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(*E*)-1-(4-Hydroxybenzylidene)-4-methylthiosemicarbazide

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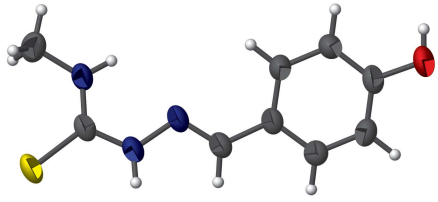
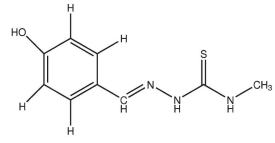
The title compound, $C_9H_{11}N_3OS$, is derived from methylthiosemicarbazide and hydroxybenzylidene fragments with a *trans* configuration at the C=N bond. The structure is stabilized by intermolecular N—H···S, N—H···O and O—H···S hydrogen bonds that form a two-dimensional network parallel to (102).

3D view



Chemical scheme



Structure description

Thiosemicarbazones are known for their diverse biological activity and are also useful as chelating ligands for transition metal ions. (Fang *et al.*, 2007). The compounds 1-(2,3,4-trihydroxybenzylidene) thiosemicarbazide (Shawish *et al.*, 2010*a*) and 1-(2,3,4-trihydroxybenzylidene)-4-ethylthiosemicarbazide (Shawish *et al.*, 2010*b*) are analogous except for the presence of the ethyl group in the later compound. The present compound (Fig. 1) is similar to these compounds but has only one hydroxy substituent of the benzylidene group and a methyl substituent of the thiocarbazide fragment. The thiourea fragment, S1/N1/N2/C8/C9, is planar with maximum deviation from the least-squares plane of 0.021 (2) Å for the N1 atom. It makes a dihedral angle of 12.01 (9)° with the benzene ring (C1–C6), considerably smaller than that in 1-(2,3,4-trihydroxybenzylidene)-4-ethylthiosemicarbazide [20.5 (1)°]. No intramolecular hydrogen bonds are observed in the molecule.

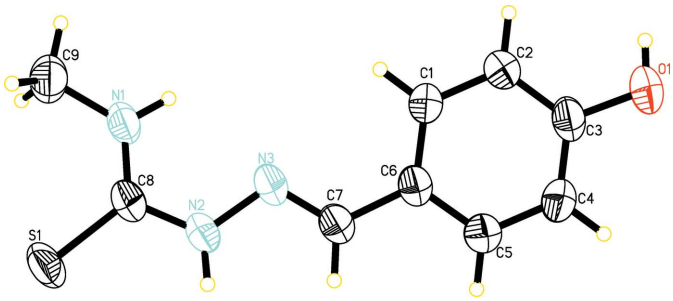


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

In the crystal, the molecules are linked by N1—H1*B*···S1, N1—H1*B*···O1 and O1—H1*A*···S1 hydrogen bonds (Table 1), to forming two-dimensional network parallel to (102) (Fig. 2).

Synthesis and crystallization

4-Methyl-3-thiosemicarbazide (0.5258 g, 0.005 mol) in an ethanol solution (15 ml) was slowly added to an ethanolic solution (15 ml) containing 4-hydroxybenzaldehyde (0.6106 g, 0.005 mol). The mixture was refluxed for 3 h and then cooled down to room temperature. Colorless crystals were collected by slow evaporation from the ethanolic mixture solution.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···S1^{i}	0.82 (2)	2.41 (2)	3.220 (2)	171 (3)
N1—H1*B*···O1^{ii}	0.86 (2)	2.47 (2)	3.018 (3)	123 (2)
N2—H2*A*···S1^{iii}	0.87 (2)	2.62 (1)	3.4177 (19)	154 (2)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_9H_{11}N_3OS$
M_r	209.27
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	302
a, *b*, *c* (Å)	5.2320 (4), 9.9727 (9), 19.9900 (18)
β (°)	97.5196 (18)
V (Å^3)	1034.05 (15)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.28
Crystal size (mm)	0.50 × 0.30 × 0.24
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.903, 0.934
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19497, 2572, 1977
R_{int}	0.062
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.670
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.048, 0.130, 1.06
No. of reflections	2572
No. of parameters	140
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.26, −0.32

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2015), *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2009).

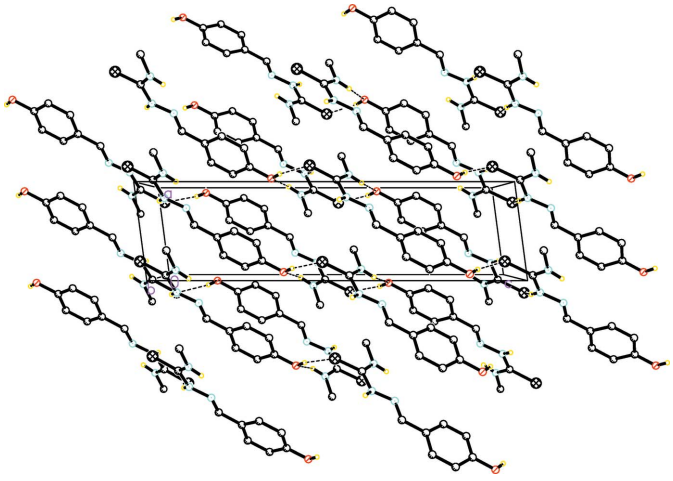

Figure 2
The crystal packing of the title compound, viewed along the *a* axis. The dashed lines indicate hydrogen bonds.

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full crystallographic data

IUCrData (2016). **1**, x161048 [https://doi.org/10.1107/S2414314616010488]

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Crystal data

$C_9H_{11}N_3OS$
M_r = 209.27
Monoclinic, $P2_1/c$
a = 5.2320 (4) Å
b = 9.9727 (9) Å
c = 19.9900 (18) Å
β = 97.5196 (18)°
V = 1034.05 (15) Å^3
Z = 4
$F(000)$ = 440
D_x = 1.344 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8733 reflections
θ = 2.9–28.3°
μ = 0.28 mm^{-1}
T = 302 K
Block, colorless
0.50 × 0.30 × 0.24 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: 'fire-focus sealed tube′
Detector resolution: 83.66 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2013)
T_{min} = 0.903, T_{max} = 0.934
19497 measured reflections
2572 independent reflections
1977 reflections with $I > 2\sigma(I)$
R_{int} = 0.062
θ_{max} = 28.4°, θ_{min} = 2.9°
h = −7→6
k = −13→13
l = −26→26

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.130
S = 1.06
2572 reflections
140 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: inferred from neighbouring sites
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2 + 0.5068P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}
Extinction correction: SHELXL2013 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.022 (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.

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses 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 observed criterion of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating -R-factor-obs 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.18138 (12)	0.81497 (6)	0.46654 (3)	0.0587 (2)
N1	0.0989 (3)	0.65738 (17)	0.56994 (9)	0.0485 (4)
N2	−0.1481 (3)	0.84494 (18)	0.55381 (8)	0.0484 (4)
N3	−0.2569 (3)	0.81887 (16)	0.61222 (8)	0.0444 (4)
O1	−0.9364 (4)	0.91660 (19)	0.85451 (9)	0.0705 (5)
C1	−0.5004 (5)	0.8075 (2)	0.73541 (11)	0.0553 (6)
H1C	−0.3699	0.7426	0.7319	0.066*
C2	−0.6242 (4)	0.8105 (2)	0.79267 (11)	0.0578 (6)
H2B	−0.5789	0.7476	0.8280	0.069*
C3	−0.8139 (4)	0.9049 (2)	0.79833 (10)	0.0485 (5)
C4	−0.8827 (4)	0.9941 (2)	0.74681 (10)	0.0499 (5)
H4A	−1.0152	1.0579	0.7503	0.060*
C5	−0.7585 (4)	0.9908 (2)	0.68979 (10)	0.0459 (5)
H5A	−0.8066	1.0531	0.6544	0.055*
C6	−0.5644 (3)	0.89803 (19)	0.68337 (9)	0.0412 (4)
C7	−0.4324 (4)	0.9023 (2)	0.62330 (9)	0.0436 (4)
H7A	−0.4793	0.9705	0.5908	0.052*
C8	0.0386 (4)	0.7664 (2)	0.53477 (9)	0.0425 (4)
C9	0.3028 (4)	0.5649 (2)	0.55772 (13)	0.0623 (6)
H9A	0.3113	0.4913	0.5904	0.094*
H9B	0.4681	0.6125	0.5626	0.094*
H9C	0.2663	0.5287	0.5119	0.094*
H1B	0.012 (4)	0.643 (2)	0.6027 (8)	0.059 (7)*
H2A	−0.175 (5)	0.9226 (14)	0.5346 (11)	0.069 (8)*
H1A	−0.894 (6)	0.854 (2)	0.8803 (14)	0.100 (12)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0796 (4)	0.0591 (4)	0.0444 (3)	−0.0017 (3)	0.0344 (3)	0.0018 (2)
N1	0.0535 (10)	0.0480 (9)	0.0491 (9)	−0.0002 (7)	0.0259 (8)	0.0027 (8)
N2	0.0575 (10)	0.0522 (10)	0.0394 (9)	0.0035 (8)	0.0218 (7)	0.0046 (8)
N3	0.0480 (9)	0.0508 (9)	0.0373 (8)	−0.0035 (7)	0.0167 (7)	−0.0012 (7)
O1	0.0869 (12)	0.0776 (12)	0.0552 (10)	0.0215 (10)	0.0402 (9)	0.0038 (9)
C1	0.0646 (13)	0.0535 (12)	0.0530 (12)	0.0185 (10)	0.0270 (10)	0.0079 (9)
C2	0.0710 (14)	0.0584 (13)	0.0486 (12)	0.0185 (11)	0.0254 (10)	0.0125 (10)
C3	0.0524 (11)	0.0528 (11)	0.0439 (10)	0.0000 (9)	0.0195 (8)	−0.0058 (9)
C4	0.0473 (11)	0.0513 (11)	0.0537 (11)	0.0088 (9)	0.0159 (9)	−0.0035 (9)
C5	0.0455 (10)	0.0479 (11)	0.0452 (10)	0.0027 (8)	0.0091 (8)	0.0017 (8)

C6	0.0418 (10)	0.0430 (10)	0.0407 (9)	−0.0037 (8)	0.0124 (7)	−0.0043 (8)
C7	0.0468 (10)	0.0472 (11)	0.0388 (9)	−0.0028 (8)	0.0126 (8)	0.0000 (8)
C8	0.0478 (10)	0.0463 (10)	0.0356 (9)	−0.0078 (8)	0.0140 (7)	−0.0048 (8)
C9	0.0595 (13)	0.0524 (12)	0.0811 (16)	0.0042 (10)	0.0317 (12)	0.0035 (12)

Geometric parameters (Å, º)

S1—C8	1.7087 (18)	C2—C3	1.383 (3)
N1—C8	1.311 (3)	C2—H2B	0.9500
N1—C9	1.454 (3)	C3—C4	1.373 (3)
N1—H1B	0.858 (10)	C4—C5	1.384 (3)
N2—C8	1.345 (3)	C4—H4A	0.9500
N2—N3	1.389 (2)	C5—C6	1.392 (3)
N2—H2A	0.868 (10)	C5—H5A	0.9500
N3—C7	1.279 (2)	C6—C7	1.462 (2)
O1—C3	1.369 (2)	C7—H7A	0.9500
O1—H1A	0.823 (10)	C9—H9A	0.9800
C1—C6	1.385 (3)	C9—H9B	0.9800
C1—C2	1.388 (3)	C9—H9C	0.9800
C1—H1C	0.9500		
C8—N1—C9	124.47 (17)	C5—C4—H4A	120.1
C8—N1—H1B	115.4 (16)	C4—C5—C6	121.23 (18)
C9—N1—H1B	120.1 (16)	C4—C5—H5A	119.4
C8—N2—N3	121.45 (17)	C6—C5—H5A	119.4
C8—N2—H2A	118.6 (17)	C1—C6—C5	118.15 (17)
N3—N2—H2A	118.5 (16)	C1—C6—C7	122.80 (17)
C7—N3—N2	113.97 (16)	C5—C6—C7	119.03 (17)
C3—O1—H1A	109 (2)	N3—C7—C6	123.38 (18)
C6—C1—C2	120.85 (19)	N3—C7—H7A	118.3
C6—C1—H1C	119.6	C6—C7—H7A	118.3
C2—C1—H1C	119.6	N1—C8—N2	117.64 (17)
C3—C2—C1	119.95 (19)	N1—C8—S1	124.30 (15)
C3—C2—H2B	120.0	N2—C8—S1	118.06 (15)
C1—C2—H2B	120.0	N1—C9—H9A	109.5
O1—C3—C4	117.05 (18)	N1—C9—H9B	109.5
O1—C3—C2	122.90 (19)	H9A—C9—H9B	109.5
C4—C3—C2	120.04 (18)	N1—C9—H9C	109.5
C3—C4—C5	119.78 (18)	H9A—C9—H9C	109.5
C3—C4—H4A	120.1	H9B—C9—H9C	109.5
C8—N2—N3—C7	−179.80 (18)	C4—C5—C6—C1	0.7 (3)
C6—C1—C2—C3	−0.2 (4)	C4—C5—C6—C7	−177.60 (18)
C1—C2—C3—O1	−177.4 (2)	N2—N3—C7—C6	−177.01 (17)
C1—C2—C3—C4	1.2 (4)	C1—C6—C7—N3	3.7 (3)
O1—C3—C4—C5	177.5 (2)	C5—C6—C7—N3	−178.03 (18)
C2—C3—C4—C5	−1.2 (3)	C9—N1—C8—N2	−177.4 (2)
C3—C4—C5—C6	0.2 (3)	C9—N1—C8—S1	2.6 (3)

C2—C1—C6—C5	−0.7 (3)	N3—N2—C8—N1	5.9 (3)
C2—C1—C6—C7	177.5 (2)	N3—N2—C8—S1	−174.09 (14)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···S1^{i}	0.82 (2)	2.41 (2)	3.220 (2)	171 (3)
N1—H1*B*···N3	0.86 (2)	2.27 (2)	2.681 (2)	109 (2)
N1—H1*B*···O1^{ii}	0.86 (2)	2.47 (2)	3.018 (3)	123 (2)
N2—H2*A*···S1^{iii}	0.87 (2)	2.62 (1)	3.4177 (19)	154 (2)

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