

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

 Yang Farina^{a*} and Jim Simpson^b

^aSchool of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia, and ^bDepartment of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand

Correspondence e-mail: farina@pkriscr.cc.ukm.my

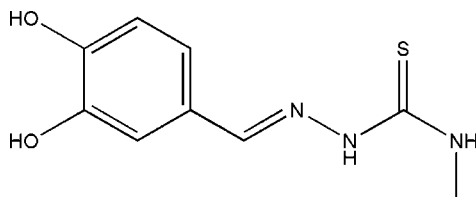
Received 9 October 2008; accepted 21 October 2008

 Key indicators: single-crystal X-ray study; $T = 92$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.045; wR factor = 0.112; data-to-parameter ratio = 24.8.

The title compound, $\text{C}_9\text{H}_{11}\text{N}_3\text{O}_2\text{S}$, adopts an *E* configuration with respect to the $\text{C}=\text{N}$ 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 $12.48(7)^\circ$. A weak intramolecular $\text{N}-\text{H}\cdots\text{N}$ interaction contributes to the planarity of the semicarbazone unit. Centrosymmetric pairs of $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{S}$ 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 $\text{O}-\text{H}\cdots\text{S}$ and $\text{C}-\text{H}\cdots\text{O}$ 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.* (2008*a,b*). For hydrogen-bonding patterns, see: Bernstein *et al.* (1995). For reference structural data, see: Allen *et al.* (1987).



Experimental

Crystal data

$\text{C}_9\text{H}_{11}\text{N}_3\text{O}_2\text{S}$
 $M_r = 225.27$
 Monoclinic, $P2_1/n$
 $a = 6.8502(9)$ Å

$b = 14.911(2)$ Å
 $c = 10.6299(13)$ Å
 $\beta = 107.894(6)^\circ$
 $V = 1033.3(2)$ Å³

$Z = 4$
 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 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$

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
 $\Delta\rho_{\text{max}} = 0.49$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.32$ e Å⁻³

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N3}-\text{H3N}\cdots\text{N1}$	0.879 (9)	2.220 (18)	2.6282 (17)	108.0 (14)
$\text{O3}-\text{H3}\cdots\text{O4}^i$	0.837 (9)	2.070 (14)	2.8071 (14)	146.5 (19)
$\text{O4}-\text{H4}\cdots\text{S1}^{ii}$	0.836 (9)	2.369 (10)	3.1899 (11)	167.1 (19)
$\text{N2}-\text{H2N}\cdots\text{S1}^{iii}$	0.876 (9)	2.785 (12)	3.5766 (13)	150.9 (15)
$\text{C9}-\text{H9A}\cdots\text{O4}^{iv}$	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).

We thank the Universiti Kebangsaan Malaysia and the Ministry of Higher Education, Malaysia, for supporting this research through grants UKM-ST-01-FRGS0022-2006 and UKM-GUP-NBT-08-27-112 and Mr M. A. I. Yim for preparing the title compound. We also thank the University of Otago for purchase of the diffractometer.

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

References

- Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
 Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
 Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Bruker (2006). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Hunter, K. A. & Simpson, J. (1999). TITAN2000. University of Otago, New Zealand.
 Kayed, S. F., Farina, Y., Baba, I. & Simpson, J. (2008). *Acta Cryst. E* **64**, o824–o825.

- 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.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sousa, G. F. de, Manso, L. C. C., Lang, E. S., Gatto, C. C. & Mahieu, B. (2007). *J. Mol. Struct.* **826**, 185–191.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Tan, K. W., Farina, Y., Ng, C. H., Maah, M. J. & Ng, S. W. (2008a). *Acta Cryst.* **E64**, o1035.
- Tan, K. W., Farina, Y., Ng, C. H., Maah, M. J. & Ng, S. W. (2008b). *Acta Cryst.* **E64**, o1073.
- Westrip, S. P. (2008). *publCIF*. In preparation.

supplementary materials

Acta Cryst. (2008). E64, o2184-o2185 [doi:10.1107/S1600536808034326]

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

Y. Farina and J. Simpson

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.

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).

Refinement

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

Figures

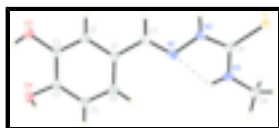


Fig. 1. The structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms. An intramolecular hydrogen bond is drawn as a dashed line.

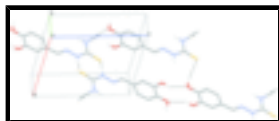


Fig. 2. Crystal packing of (I) viewed down the *c* axis with hydrogen bonds drawn as dashed lines. H-atoms not involved in H-bonding have been excluded.

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

Crystal data

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

Data collection

Bruker APEXII CCD area-detector diffractometer	3696 independent reflections
Radiation source: fine-focus sealed tube	2974 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.044$
$T = 92(2) \text{ K}$	$\theta_{\text{max}} = 33.0^\circ$
ω scans	$\theta_{\text{min}} = 3.4^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2006)	$h = -10 \rightarrow 10$
$T_{\text{min}} = 0.799$, $T_{\text{max}} = 0.962$	$k = -22 \rightarrow 18$
17952 measured reflections	$l = -16 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.045$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.112$	$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 0.5756P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
3696 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
149 parameters	$\Delta\rho_{\text{max}} = 0.49 \text{ e \AA}^{-3}$
4 restraints	$\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (\AA^2)

	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)

supplementary materials

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 (\AA , $^\circ$)

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, °)

<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>
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) $x, y, z+1$.

Fig. 1

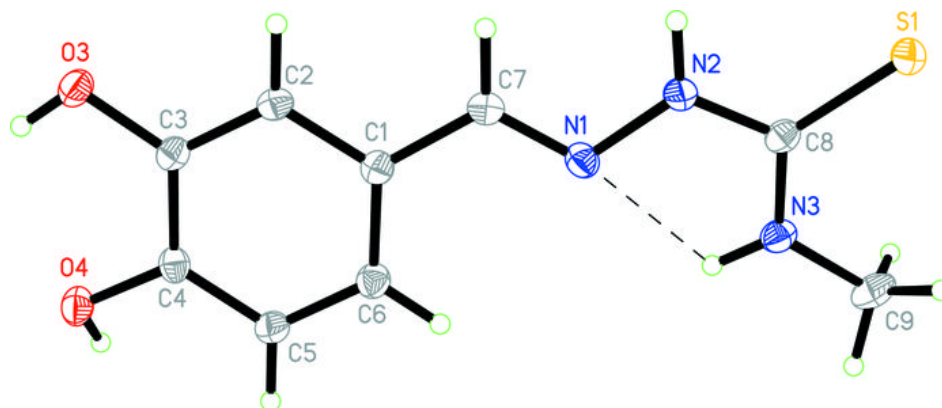


Fig. 2

