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3,4-Dihydroxybenzaldehyde 4-phenyl-thiosemicarbazone

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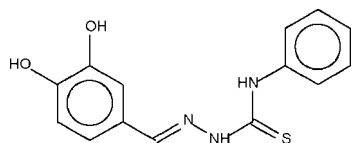
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.045; wR factor = 0.115; data-to-parameter ratio = 15.9.

Molecules of the title compound, $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2\text{S}$, are linked by intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds into centrosymmetric dimers forming $R_2^2(4)$ rings which are further linked by $\text{O}-\text{H}\cdots\text{S}$ hydrogen bonds and weaker $\text{N}-\text{H}\cdots\text{S}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds to form a three-dimensional network.

Related literature

For the structure of 2,3-dihydroxybenzaldehyde thiosemicarbazone hemihydrate, see: Swesi *et al.* (2006). For metal derivatives of the title compound, see: Zhu *et al.* (1997). The graph-set notation is given by Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2\text{S}$
 $M_r = 287.33$
 Monoclinic, $P2_1/c$
 $a = 9.7261$ (2) Å
 $b = 13.1863$ (3) Å
 $c = 10.7732$ (3) Å
 $\beta = 99.055$ (2)°

$V = 1364.46$ (6) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.24$ mm⁻¹
 $T = 100$ (2) K
 $0.40 \times 0.30 \times 0.20$ mm

Data collection

Bruker SMART APEX
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.909$, $T_{\max} = 0.953$

16724 measured reflections
 3132 independent reflections
 2358 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.078$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.115$
 $S = 1.04$
 3132 reflections
 197 parameters
 4 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.40$ e Å⁻³
 $\Delta\rho_{\min} = -0.32$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1}o\cdots\text{O2}^i$	0.85 (1)	2.03 (2)	2.737 (2)	141 (2)
$\text{O2}-\text{H2}o\cdots\text{S1}^{ii}$	0.85 (1)	2.34 (1)	3.134 (1)	156 (2)
$\text{N2}-\text{H2}n\cdots\text{S1}^{iii}$	0.85 (1)	2.73 (1)	3.487 (2)	150 (2)
$\text{N2}-\text{H2}n\cdots\text{O1}^{iv}$	0.85 (1)	2.56 (2)	3.022 (2)	115 (2)

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: X-SEED (Barbour, 2001); software used to prepare material for publication: publCIF (Westrip, 2008).

We thank the University of Malaya (P0265/2007 A) for supporting this study; KWT thanks the Ministry of Higher Education for an SLAI scholarship in this research.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2625).

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supplementary materials

Acta Cryst. (2008). E64, o1035 [doi:10.1107/S1600536808013287]

3,4-Dihydroxybenzaldehyde 4-phenylthiosemicarbazone

K. W. Tan, Y. Farina, C. H. Ng, M. J. Maah and S. W. Ng

Comment

A previous study of the Schiff bases derived by condensing substituted benzaldehydes with 4-phenylthiosemicarbazides reported the 2,3-dihydroxy compound, which crystallizes as a hemihydrate. The compound features extensive hydrogen bond (Swesi *et al.*, 2006). In the title 3,4-dihydroxy isomer the 4-hydroxy group functions as hydrogen-bond donor to the 3-hydroxy group of a symmetry-related molecule forming $R_2^2(4)$ rings (Bernstein *et al.*, 1995). In addition, the 3-hydroxy group is a donor to the sulfur atom of another molecule; the hydrogen bonding arrangement furnishes a three-dimensional network motif. The amino groups are involved in weaker hydrogen bond interactions.

Further work will investigate the formation of metal derivatives of the ligand; some metal complexes have been reported by others but these have not characterized by crystallography yet (Zhu *et al.*, 1997).

Experimental

4-Phenylthiosemicarbazide (0.17 g, 1 mmol) and 3,4-dihydroxybenzaldehyde (0.14 g, 1 mmol) were heated in ethanol (20 ml) for 3 h. Slow evaporation of the solvent yielded yellow crystals.

Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.95 Å) and were included in the refinement in the riding model approximation, with $U_{\text{iso}}(\text{H})$ set to 1.2 $U_{\text{eq}}(\text{C})$. The hydroxy and amino H-atoms were located in a difference Fourier map, and were refined with a distance restraint of O—H = N—H = 0.85±0.01 Å; their temperature factors were similarly tied.

Figures

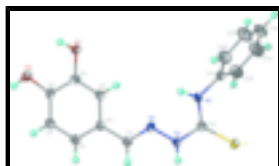


Fig. 1. Thermal ellipsoid (Barbour, 2001) plot of $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2\text{S}$ at the 70% probability level. Hydrogen atoms are drawn as spheres of arbitrary radii.

3,4-Dihydroxybenzaldehyde 4-phenylthiosemicarbazone

Crystal data

$\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2\text{S}$

$M_r = 287.33$

Monoclinic, $P2_1/c$

$F_{000} = 600$

$D_x = 1.399 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

supplementary materials

Hall symbol: -P 2ybc

$a = 9.7261$ (2) Å

$b = 13.1863$ (3) Å

$c = 10.7732$ (3) Å

$\beta = 99.055$ (2)°

$V = 1364.46$ (6) Å³

$Z = 4$

Cell parameters from 2291 reflections

$\theta = 2.5$ – 23.4 °

$\mu = 0.24$ mm⁻¹

$T = 100$ (2) K

Block, yellow

$0.40 \times 0.30 \times 0.20$ mm

Data collection

Bruker SMART APEX
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 100$ (2) K

ω scans

Absorption correction: Multi-scan
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.910$, $T_{\max} = 0.953$

16724 measured reflections

3132 independent reflections

2358 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.078$

$\theta_{\max} = 27.5$ °

$\theta_{\min} = 2.1$ °

$h = -12 \rightarrow 12$

$k = -17 \rightarrow 16$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.115$

$S = 1.04$

3132 reflections

197 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

$$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.2883P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.40$ e Å⁻³

$\Delta\rho_{\min} = -0.32$ e Å⁻³

Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	1.08441 (5)	0.12769 (4)	0.40212 (5)	0.02006 (15)
O1	0.65919 (15)	0.45705 (10)	0.89678 (14)	0.0221 (3)
O2	0.40955 (14)	0.39195 (11)	0.94986 (14)	0.0231 (3)
N1	0.83208 (16)	0.18905 (12)	0.63925 (15)	0.0187 (4)
N2	0.90695 (16)	0.13520 (12)	0.56294 (16)	0.0185 (4)
N3	1.03542 (19)	0.27810 (13)	0.55853 (18)	0.0258 (4)
C1	0.64419 (19)	0.20682 (14)	0.75172 (18)	0.0172 (4)
C2	0.6914 (2)	0.30261 (14)	0.79586 (18)	0.0177 (4)

H2	0.7798	0.3262	0.7814	0.021*
C3	0.61093 (19)	0.36257 (14)	0.85974 (18)	0.0168 (4)
C4	0.48283 (19)	0.32692 (15)	0.88517 (18)	0.0175 (4)
C5	0.4360 (2)	0.23207 (15)	0.84415 (19)	0.0207 (4)
H5	0.3492	0.2077	0.8620	0.025*
C6	0.5160 (2)	0.17194 (15)	0.77643 (19)	0.0204 (4)
H6	0.4831	0.1071	0.7471	0.024*
C7	0.72652 (19)	0.14733 (15)	0.67561 (19)	0.0190 (4)
H7	0.7022	0.0792	0.6536	0.023*
C8	1.00702 (19)	0.18502 (14)	0.51400 (19)	0.0177 (4)
C9	1.1227 (2)	0.35150 (15)	0.5122 (2)	0.0212 (4)
C10	1.2393 (2)	0.38550 (18)	0.5909 (2)	0.0304 (5)
H10	1.2651	0.3565	0.6719	0.037*
C11	1.3183 (3)	0.4624 (2)	0.5504 (2)	0.0386 (6)
H11	1.3986	0.4863	0.6042	0.046*
C12	1.2821 (2)	0.50451 (18)	0.4336 (2)	0.0339 (6)
H12	1.3366	0.5576	0.4070	0.041*
C13	1.1657 (2)	0.46947 (18)	0.3545 (2)	0.0348 (6)
H13	1.1410	0.4977	0.2729	0.042*
C14	1.0858 (2)	0.39327 (17)	0.3946 (2)	0.0287 (5)
H14	1.0053	0.3696	0.3410	0.034*
H1O	0.602 (2)	0.4875 (17)	0.935 (2)	0.035 (7)*
H2O	0.3276 (14)	0.3698 (18)	0.950 (3)	0.043 (8)*
H2N	0.890 (2)	0.0737 (9)	0.542 (2)	0.036 (7)*
H3N	0.995 (2)	0.2960 (17)	0.6187 (16)	0.027 (6)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0175 (2)	0.0195 (3)	0.0249 (3)	0.00003 (19)	0.00859 (19)	-0.0035 (2)
O1	0.0209 (7)	0.0162 (7)	0.0316 (9)	-0.0015 (6)	0.0116 (6)	-0.0063 (6)
O2	0.0158 (7)	0.0226 (8)	0.0328 (9)	-0.0011 (6)	0.0093 (6)	-0.0075 (6)
N1	0.0181 (8)	0.0188 (9)	0.0207 (9)	0.0021 (7)	0.0081 (7)	-0.0017 (7)
N2	0.0173 (8)	0.0148 (9)	0.0250 (9)	-0.0013 (7)	0.0086 (7)	-0.0043 (7)
N3	0.0313 (10)	0.0202 (9)	0.0310 (11)	-0.0081 (8)	0.0202 (8)	-0.0076 (8)
C1	0.0159 (9)	0.0187 (10)	0.0178 (10)	-0.0003 (7)	0.0048 (8)	-0.0011 (8)
C2	0.0146 (9)	0.0178 (10)	0.0216 (10)	-0.0011 (7)	0.0056 (8)	-0.0001 (8)
C3	0.0169 (9)	0.0148 (10)	0.0184 (10)	-0.0004 (7)	0.0016 (7)	0.0000 (7)
C4	0.0148 (9)	0.0204 (10)	0.0183 (10)	0.0026 (7)	0.0052 (7)	-0.0008 (8)
C5	0.0141 (9)	0.0206 (10)	0.0285 (12)	-0.0020 (8)	0.0064 (8)	-0.0007 (8)
C6	0.0199 (10)	0.0175 (10)	0.0246 (11)	-0.0030 (8)	0.0061 (8)	-0.0026 (8)
C7	0.0185 (10)	0.0168 (10)	0.0223 (11)	-0.0018 (8)	0.0054 (8)	-0.0027 (8)
C8	0.0145 (9)	0.0167 (10)	0.0224 (10)	0.0011 (7)	0.0046 (8)	-0.0002 (8)
C9	0.0204 (10)	0.0170 (10)	0.0287 (12)	-0.0037 (8)	0.0114 (8)	-0.0041 (8)
C10	0.0317 (12)	0.0345 (13)	0.0248 (12)	-0.0058 (10)	0.0034 (9)	0.0012 (10)
C11	0.0328 (13)	0.0442 (15)	0.0381 (15)	-0.0193 (11)	0.0032 (11)	-0.0047 (11)
C12	0.0323 (13)	0.0250 (12)	0.0474 (16)	-0.0093 (10)	0.0155 (11)	0.0037 (11)
C13	0.0336 (13)	0.0312 (13)	0.0396 (15)	0.0016 (10)	0.0059 (11)	0.0148 (11)

supplementary materials

C14 0.0211 (10) 0.0310 (12) 0.0328 (13) -0.0033 (9) 0.0011 (9) 0.0030 (10)

Geometric parameters (Å, °)

S1—C8	1.696 (2)	C3—C4	1.398 (3)
O1—C3	1.368 (2)	C4—C5	1.380 (3)
O1—H1O	0.85 (1)	C5—C6	1.395 (3)
O2—C4	1.373 (2)	C5—H5	0.9500
O2—H2O	0.85 (1)	C6—H6	0.9500
N1—C7	1.279 (2)	C7—H7	0.9500
N1—N2	1.378 (2)	C9—C14	1.376 (3)
N2—C8	1.348 (2)	C9—C10	1.380 (3)
N2—H2N	0.85 (1)	C10—C11	1.383 (3)
N3—C8	1.331 (3)	C10—H10	0.9500
N3—C9	1.428 (3)	C11—C12	1.370 (3)
N3—H3N	0.84 (1)	C11—H11	0.9500
C1—C6	1.393 (3)	C12—C13	1.385 (3)
C1—C2	1.401 (3)	C12—H12	0.9500
C1—C7	1.461 (3)	C13—C14	1.381 (3)
C2—C3	1.372 (3)	C13—H13	0.9500
C2—H2	0.9500	C14—H14	0.9500
C3—O1—H1O	110.7 (17)	C5—C6—H6	119.9
C4—O2—H2O	110.6 (18)	N1—C7—C1	118.55 (17)
C7—N1—N2	119.07 (16)	N1—C7—H7	120.7
C8—N2—N1	117.64 (16)	C1—C7—H7	120.7
C8—N2—H2N	119.3 (17)	N3—C8—N2	115.47 (17)
N1—N2—H2N	123.0 (17)	N3—C8—S1	125.24 (15)
C8—N3—C9	126.89 (17)	N2—C8—S1	119.28 (15)
C8—N3—H3N	116.2 (16)	C14—C9—C10	120.35 (19)
C9—N3—H3N	116.9 (16)	C14—C9—N3	120.67 (19)
C6—C1—C2	119.21 (17)	C10—C9—N3	118.8 (2)
C6—C1—C7	121.05 (18)	C9—C10—C11	119.2 (2)
C2—C1—C7	119.68 (17)	C9—C10—H10	120.4
C3—C2—C1	120.50 (17)	C11—C10—H10	120.4
C3—C2—H2	119.7	C12—C11—C10	120.8 (2)
C1—C2—H2	119.7	C12—C11—H11	119.6
O1—C3—C2	118.33 (17)	C10—C11—H11	119.6
O1—C3—C4	121.62 (17)	C11—C12—C13	119.8 (2)
C2—C3—C4	120.06 (17)	C11—C12—H12	120.1
O2—C4—C5	123.84 (17)	C13—C12—H12	120.1
O2—C4—C3	116.05 (17)	C14—C13—C12	119.7 (2)
C5—C4—C3	120.10 (18)	C14—C13—H13	120.1
C4—C5—C6	119.95 (18)	C12—C13—H13	120.1
C4—C5—H5	120.0	C9—C14—C13	120.1 (2)
C6—C5—H5	120.0	C9—C14—H14	119.9
C1—C6—C5	120.14 (18)	C13—C14—H14	119.9
C1—C6—H6	119.9		
C7—N1—N2—C8	172.24 (18)	C2—C1—C7—N1	-7.8 (3)
C6—C1—C2—C3	-1.7 (3)	C9—N3—C8—N2	-171.35 (19)

C7—C1—C2—C3	175.33 (18)	C9—N3—C8—S1	7.8 (3)
C1—C2—C3—O1	-177.55 (17)	N1—N2—C8—N3	8.7 (3)
C1—C2—C3—C4	2.2 (3)	N1—N2—C8—S1	-170.51 (13)
O1—C3—C4—O2	-0.4 (3)	C8—N3—C9—C14	66.2 (3)
C2—C3—C4—O2	179.82 (17)	C8—N3—C9—C10	-118.6 (2)
O1—C3—C4—C5	178.64 (18)	C14—C9—C10—C11	0.3 (3)
C2—C3—C4—C5	-1.1 (3)	N3—C9—C10—C11	-174.9 (2)
O2—C4—C5—C6	178.51 (18)	C9—C10—C11—C12	-0.2 (4)
C3—C4—C5—C6	-0.5 (3)	C10—C11—C12—C13	-0.5 (4)
C2—C1—C6—C5	0.1 (3)	C11—C12—C13—C14	1.0 (4)
C7—C1—C6—C5	-176.89 (18)	C10—C9—C14—C13	0.1 (3)
C4—C5—C6—C1	1.0 (3)	N3—C9—C14—C13	175.3 (2)
N2—N1—C7—C1	-177.22 (16)	C12—C13—C14—C9	-0.8 (4)
C6—C1—C7—N1	169.23 (19)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H10 \cdots O2 ⁱ	0.85 (1)	2.03 (2)	2.737 (2)	141 (2)
O2—H2O \cdots S1 ⁱⁱ	0.85 (1)	2.34 (1)	3.134 (1)	156 (2)
N2—H2N \cdots S1 ⁱⁱⁱ	0.85 (1)	2.73 (1)	3.487 (2)	150 (2)
N2—H2N \cdots O1 ^{iv}	0.85 (1)	2.56 (2)	3.022 (2)	115 (2)

Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $x-1, -y+1/2, z+1/2$; (iii) $-x+2, -y, -z+1$; (iv) $x, -y+1/2, z-1/2$.

Fig. 1

