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1-[(*E*)-(3-Hydroxy-4-methoxybenzylidene)amino]-3-methylthiourea

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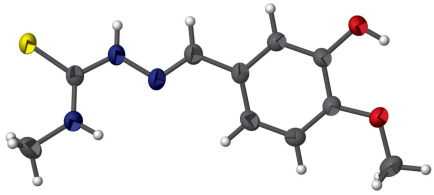
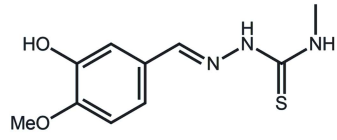
Structural data: full structural data are available from iucrdata.iucr.org

In the title thiosemicarbazone Schiff base compound, $C_{10}H_{13}N_3O_2S$, the dihedral angle between the benzene ring and methyl carbothioamide side arm was found to be 17.4 (4)°. The presence of two intramolecular hydrogen bonds is noted, namely hydroxy-O—$H\cdots O$(methoxy) and amine-N—$H\cdots N$(imine). In the crystal, pairwise amine-N—H$\cdots$S hydrogen bonds give rise to centrosymmetric $\{\cdots HNCS\}_2$ synthons, which lead to dimeric aggregates.

3D view



Chemical scheme



Structure description

The molecule of the title compound (Fig. 1) is not completely planar, as indicated by the dihedral angle of 17.4 (4)° between the benzene ring and carbothioamide side chain. The crystal packing is reinforced by pairwise N—H$\cdots$S hydrogen bonds, which connect molecules into dimeric aggregates, Fig. 2 and Table 1.

Similar structures of carbothioamide Schiff base compounds have been reported (Qasem Ali *et al.*, 2012; Tayamon *et al.*, 2012; Li, 2010; Shankara *et al.*, 2013; Adam *et al.*, 2015; de Oliveira *et al.*, 2015). These molecules can coordinate metals in neutral and deprotonated forms, leading to biologically active species (Zhang *et al.*, 2011).

Synthesis and crystallization

3-Hydroxy-4-methoxybenzaldehyde (0.761 g, 5 mmol) was dissolved in methanol (20 ml). Then, glacial acetic acid (0.2 ml) was added, followed by refluxing for 30 min. Separately, *N*-methylhydrazinecarbothioamide (0.526 g, 5 mmol) was dissolved in methanol (15 ml) and the solution was added dropwise with stirring to the aldehyde solution. The resulting colourless solution was refluxed for 4 h. The product was filtered and dried under reduced pressure overnight and washed with a mixture of methanol and *n*-hexane (1:3).

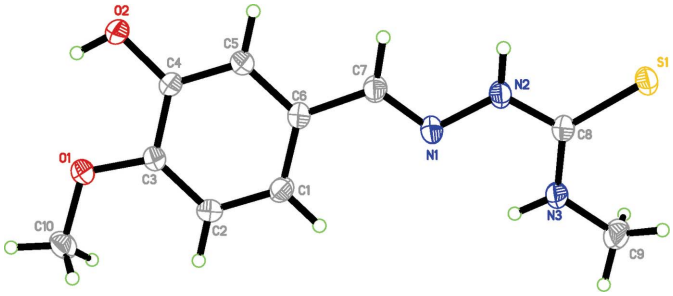


Figure 1
The molecular structure of the title compound, showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level. The intramolecular O—H···O hydrogen bond should be shown

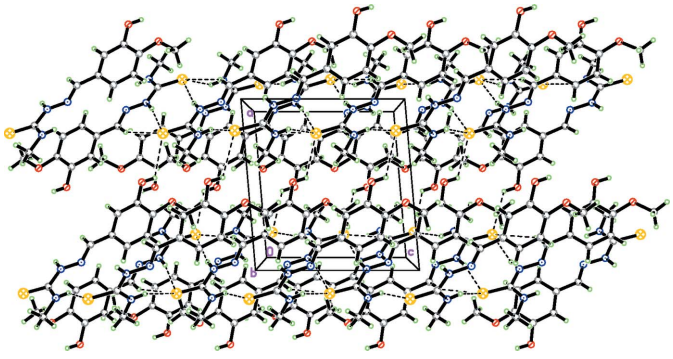


Figure 2
The packing of the title compound viewed along the *b* axis. Hydrogen bonds are shown as dashed lines.

The recovered product was recrystallized from methanol solution to yield colourless crystals suitable for X-ray diffraction. Yield: 95%; M.p: 512–513 K.

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
O2—H1*O2*···O1	0.85 (3)	2.18 (3)	2.6564 (19)	115 (2)
N3—H1*N3*···N1	0.847 (19)	2.32 (2)	2.682 (2)	106.1 (16)
N2—H1*N2*···S1^{i}	0.86 (2)	2.63 (2)	3.4753 (16)	167.8 (16)
N3—H1*N3*···S1^{ii}	0.847 (19)	2.85 (2)	3.4839 (16)	133.5 (17)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{10}H_{13}N_3O_2S$
M_r	239.29
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	9.4893 (13), 13.5903 (19), 9.0554 (12)
β (°)	94.896 (2)
V (Å^3)	1163.5 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.27
Crystal size (mm)	0.41 × 0.27 × 0.18
Data collection	
Diffractometer	Bruker APEXII CCD
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25305, 3429, 2573
R_{int}	0.045
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.707
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.121, 1.06
No. of reflections	3429
No. of parameters	159
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, −0.25

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXS97* and *SHELXTL* (Sheldrick 2008) and *SHELXL2014* (Sheldrick, 2015).

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full crystallographic data

IUCrData (2016). **1**, x161599 [https://doi.org/10.1107/S2414314616015996]

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Crystal data

$C_{10}H_{13}N_3O_2S$
M_r = 239.29
Monoclinic, $P2_1/c$
a = 9.4893 (13) Å
b = 13.5903 (19) Å
c = 9.0554 (12) Å
β = 94.896 (2)°
V = 1163.5 (3) Å^3
Z = 4
$F(000)$ = 504
D_x = 1.366 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5445 reflections
θ = 2.6–27.0°
μ = 0.27 mm^{-1}
T = 100 K
Block, colourless
0.41 × 0.27 × 0.18 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
25305 measured reflections
3429 independent reflections
2573 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 30.2°, θ_{min} = 2.2°
h = −13→13
k = −19→19
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.121
S = 1.06
3429 reflections
159 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 0.4456P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 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	−0.17921 (5)	0.60009 (3)	−0.56327 (4)	0.04224 (14)
O1	0.39288 (13)	0.61470 (9)	0.46152 (13)	0.0438 (3)

O2	0.51572 (14)	0.51474 (12)	0.25548 (15)	0.0540 (4)
N1	0.01610 (15)	0.61303 (10)	−0.16455 (14)	0.0362 (3)
N2	−0.02765 (16)	0.58746 (11)	−0.30889 (16)	0.0392 (3)
N3	−0.19422 (16)	0.70885 (11)	−0.32064 (17)	0.0419 (3)
C1	0.11997 (17)	0.63490 (12)	0.14732 (18)	0.0375 (3)
H1A	0.0295	0.6629	0.1217	0.045*
C2	0.18498 (18)	0.64841 (12)	0.28869 (18)	0.0380 (4)
H2A	0.1391	0.6854	0.3596	0.046*
C3	0.31735 (17)	0.60775 (11)	0.32641 (16)	0.0334 (3)
C4	0.38462 (17)	0.55389 (12)	0.22168 (17)	0.0352 (3)
C5	0.31840 (17)	0.53995 (12)	0.08188 (17)	0.0359 (3)
H5A	0.3636	0.5021	0.0114	0.043*
C6	0.18565 (16)	0.58084 (11)	0.04272 (17)	0.0328 (3)
C7	0.12370 (18)	0.56569 (12)	−0.10845 (18)	0.0369 (3)
H7A	0.1655	0.5182	−0.1681	0.044*
C8	−0.13334 (16)	0.63533 (11)	−0.38644 (17)	0.0334 (3)
C9	−0.3040 (2)	0.77017 (18)	−0.3935 (3)	0.0679 (7)
H9A	−0.3534	0.8053	−0.3187	0.102*
H9B	−0.3715	0.7289	−0.4534	0.102*
H9C	−0.2615	0.8179	−0.4576	0.102*
C10	0.3315 (2)	0.66986 (15)	0.57408 (19)	0.0497 (5)
H10A	0.3935	0.6667	0.6662	0.075*
H10B	0.2389	0.6421	0.5907	0.075*
H10C	0.3201	0.7386	0.5425	0.075*
H1N2	0.013 (2)	0.5400 (15)	−0.352 (2)	0.046 (5)*
H1N3	−0.162 (2)	0.7251 (16)	−0.234 (2)	0.051 (6)*
H1O2	0.542 (3)	0.5280 (18)	0.345 (3)	0.069 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0469 (3)	0.0460 (2)	0.0318 (2)	0.00772 (18)	−0.00814 (17)	−0.00491 (16)
O1	0.0449 (7)	0.0545 (7)	0.0308 (6)	0.0104 (6)	−0.0032 (5)	−0.0084 (5)
O2	0.0429 (7)	0.0768 (10)	0.0400 (7)	0.0263 (7)	−0.0101 (6)	−0.0146 (6)
N1	0.0384 (7)	0.0378 (7)	0.0310 (6)	−0.0014 (5)	−0.0052 (5)	−0.0004 (5)
N2	0.0431 (8)	0.0402 (7)	0.0325 (7)	0.0075 (6)	−0.0081 (6)	−0.0037 (6)
N3	0.0404 (8)	0.0465 (8)	0.0370 (7)	0.0071 (6)	−0.0071 (6)	−0.0097 (6)
C1	0.0308 (8)	0.0407 (8)	0.0408 (8)	0.0046 (6)	0.0014 (6)	0.0026 (7)
C2	0.0373 (8)	0.0417 (8)	0.0357 (8)	0.0057 (7)	0.0064 (6)	−0.0027 (6)
C3	0.0350 (8)	0.0360 (8)	0.0289 (7)	0.0010 (6)	0.0004 (6)	−0.0009 (6)
C4	0.0314 (8)	0.0395 (8)	0.0340 (8)	0.0063 (6)	−0.0008 (6)	−0.0013 (6)
C5	0.0373 (8)	0.0381 (8)	0.0319 (7)	0.0047 (6)	0.0005 (6)	−0.0040 (6)
C6	0.0328 (8)	0.0324 (7)	0.0324 (7)	−0.0019 (6)	−0.0021 (6)	0.0023 (6)
C7	0.0388 (8)	0.0358 (8)	0.0349 (8)	0.0014 (6)	−0.0032 (6)	−0.0012 (6)
C8	0.0323 (8)	0.0337 (7)	0.0333 (7)	−0.0029 (6)	−0.0024 (6)	0.0011 (6)
C9	0.0590 (13)	0.0712 (14)	0.0689 (14)	0.0316 (11)	−0.0215 (11)	−0.0248 (11)
C10	0.0649 (12)	0.0499 (10)	0.0345 (8)	0.0086 (9)	0.0041 (8)	−0.0075 (7)

Geometric parameters (Å, º)

S1—C8	1.6923 (16)	C2—C3	1.388 (2)
O1—C3	1.3675 (18)	C2—H2A	0.9500
O1—C10	1.429 (2)	C3—C4	1.395 (2)
O2—C4	1.3636 (19)	C4—C5	1.377 (2)
O2—H1O2	0.85 (2)	C5—C6	1.395 (2)
N1—C7	1.275 (2)	C5—H5A	0.9500
N1—N2	1.3816 (18)	C6—C7	1.458 (2)
N2—C8	1.342 (2)	C7—H7A	0.9500
N2—H1N2	0.86 (2)	C9—H9A	0.9800
N3—C8	1.321 (2)	C9—H9B	0.9800
N3—C9	1.448 (2)	C9—H9C	0.9800
N3—H1N3	0.85 (2)	C10—H10A	0.9800
C1—C2	1.385 (2)	C10—H10B	0.9800
C1—C6	1.388 (2)	C10—H10C	0.9800
C1—H1A	0.9500		
C3—O1—C10	117.40 (13)	C6—C5—H5A	119.7
C4—O2—H1O2	108.9 (17)	C1—C6—C5	119.07 (14)
C7—N1—N2	114.56 (14)	C1—C6—C7	123.17 (14)
C8—N2—N1	121.58 (14)	C5—C6—C7	117.75 (14)
C8—N2—H1N2	118.1 (13)	N1—C7—C6	123.22 (15)
N1—N2—H1N2	120.3 (13)	N1—C7—H7A	118.4
C8—N3—C9	123.71 (15)	C6—C7—H7A	118.4
C8—N3—H1N3	118.7 (14)	N3—C8—N2	117.80 (14)
C9—N3—H1N3	117.3 (14)	N3—C8—S1	123.62 (12)
C2—C1—C6	120.69 (15)	N2—C8—S1	118.57 (13)
C2—C1—H1A	119.7	N3—C9—H9A	109.5
C6—C1—H1A	119.7	N3—C9—H9B	109.5
C1—C2—C3	119.80 (15)	H9A—C9—H9B	109.5
C1—C2—H2A	120.1	N3—C9—H9C	109.5
C3—C2—H2A	120.1	H9A—C9—H9C	109.5
O1—C3—C2	125.93 (14)	H9B—C9—H9C	109.5
O1—C3—C4	114.16 (14)	O1—C10—H10A	109.5
C2—C3—C4	119.91 (14)	O1—C10—H10B	109.5
O2—C4—C5	119.24 (14)	H10A—C10—H10B	109.5
O2—C4—C3	120.91 (14)	O1—C10—H10C	109.5
C5—C4—C3	119.85 (14)	H10A—C10—H10C	109.5
C4—C5—C6	120.67 (14)	H10B—C10—H10C	109.5
C4—C5—H5A	119.7		
C7—N1—N2—C8	−175.40 (16)	C2—C1—C6—C5	0.1 (2)
C6—C1—C2—C3	0.1 (3)	C2—C1—C6—C7	−178.82 (15)
C10—O1—C3—C2	−0.9 (2)	C4—C5—C6—C1	−0.8 (2)
C10—O1—C3—C4	179.23 (15)	C4—C5—C6—C7	178.14 (15)
C1—C2—C3—O1	−179.53 (15)	N2—N1—C7—C6	−179.36 (15)
C1—C2—C3—C4	0.3 (3)	C1—C6—C7—N1	11.6 (3)

O1—C3—C4—O2	−1.3 (2)	C5—C6—C7—N1	−167.35 (16)
C2—C3—C4—O2	178.84 (16)	C9—N3—C8—N2	176.56 (19)
O1—C3—C4—C5	178.83 (15)	C9—N3—C8—S1	−2.2 (3)
C2—C3—C4—C5	−1.0 (2)	N1—N2—C8—N3	0.5 (2)
O2—C4—C5—C6	−178.58 (15)	N1—N2—C8—S1	179.36 (12)
C3—C4—C5—C6	1.3 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1*O*2···O1	0.85 (3)	2.18 (3)	2.6564 (19)	115 (2)
N3—H1*N*3···N1	0.847 (19)	2.32 (2)	2.682 (2)	106.1 (16)
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N3—H1*N*3···S1^{ii}	0.847 (19)	2.85 (2)	3.4839 (16)	133.5 (17)

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