Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3,4-Dihydroxybenzaldehyde 4-phenylthiosemicarbazone

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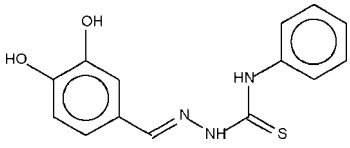
Received 30 April 2008; accepted 6 May 2008

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.045; wR factor = 0.115; data-to-parameter ratio = 15.9.

Molecules of the title compound, $C_{14}H_{13}N_3O_2S$, are linked by intermolecular O—H···O hydrogen bonds into centrosymmetric dimers forming $R_2^2(4)$ rings which are further linked by O—H···S hydrogen bonds and weaker N—H···S and N—H···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

$C_{14}H_{13}N_3O_2S$
M_r = 287.33
Monoclinic, $P2_1/c$
a = 9.7261 (2) Å
b = 13.1863 (3) Å
c = 10.7732 (3) Å
β = 99.055 (2)°
V = 1364.46 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 100 (2) K
0.40 × 0.30 × 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_{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—H···A	D—H	H···A	D···A	D—H···A
O1—H1*o*···O2^{i}	0.85 (1)	2.03 (2)	2.737 (2)	141 (2)
O2—H2*o*···S1^{ii}	0.85 (1)	2.34 (1)	3.134 (1)	156 (2)
N2—H2*n*···S1^{iii}	0.85 (1)	2.73 (1)	3.487 (2)	150 (2)
N2—H2*n*···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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supporting information

Acta Cryst. (2008). E**64**, o1035 [doi:10.1107/S1600536808013287]

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S1. 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 deratives of the ligand; some metal complexes have been reported by others but these have not characterized by crystallography yet (Zhu *et al.*, 1997).

S2. 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.

S3. 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_{iso}(H) set to 1.2 U_{eq}(C). The hydroxy and amino H-atoms were located in a difference Fourier map, and were refined with a distance retraint of O–H = N–H = 0.85±0.01 Å; their temperature factors were similarly tied.

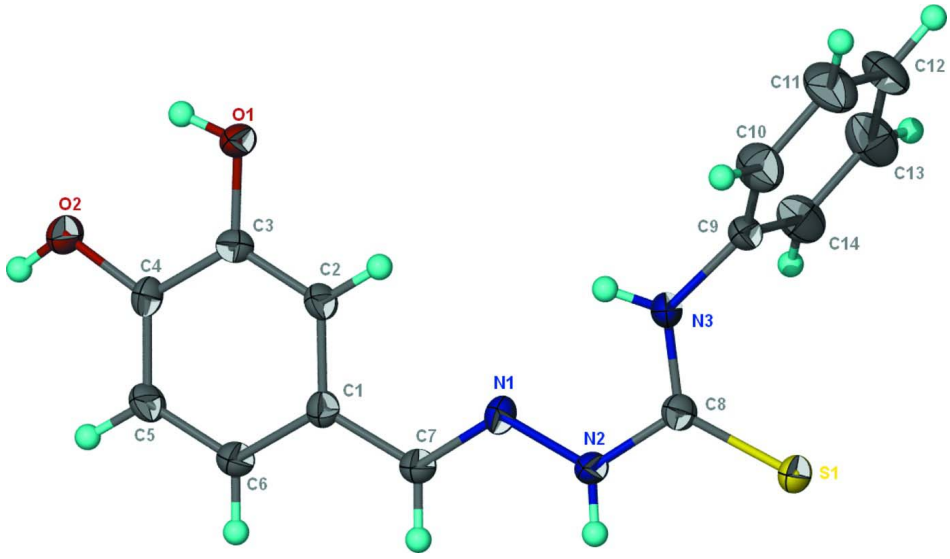

Figure 1

Thermal ellipsoid (Barbour, 2001) plot of $C_{14}H_{13}N_3O_2S$ at the 70% probability level. Hydrogen atoms are drawn as spheres of arbitrary radii.

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Crystal data

$C_{14}H_{13}N_3O_2S$
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Monoclinic, $P2_1/c$
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) Å^3
$Z = 4$
$F(000) = 600$
$D_x = 1.399$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2291 reflections
$\theta = 2.5$–$23.4°$
$\mu = 0.24$ mm^{-1}
$T = 100$ K
Block, yellow
0.40 × 0.30 × 0.20 mm

Data collection

Bruker SMART APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
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 $I > 2\sigma(I)$
$R_{int} = 0.078$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.1°$
$h = -12 \rightarrow 12$
$k = -17 \rightarrow 16$
$l = -13 \rightarrow 13$

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}

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

	x	*y*	*z*	U_{iso}*/U_{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 (Å²)

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

Geometric parameters (Å, º)

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, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···O2^{i}	0.85 (1)	2.03 (2)	2.737 (2)	141 (2)
O2—H2*O*···S1^{ii}	0.85 (1)	2.34 (1)	3.134 (1)	156 (2)
N2—H2*N*···S1^{iii}	0.85 (1)	2.73 (1)	3.487 (2)	150 (2)
N2—H2*N*···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.