

(*E*)-2-(2-Hydroxy-3-methylbenzylidene)-*N*-methylhydrazine-1-carbothioamide: supramolecular assemblies in two-dimensions mediated by N—H···S and C—H··· π interactions

Md. Azharul Arafath,^{a*} Huey Chong Kwong^b and Farook Adam^{b*}

Received 4 March 2019

Accepted 1 April 2019

Edited by M. Nieger, University of Helsinki, Finland

Keywords: crystal structure; hydrazine carbothioamide; Schiff base; intermolecular interaction.

CCDC reference: 1485713

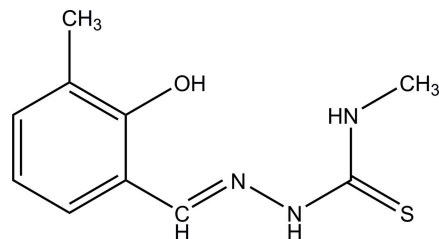
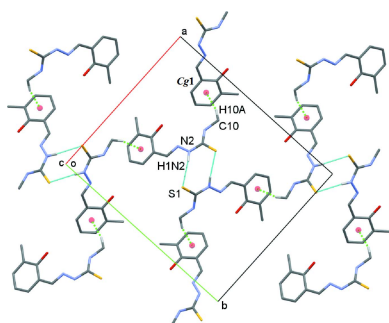
Supporting information: this article has supporting information at journals.iucr.org/e

^aDepartment of Chemistry, Shahjalal University of Science and Technology, Sylhet 3114, Bangladesh, and ^bSchool of Chemical Sciences, Universiti Sains Malaysia, Penang 11800 USM, Malaysia. *Correspondence e-mail: arafath.usm@gmail.com, farook@usm.my

In the title compound, C₁₀H₁₃N₃OS, the azomethine C=N double bond has an *E* configuration. The phenyl ring and methylhydrazine carbothioamide moiety [maximum deviation = 0.008 (2) Å] are twisted slightly with a dihedral angle of 14.88 (10)°. In the crystal, molecules are linked into sheets parallel to the *ab* plane via N—H···S hydrogen bonds and C—H··· π interactions.

1. Chemical context

Schiff base compounds are very important and can be used for multidisciplinary applications. They are widely used in the food and dye industries and exhibit many types of biological activity (Gaur, 2000) such as antibacterial, antifungal, and antimalarial (Annapoorani & Krishnan, 2013). The azomethine C=N group of Schiff bases plays an important role in the biological activity. Metal complexes of thiosemicarbazones have also received much attention. The metal chelation typically improves the lipophilicity of the ligand and facilitates the penetration of the complexes into bacterial membranes (Lobana *et al.*, 2009; Rogolino *et al.*, 2017). Thiosemicarbazones have multi-donor characteristics because of the presence of nitrogen and sulfur atoms in their molecular backbone. This results in a variety of coordination modes and many different physiochemical properties (Sharma *et al.*, 2016). As part of our ongoing studies on thiosemicarbazone Schiff bases (Arafath *et al.*, 2018a), we report herein the synthesis and structural determination of the title compound.



2. Structural commentary

The title compound (I) crystallizes in the non-centrosymmetric orthorhombic space group *Iba*2 and exhibits an *E* configuration with respect to the azomethine C=N double

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C1–C6 phenyl ring.

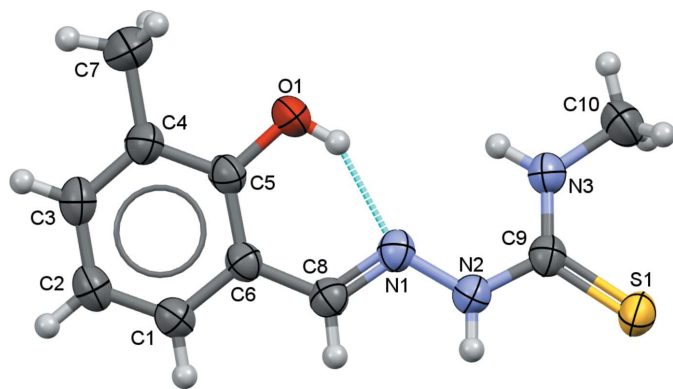
<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O1–H1O1...N1	0.84 (4)	1.94 (4)	2.681 (3)	147 (4)
N2–H1N2...S1 ⁱ	0.89 (3)	2.51 (3)	3.387 (2)	173 (3)
C10–H10A...Cg1 ⁱⁱ	0.96	2.70	3.577 (4)	152

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

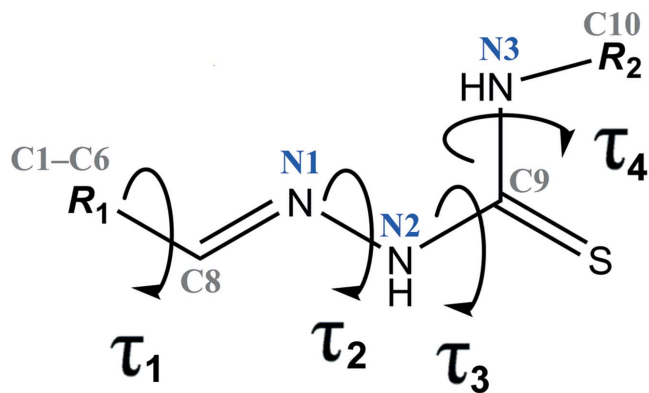
bond (Fig. 1). The C8=N1 and C9=S1 bond lengths of 1.288 (3) and 1.689 (2) Å, respectively, confirm the presence of the double bonds while the C6–C8, N2–C9 and C9–N3 bond lengths of 1.452 (3), 1.354 (3) and 1.321 (3) Å, respectively, confirm their single-bond character. The C6–C8–N1 and N2–C9–N3 angles are 122.5 (2) and 117.8 (2)°, respectively, and are consistent with an sp^2 -hybridized character for atom C8 and C9 (Arafath *et al.*, 2018b; Khalaji *et al.*, 2012). The unique molecular conformation of (I) can be characterized by four torsion angles, *viz.* τ_1 (C5–C6–C8–N1), τ_2 (C8–N1–N2–C9), τ_3 (N1–N2–C9–N3) and τ_4 (N2–C9–N3–C10), respectively (Fig. 2). The torsion angles τ_3 and τ_4 are 0.4 (3) and 179.9 (2)°, signifying the planarity of the methylhydrazine carbothioamide moiety [N1–N2–(C9=S1)–N3–C10; mean deviation $\sigma = 0.002$ Å, maximum deviation = 0.008 (2) Å for atom C9]. τ_1 and τ_2 are slightly twisted [$\tau_1 = -4.2$ (3) and $\tau_2 = 170.4$ (2)°, respectively], and the C1–C6 phenyl ring and the methylhydrazine carbothioamide moiety subtend a dihedral angle of 14.88 (10)°. In the molecule, the hydroxy group acts as a hydrogen-bond donor for the adjacent hydrazine group, forming an intramolecular hydrogen bond with an *S*(6) ring motif (Fig. 1, Table 1).

3. Supramolecular features

In the crystal, molecules are linked into dimers with an $R_2^2(8)$ ring motif *via* N2–H1N2...S1 hydrogen bonds (Fig. 3a, Table 1). The dimers are then connected into sheets parallel to the *ab* plane through C–H... π interactions (Fig. 3b, Table 1).


Figure 1

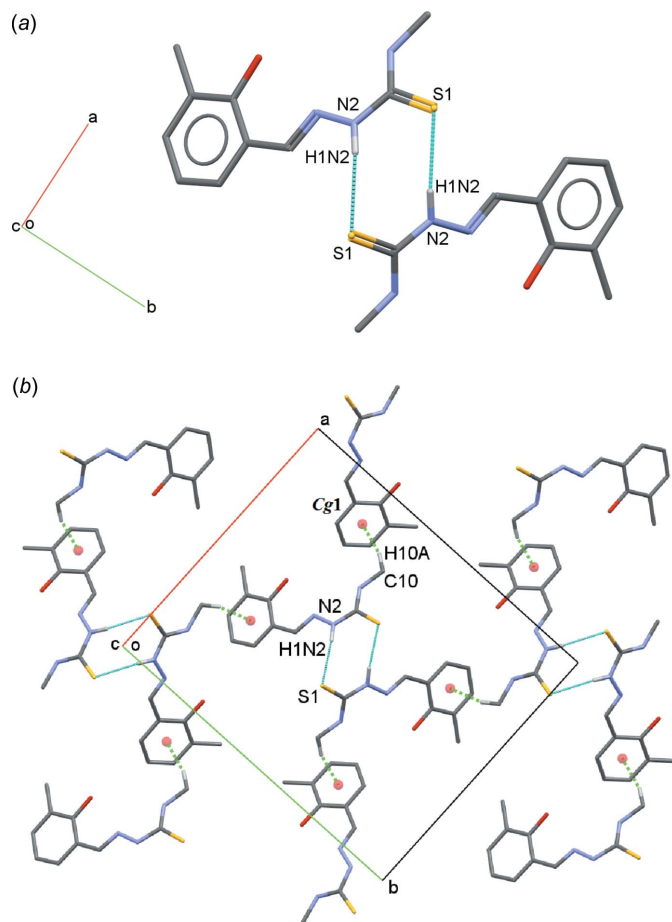
The atom labelling scheme and displacement ellipsoids of the molecular structure at the 50% probability level.


Figure 2

General chemical diagram showing torsion angles, τ_1 , τ_2 , τ_3 and τ_4 in the title compound.

4. Database survey

A search of the Cambridge Structural Database (CSD version 5.39, last update February 2018; Groom *et al.*, 2016) using (*E*)-2-(2-hydroxybenzylidene)-*N*-(λ^1 -methyl)hydrazine-1-carbothioamide as reference moiety found 44 structures containing the 2-(2-hydroxybenzylidene)hydrazinecarbothioamide


Figure 3

(a) A view of a dimer of $C_{10}H_{13}N_3OS$ with N2–H1N2...S1 hydrogen bonds shown as cyan dotted lines. (b) A view of a dimeric sheet with C10–H10A...Cg1 interactions shown as green dotted lines. Hydrogen atoms not involved in with these interactions are omitted for clarity.

Table 2
Torsion angles τ_1 , τ_2 , τ_3 and τ_4 (°).

Compound	R_1	R_2	τ_1	τ_2	τ_3	τ_4
(I)	2-hydroxy-3-methylbenzylidenyl	methyl	4	170	0	180
AWAZOP (Hussein & Guan, 2015)	5-bromo-2-hydroxybenzylidenyl	methyl	1	175	12	179
AWEBEL (Hussein & Guan, 2015)	3-ethoxy-2-hydroxybenzylidenyl	methyl	176	174	4	180
CIVZAK (Hussein <i>et al.</i> , 2014b)	5-(<i>tert</i> -butyl)-2-hydroxybenzylidenyl	ethyl	2	174	15	180
CIWBAN (Hussein <i>et al.</i> , 2014b)	5-allyl-3-ethyl-2-hydroxybenzylidenyl	methyl	169	173	5	178
DAGVOZ (Arafath <i>et al.</i> , 2017b)	2-hydroxy-5-methoxy-3-nitrobenzylidenyl	methyl	177	176	7	179
EFUPAX (Rubčić <i>et al.</i> , 2008)	2-hydroxy-4-methoxybenzylidenyl	phenyl	2	173	4	174
EROVIR (Lo & Ng, 2011)	5-chloro-2-hydroxybenzylidenyl	ethyl	8	172	14	176
GOZQIX (Hussein <i>et al.</i> , 2015a)	2-hydroxy-5-methoxybenzylidenyl	methyl	3	175	14	180
GOZQIX01 (Salam <i>et al.</i> , 2016)	2-hydroxy-5-methoxybenzylidenyl	methyl	3	175	15	180
GOZQIX02 (Subhashree <i>et al.</i> , 2017)	2-hydroxy-5-methoxybenzylidenyl	methyl	2	175	13	180
HABDEW (Hussein <i>et al.</i> , 2015c)	3-ethoxy-2-hydroxybenzylidenyl	ethyl	177	176	5	180
HABFEY (Hussein <i>et al.</i> , 2015c)	5-allyl-2-hydroxy-3-methoxybenzylidenyl	ethyl	173, 173	176, 179	6, 8	178, 177
HAXROO (Vrdoljak <i>et al.</i> , 2005)	2-hydroxybenzylidenyl	methyl	1	176	11	178
HAXROO01 (Liu, 2015)	2-hydroxybenzylidenyl	methyl	2	175	11	178
HAXSAB (Vrdoljak <i>et al.</i> , 2005)	2-hydroxy-3-methoxybenzylidenyl	methyl	177	174	5	178
IBAZUJ (Haque <i>et al.</i> , 2015)	2,3-dihydroxybenzylidenyl	methyl	1	170	1	175
IBEDOL (Haque <i>et al.</i> , 2015)	2-hydroxy-5-methylbenzylidenyl	methyl	3, 2	175, 173	16, 16	175, 175
IFUXEN (Tan <i>et al.</i> , 2008b)	2,4-dihydroxybenzylidenyl	ethyl	2	179	0	176
IFUXEN01 (Hussein <i>et al.</i> , 2014b)	2,4-dihydroxybenzylidenyl	ethyl	2	179	0	176
IFUXEN02 (Ramaiyer & Frank, 2015)	2,4-dihydroxybenzylidenyl	ethyl	1	175	4	179
IFUXEN03 (Ramaiyer & Frank, 2015)	2,4-dihydroxybenzylidenyl	ethyl	5	171	6	178
IGALUY (Tan <i>et al.</i> , 2008c)	2,4-dihydroxybenzylidenyl	methyl	5	174	9	176
IGALUY01 (Salam <i>et al.</i> , 2015)	2,4-dihydroxybenzylidenyl	methyl	2	177	16	178
IMAFIN (El-Asmy <i>et al.</i> , 2016)	2-hydroxybenzylidenyl	ethyl	1	177	13	177
JAJHUA (Li <i>et al.</i> , 2016)	5-bromo-2-hydroxybenzylidenyl	methyl	1	175	12	179
JOFHIW (Tan <i>et al.</i> , 2008a)	2,5-dihydroxybenzylidenyl	methyl	1	175	11	178
KOCLİY (Đilović <i>et al.</i> , 2008)	4-(diethylamino)-2-hydroxybenzylidenyl	phenyl	2	172	12	174
LAQCIR (Jacob & Kurup, 2012)	5-bromo-2-hydroxy-3-methoxybenzylidenyl	cyclohexyl	172	177	4	179
NUQNAP (Shawish <i>et al.</i> , 2010)	2,3,4-trihydroxybenzylidenyl	ethyl	167	176	8	174
OBOLOJ (Arafath <i>et al.</i> , 2017a)	5-chloro-2-hydroxybenzylidenyl	cyclohexyl	175	176	6	177
PAXCAU (Jacob <i>et al.</i> , 2012)	5-bromo-2-hydroxy-3-methoxybenzylidenyl	phenyl	177	180	6	177
RIVFAE (Seena <i>et al.</i> , 2008)	2-hydroxybenzylidenyl	phenyl	2, 5, 2	179, 175, 178	12, 9, 2	171, 177, 180
RIVFAE01 (Rubčić <i>et al.</i> , 2008)	2-hydroxybenzylidenyl	phenyl	11, 3	177, 171	2, 2	175, 170
SUKQOG (Hussein <i>et al.</i> , 2015d)	5-allyl-2-hydroxy-3-methoxybenzylidenyl	phenyl	168	172	4	179
WEXDAG (Orsyk <i>et al.</i> , 2013)	2-hydroxybenzylidenyl	allyl	4	170	7	173
XOTPED (Hussein <i>et al.</i> , 2015b)	2-hydroxy-3-methylbenzylidenyl	ethyl	2	179	7	179
YOCJOR (Chumakov <i>et al.</i> , 2014)	5-bromo-2-hydroxybenzylidenyl	pyridin-2-yl	0	179	178	1
YOCJUX (Chumakov <i>et al.</i> , 2014)	2-hydroxy-3-methoxybenzylidenyl	pyridin-2-yl	3	178	177	3
YOPHUI (Hussein <i>et al.</i> , 2014a)	3-(<i>tert</i> -butyl)-2-hydroxybenzylidenyl	ethyl	4, 8	171, 169	4, 18	179, 180
YOPLIA (Hussein <i>et al.</i> , 2014a)	2-hydroxy-5-methylbenzylidenyl	ethyl	4	171	10	180
YUKYOU (Salam & Haque, 2015)	3,5-dichloro-2-hydroxybenzylidenyl	ethyl	179	180	2	178
YUXJOS (Arafath <i>et al.</i> , 2018a)	3-(<i>tert</i> -butyl)-2-hydroxybenzylidenyl	cyclohexyl	12	170	12	176
ZIJKIO (Li & Sato, 2013)	5-bromo-2-hydroxybenzylidenyl	ethyl	6	172	12	176
ZIJKIO02 (Hussein <i>et al.</i> , 2015b)	5-bromo-2-hydroxybenzylidenyl	ethyl	7	173	13	177

Note: there is more than one torsion angle for compounds HABFEY, IBEDOL, RIVFAE, RIVFAE01 and YOPHUI because there are more than one independent molecules in their asymmetric units.

moiety with different substituents. The basic structural motif (*E*)-2-(2-hydroxybenzylidene)-*N*-(λ^1 -methyl)hydrazine-1-carbothioamide is shown in Fig. 2 and the different substituents (R_1 and R_2) together with the torsion angles of the C—CH=N—NH—C(=S)—NH—C backbone are summarized in Table 2. In these structures, the torsion angle τ_1 exists in either the *syn-periplanar* (range from 0 to 12°) or *anti-periplanar* (range from 167 to 179°) conformation. As for the torsion angle τ_2 , all structures adopt an *anti-periplanar* conformation (169–179°). Similar to the title compound, torsion angles τ_3 and τ_4 for most of the structures are *syn-periplanar* (0–16°) and *anti-periplanar* (171–180°), respectively. However, there are two outliers (YOCJOR and YOCJUX; (Chumakov *et al.*, 2014)) where the 2-(2-hydroxybenzylidene)hydrazinecarbothioamide is substituted with a pyridine ring. In contrast to most of the structures, torsion angles τ_3 and τ_4

for YOCJOR and YOCJUX are *anti-periplanar* (178 and 177°, respectively) and *syn-periplanar* (1 and 3°, respectively).

5. Synthesis and crystallization

2-Hydroxy-3-methylbenzaldehyde (0.68 g, 5.00 mmol) was dissolved in 20.0 mL of methanol. 0.20 mL of glacial acetic acid was added and the mixture was refluxed for 30 minutes. A solution of 0.52 g (5.00 mmol) of *N*-methyl hydrazinecarbothioamide in 20.0 mL of methanol was added dropwise with stirring to the aldehyde solution (Fig. 4). The resulting colourless solution was heated under reflux for 4 h with stirring. The crude product was washed with 5.0 mL of *n*-hexane. The recovered product was dissolved in DMSO for purification and recrystallization. Light-yellow single crystals (m.p.

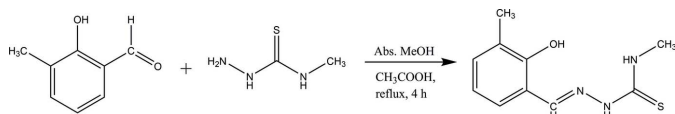


Figure 4
Reaction scheme for the synthesis of $C_{10}H_{13}N_3OS$.

454–455 K; yield 94%) suitable for X-ray diffraction were obtained by slow evaporation of the solvent.

Analysis calculated for $C_{10}H_{13}N_3OS$ (FW: 223.29 g mol⁻¹); C, 53.74; H, 5.83; N, 18.81; found: C, 53.71; H, 5.79; N, 18.83%. ¹H NMR (500 MHz, DMSO-*d*₆, Me₄Si ppm): δ 11.38 (*s*, N–NH), δ 9.39 (*s*, OH), δ 8.34 (*s*, HC=N), δ 8.44 (*q*, CS–NH), δ 7.42–6.81 (multiplet, aromatic), δ 3.00 (*d*, *J* = 4.5 Hz, N–CH₃), δ 2.20 (*s*, Ph–CH₃). ¹³C NMR (DMSO-*d*₆, Me₄Si ppm): δ 177.48 (C=S), δ 154.24 (C=N), δ 143.64–119.10 (C-aromatic), δ 31.05 (N–CH₃), δ 15.91 (Ph–CH₃) ppm. IR (KBr pellets $\nu_{\max}/\text{cm}^{-1}$): 3418 ν (NH), 3133 ν (OH), 2983 (NC–H₃, *sp*³), 1618 ν (C=N), 1553 ν (C=C, aromatic), 1270 ν (C=S), 1251 ν (CH, bend., aromatic), 1085 ν (C–O). 1043 ν (C–N).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. C-bound H atoms were positioned geometrically (C–H = 0.93–0.96 Å) and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5 U_{\text{eq}}(\text{C})$. All N- and O-bound H atoms were located from a difference-Fourier map and freely refined.

Funding information

This research was supported financially by the RU grant No. 1001/PKIMIA/811269 from Universiti Sains Malaysia. The authors wish to thank Universiti Sains Malaysia and The World Academy of Science for a USM–TWAS fellowship to MdAA. HCK would like to thank the Malaysian Government for a MyBrain15 scholarship.

References

Annapoorani, S. & Krishnan, C. (2013). *Synthesis*, **5**, 180–185.
 Arafath, M. A., Adam, F. & Razali, M. R. (2017a). *IUCrData*, **2**, x161997.
 Arafath, M. A., Adam, F., Razali, M. R., Ahmed Hassan, L. E., Ahamed, M. B. K. & Majid, A. M. S. A. (2017b). *J. Mol. Struct.* **1130**, 791–798.
 Arafath, M. A., Kwong, H. C., Adam, F. & Razali, M. R. (2018a). *Acta Cryst.* **E74**, 687–690.
 Arafath, M. A., Kwong, H. C., Adam, F. & Razali, M. R. (2018b). *Acta Cryst.* **E74**, 1460–1462.
 Bruker (2012). Bruker AXS Inc., Madison, Wisconsin, USA.
 Chumakov, Y. M., Petrenko, P. A., Codita, T. B., Tsapkov, V. I., Poirier, D. & Gulea, A. P. (2014). *Crystallogr. Rep.* **59**, 207–212.
 Đilović, I., Rubčić, M., Vrdoljak, V., Pavelić, S. K., Kralj, M., Piantanida, I. & Cindrić, M. (2008). *Bioorg. Med. Chem.* **16**, 5189–5198.
 El-Asmy, A. A., Jeragh, B. & Ali, M. S. (2016). Private communication (Refcode CCDC 1478956. CCDC, Cambridge, England.
 Gaur, S. (2000). *Asian J. Chem.* **43**, 250–254.

Table 3
Experimental details.

Crystal data	$C_{10}H_{13}N_3OS$
Chemical formula	223.29
M_r	Orthorhombic, <i>Iba</i> 2
Crystal system, space group	296
Temperature (K)	14.6474 (14), 17.522 (2), 8.9048 (8)
a, b, c (Å)	2285.4 (4)
V (Å ³)	8
Z	Mo $K\alpha$
Radiation type	μ (mm ⁻¹)
μ (mm ⁻¹)	0.26
Crystal size (mm)	0.46 × 0.26 × 0.16
Data collection	
Diffractometer	Bruker APEXII DUO CCD area-detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2012)
T_{\min} , T_{\max}	0.853, 0.879
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14825, 3359, 2949
R_{int}	0.020
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.705
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.094, 1.06
No. of reflections	3359
No. of parameters	150
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 ⁻³)	0.17, -0.16
Absolute structure	Flack parameter determined using 1222 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.04 (3)

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2006) and *PLATON* (Spek, 2009).

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
 Haque, R. A., Salam, M. A. & Arafath, M. A. (2015). *J. Coord. Chem.* **68**, 2953–2967.
 Hussein, M. A. & Guan, T. S. (2015). *Eur. J. Chem.* **6**, 451–460.
 Hussein, M. A., Guan, T. S., Haque, R. A., Ahamed, M. B. K. & Majid, A. M. S. A. (2015a). *Polyhedron*, **85**, 93–103.
 Hussein, M. A., Guan, T. S., Haque, R. A., Khadeer Ahamed, M. B. & Abdul Majid, A. M. S. (2014a). *Inorg. Chim. Acta*, **421**, 270–283.
 Hussein, M. A., Guan, T. S., Haque, R. A., Khadeer Ahamed, M. B. & Abdul Majid, A. M. S. (2015b). *Spectrochim. Acta A*, **136**, 1335–1348.
 Hussein, M. A., Iqbal, M. A., Asif, M., Haque, R. A., Ahamed, M. B. K., Majid, A. M. S. A. & Guan, T. S. (2015c). *Phosphorus Sulfur Silicon*, **190**, 1498–1508.
 Hussein, M. A., Iqbal, M. A., Umar, M. I., Haque, R. A. & Guan, T. S. (2015d). *Arab. J. Chem.* In the Press.
 Hussein, M. A., Guan, T. S., Haque, R. A., Ahamed, M. B. K. & Majid, A. M. S. A. (2014b). *J. Coord. Chem.* **67**, 714–727.
 Jacob, J. M. & Kurup, M. R. P. (2012). *Acta Cryst.* **E68**, o836–o837.
 Jacob, J. M., Sithambaresan, M. & Kurup, M. R. P. (2012). *Acta Cryst.* **E68**, o1871–o1872.
 Khalaji, A. D., Fejfarova, K. & Dusek, M. (2012). *J. Chem. Crystallogr.* **42**, 263–266.
 Li, Z. & Sato, O. (2013). *Acta Cryst.* **E69**, o762.
 Li, Z.-Y., Ohtsu, H., Kojima, T., Dai, J.-W., Yoshida, T., Breedlove, B. K., Zhang, W.-X., Iguchi, H., Sato, O., Kawano, M. & Yamashita, M. (2016). *Angew. Chem. Int. Ed.* **55**, 5184–5189.

- Liu, Z.-X. (2015). *J. Struct. Chem.* **56**, 1420–1425.
- Lo, K. M. & Ng, S. W. (2011). *Acta Cryst.* **E67**, o1453.
- Lobana, T. S., Sharma, R., Bawa, G. & Khanna, S. (2009). *Coord. Chem. Rev.* **253**, 977–1055.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Orysyk, S. I., Bon, V. V., Zholob, O. O., Pekhnyo, V. I., Orysyk, V. V., Zborovskii, Y. L. & Vovk, M. V. (2013). *Polyhedron*, **51**, 211–221.
- Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
- Ramaiyer, V. & Frank, R. (2015). Private communication (Refcode CCDC 1058555. CCDC, Cambridge, England).
- Rogolino, D., Gatti, A., Carcelli, M., Pelosi, G., Bisceglie, F., Restivo, F. M., Degola, F., Buschini, A., Montalbano, S., Ferretti, D. & Zani, C. (2017). *Sci. Rep.* **7**, 11214.
- Rubčić, M., Đilović, I., Cindrić, M. & Matković-Čalogović, D. (2008). *Acta Cryst.* **C64**, o570–o573.
- Salam, M. A. & Haque, R. A. (2015). *Inorg. Chim. Acta*, **435**, 103–108.
- Salam, M. A., Hussein, M. A., Ramli, I. & Islam, M. S. (2016). *J. Organomet. Chem.* **813**, 71–77.
- Salam, M. A., Hussein, M. A. & Tiekink, E. R. T. (2015). *Acta Cryst.* **E71**, 58–61.
- Seena, E. B., Prathapachandra Kurup, M. R. & Suresh, E. (2008). *J. Chem. Crystallogr.* **38**, 93–96.
- Sharma, R., Lobana, T. S., Kaur, M., Thathai, N., Hundal, G., Jasinski, J. P. & Butcher, R. J. (2016). *J. Chem. Sci.* **128**, 1103–1112.
- Shawish, H. B., Maah, M. J. & Ng, S. W. (2010). *Acta Cryst.* **E66**, o1151.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Subhashree, G. R., Haribabu, J., Saranya, S., Yuvaraj, P., Anantha Krishnan, D., Karvembu, R. & Gayathri, D. (2017). *J. Mol. Struct.* **1145**, 160–169.
- Tan, K. W., Ng, C. H., Maah, M. J. & Ng, S. W. (2008a). *Acta Cryst.* **E64**, o1344.
- Tan, K. W., Ng, C. H., Maah, M. J. & Ng, S. W. (2008b). *Acta Cryst.* **E64**, o2123.
- Tan, K. W., Ng, C. H., Maah, M. J. & Ng, S. W. (2008c). *Acta Cryst.* **E64**, o2224.
- Vrdoljak, V., Cindrić, M., Milić, D., Matković-Čalogović, D., Novak, P. & Kamenar, B. (2005). *Polyhedron*, **24**, 1717–1726.

supporting information

Acta Cryst. (2019). E75, 571-575 [https://doi.org/10.1107/S2056989019004444]

(*E*)-2-(2-Hydroxy-3-methylbenzylidene)-*N*-methylhydrazine-1-carbothioamide: supramolecular assemblies in two-dimensions mediated by N—H \cdots S and C—H \cdots π interactions

Md. Azharul Arafath, Huey Chong Kwong and Farook Adam

Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINTE* (Bruker, 2012); data reduction: *SAINTE* (Bruker, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *SHELXL2013* (Sheldrick, 2015) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL2013* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

(*E*)-2-(2-Hydroxy-3-methylbenzylidene)-*N*-methylhydrazine-1-carbothioamide

Crystal data

$C_{10}H_{13}N_3OS$	$D_x = 1.298 \text{ Mg m}^{-3}$
$M_r = 223.29$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Orthorhombic, <i>Iba</i> 2	Cell parameters from 5563 reflections
$a = 14.6474 (14) \text{ \AA}$	$\theta = 2.3\text{--}29.5^\circ$
$b = 17.522 (2) \text{ \AA}$	$\mu = 0.26 \text{ mm}^{-1}$
$c = 8.9048 (8) \text{ \AA}$	$T = 296 \text{ K}$
$V = 2285.4 (4) \text{ \AA}^3$	Block, yellow
$Z = 8$	$0.46 \times 0.26 \times 0.16 \text{ mm}$
$F(000) = 944$	

Data collection

Bruker APEXII DUO CCD area-detector diffractometer	14825 measured reflections
Radiation source: fine-focus sealed tube	3359 independent reflections
Graphite monochromator	2949 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.020$
Absorption correction: multi-scan (SADABS; Bruker, 2012)	$\theta_{\text{max}} = 30.1^\circ$, $\theta_{\text{min}} = 1.8^\circ$
$T_{\text{min}} = 0.853$, $T_{\text{max}} = 0.879$	$h = -20 \rightarrow 20$
	$k = -23 \rightarrow 24$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.033$	$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2 + 0.3888P]$
$wR(F^2) = 0.094$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{\text{max}} = 0.001$
3359 reflections	$\Delta\rho_{\text{max}} = 0.17 \text{ e \AA}^{-3}$
150 parameters	$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$
1 restraint	

Absolute structure: Flack parameter determined
using 1222 quotients $[(F^-)-(F)]/[(F^+)+(F)]$
(Parsons *et al.*, 2013)
Absolute structure parameter: 0.04 (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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.35594 (4)	0.50006 (3)	0.20442 (10)	0.05018 (16)
O1	0.45729 (12)	0.77741 (11)	0.6162 (3)	0.0621 (6)
N1	0.48391 (12)	0.65142 (9)	0.4511 (3)	0.0414 (4)
N2	0.46275 (13)	0.59332 (10)	0.3526 (2)	0.0436 (4)
N3	0.31035 (13)	0.60707 (11)	0.4029 (2)	0.0459 (4)
C1	0.69785 (15)	0.72085 (14)	0.6081 (2)	0.0443 (5)
H1A	0.735599	0.683585	0.567182	0.053*
C2	0.73506 (15)	0.77658 (13)	0.6987 (3)	0.0493 (5)
H2A	0.797160	0.776261	0.720393	0.059*
C3	0.67936 (16)	0.83287 (14)	0.7568 (3)	0.0492 (5)
H3A	0.704945	0.871242	0.815398	0.059*
C4	0.58596 (16)	0.83349 (12)	0.7297 (3)	0.0479 (5)
C5	0.54896 (14)	0.77591 (12)	0.6405 (3)	0.0424 (4)
C6	0.60427 (14)	0.71939 (12)	0.5768 (2)	0.0380 (4)
C7	0.5255 (2)	0.89533 (18)	0.7931 (5)	0.0783 (10)
H7A	0.491901	0.918970	0.713173	0.117*
H7B	0.562565	0.932944	0.842504	0.117*
H7C	0.483746	0.873420	0.864103	0.117*
C8	0.56962 (15)	0.65960 (11)	0.4793 (3)	0.0410 (4)
H8A	0.610876	0.625925	0.435625	0.049*
C9	0.37548 (14)	0.57095 (11)	0.3289 (2)	0.0397 (4)
C10	0.21430 (16)	0.58990 (19)	0.3892 (4)	0.0647 (7)
H10A	0.179253	0.629791	0.435460	0.097*
H10B	0.201496	0.542285	0.438227	0.097*
H10C	0.198298	0.586205	0.284940	0.097*
H1N2	0.5065 (18)	0.5680 (16)	0.307 (4)	0.056 (8)*
H1N3	0.3243 (19)	0.6428 (16)	0.471 (4)	0.054 (7)*
H1O1	0.444 (3)	0.7429 (19)	0.555 (5)	0.076 (10)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0523 (3)	0.0455 (3)	0.0527 (3)	-0.0030 (2)	-0.0095 (3)	-0.0097 (2)
O1	0.0328 (8)	0.0601 (11)	0.0936 (16)	-0.0015 (7)	-0.0014 (8)	-0.0230 (10)
N1	0.0439 (9)	0.0367 (7)	0.0436 (8)	-0.0042 (6)	-0.0024 (9)	0.0006 (9)

N2	0.0412 (9)	0.0404 (9)	0.0491 (10)	0.0001 (7)	-0.0030 (8)	-0.0060 (8)
N3	0.0409 (9)	0.0495 (10)	0.0475 (9)	0.0000 (8)	-0.0055 (7)	-0.0078 (8)
C1	0.0380 (10)	0.0490 (12)	0.0460 (11)	0.0012 (9)	0.0008 (9)	0.0009 (9)
C2	0.0379 (9)	0.0576 (12)	0.0525 (11)	-0.0059 (9)	-0.0058 (10)	0.0016 (12)
C3	0.0478 (12)	0.0485 (11)	0.0513 (11)	-0.0119 (10)	-0.0057 (10)	-0.0017 (9)
C4	0.0446 (11)	0.0416 (10)	0.0575 (15)	-0.0049 (9)	0.0020 (9)	-0.0064 (9)
C5	0.0327 (10)	0.0401 (10)	0.0544 (12)	-0.0048 (8)	0.0031 (8)	0.0002 (9)
C6	0.0357 (9)	0.0380 (10)	0.0401 (10)	-0.0037 (8)	0.0010 (8)	0.0033 (8)
C7	0.0642 (17)	0.0641 (17)	0.107 (3)	0.0081 (14)	-0.0021 (18)	-0.0325 (17)
C8	0.0413 (10)	0.0387 (9)	0.0428 (11)	-0.0008 (8)	-0.0006 (8)	0.0020 (8)
C9	0.0439 (10)	0.0365 (9)	0.0387 (9)	-0.0016 (8)	-0.0064 (8)	0.0033 (8)
C10	0.0403 (12)	0.0802 (18)	0.0736 (17)	-0.0043 (12)	-0.0015 (12)	-0.0148 (15)

Geometric parameters (Å, °)

S1—C9	1.689 (2)	C2—H2A	0.9300
O1—C5	1.360 (3)	C3—C4	1.389 (3)
O1—H1O1	0.84 (4)	C3—H3A	0.9300
N1—C8	1.288 (3)	C4—C5	1.393 (3)
N1—N2	1.379 (3)	C4—C7	1.509 (4)
N2—C9	1.354 (3)	C5—C6	1.400 (3)
N2—H1N2	0.88 (3)	C6—C8	1.452 (3)
N3—C9	1.321 (3)	C7—H7A	0.9600
N3—C10	1.444 (3)	C7—H7B	0.9600
N3—H1N3	0.90 (3)	C7—H7C	0.9600
C1—C2	1.379 (3)	C8—H8A	0.9300
C1—C6	1.399 (3)	C10—H10A	0.9600
C1—H1A	0.9300	C10—H10B	0.9600
C2—C3	1.381 (4)	C10—H10C	0.9600
C5—O1—H1O1	108 (3)	C4—C5—C6	121.21 (19)
C8—N1—N2	115.18 (18)	C1—C6—C5	118.25 (19)
C9—N2—N1	121.68 (18)	C1—C6—C8	118.35 (19)
C9—N2—H1N2	118.0 (19)	C5—C6—C8	123.40 (18)
N1—N2—H1N2	120.2 (19)	C4—C7—H7A	109.5
C9—N3—C10	124.2 (2)	C4—C7—H7B	109.5
C9—N3—H1N3	120.5 (18)	H7A—C7—H7B	109.5
C10—N3—H1N3	115.1 (18)	C4—C7—H7C	109.5
C2—C1—C6	121.1 (2)	H7A—C7—H7C	109.5
C2—C1—H1A	119.4	H7B—C7—H7C	109.5
C6—C1—H1A	119.4	N1—C8—C6	122.5 (2)
C1—C2—C3	119.4 (2)	N1—C8—H8A	118.7
C1—C2—H2A	120.3	C6—C8—H8A	118.7
C3—C2—H2A	120.3	N3—C9—N2	117.8 (2)
C2—C3—C4	121.5 (2)	N3—C9—S1	123.86 (17)
C2—C3—H3A	119.3	N2—C9—S1	118.37 (16)
C4—C3—H3A	119.3	N3—C10—H10A	109.5
C3—C4—C5	118.4 (2)	N3—C10—H10B	109.5

C3—C4—C7	121.2 (2)	H10A—C10—H10B	109.5
C5—C4—C7	120.3 (2)	N3—C10—H10C	109.5
O1—C5—C4	117.4 (2)	H10A—C10—H10C	109.5
O1—C5—C6	121.4 (2)	H10B—C10—H10C	109.5
C8—N1—N2—C9	170.4 (2)	O1—C5—C6—C1	-179.2 (2)
C6—C1—C2—C3	-1.4 (4)	C4—C5—C6—C1	1.7 (3)
C1—C2—C3—C4	1.9 (4)	O1—C5—C6—C8	1.1 (3)
C2—C3—C4—C5	-0.6 (3)	C4—C5—C6—C8	-178.0 (2)
C2—C3—C4—C7	-179.8 (3)	N2—N1—C8—C6	178.06 (19)
C3—C4—C5—O1	179.6 (2)	C1—C6—C8—N1	176.1 (2)
C7—C4—C5—O1	-1.1 (4)	C5—C6—C8—N1	-4.2 (3)
C3—C4—C5—C6	-1.2 (3)	C10—N3—C9—N2	179.9 (2)
C7—C4—C5—C6	178.0 (3)	C10—N3—C9—S1	1.2 (3)
C2—C1—C6—C5	-0.3 (3)	N1—N2—C9—N3	0.4 (3)
C2—C1—C6—C8	179.4 (2)	N1—N2—C9—S1	179.17 (16)

Hydrogen-bond geometry (Å, °)

*Cg*1 is the centroid of the C1—C6 phenyl ring.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1O1...N1	0.84 (4)	1.94 (4)	2.681 (3)	147 (4)
N2—H1N2...S1 ⁱ	0.89 (3)	2.51 (3)	3.387 (2)	173 (3)
C10—H10A... <i>Cg</i> 1 ⁱⁱ	0.96	2.70	3.577 (4)	152

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