Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(*E*)-2-Hydroxy-3-methoxybenzaldehyde thiosemicarbazone

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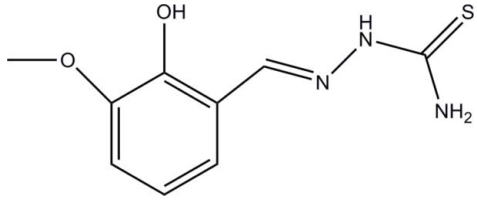
Received 6 May 2008; accepted 14 May 2008

Key indicators: single-crystal X-ray study; T = 273 K; mean σ(C–C) = 0.006 Å; R factor = 0.060; wR factor = 0.163; data-to-parameter ratio = 13.6.

In the title compound, $C_9H_{11}N_3O_2S$, intramolecular O—H···O and N—H···N hydrogen bonds contribute to the planarity of the molecular skeleton. Intermolecular N—H···O hydrogen bonds link the molecules into zigzag chains along the b axis; these molecules are futher paired by π–π interactions [centroid–centroid distance 4.495 (5) Å]. The crystal structure also exhibits weak intermolecular N—H···S and O—H···S hydrogen bonds.

Related literature

For related crystal structures, see: Joseph *et al.* (2006). For biological activities of thiosemicarbazone Schiff bases, see: Kasuga *et al.* (2001); Fonari *et al.* (2003).



Experimental

Crystal data

$C_9H_{11}N_3O_2S$
M_r = 225.27
Monoclinic, $P2_1/c$
a = 7.057 (3) Å
b = 14.673 (5) Å
c = 10.738 (4) Å
β = 108.412 (7)°
V = 1055.0 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.29 mm^{-1}
T = 273 (2) K
0.15 × 0.12 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.958, T_{max} = 0.972
5510 measured reflections
1872 independent reflections
1023 reflections with $I > 2\sigma(I)$
R_{int} = 0.071

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.163
S = 1.10
1872 reflections
138 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2	0.82	2.14	2.610 (4)	116
N3—H3A···N1	0.86	2.23	2.592 (5)	105
O1—H1···S1^{ii}	0.82	2.69	3.290 (3)	131
N2—H2···S1^{iii}	0.86	2.62	3.470 (4)	172
N3—H3B···O1^{iv}	0.86	2.28	2.943 (4)	134

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The authors thank the Postgraduate Foundation of Taishan University for financial support (grant No. Y06–2-12).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2411).

References

Fonari, M. S., Simonov, Y. A., Kravtsov, V. C., Lipkowski, J., Ganin, E. V. & Yavolovskii, A. A. (2003). *J. Mol. Struct.* **647**, 129–140.
Joseph, M., Kuriakose, M., Kurup, M. R. P., Suresh, E., Kishore, A. & Bhat, S. G. (2006). *Polyhedron*, **25**, 61–70.
Kasuga, N. C., Sekino, K., Koumo, C., Shimada, N., Ishikawa, M. & Nomiya, K. (2001). *J. Inorg. Biochem.* **84**, 55–65.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

supporting information

Acta Cryst. (2008). E**64**, o1113 [doi:10.1107/S1600536808014475]

(*E*)-2-Hydroxy-3-methoxybenzaldehyde thiosemicarbazone

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S1. Comment

Thiosemicarbazone Schiff-bases have been investigated in terms of their chemistry and potentially beneficial biological activities, such as antitumor, antibacterial, antiviral and antimalarial activities (Kasuga *et al.*, 2001; Fonari *et al.*, 2003). In continuation of our studies on thiosemicarbazone Schiff-bases, we report the synthesis and crystal structure of the title compound, (I).

In (I) (Fig. 1), all bond lengths and angles are normal and in a good agreement with those found in the literature (Joseph *et al.*, 2006). The intramolecular O—H···O and N—H···N hydrogen bonds (Table 2) contribute to the planarity of molecular skeleton. The intermolecular N—H···O hydrogen bonds (Table 2) link the molecules into zigzag chains along *b* axis, which are futher paired by $\pi\cdots\pi$ interactions proved by short intermolecular C···C distances (Table 1). The crystal packing exhibits also weak intermolecular N—H···S and O—H···S hydrogen bonds (Table 2).

S2. Experimental

The title compound was synthesized by the reaction of 2-hydroxy-3-methoxybenzaldehyde (0.152 g, 1 mmol) and hydrazinecarbothioamide (0.091 g, 1 mmol) in ethanol solution and stirred under reflux conditions (353 K) for 6 h. When cooled to the room temperature, the solution was filtered off and after a week orange crystals suitable for X-ray diffraction study were obtained. Yield, 0.199 g, 82%. m.p. 358–360 K.

Analysis found: C 47.94, H 4.95, N 18.62%; $C_9H_{11}N_3O_2S$ requires: C 47.99, H 4.92, N 18.65%.

S3. Refinement

The H-atoms were geometrically positioned (C-H 0.93-0.96 Å, N-H 0.86 Å, O-H 0.82 Å), and refined as riding on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C-aromatic and N) and U_{iso}(H) = 1.5U_{eq}(*C*-methyl and O).

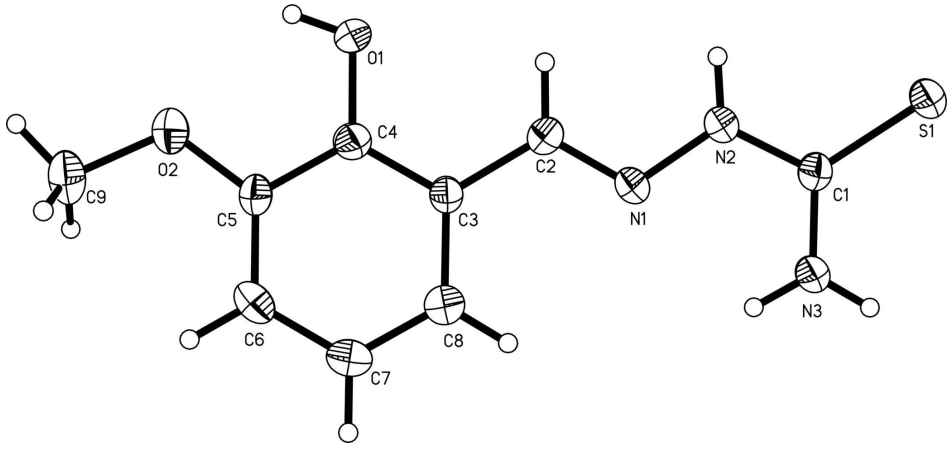

Figure 1

The molecular structure of (I) showing the atomic numbering and 30% probability displacement ellipsoids.

(*E*)-2-Hydroxy-3-methoxybenzaldehyde thiosemicarbazone

Crystal data

$C_9H_{11}N_3O_2S$
$M_r = 225.27$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 7.057$ (3) Å
$b = 14.673$ (5) Å
$c = 10.738$ (4) Å
$\beta = 108.412$ (7)°
$V = 1055.0$ (7) Å^3
$Z = 4$
$F(000) = 472$
$D_x = 1.418$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 511 reflections
$\theta = 2.4$–19.8°
$\mu = 0.29$ mm^{-1}
$T = 273$ K
Block, orange
0.15 × 0.12 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.958$, $T_{max} = 0.972$
5510 measured reflections
1872 independent reflections
1023 reflections with $I > 2\sigma(I)$
$R_{int} = 0.071$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.4°$
$h = -8\rightarrow6$
$k = -17\rightarrow17$
$l = -9\rightarrow12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.163$
$S = 1.10$
1872 reflections
138 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
$w = 1/[\sigma^2(F_o^2) + (0.0641P)^2 + 0.0089P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.005 (2)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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 $F^2 > \sigma(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	1.0171 (2)	0.35387 (8)	0.55909 (10)	0.0534 (5)
O1	0.8111 (5)	0.65121 (18)	−0.0190 (3)	0.0600 (10)
H1	0.7915	0.6940	−0.0706	0.090*
O2	0.6495 (5)	0.6610 (2)	−0.2733 (3)	0.0637 (10)
N1	0.8421 (5)	0.4185 (2)	0.1879 (3)	0.0423 (10)
N2	0.9111 (5)	0.4247 (2)	0.3218 (3)	0.0464 (10)
H2	0.9351	0.4771	0.3595	0.056*
N3	0.9079 (6)	0.2710 (2)	0.3278 (3)	0.0583 (12)
H3A	0.8692	0.2716	0.2434	0.070*
H3B	0.9248	0.2199	0.3692	0.070*
C1	0.9411 (7)	0.3481 (3)	0.3936 (4)	0.0425 (11)
C2	0.8215 (7)	0.4935 (3)	0.1257 (4)	0.0442 (12)
H2A	0.8580	0.5480	0.1712	0.053*
C3	0.7403 (6)	0.4938 (3)	−0.0173 (4)	0.0383 (11)
C4	0.7340 (7)	0.5738 (3)	−0.0851 (4)	0.0410 (11)
C5	0.6465 (7)	0.5770 (3)	−0.2212 (4)	0.0443 (12)
C6	0.5703 (8)	0.4995 (3)	−0.2877 (4)	0.0556 (14)
H6	0.5123	0.5011	−0.3784	0.067*
C7	0.5789 (8)	0.4183 (3)	−0.2207 (4)	0.0625 (15)
H7	0.5275	0.3655	−0.2669	0.075*
C8	0.6621 (7)	0.4148 (3)	−0.0874 (4)	0.0552 (14)
H8	0.6667	0.3599	−0.0434	0.066*
C9	0.5673 (8)	0.6720 (3)	−0.4120 (4)	0.0628 (15)
H9A	0.6335	0.6316	−0.4551	0.094*
H9B	0.5859	0.7339	−0.4351	0.094*
H9C	0.4272	0.6582	−0.4392	0.094*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0790 (10)	0.0454 (7)	0.0340 (6)	0.0035 (7)	0.0154 (6)	0.0006 (5)
O1	0.100 (3)	0.0310 (16)	0.0406 (17)	−0.0114 (18)	0.0107 (17)	−0.0004 (14)
O2	0.092 (3)	0.054 (2)	0.0415 (19)	−0.0039 (19)	0.0147 (17)	0.0101 (15)
N1	0.055 (3)	0.041 (2)	0.0303 (19)	0.0000 (18)	0.0133 (17)	−0.0019 (16)
N2	0.068 (3)	0.038 (2)	0.032 (2)	0.000 (2)	0.0133 (18)	−0.0004 (16)
N3	0.098 (4)	0.039 (2)	0.032 (2)	−0.001 (2)	0.012 (2)	0.0005 (16)

C1	0.053 (3)	0.037 (2)	0.036 (2)	0.003 (2)	0.012 (2)	0.005 (2)
C2	0.056 (4)	0.035 (2)	0.042 (2)	0.000 (2)	0.016 (2)	0.0029 (19)
C3	0.046 (3)	0.036 (3)	0.032 (2)	0.004 (2)	0.011 (2)	0.0028 (18)
C4	0.043 (3)	0.038 (3)	0.040 (2)	0.003 (2)	0.012 (2)	−0.001 (2)
C5	0.056 (3)	0.042 (3)	0.035 (2)	0.001 (2)	0.014 (2)	0.008 (2)
C6	0.069 (4)	0.061 (3)	0.033 (3)	−0.004 (3)	0.010 (2)	−0.006 (2)
C7	0.087 (4)	0.045 (3)	0.049 (3)	−0.006 (3)	0.013 (3)	−0.011 (2)
C8	0.074 (4)	0.043 (3)	0.045 (3)	−0.003 (3)	0.013 (2)	−0.001 (2)
C9	0.063 (4)	0.074 (3)	0.047 (3)	0.004 (3)	0.011 (2)	0.017 (2)

Geometric parameters (Å, º)

S1—C1	1.688 (4)	C2—H2A	0.9300
O1—C4	1.358 (4)	C3—C4	1.375 (5)
O1—H1	0.8200	C3—C8	1.396 (5)
O2—C5	1.357 (5)	C4—C5	1.397 (5)
O2—C9	1.426 (5)	C5—C6	1.360 (6)
N1—C2	1.271 (5)	C6—C7	1.382 (6)
N1—N2	1.367 (4)	C6—H6	0.9300
N2—C1	1.342 (5)	C7—C8	1.365 (6)
N2—H2	0.8600	C7—H7	0.9300
N3—C1	1.315 (5)	C8—H8	0.9300
N3—H3A	0.8600	C9—H9A	0.9600
N3—H3B	0.8600	C9—H9B	0.9600
C2—C3	1.460 (5)	C9—H9C	0.9600
C1···C9^{i}	3.425 (7)	C2···C4^{i}	3.445 (7)
C4—O1—H1	109.5	C3—C4—C5	120.8 (4)
C5—O2—C9	118.7 (3)	O2—C5—C6	126.7 (4)
C2—N1—N2	116.0 (3)	O2—C5—C4	113.7 (4)
C1—N2—N1	119.2 (3)	C6—C5—C4	119.5 (4)
C1—N2—H2	120.4	C5—C6—C7	120.1 (4)
N1—N2—H2	120.4	C5—C6—H6	119.9
C1—N3—H3A	120.0	C7—C6—H6	119.9
C1—N3—H3B	120.0	C8—C7—C6	120.8 (4)
H3A—N3—H3B	120.0	C8—C7—H7	119.6
N3—C1—N2	116.3 (4)	C6—C7—H7	119.6
N3—C1—S1	123.5 (3)	C7—C8—C3	120.0 (4)
N2—C1—S1	120.2 (3)	C7—C8—H8	120.0
N1—C2—C3	119.8 (4)	C3—C8—H8	120.0
N1—C2—H2A	120.1	O2—C9—H9A	109.5
C3—C2—H2A	120.1	O2—C9—H9B	109.5
C4—C3—C8	118.8 (4)	H9A—C9—H9B	109.5
C4—C3—C2	119.7 (4)	O2—C9—H9C	109.5
C8—C3—C2	121.4 (4)	H9A—C9—H9C	109.5
O1—C4—C3	119.8 (4)	H9B—C9—H9C	109.5
O1—C4—C5	119.4 (4)		

C2—N1—N2—C1	−178.4 (4)	C9—O2—C5—C4	178.9 (4)
N1—N2—C1—N3	2.5 (6)	O1—C4—C5—O2	0.0 (7)
N1—N2—C1—S1	−177.5 (3)	C3—C4—C5—O2	179.1 (4)
N2—N1—C2—C3	−177.3 (4)	O1—C4—C5—C6	179.6 (4)
N1—C2—C3—C4	−174.4 (4)	C3—C4—C5—C6	−1.3 (7)
N1—C2—C3—C8	7.7 (7)	O2—C5—C6—C7	179.7 (5)
C8—C3—C4—O1	−179.3 (4)	C4—C5—C6—C7	0.2 (8)
C2—C3—C4—O1	2.8 (7)	C5—C6—C7—C8	0.5 (9)
C8—C3—C4—C5	1.7 (7)	C6—C7—C8—C3	−0.2 (8)
C2—C3—C4—C5	−176.3 (4)	C4—C3—C8—C7	−0.9 (7)
C9—O2—C5—C6	−0.6 (7)	C2—C3—C8—C7	177.0 (5)

Symmetry code: (i) −*x*+2, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.82	2.14	2.610 (4)	116
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