organic compounds

(E)-3,4-Dihydroxybenzaldehyde 4-methylthiosemicarbazone

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The title compound, $C_9H_{11}N_3O_2S$, adopts an E configuration with respect to the C=N bond. The molecule is approximately planar, with an r.m.s. deviation from the mean plane through all 15 non-H atoms of 0.152 Å; the dihedral angle between the benzene ring plane and the least-squares plane through the thiosemicarbazone unit is 12.48 (7)°. A weak intramolecular N—H···N interaction contributes to the planarity of the semicarbazone unit. Centrosymmetric pairs of O—H···O and N—H···S hydrogen bonds form chains along c, generating $R_2^2(10)$ and $R_2^2(8)$ ring motifs, respectively. In the crystal structure, these chains are further linked by intermolecular O—H···S and C—H···O interactions, forming stacks down the c axis.

Related literature

For the biological activity of thiosemicarbazones, see: de Sousa *et al.* (2007). For related structures, see: Kayed *et al.* (2008); Tan *et al.* (2008a,b). For hydrogen-bonding patterns, see: Bernstein *et al.* (1995). For reference structural data, see: Allen *et al.* (1987).
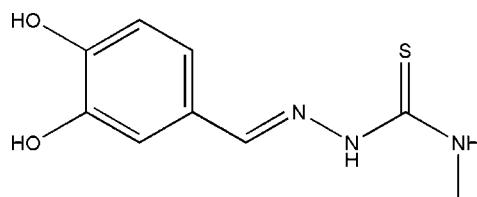
Experimental

Crystal data

$C_9H_{11}N_3O_2S$
$M_r = 225.27$
Monoclinic, $P2_1/n$
$a = 6.8502$ (9) Å

$b = 14.911$ (2) Å
$c = 10.6299$ (13) Å
$\beta = 107.894$ (6)°
$V = 1033.3$ (2) Å^3

$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.30$ mm^{-1}

$T = 92$ (2) K
$0.23 \times 0.15 \times 0.13$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)
$T_{min} = 0.799$, $T_{max} = 0.962$

17952 measured reflections
3696 independent reflections
2974 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.112$
$S = 1.07$
3696 reflections
149 parameters
4 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3N···N1	0.879 (9)	2.220 (18)	2.6282 (17)	108.0 (14)
O3—H3···O4^i	0.837 (9)	2.070 (14)	2.8071 (14)	146.5 (19)
O4—H4···S1^{ii}	0.836 (9)	2.369 (10)	3.1899 (11)	167.1 (19)
N2—H2N···S1^{iii}	0.876 (9)	2.785 (12)	3.5766 (13)	150.9 (15)
C9—H9A···O4^{iv}	0.98	2.56	3.435 (2)	148

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2* and *SAINT* (Bruker 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *TITAN* (Hunter & Simpson, 1999); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*, *enCIFer* (Allen *et al.*, 2004), *PLATON* (Spek, 2003) and *publCIF* (Westrip, 2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2112).

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supporting information

(*E*)-3,4-Dihydroxybenzaldehyde 4-methylthiosemicarbazone

Yang Farina and Jim Simpson

S1. Comment

Thiosemicarbazones are a class of compounds that have been extensively investigated because of their biological activity (de Sousa *et al.*, 2007). As a continuation of our work on thiosemicarbazone compounds as potential ligands in transition metal chemistry (Kayed *et al.*, 2008; Tan *et al.*, 2008*a*,*b*) we report here the structure of the title compound, (I).

The molecule of (I) (Fig. 1) is approximately planar with a dihedral angle of 12.48 (7)° between the phenyl ring plane and the least squares plane through the C7/N1/N2/C8/S2/N3 thiosemicarbazone moiety. The planarity of this section of the molecule is aided by a weak intramolecular N3—H3N···N1 interaction. The molecule adopts an *E* configuration with respect to the C=N bond and bond distances are normal (Allen *et al.*, 1987).

Pairs of O3—H3···O4 hydrogen bonds generate a centrosymmetric $R^2_2(10)$ ring motif (Bernstein *et al.*, 1995) and, together with the $R^2_2(8)$ ring generated by N2—H2N···S1 interactions, form an unusual molecular trimer. The crystal structure is further stabilized by O4—H4···S1 and C9—H9A···O4 contacts, Table 1, Fig. 2.

S2. Experimental

A 1:1 mixture of 3,4-dihydroxybenzaldehyde and N-methylhydrazinecarbothioamide was heated under reflux in ethanol for 2 hours. The solid product which separated upon cooling was filtered and recrystallised from methanol to afford colourless blocks of (I) in 54% yield (m.p. 418-419 K).

S3. Refinement

The H atoms bound to N and O atoms were located in a difference electron density map and refined freely with $U_{iso} = 1.2U_{eq}$ (N) and $U_{iso} = 1.5U_{eq}$ (O). All other H-atoms were refined using a riding model with d(C—H) = 0.95 Å, $U_{iso} = 1.2U_{eq}$ (C) for aryl and 0.98 Å, $U_{iso} = 1.5U_{eq}$ (C) for methyl H atoms.
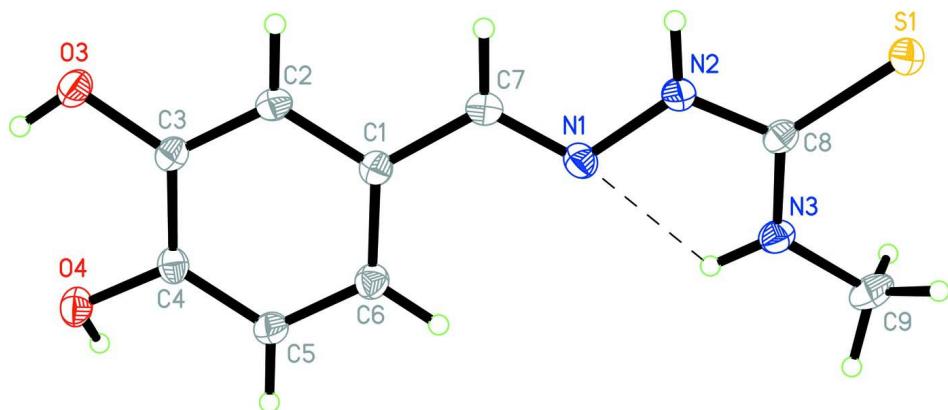
Figure 1

The structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms. An intramolecular hydrogen bond is drawn as a dashed line.
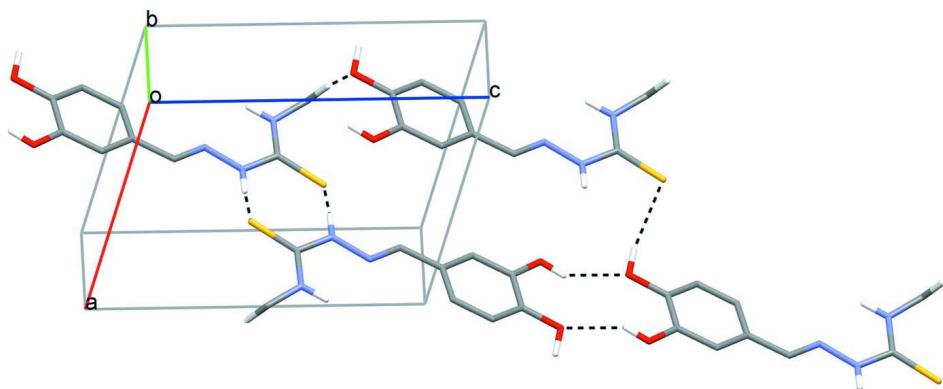
Figure 2

Crystal packing of (I) viewed down the *c* axis with hydrogen bonds drawn as dashed lines. H-atoms not involved in H-bonding have been excluded.

(*E*)-3,4-Dihydroxybenzaldehyde 4-methylthiosemicarbazone

Crystal data

$C_9H_{11}N_3O_2S$	$F(000) = 472$
$M_r = 225.27$	$D_x = 1.448$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 3847 reflections
$a = 6.8502$ (9) Å	$\theta = 2.4$–29.8°
$b = 14.911$ (2) Å	$\mu = 0.30$ mm^{-1}
$c = 10.6299$ (13) Å	$T = 92$ K
$\beta = 107.894$ (6)°	Plate, colourless
$V = 1033.3$ (2) Å^3	$0.23 \times 0.15 \times 0.13$ mm
$Z = 4$	

Data collection

Bruker APEXII CCD area-detector diffractometer	ω scans
Radiation source: fine-focus sealed tube	Absorption correction: multi-scan (*SADABS*; Bruker, 2006)
Graphite monochromator	$T_{min} = 0.799$, $T_{max} = 0.962$

17952 measured reflections
3696 independent reflections
2974 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$

$\theta_{max} = 33.0°$, $\theta_{min} = 3.4°$
$h = -10 \rightarrow 10$
$k = -22 \rightarrow 18$
$l = -16 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.112$
$S = 1.07$
3696 reflections
149 parameters
4 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 0.5756P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.2002 (2)	0.06919 (9)	−0.01216 (13)	0.0157 (2)
C2	0.2338 (2)	0.00229 (9)	−0.09567 (13)	0.0165 (2)
H2	0.3237	−0.0460	−0.0590	0.020*
C3	0.1378 (2)	0.00557 (9)	−0.23119 (13)	0.0160 (2)
O3	0.17512 (16)	−0.06151 (7)	−0.30786 (10)	0.0213 (2)
H3	0.110 (3)	−0.0532 (14)	−0.3876 (10)	0.032*
C4	0.0039 (2)	0.07616 (9)	−0.28381 (13)	0.0166 (2)
O4	−0.09897 (16)	0.07447 (7)	−0.41779 (10)	0.0206 (2)
H4	−0.2160 (18)	0.0940 (13)	−0.424 (2)	0.031*
C5	−0.0247 (2)	0.14471 (9)	−0.20207 (13)	0.0183 (3)
H5	−0.1111	0.1940	−0.2392	0.022*
C6	0.0727 (2)	0.14133 (10)	−0.06654 (14)	0.0180 (3)
H6	0.0523	0.1881	−0.0111	0.022*
C7	0.2988 (2)	0.05936 (9)	0.13036 (13)	0.0168 (2)
H7	0.3900	0.0107	0.1623	0.020*
N1	0.26441 (18)	0.11527 (8)	0.21297 (11)	0.0174 (2)
N2	0.36894 (18)	0.09854 (8)	0.34422 (11)	0.0182 (2)
H2N	0.456 (2)	0.0539 (9)	0.3669 (17)	0.022*
C8	0.3229 (2)	0.14654 (9)	0.43924 (13)	0.0163 (2)
S1	0.46023 (5)	0.12889 (2)	0.60055 (3)	0.01943 (10)

N3	0.17327 (18)	0.20621 (8)	0.39921 (12)	0.0188 (2)
H3N	0.107 (3)	0.2075 (12)	0.3142 (10)	0.023*
C9	0.1019 (2)	0.26414 (10)	0.48622 (16)	0.0259 (3)
H9A	0.0204	0.2289	0.5298	0.039*
H9B	0.0171	0.3123	0.4343	0.039*
H9C	0.2202	0.2902	0.5532	0.039*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0148 (5)	0.0165 (6)	0.0166 (5)	−0.0009 (5)	0.0061 (4)	−0.0004 (5)
C2	0.0158 (6)	0.0143 (6)	0.0202 (6)	0.0002 (5)	0.0067 (5)	0.0006 (5)
C3	0.0160 (6)	0.0148 (6)	0.0182 (6)	−0.0020 (5)	0.0067 (5)	−0.0019 (5)
O3	0.0239 (5)	0.0197 (5)	0.0194 (5)	0.0032 (4)	0.0055 (4)	−0.0040 (4)
C4	0.0149 (5)	0.0199 (6)	0.0153 (5)	−0.0006 (5)	0.0052 (4)	−0.0007 (5)
O4	0.0190 (5)	0.0258 (5)	0.0164 (4)	0.0032 (4)	0.0044 (4)	−0.0027 (4)
C5	0.0189 (6)	0.0172 (6)	0.0184 (6)	0.0031 (5)	0.0052 (5)	0.0000 (5)
C6	0.0172 (6)	0.0188 (6)	0.0182 (6)	0.0013 (5)	0.0058 (5)	−0.0009 (5)
C7	0.0157 (6)	0.0158 (6)	0.0187 (6)	0.0002 (5)	0.0050 (5)	0.0016 (5)
N1	0.0163 (5)	0.0198 (6)	0.0152 (5)	0.0012 (4)	0.0037 (4)	0.0011 (4)
N2	0.0200 (5)	0.0181 (6)	0.0160 (5)	0.0049 (4)	0.0050 (4)	0.0005 (4)
C8	0.0165 (6)	0.0141 (6)	0.0193 (6)	−0.0018 (5)	0.0072 (5)	−0.0010 (5)
S1	0.02201 (17)	0.01991 (18)	0.01649 (16)	0.00247 (12)	0.00609 (12)	−0.00049 (12)
N3	0.0184 (5)	0.0162 (5)	0.0214 (5)	0.0019 (4)	0.0056 (4)	−0.0010 (4)
C9	0.0277 (7)	0.0185 (7)	0.0348 (8)	0.0044 (6)	0.0148 (6)	−0.0034 (6)

Geometric parameters (Å, º)

C1—C6	1.3943 (19)	C6—H6	0.9500
C1—C2	1.4006 (18)	C7—N1	1.2841 (18)
C1—C7	1.4642 (18)	C7—H7	0.9500
C2—C3	1.3886 (18)	N1—N2	1.3812 (15)
C2—H2	0.9500	N2—C8	1.3518 (17)
C3—O3	1.3632 (16)	N2—H2N	0.876 (9)
C3—C4	1.3952 (19)	C8—N3	1.3251 (18)
O3—H3	0.837 (9)	C8—S1	1.7038 (14)
C4—O4	1.3815 (16)	N3—C9	1.4556 (18)
C4—C5	1.3937 (19)	N3—H3N	0.879 (9)
O4—H4	0.836 (9)	C9—H9A	0.9800
C5—C6	1.3901 (19)	C9—H9B	0.9800
C5—H5	0.9500	C9—H9C	0.9800
C6—C1—C2	119.39 (12)	N1—C7—C1	121.28 (12)
C6—C1—C7	122.50 (12)	N1—C7—H7	119.4
C2—C1—C7	118.10 (12)	C1—C7—H7	119.4
C3—C2—C1	120.98 (12)	C7—N1—N2	115.24 (12)
C3—C2—H2	119.5	C8—N2—N1	119.45 (11)
C1—C2—H2	119.5	C8—N2—H2N	119.4 (12)

O3—C3—C2	118.57 (12)	N1—N2—H2N	120.9 (12)
O3—C3—C4	122.33 (12)	N3—C8—N2	116.78 (12)
C2—C3—C4	119.08 (12)	N3—C8—S1	124.08 (11)
C3—O3—H3	111.0 (14)	N2—C8—S1	119.13 (10)
O4—C4—C5	122.08 (12)	C8—N3—C9	124.91 (13)
O4—C4—C3	117.63 (12)	C8—N3—H3N	116.8 (12)
C5—C4—C3	120.28 (12)	C9—N3—H3N	118.1 (12)
C4—O4—H4	104.4 (14)	N3—C9—H9A	109.5
C6—C5—C4	120.34 (13)	N3—C9—H9B	109.5
C6—C5—H5	119.8	H9A—C9—H9B	109.5
C4—C5—H5	119.8	N3—C9—H9C	109.5
C5—C6—C1	119.83 (13)	H9A—C9—H9C	109.5
C5—C6—H6	120.1	H9B—C9—H9C	109.5
C1—C6—H6	120.1		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*N*···N1	0.88 (1)	2.22 (2)	2.6282 (17)	108 (1)
O3—H3···O4ⁱ	0.84 (1)	2.07 (1)	2.8071 (14)	147 (2)
O4—H4···S1ⁱⁱ	0.84 (1)	2.37 (1)	3.1899 (11)	167 (2)
N2—H2*N*···S1ⁱⁱⁱ	0.88 (1)	2.79 (1)	3.5766 (13)	151 (2)
C9—H9*A*···O4ⁱᵛ	0.98	2.56	3.435 (2)	148

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