reflections | 3270 |
| No. of parameters | 206 |
| No. of restraints | 2 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.33, −0.24 |

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

## 6. Synthesis and crystallization

Following procedures adapted from the literature (Ali & Tarafder, 1977), *S*-benzyldithiocarbazate (SBDTC) (1.98 g, 0.01 mol) was dissolved in hot absolute ethanol (100 cm$^3$) and added to an equimolar amount of 2-hydroxy-3-methoxy-benzaldehyde (Merck, 1.52 g) in absolute ethanol (20 cm$^3$). The mixture was heated with continuous stirring for about 30 min and was then allowed to stand overnight. The light-yellow crystals that formed were filtered and washed with absolute ethanol at room temperature. Yield: 70%. M.p.: 446–447 K. Analysis calculated for $C_{16}H_{16}N_2O_2S_2$: C, 57.81; H, 4.85; N, 8.43. Found: C, 58.21; H, 4.87; N, 8.28%. FT–IR (ATR, cm$^{-1}$): 3089, $\nu$(N—H); 1598, $\nu$(C═N); 1030, $\nu$(N—N); 720, $\nu$(C═S). $^{13}$C NMR (DMSO-$d_6$) $\delta$ (p.p.m.): 196.09 (C=S), 148.59 (C═N); 147.45–114.43 (aromatic-C), 56.43 ($CH_3$),

38.10 ($CH_2$). *m*/*z* calculated for $C_{16}H_{16}N_2O_2S_2$ 332.44, found 332.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. 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 $U_{iso}$(H) set to 1.2$U_{eq}$(C). The oxygen- and nitrogen-bound H-atoms were located in a difference Fourier map but were refined with distance restraints of O—H = 0.84±0.01 Å and N—H = 0.88±0.01 Å, and with $U_{iso}$(H) set to 1.5$U_{eq}$(O) and 1.2$U_{eq}$(N).

## Acknowledgements

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## References

Agilent (2011). *CrysAlis PRO*. Agilent Technologies, Yarnton, England.
Ali, M. A. & Livingstone, S. E. (1974). *Coord. Chem. Rev*. **13**, 101–132.
Ali, M. A. & Tarafder, M. T. H. (1977). *J. Inorg. Nucl. Chem*. **39**, 1785–1791.
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.
Begum, M. S., Howlader, M. B. H., Sheikh, M. C., Miyatake, R. & Zangrando, E. (2016). *Acta Cryst.* E**72**, 290–292.
Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Fan, Z., Huang, Y.-L., Wang, Z., Guo, H.-Q. & Shan, S. (2011*a*). *Acta Cryst.* E**67**, o3011.
Fan, Z., Huang, Y.-L., Wang, Z., Guo, H.-Q. & Shan, S. (2011*b*). *Acta Cryst.* E**67**, o3015.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
Jayatilaka, D., Grimwood, D. J., Lee, A., Lemay, A., Russel, A. J., Taylor, C., Wolff, S. K., Cassam-Chenai, P. & Whitton, A. (2005). *TONTO*. Available at: http://hirshfeldsurface.net/
Jelsch, C., Ejsmont, K. & Huder, L. (2014). *IUCrJ*, **1**, 119–128.
Liu, Z., Wang, W., Xu, H., Sheng, L., Chen, S., Huang, D. & Sun, F. (2015). *Inorg. Chem. Commun.* **62**, 19–23.
Madanhire, T., Abrahams, A., Hosten, E. C. & Betz, R. (2015). *Z. Kristallogr. New Cryst. Struct*. **230**, 13–14.
Rohl, A. L., Moret, M., Kaminsky, W., Claborn, K., McKinnon, J. J. & Kahr, B. (2008). *Cryst. Growth Des.* **8**, 4517–4525.
Sethuraman, G., Yamin, B. M., Shamsuddin, M., Usman, A., Razak, I. A. & Fun, H.-K. (2002). *Acta Cryst.* E**58**, o649–o651.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Spackman, M. A., McKinnon, J. J. & Jayatilaka, D. (2008). *CrystEngComm*, **10**, 377–388.
Tan, Y.-F., Break, M. K. bin, Tahir, M. I. M. & Khoo, T.-J. (2015). *Acta Cryst.* E**71**, 238–240.
Vijayan, P., Viswanathamurthi, P., Sugumar, P., Ponnuswamy, M. N., Balakumaran, M. D., Kalaichelvan, P. T., Velmurugan, K., Nandhakumar, R. & Butcher, R. J. (2015). *Inorg. Chem. Front.* **2**, 620–639.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Wise, C. F., Liu, D., Mayer, K. J., Crossland, P. M., Hartley, C. L. & McNamara, W. R. (2015). *Dalton Trans.* **44**, 14265–14271.
Wolff, S. K., Grimwood, D. J., McKinnon, J. J., Turner, M. J., Jayatilaka, D. & Spackman, M. A. (2012). *Crystal Explorer*. The University of Western Australia.
Yusof, E. N. M., Ravoof, T. B. S. A., Jamsari, J., Tiekink, E. R. T., Veerakumarasivam, A., Crouse, K. A., Tahir, M. I. M. & Ahmad, H. (2015). *Inorg. Chim. Acta*, **438**, 85–93.
Yusof, E. N. M., Ravoof, T. B. S. A., Tiekink, E. R. T., Veerakumarasivam, A., Crouse, K. A., Tahir, M. I. M. & Ahmad, H. (2015). *Int. J. Molec. Sci.* **16**, 11034–11054.

# supporting information

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## 2-[(1*E*)-({[(Benzylsulfanyl)methanethioyl]amino}imino)methyl]-6-methoxyphenol: crystal structure and Hirshfeld surface analysis

**Enis Nadia Md Yusof, Mukesh M. Jotani, Edward R. T. Tiekink and Thahira B. S. A. Ravoof**

### 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).

### 2-[(1*E*)-({[(Benzylsulfanyl)methanethioyl]amino}imino)methyl]-6-methoxyphenol

*Crystal data*

$C_{16}H_{16}N_2O_2S_2$
$M_r$ = 332.43
Monoclinic, $C2/c$
$a$ = 20.7896 (10) Å
$b$ = 4.6965 (2) Å
$c$ = 32.5217 (13) Å
$\beta$ = 95.004 (4)°
$V$ = 3163.3 (2) Å$^3$
$Z$ = 8
$F(000)$ = 1392
$D_x$ = 1.396 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 2185 reflections
$\theta$ = 2–29°
$\mu$ = 0.35 mm$^{-1}$
$T$ = 100 K
Plate, light-yellow
0.25 × 0.15 × 0.07 mm

*Data collection*

Agilent Xcalibur Eos Gemini diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.1952 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2011)
$T_{min}$ = 0.87, $T_{max}$ = 0.98
6979 measured reflections
3270 independent reflections
2595 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.033
$\theta_{max}$ = 26.5°, $\theta_{min}$ = 2.4°
$h$ = −25→26
$k$ = −5→5
$l$ = −27→40

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.097
$S$ = 1.06
3270 reflections
206 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 1.7624P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.33 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.24 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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.22247 (2) | 0.46299 (12) | 0.61684 (2) | 0.02185 (15) |
| S2 | 0.17478 (3) | 0.80851 (12) | 0.54164 (2) | 0.02258 (15) |
| O1 | 0.35672 (7) | −0.0373 (3) | 0.63252 (4) | 0.0239 (3) |
| H1O | 0.3342 (10) | 0.086 (4) | 0.6194 (7) | 0.036* |
| O2 | 0.43677 (8) | −0.4115 (3) | 0.66547 (5) | 0.0305 (4) |
| N1 | 0.27458 (8) | 0.4630 (4) | 0.54712 (5) | 0.0203 (4) |
| H1N | 0.2819 (10) | 0.519 (5) | 0.5223 (4) | 0.024* |
| N2 | 0.31479 (8) | 0.2682 (4) | 0.56753 (5) | 0.0194 (4) |
| C1 | 0.22604 (9) | 0.5777 (4) | 0.56594 (6) | 0.0179 (4) |
| C2 | 0.15287 (10) | 0.6579 (5) | 0.63209 (6) | 0.0237 (5) |
| H2A | 0.1579 | 0.8639 | 0.6268 | 0.028* |
| H2B | 0.1130 | 0.5907 | 0.6161 | 0.028* |
| C3 | 0.14873 (10) | 0.6059 (5) | 0.67741 (6) | 0.0223 (5) |
| C4 | 0.18779 (13) | 0.7499 (6) | 0.70649 (8) | 0.0395 (6) |
| H4 | 0.2181 | 0.8838 | 0.6979 | 0.047* |
| C5 | 0.18365 (13) | 0.7029 (6) | 0.74845 (8) | 0.0432 (7) |
| H5 | 0.2108 | 0.8059 | 0.7682 | 0.052* |
| C6 | 0.14056 (12) | 0.5086 (5) | 0.76139 (7) | 0.0356 (6) |
| H6 | 0.1381 | 0.4735 | 0.7900 | 0.043* |
| C7 | 0.10141 (14) | 0.3670 (7) | 0.73262 (8) | 0.0502 (8) |
| H7 | 0.0708 | 0.2346 | 0.7413 | 0.060* |
| C8 | 0.10538 (13) | 0.4127 (6) | 0.69076 (8) | 0.0404 (7) |
| H8 | 0.0779 | 0.3096 | 0.6712 | 0.048* |
| C9 | 0.35930 (10) | 0.1553 (4) | 0.54759 (6) | 0.0192 (4) |
| H9 | 0.3635 | 0.2118 | 0.5199 | 0.023* |
| C10 | 0.40308 (9) | −0.0564 (4) | 0.56664 (6) | 0.0188 (4) |
| C11 | 0.40002 (9) | −0.1423 (4) | 0.60766 (6) | 0.0191 (4) |
| C12 | 0.44376 (10) | −0.3469 (5) | 0.62508 (7) | 0.0236 (5) |
| C13 | 0.48986 (10) | −0.4610 (5) | 0.60167 (7) | 0.0282 (5) |
| H13 | 0.5196 | −0.5984 | 0.6134 | 0.034* |
| C14 | 0.49292 (11) | −0.3747 (5) | 0.56070 (7) | 0.0286 (5) |
| H14 | 0.5246 | −0.4541 | 0.5448 | 0.034* |
| C15 | 0.45042 (10) | −0.1762 (5) | 0.54345 (7) | 0.0239 (5) |
| H15 | 0.4529 | −0.1189 | 0.5156 | 0.029* |
| C16 | 0.47583 (12) | −0.6366 (5) | 0.68359 (8) | 0.0346 (6) |
| H16A | 0.4679 | −0.8109 | 0.6674 | 0.052* |
| H16B | 0.4649 | −0.6693 | 0.7119 | 0.052* |
| H16C | 0.5215 | −0.5840 | 0.6839 | 0.052* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0221 (3) | 0.0271 (3) | 0.0169 (3) | 0.0071 (2) | 0.0051 (2) | 0.0040 (2) |
| S2 | 0.0225 (3) | 0.0273 (3) | 0.0180 (3) | 0.0075 (2) | 0.0024 (2) | 0.0047 (2) |
| O1 | 0.0258 (8) | 0.0281 (9) | 0.0183 (7) | 0.0072 (7) | 0.0044 (6) | 0.0034 (7) |
| O2 | 0.0399 (9) | 0.0269 (9) | 0.0238 (8) | 0.0075 (7) | −0.0035 (7) | 0.0064 (7) |
| N1 | 0.0206 (9) | 0.0253 (10) | 0.0154 (8) | 0.0044 (8) | 0.0040 (7) | 0.0058 (8) |
| N2 | 0.0180 (8) | 0.0208 (9) | 0.0194 (9) | 0.0039 (7) | 0.0024 (7) | 0.0026 (8) |
| C1 | 0.0181 (10) | 0.0179 (10) | 0.0176 (10) | −0.0018 (8) | 0.0016 (8) | 0.0000 (9) |
| C2 | 0.0239 (11) | 0.0257 (12) | 0.0222 (11) | 0.0080 (9) | 0.0061 (9) | 0.0038 (10) |
| C3 | 0.0234 (11) | 0.0231 (12) | 0.0212 (11) | 0.0093 (9) | 0.0059 (9) | 0.0005 (9) |
| C4 | 0.0430 (15) | 0.0457 (16) | 0.0293 (13) | −0.0093 (13) | 0.0010 (12) | 0.0040 (12) |
| C5 | 0.0523 (17) | 0.0504 (17) | 0.0258 (13) | −0.0002 (14) | −0.0034 (12) | −0.0029 (13) |
| C6 | 0.0411 (14) | 0.0470 (16) | 0.0200 (11) | 0.0152 (12) | 0.0103 (11) | 0.0032 (12) |
| C7 | 0.0549 (18) | 0.066 (2) | 0.0310 (14) | −0.0188 (16) | 0.0104 (13) | 0.0078 (14) |
| C8 | 0.0493 (16) | 0.0480 (16) | 0.0244 (12) | −0.0172 (13) | 0.0063 (12) | −0.0001 (12) |
| C9 | 0.0225 (10) | 0.0203 (11) | 0.0150 (10) | −0.0017 (9) | 0.0028 (9) | 0.0010 (9) |
| C10 | 0.0184 (10) | 0.0170 (10) | 0.0210 (10) | −0.0013 (9) | 0.0015 (8) | −0.0030 (9) |
| C11 | 0.0185 (10) | 0.0189 (11) | 0.0197 (10) | −0.0013 (8) | 0.0004 (9) | −0.0039 (9) |
| C12 | 0.0264 (11) | 0.0194 (11) | 0.0239 (11) | −0.0004 (9) | −0.0046 (9) | −0.0011 (9) |
| C13 | 0.0239 (11) | 0.0238 (12) | 0.0355 (13) | 0.0068 (10) | −0.0067 (10) | −0.0046 (11) |
| C14 | 0.0228 (11) | 0.0301 (13) | 0.0331 (13) | 0.0063 (10) | 0.0035 (10) | −0.0077 (11) |
| C15 | 0.0223 (11) | 0.0269 (12) | 0.0228 (11) | 0.0012 (9) | 0.0041 (9) | −0.0030 (10) |
| C16 | 0.0411 (14) | 0.0237 (13) | 0.0363 (14) | −0.0008 (11) | −0.0129 (12) | 0.0070 (11) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—C1 | 1.749 (2) | C6—C7 | 1.359 (4) |
| S1—C2 | 1.817 (2) | C6—H6 | 0.9500 |
| S2—C1 | 1.670 (2) | C7—C8 | 1.388 (3) |
| O1—C11 | 1.354 (2) | C7—H7 | 0.9500 |
| O1—H1O | 0.836 (10) | C8—H8 | 0.9500 |
| O2—C12 | 1.368 (3) | C9—C10 | 1.450 (3) |
| O2—C16 | 1.429 (3) | C9—H9 | 0.9500 |
| N1—C1 | 1.338 (2) | C10—C11 | 1.401 (3) |
| N1—N2 | 1.371 (2) | C10—C15 | 1.408 (3) |
| N1—H1N | 0.874 (9) | C11—C12 | 1.408 (3) |
| N2—C9 | 1.290 (2) | C12—C13 | 1.383 (3) |
| C2—C3 | 1.504 (3) | C13—C14 | 1.400 (3) |
| C2—H2A | 0.9900 | C13—H13 | 0.9500 |
| C2—H2B | 0.9900 | C14—C15 | 1.370 (3) |
| C3—C4 | 1.370 (3) | C14—H14 | 0.9500 |
| C3—C8 | 1.376 (3) | C15—H15 | 0.9500 |
| C4—C5 | 1.392 (3) | C16—H16A | 0.9800 |
| C4—H4 | 0.9500 | C16—H16B | 0.9800 |
| C5—C6 | 1.370 (4) | C16—H16C | 0.9800 |
| C5—H5 | 0.9500 | | |

| | | | |
|---|---|---|---|
| C1—S1—C2 | 101.75 (10) | C3—C8—C7 | 120.5 (2) |
| C11—O1—H1O | 108.6 (16) | C3—C8—H8 | 119.7 |
| C12—O2—C16 | 117.13 (17) | C7—C8—H8 | 119.7 |
| C1—N1—N2 | 119.96 (16) | N2—C9—C10 | 121.21 (18) |
| C1—N1—H1N | 120.0 (15) | N2—C9—H9 | 119.4 |
| N2—N1—H1N | 120.0 (15) | C10—C9—H9 | 119.4 |
| C9—N2—N1 | 117.70 (17) | C11—C10—C15 | 119.1 (2) |
| N1—C1—S2 | 121.37 (15) | C11—C10—C9 | 121.72 (18) |
| N1—C1—S1 | 113.89 (15) | C15—C10—C9 | 119.15 (18) |
| S2—C1—S1 | 124.74 (11) | O1—C11—C10 | 123.47 (19) |
| C3—C2—S1 | 107.49 (14) | O1—C11—C12 | 116.60 (18) |
| C3—C2—H2A | 110.2 | C10—C11—C12 | 119.92 (18) |
| S1—C2—H2A | 110.2 | O2—C12—C13 | 125.4 (2) |
| C3—C2—H2B | 110.2 | O2—C12—C11 | 114.77 (18) |
| S1—C2—H2B | 110.2 | C13—C12—C11 | 119.8 (2) |
| H2A—C2—H2B | 108.5 | C12—C13—C14 | 120.2 (2) |
| C4—C3—C8 | 118.2 (2) | C12—C13—H13 | 119.9 |
| C4—C3—C2 | 121.0 (2) | C14—C13—H13 | 119.9 |
| C8—C3—C2 | 120.8 (2) | C15—C14—C13 | 120.4 (2) |
| C3—C4—C5 | 121.0 (2) | C15—C14—H14 | 119.8 |
| C3—C4—H4 | 119.5 | C13—C14—H14 | 119.8 |
| C5—C4—H4 | 119.5 | C14—C15—C10 | 120.6 (2) |
| C6—C5—C4 | 120.3 (3) | C14—C15—H15 | 119.7 |
| C6—C5—H5 | 119.8 | C10—C15—H15 | 119.7 |
| C4—C5—H5 | 119.8 | O2—C16—H16A | 109.5 |
| C7—C6—C5 | 118.8 (2) | O2—C16—H16B | 109.5 |
| C7—C6—H6 | 120.6 | H16A—C16—H16B | 109.5 |
| C5—C6—H6 | 120.6 | O2—C16—H16C | 109.5 |
| C6—C7—C8 | 121.1 (3) | H16A—C16—H16C | 109.5 |
| C6—C7—H7 | 119.4 | H16B—C16—H16C | 109.5 |
| C8—C7—H7 | 119.4 | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1*O*···N2 | 0.84 (2) | 1.90 (2) | 2.639 (2) | 146 (2) |
| N1—H1*N*···S2$^{i}$ | 0.88 (2) | 2.47 (2) | 3.3351 (18) | 168 (2) |
| C6—H6···O1$^{ii}$ | 0.95 | 2.51 | 3.453 (3) | 170 |

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