CRYSTALLOGRAPHIC
COMMUNICATIONS

ISSN 2056-9890

# Crystal structure and Hirshfeld surface analysis of (*E*)-2-(5-bromo-2-hydroxybenzylidene)hydrazinecarbothioamide dimethyl sulfoxide monosolvate

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Received 8 December 2017
Accepted 4 January 2018

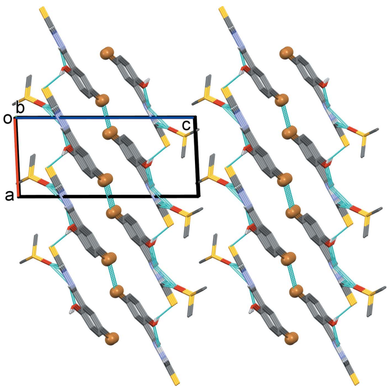
Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

**Keywords:** crystal structure; Schiff base; hydrazinecarbothioamide; hydrogen bonding; Hirshfeld surface analysis.

**CCDC reference**: 1587285

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

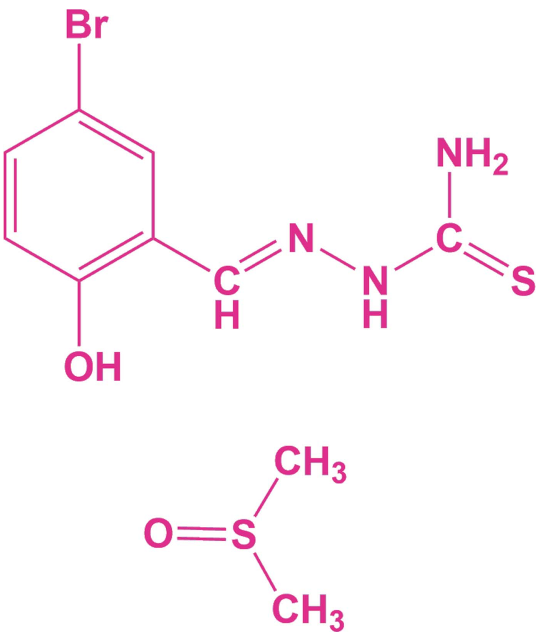
The molecule of the title Schiff base, $C_8H_8BrN_3OS{\cdot}C_2H_6OS$, which crystallizes as a dimethyl sulfoxide (DMSO) monosolvate, displays an *E* configuration with respect to the C═N bond, with a dihedral angle of 14.54 (11)° between the benzene ring and the mean plane of the N—N—C(N)═S unit. In the crystal, molecules are linked by N—H⋯O hydrogen bonds, forming chains propagating along the *b*-axis direction. Within the chains there are $R_3^2(11)$ ring motifs, which are reinforced by C—H⋯O$_{\rm DMSO}$ hydrogen bonds enclosing secondary $R_2^1(6)$ and $R_3^2(9)$ loops. The chains are linked by O—H$_{\rm hydroxyl}$⋯S hydrogen bonds, forming layers parallel to (011). Inversion-related layers are linked by short Br⋯Br interactions [3.5585 (5) Å], forming slabs parallel to (011). The intermolecular interactions have been investigated using Hirshfeld surface studies and two-dimensional fingerprint plots. The crystal structure of the unsolvated form of the title compound has been reported previously [Kargar *et al.* (2010). Acta Cryst. E**66**, o2999], and its solid-state structure is compared with that of the title solvated form.



## 1. Chemical context

Schiff bases are nitrogen-containing active organic compounds that play a vital role in enzymatic reactions involving interaction of an enzyme with a carbonyl group of a substrate (Tidwell, 2008). Thiosemicarbazones exhibit interesting pharmacological properties and biological activities. Thiosemicarbazone derivatives have gained special importance because of their role in drug development; for example they are used as antiviral, antitubercular, anti-bacterial infection, analgesic and antiallergic agents and in the treatment of central nervous system disorders and as sodium channel blockers and show antitumorous activity. The pharmacological versatility of semicarbazones, thiosemicarbazones and their metal complexes have been reviewed by Beraldo & Gambino (2004).

Thiosemicarbazones are formed by the condensation of thiosemicarbazides with aldehydes or ketones (Sriram *et al.*, 2006; Scovill *et al.*, 1982). They are also used in most branches of chemistry, for example, as dyes, photographic films, plastics and in the textile industry. These types of compounds also act as ligands for a variety of transition metals, often as high propensity multi-dentate chelating agents (Al-Karawi *et al.*, 2009). Herein, we report on the crystal structure of the title thiosemicarbazone that crystallizes as a dimethyl sulfoxide monosolvate. The crystal structure of the unsolvated form of the title Schiff base has been reported previously (Kargar *et* *al.*, 2010*a*), and its solid-state structure is compared with that of the title solvated form.



## 2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The thiosemicarbazone molecule has an *E* configurationabout the C7═N1 bond. The molecule is twisted with a dihedral angle of 14.54 (11)° between the benzene ring and the mean plane of the N1/N2/C8/N3/S1 unit. The C8—-S1 bond distance of 1.698 (2) Å is close to that expected for a C═S bond (Cambridge Structural Database; Groom *et al.*, 2016). This confirms the existence of the compound in the thioamido form in the solid state, similar to the situation observed in some related compounds, *viz*. (*E*)-2-(2,4-dihydroxybenzylidene)thiosemicarbazone and (*E*)-2-[(1*H*-indol-3-yl)methylene]thiosemicarbazone (Yıldız *et al.*, 2009). The C1—N7 bond distance is 1.278 (3) Å, close to that of a C═N double bond, confirming the azomethine bond formation, again similar to the situation observed in related compounds, *viz*. (*E*)-1-[4-(dimethylamino)benzylidene]thiosemicarbazide (Sun *et al.* 2009) and 2-[(2-hydroxynaphthalen-1-yl)methylene]hydrazinecarbothioamide (Sivajeyanthi *et al.* 2017).

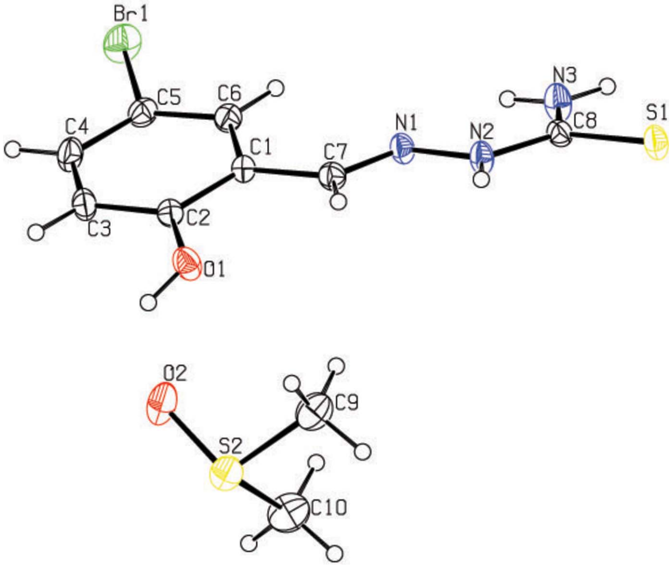


**Figure 1**
A view of the molecular structure of the title compound, with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1···S1$^{i}$ | 0.82 | 2.40 | 3.1655 (17) | 157 |
| N2—H2···O2$^{ii}$ | 0.86 | 2.10 | 2.897 (2) | 155 |
| N3—H3*A*···O1$^{iii}$ | 0.86 | 2.37 | 3.048 (2) | 136 |
| N3—H3*B*···O2$^{iv}$ | 0.86 | 2.11 | 2.930 (3) | 160 |
| C7—H7···O2$^{ii}$ | 0.93 | 2.53 | 3.315 (3) | 142 |

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

In the molecular structure of the unsolvated form of the title compound (Kargar *et al.*, 2010*a*), an intramolecular O—H···N hydrogen bond is present enclosing an *S*(6) ring motif. Comparing the two molecules, as shown in the structural overlay of Fig. 2, it can be seen that the benzene ring of the title solvated compound is rotated by *ca.* 180° with respect to that in the unsolvated form of the molecule. The bond lengths and bond angles of the two molecules are similar. In the title compound, the dihedral angle between the benzene ring and the mean plane of the N—N—C(N)═S hydrazinecarbothioamide unit is 14.54 (11)° compared to *ca* 7.05° in the unsolvated phase. Kargar *et al.* (2010*b*) have also reported the crystal structure of the unsolvated chloro-substituted analogue. This molecule has the same conformation as the unsolvated bromo-substituted analogue (Kargar *et al.*, 2010*a*), but in contrast it crystallizes in the monoclinic space group $P2_1/c$, while the unsolvated bromo compound crystallizes in the chiral orthorhombic space group $P2_12_12_1$.

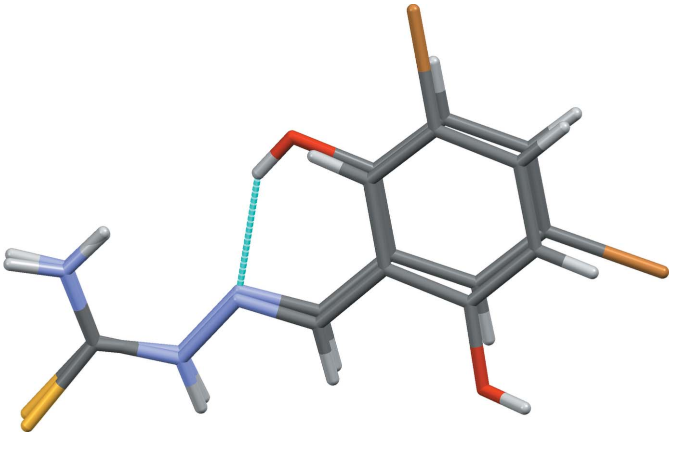


**Figure 2**
The structural overlay of the title molecule with that of the unsolvated form (CEDPAE; Kargar *et al.*, 2010*a*), showing the presence of the intramolecular O—H···N hydrogen bond (dashed line) in CEDPAE.

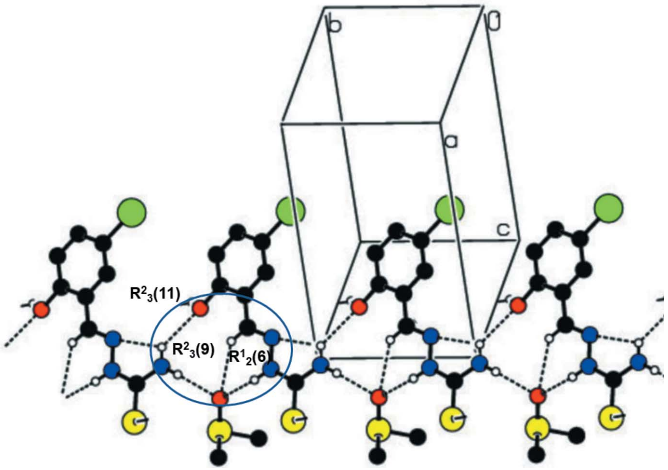


**Figure 3**
A partial view, almost normal to the (011) plane, of the hydrogen-bonded chain (dashed lines; see Table 1) propagating along the [010] direction. In this and subsequent figures, only the H atoms involved in hydrogen bonding have been included.

## 3. Supramolecular features

In the crystal, the Schiff base hydrazone is hydrogen bonded (see Table 1) to the dimethyl sulfoxide solvate molecule, forming a chain propagating along the *b*-axis direction, as shown in Fig. 3. Within the chains there are $R_3^2(11)$ ring motifs, which are reinforced by C—H$\cdots$O$_{\rm DMSO}$ hydrogen bonds enclosing secondary $R_2^1(6)$ and $R_3^2(9)$ ring motifs (Table 1). The $R_3^2(11)$ ring motif is formed by N2—H2$\cdots$O2$^{\rm ii}$, N3—H3*A*$\cdots$O1$^{\rm iii}$ and N3—H3*B*$\cdots$O2$^{\rm iv}$ hydrogen-bonding interactions, and the $R_2^1(6)$ ring motif is formed *via* C7—H7$\cdots$O2$^{\rm ii}$ and N2—H2$\cdots$O2$^{\rm ii}$ hydrogen-bonding interactions. Hence, atom O2 of the dimethyl sulfoxide acts as a trifurcated acceptor (Fig. 3, Table 1). The chains are linked by O1—H1$\cdots$S$^{\rm i}$ hydrogen bonds, forming layers parallel to plane (011); see Fig. 4 and Table 1. Inversion-related layers are linked by short Br$\cdots$Br($-x$, $-y + 1$, $-z + 1$) interactions of 3.5585 (5) Å, forming slabs parallel to (011), as illustrated in Fig. 5.

## 4. Hirshfeld surface analysis

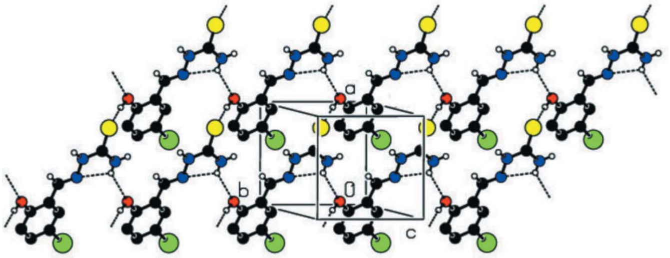


**Figure 4**
A view, almost normal to (011), of the hydrogen-bonded sheets parallel to (011). The hydrogen bonds are shown as dashed lines and details are given in Table 1.

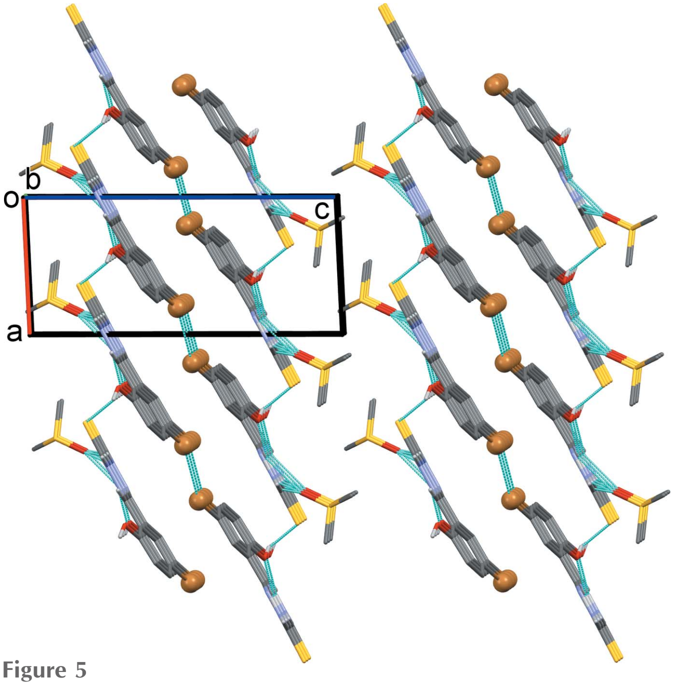


**Figure 5**
A view along the *b* axis of the crystal packing of the title compound. The hydrogen bonds (see Table 1) and the short Br$\cdots$Br interactions are shown as dashed lines.

The three-dimensional $d_{\rm norm}$ surface is a useful tool to analyse and visualize the inter-molecular interactions. $d_{\rm norm}$ takes negative or positive values depending on whether the intermolecular contact is shorter or longer than the van der Waals radii (Spackman & Jayatilaka, 2009; McKinnon *et al.*, 2007). The three-dimensional $d_{\rm norm}$ surface of the title compound is shown in Fig. 6. The red points, which represent closer contacts and negative $d_{\rm norm}$ values on the surface, correspond to the N—H$\cdots$O, O—H$\cdots$S and C—H$\cdots$O interactions. The percentage contributions of various contacts to the total Hirshfeld surface are as follows: H$\cdots$H (32.9%), S$\cdots$H/H$\cdots$S (18.8%), O$\cdots$H/H$\cdots$O (13.3%), Br$\cdots$H/H$\cdots$Br (11.6), C$\cdots$H/H$\cdots$C (8.8%), N$\cdots$H/H$\cdots$N (3.4%), C$\cdots$C (2.8%), Br$\cdots$N/N$\cdots$Br (2.0%), Br$\cdots$Br (1.5%), Br$\cdots$O/O$\cdots$Br (1.1%), Br$\cdots$C/C$\cdots$Br (1.1%), C$\cdots$N/N$\cdots$C (1.0%), S$\cdots$S (0.7%), S$\cdots$N/N$\cdots$S (0.6%) and S$\cdots$C/C$\cdots$S (0.2%), as shown in the two-dimensional fingerprint plots in Fig. 7.

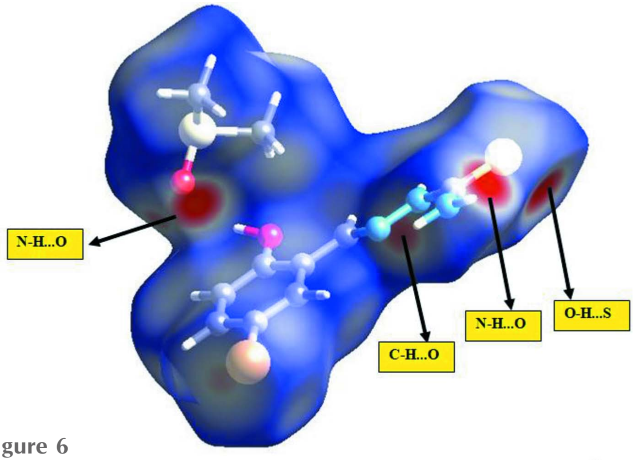


**Figure 6**
Hirshfeld surfaces mapped over $d_{\rm norm}$ for the title compound.

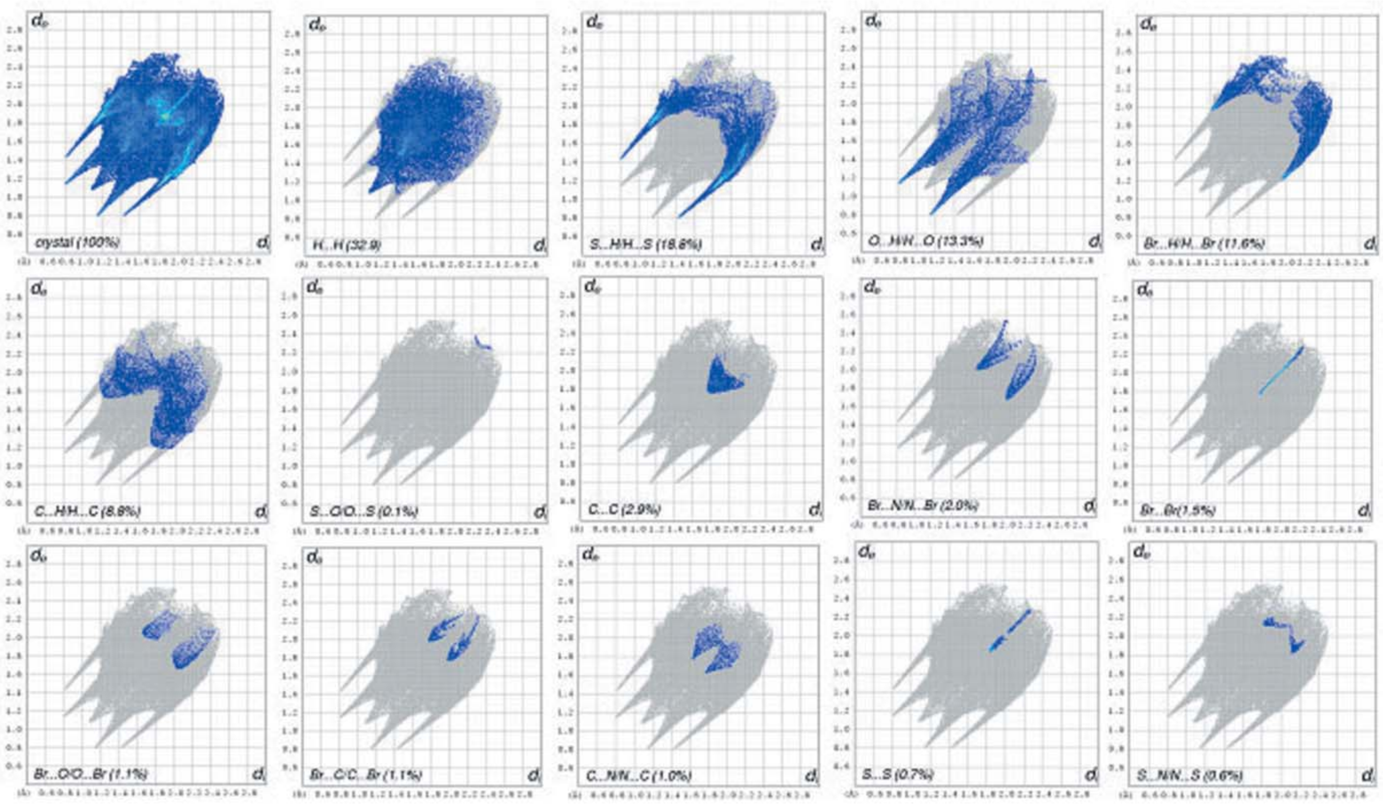


**Figure 7**
Two-dimensional fingerprint plots of the crystal and the relative contributions of the atom pairs to the Hirshfeld surface.

## 5. Database survey

A search of the Cambridge Structural Database (Version 5.38, update May 2017; Groom *et al.*, 2016) for the 2-hydroxybenzaldehyde thiosemicarbazone skeleton (or salicylaldehyde thiosemicarbazone) yielded 25 hits. These include the unsolvated bromo- and chloro-substituted analogues of the title compound mentioned above, *viz*. 5-bromo-2-hydroxybenzaldehyde thiosemicarbazone (CEDPAE; Kargar *et al.*, 2010*a*) and 2-(5-chloro-2-hydroxybenzylidene)hydrazinecarbothioamide (VACGUD; Kargar *et al.*, 2010*b*). The crystal structure of salicylaldehyde thiosemicarbazone has also been reported at 295 K (GEXKID; Chattopadhyay *et al.*, 1988) and at 100 K (GEXKID01; Novaković *et al.*, 2007). The crystal structures of various hydrated forms of salicylaldehydethiosemicarbazone [(*E*)-2-(2-hydroxybenzylidene)-hydrazinecarbothioamide hydrate] have been reported at 100 K (UJIPIN) and 203 K (UJIPOT and UJIPUZ) by Monfared *et al.* (2010). In the majority of the hits, the 2-hydroxy group forms an intramolecular O—H$\cdots$N hydrogen bond, as shown for CEDPAE in Fig. 2. Consequently, in the compounds mentioned above, the dihedral angle between the benzene ring and the mean plane of the N—N—C(N)=S hydrazinecarbothioamide unit is relatively small, varying from *ca* 5.62 to 10.10°, compared to 14.54 (11)° in the title compound.

## 6. Synthesis and crystallization

The title compound was synthesized by refluxing for 8 h a 1:1 molar ratio of a hot ethanolic solution (20 ml) of thiosemicarbazide (0.091 mg, Aldrich) and a hot ethanolic solution of 5-bromosalicylaldehyde (0.196 mg, Aldrich). The solution was then cooled and kept at room temperature. The precipitate that formed was filtered off and recrystallized from dimethyl sulfoxide. Colourless block-like crystals, suitable for the X-ray analysis, were obtained in a few days on slow evaporation of the solvent.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydrogen atoms were fixed geometrically (O—H = 0.82, N—H = 0.86, C—H = 0.93–0.96 Å) and allowed to ride on their parent atoms with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O-hydroxyl, C-methyl) and 1.2$U_{\rm eq}$(N,C) for other H atoms.

## Funding information

KB and PS thank the Department of Science and Technology (DST–SERB), grant No. SB/FT/CS-058/2013, New Delhi, India, for financial support.

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_8H_8BrN_3OS \cdot C_2H_6OS$ |
| $M_r$ | 352.26 |
| Crystal system, space group | Triclinic, $P\overline{1}$ |
| Temperature (K) | 296 |
| $a$, $b$, $c$ (Å) | 6.5411 (4), 7.3889 (6), 15.0662 (12) |
| $\alpha$, $\beta$, $\gamma$ (°) | 78.772 (3), 86.872 (3), 87.376 (3) |
| $V$ (Å$^3$) | 712.71 (9) |
| $Z$ | 2 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 3.17 |
| Crystal size (mm) | 0.30 × 0.20 × 0.20 |
| Data collection | |
| Diffractometer | Bruker Kappa APEXII CCD |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2004) |
| $T_{min}$, $T_{max}$ | 0.449, 0.569 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 6030, 3299, 2661 |
| $R_{int}$ | 0.018 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.666 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.030, 0.106, 0.79 |
| No. of reflections | 3299 |
| No. of parameters | 165 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.27, −0.34 |

Computer programs: *APEX2*, *SAINT* and *XPREP* (Bruker, 2004), *SIR92* (Altomare *et al.*, 1993), *SHELXL2017/1* (Sheldrick, 2015), *PLATON* (Spek 2009), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

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# supporting information

*Acta Cryst.* (2018). E**74**, 119-123 [https://doi.org/10.1107/S2056989018000233]

## Crystal structure and Hirshfeld surface analysis of (*E*)-2-(5-bromo-2-hydroxybenzylidene)hydrazinecarbothioamide dimethyl sulfoxide monosolvate

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### Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL2017/1* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2017/1* (Sheldrick, 2015), *PLATON* (Spek 2009) and *publCIF* (Westrip, 2010).

### (*E*)-2-(5-Bromo-2-hydroxybenzylidene)hydrazinecarbothioamide dimethyl sulfoxide monosolvate

*Crystal data*

$C_8H_8BrN_3OS{\cdot}C_2H_6OS$
$M_r = 352.26$
Triclinic, $P\overline{1}$
$a = 6.5411\ (4)$ Å
$b = 7.3889\ (6)$ Å
$c = 15.0662\ (12)$ Å
$\alpha = 78.772\ (3)°$
$\beta = 86.872\ (3)°$
$\gamma = 87.376\ (3)°$
$V = 712.71\ (9)$ Å$^3$
$Z = 2$
$F(000) = 356$
$D_x = 1.637$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2934 reflections
$\theta = 5.5–55.9°$
$\mu = 3.17$ mm$^{-1}$
$T = 296$ K
Block, colourless
0.30 × 0.20 × 0.20 mm

*Data collection*

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
$\omega$ and $\varphi$ scan
Absorption correction: multi-scan (SADABS; Bruker, 2004)
$T_{min} = 0.449$, $T_{max} = 0.569$
6030 measured reflections
3299 independent reflections
2661 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 28.3°$, $\theta_{min} = 3.4°$
$h = -8 \rightarrow 6$
$k = -9 \rightarrow 9$
$l = -17 \rightarrow 19$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.106$
$S = 0.79$
3299 reflections
165 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.27$ e Å$^{-3}$
$\Delta\rho_{min} = -0.34$ e Å$^{-3}$

*Special details*

**Geometry**. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

**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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.20262 (4) | 0.63938 (4) | 0.51812 (2) | 0.0512 (1) |
| S1 | 1.36501 (8) | 0.37819 (8) | 0.83370 (4) | 0.0359 (2) |
| S2 | 0.24643 (10) | 0.89596 (8) | 0.93448 (4) | 0.0421 (2) |
| O1 | 0.6312 (2) | 1.1359 (2) | 0.71559 (12) | 0.0382 (5) |
| N1 | 0.8705 (3) | 0.6223 (3) | 0.72520 (13) | 0.0300 (5) |
| N2 | 1.0553 (3) | 0.5884 (2) | 0.76701 (13) | 0.0305 (5) |
| N3 | 1.0303 (3) | 0.2820 (3) | 0.76421 (15) | 0.0389 (6) |
| C1 | 0.6169 (3) | 0.8495 (3) | 0.66806 (14) | 0.0267 (6) |
| O2 | 0.1487 (3) | 0.9012 (2) | 0.84564 (14) | 0.0512 (6) |
| C2 | 0.5325 (3) | 1.0274 (3) | 0.66902 (15) | 0.0287 (6) |
| C3 | 0.3559 (3) | 1.0884 (3) | 0.62389 (16) | 0.0346 (7) |
| C4 | 0.2574 (4) | 0.9727 (3) | 0.57957 (17) | 0.0385 (7) |
| C5 | 0.3383 (3) | 0.7961 (3) | 0.58003 (15) | 0.0325 (6) |
| C6 | 0.5159 (3) | 0.7339 (3) | 0.62232 (15) | 0.0309 (6) |
| C7 | 0.8054 (3) | 0.7906 (3) | 0.71317 (15) | 0.0300 (6) |
| C8 | 1.1348 (3) | 0.4159 (3) | 0.78513 (14) | 0.0274 (6) |
| C9 | 0.5074 (4) | 0.8287 (4) | 0.9172 (2) | 0.0493 (9) |
| C10 | 0.1671 (5) | 0.6884 (4) | 1.0067 (2) | 0.0578 (10) |
| H1 | 0.54961 | 1.21258 | 0.73121 | 0.0570* |
| H2 | 1.11849 | 0.67747 | 0.78122 | 0.0360* |
| H3 | 0.30338 | 1.20764 | 0.62341 | 0.0410* |
| H3A | 0.91417 | 0.30700 | 0.73958 | 0.0470* |
| H3B | 1.07844 | 0.17008 | 0.77525 | 0.0470* |
| H4 | 0.13811 | 1.01311 | 0.54976 | 0.0460* |
| H6 | 0.56908 | 0.61567 | 0.62069 | 0.0370* |
| H7 | 0.88039 | 0.87680 | 0.73376 | 0.0360* |
| H9A | 0.51533 | 0.72024 | 0.89072 | 0.0740* |
| H9B | 0.57191 | 0.80243 | 0.97422 | 0.0740* |
| H9C | 0.57610 | 0.92693 | 0.87721 | 0.0740* |
| H10A | 0.02145 | 0.69522 | 1.01827 | 0.0870* |
| H10B | 0.23443 | 0.67244 | 1.06288 | 0.0870* |
| H10C | 0.20263 | 0.58551 | 0.97788 | 0.0870* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.0489 (2) | 0.0567 (2) | 0.0538 (2) | −0.0095 (1) | −0.0172 (1) | −0.0193 (1) |
| S1 | 0.0323 (3) | 0.0315 (3) | 0.0469 (4) | 0.0088 (2) | −0.0164 (2) | −0.0132 (2) |
| S2 | 0.0571 (4) | 0.0295 (3) | 0.0432 (4) | −0.0032 (3) | −0.0125 (3) | −0.0124 (3) |
| O1 | 0.0344 (8) | 0.0356 (8) | 0.0498 (10) | 0.0071 (7) | −0.0122 (7) | −0.0203 (7) |
| N1 | 0.0244 (8) | 0.0301 (9) | 0.0365 (10) | 0.0043 (7) | −0.0081 (7) | −0.0086 (7) |
| N2 | 0.0273 (9) | 0.0241 (8) | 0.0417 (11) | 0.0023 (7) | −0.0132 (7) | −0.0082 (7) |
| N3 | 0.0374 (10) | 0.0260 (9) | 0.0566 (14) | 0.0019 (8) | −0.0182 (9) | −0.0123 (9) |
| C1 | 0.0254 (10) | 0.0273 (10) | 0.0267 (10) | 0.0031 (8) | −0.0038 (7) | −0.0040 (8) |
| O2 | 0.0724 (13) | 0.0296 (8) | 0.0554 (12) | 0.0027 (8) | −0.0339 (10) | −0.0099 (8) |
| C2 | 0.0294 (10) | 0.0280 (10) | 0.0288 (11) | 0.0017 (8) | −0.0032 (8) | −0.0057 (8) |
| C3 | 0.0341 (11) | 0.0302 (11) | 0.0390 (13) | 0.0091 (9) | −0.0089 (9) | −0.0059 (9) |
| C4 | 0.0303 (11) | 0.0460 (13) | 0.0373 (13) | 0.0063 (10) | −0.0115 (9) | −0.0024 (10) |
| C5 | 0.0314 (10) | 0.0377 (11) | 0.0289 (11) | −0.0033 (9) | −0.0054 (8) | −0.0063 (9) |
| C6 | 0.0328 (11) | 0.0306 (10) | 0.0297 (11) | 0.0012 (8) | −0.0047 (8) | −0.0063 (9) |
| C7 | 0.0306 (11) | 0.0290 (10) | 0.0314 (11) | 0.0008 (8) | −0.0039 (8) | −0.0084 (8) |
| C8 | 0.0283 (10) | 0.0249 (10) | 0.0301 (11) | 0.0030 (8) | −0.0031 (8) | −0.0083 (8) |
| C9 | 0.0524 (16) | 0.0504 (15) | 0.0462 (16) | −0.0097 (12) | −0.0098 (12) | −0.0079 (12) |
| C10 | 0.0619 (18) | 0.0567 (17) | 0.0521 (18) | −0.0143 (14) | 0.0035 (13) | −0.0025 (14) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Br1—C5 | 1.898 (2) | N3—H3B | 0.8600 |
| S1—C8 | 1.698 (2) | C3—C4 | 1.383 (3) |
| S2—C10 | 1.780 (3) | N3—H3A | 0.8600 |
| S2—O2 | 1.508 (2) | C4—C5 | 1.384 (3) |
| S2—C9 | 1.776 (3) | C5—C6 | 1.373 (3) |
| O1—C2 | 1.367 (3) | C3—H3 | 0.9300 |
| N1—N2 | 1.384 (3) | C4—H4 | 0.9300 |
| N1—C7 | 1.278 (3) | C6—H6 | 0.9300 |
| O1—H1 | 0.8200 | C7—H7 | 0.9300 |
| N2—C8 | 1.338 (3) | C9—H9A | 0.9600 |
| N3—C8 | 1.324 (3) | C9—H9B | 0.9600 |
| C1—C7 | 1.449 (3) | C9—H9C | 0.9600 |
| C1—C2 | 1.405 (3) | C10—H10A | 0.9600 |
| C1—C6 | 1.404 (3) | C10—H10B | 0.9600 |
| C2—C3 | 1.385 (3) | C10—H10C | 0.9600 |
| N2—H2 | 0.8600 | | |
| | | | |
| C9—S2—C10 | 97.89 (14) | S1—C8—N2 | 118.69 (16) |
| O2—S2—C9 | 105.88 (12) | N2—C8—N3 | 118.41 (19) |
| O2—S2—C10 | 105.84 (12) | S1—C8—N3 | 122.90 (18) |
| N2—N1—C7 | 114.45 (19) | C2—C3—H3 | 120.00 |
| C2—O1—H1 | 110.00 | C4—C3—H3 | 120.00 |
| N1—N2—C8 | 119.44 (18) | C5—C4—H4 | 120.00 |
| C2—C1—C7 | 119.58 (19) | C3—C4—H4 | 120.00 |

| | | | |
|---|---|---|---|
| C2—C1—C6 | 118.62 (19) | C1—C6—H6 | 120.00 |
| C6—C1—C7 | 121.8 (2) | C5—C6—H6 | 120.00 |
| O1—C2—C3 | 122.0 (2) | N1—C7—H7 | 119.00 |
| C1—C2—C3 | 120.5 (2) | C1—C7—H7 | 119.00 |
| N1—N2—H2 | 120.00 | S2—C9—H9A | 109.00 |
| C8—N2—H2 | 120.00 | S2—C9—H9B | 110.00 |
| O1—C2—C1 | 117.53 (18) | S2—C9—H9C | 109.00 |
| H3A—N3—H3B | 120.00 | H9A—C9—H9B | 109.00 |
| C2—C3—C4 | 120.3 (2) | H9A—C9—H9C | 109.00 |
| C8—N3—H3B | 120.00 | H9B—C9—H9C | 109.00 |
| C8—N3—H3A | 120.00 | S2—C10—H10A | 109.00 |
| C3—C4—C5 | 119.3 (2) | S2—C10—H10B | 109.00 |
| Br1—C5—C6 | 119.57 (17) | S2—C10—H10C | 109.00 |
| Br1—C5—C4 | 118.85 (17) | H10A—C10—H10B | 109.00 |
| C4—C5—C6 | 121.6 (2) | H10A—C10—H10C | 109.00 |
| C1—C6—C5 | 119.8 (2) | H10B—C10—H10C | 109.00 |
| N1—C7—C1 | 121.2 (2) | | |

| | | | |
|---|---|---|---|
| C7—N1—N2—C8 | 178.2 (2) | C2—C1—C7—N1 | 169.6 (2) |
| N2—N1—C7—C1 | 178.29 (19) | C6—C1—C7—N1 | −10.9 (3) |
| N1—N2—C8—S1 | 178.26 (15) | O1—C2—C3—C4 | −178.3 (2) |
| N1—N2—C8—N3 | −1.7 (3) | C1—C2—C3—C4 | 1.9 (3) |
| C6—C1—C2—O1 | 178.65 (19) | C2—C3—C4—C5 | −0.7 (4) |
| C6—C1—C2—C3 | −1.5 (3) | C3—C4—C5—Br1 | −179.52 (18) |
| C7—C1—C2—O1 | −1.9 (3) | C3—C4—C5—C6 | −1.0 (4) |
| C7—C1—C2—C3 | 178.0 (2) | Br1—C5—C6—C1 | 179.90 (16) |
| C2—C1—C6—C5 | −0.1 (3) | C4—C5—C6—C1 | 1.4 (3) |
| C7—C1—C6—C5 | −179.6 (2) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1···S1$^{i}$ | 0.82 | 2.40 | 3.1655 (17) | 157 |
| N2—H2···O2$^{ii}$ | 0.86 | 2.10 | 2.897 (2) | 155 |
| N3—H3*A*···O1$^{iii}$ | 0.86 | 2.37 | 3.048 (2) | 136 |
| N3—H3*A*···N1 | 0.86 | 2.30 | 2.648 (3) | 104 |
| N3—H3*B*···O2$^{iv}$ | 0.86 | 2.11 | 2.930 (3) | 160 |
| C7—H7···O1 | 0.93 | 2.44 | 2.752 (3) | 100 |
| C7—H7···O2$^{ii}$ | 0.93 | 2.53 | 3.315 (3) | 142 |

Symmetry codes: (i) *x*−1, *y*+1, *z*; (ii) *x*+1, *y*, *z*; (iii) *x*, *y*−1, *z*; (iv) *x*+1, *y*−1, *z*.