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2,5-Dihydroxybenzaldehyde 4-methylthiosemicarbazone

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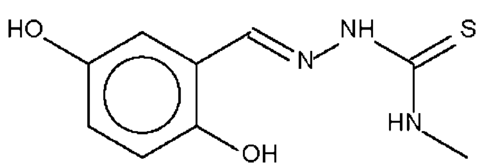
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.055; wR factor = 0.124; data-to-parameter ratio = 14.8.

The planar molecules of the title compound, $C_9H_{11}N_3O_2S$, are linked into a supramolecualr chain *via* O—H···S hydrogen bonds. These chains are connected into a two-dimensional array via N—H···O hydrogen bonds; an intramolecular O—H···N hydrogen bond is also present.

Related literature

For the medicinal activity of 2,5-dihydroxybenzaldehyde thiosemicarbazone, see: Libermann *et al.* (1953); Taniyama & Tanaka (1965); Xue *et al.* (2007). For the structure of 2-hydroxybenzaldehyde 4-methylthiosemicarbazone, see: Vrdoljak *et al.* (2005). For the structure of 3,4-dihydroxybenzaldehyde 4-ethylthiosemicarbazone, see: Kayed *et al.* (2008).



Experimental

Crystal data

$C_9H_{11}N_3O_2S$
M_r = 225.27
Triclinic, $P\bar{1}$
a = 5.9932 (4) Å
b = 8.5207 (6) Å
c = 10.3272 (6) Å
α = 78.552 (4)°
β = 74.181 (4)°
γ = 81.743 (4)°
V = 495.06 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 100 (2) K
0.24 × 0.16 × 0.02 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.929, T_{max} = 0.994
4189 measured reflections
2258 independent reflections
1580 reflections with $I > 2\sigma(I)$
R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.123
S = 1.03
2258 reflections
153 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*o*···N3	0.84 (3)	1.97 (2)	2.698 (3)	144 (3)
O2—H2*o*···S1^{i}	0.84 (3)	2.46 (2)	3.182 (2)	144 (3)
N2—H2*n*···O1^{ii}	0.84 (3)	2.47 (3)	3.111 (3)	134 (3)

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

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).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2278).

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Acta Cryst. (2008). E**64**, o1344 [doi:10.1107/S1600536808018801]

2,5-Dihydroxybenzaldehyde 4-methylthiosemicarbazone

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S1. Comment

The title compound (I, Fig. 1) possesses useful medicinal properties (Libermann *et al.*, 1953; Taniyama & Tanaka, 1965; Xue *et al.*, 2007). The molecules are linked into supramolecular chains by O-H···S hydrogen bonds involving the O2-hydroxy group, Table 1. The hydrogen-bonded chains are consolidated into a layer motif via N-NH···O hydrogen bond, involving the O1-hydroxy group. An intramolecular N-H···O hydrogen bond, also involving the O1-hydroxy group is also noted. In contrast, 2-hydroxybenzaldehyde 4-methylthiosemicarbazone, which features an intramolecular O–H···N hydrogen bond, adopts a chain structure (Vrdoljak *et al.*, 2005) as it lacks a second hydroxy substituent for layer formation.

S2. Experimental

4-Methylthiosemicarbazide (0.11 g, 1 mmol) and 2,5-dihydroxybenzaldehyde (0.14 g, 1 mmol) were heated in ethanol (10 ml) for 1 h. Slow evaporation of the solvent yielded yellow crystals of (I).

S3. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.95 to 0.98 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2-1.5 U_{eq}(C). The hydroxy and amino H-atoms were located in a difference Fourier map, and were refined isotropically with distance restraints of O–H, N–H = 0.85±0.01 Å.

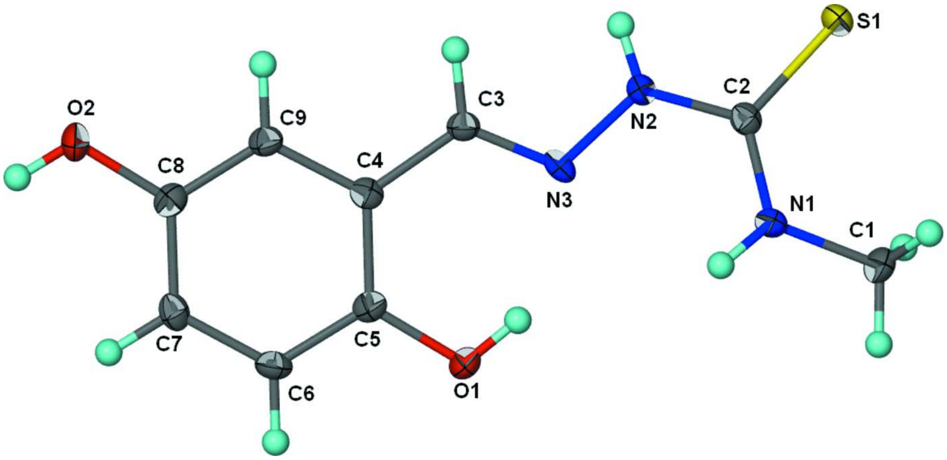

Figure 1

Thermal ellipsoid plot of (I) at the 70% probability level showing atom labeling. Hydrogen atoms are drawn as spheres of arbitrary radii.

2,5-Dihydroxybenzaldehyde 4-methylthiosemicarbazone

Crystal data

$C_9H_{11}N_3O_2S$
M_r = 225.27
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 5.9932 (4) Å
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c = 10.3272 (6) Å
α = 78.552 (4)°
β = 74.181 (4)°
γ = 81.743 (4)°
V = 495.06 (6) Å^3
Z = 2
F(000) = 236
D_x = 1.511 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 558 reflections
θ = 2.9–23.0°
μ = 0.31 mm^{-1}
T = 100 K
Plate, yellow
0.24 × 0.16 × 0.02 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} = 0.929, T_{max} = 0.994
4189 measured reflections
2258 independent reflections
1580 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 27.5°, θ_{min} = 2.5°
h = −7→7
k = −11→8
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.123
S = 1.03
2258 reflections
153 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
$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.44298 (12)	0.47335 (9)	0.72966 (7)	0.0189 (2)
O1	1.3132 (3)	0.8655 (2)	0.47568 (18)	0.0188 (4)
O2	1.2446 (3)	1.1893 (2)	−0.03406 (18)	0.0200 (5)
N1	0.8637 (4)	0.5405 (3)	0.7312 (2)	0.0147 (5)
N2	0.7415 (4)	0.6387 (3)	0.5359 (2)	0.0159 (5)
N3	0.9289 (4)	0.7298 (3)	0.4833 (2)	0.0145 (5)
C1	0.8391 (5)	0.4576 (3)	0.8709 (2)	0.0188 (6)
H1A	0.9802	0.4633	0.8996	0.028*
H1B	0.8160	0.3447	0.8763	0.028*
H1C	0.7044	0.5088	0.9310	0.028*
C2	0.7001 (4)	0.5552 (3)	0.6642 (2)	0.0134 (6)
C3	0.9368 (4)	0.8121 (3)	0.3637 (2)	0.0136 (6)

H3	0.8213	0.8018	0.3194	0.016*
C4	1.1147 (4)	0.9200 (3)	0.2937 (2)	0.0133 (6)
C5	1.2915 (4)	0.9450 (3)	0.3503 (2)	0.0140 (6)
C6	1.4505 (5)	1.0551 (3)	0.2796 (2)	0.0157 (6)
H6	1.5673	1.0745	0.3193	0.019*
C7	1.4389 (5)	1.1372 (3)	0.1504 (3)	0.0153 (6)
H7	1.5496	1.2111	0.1016	0.018*
C8	1.2669 (4)	1.1117 (3)	0.0929 (2)	0.0149 (6)
C9	1.1055 (4)	1.0049 (3)	0.1638 (2)	0.0146 (6)
H9	0.9866	0.9887	0.1243	0.018*
H1o	1.206 (4)	0.805 (3)	0.511 (3)	0.048 (12)*
H2o	1.352 (5)	1.245 (4)	−0.082 (3)	0.059 (13)*
H1n	0.988 (3)	0.581 (4)	0.689 (3)	0.032 (9)*
H2n	0.640 (4)	0.656 (4)	0.491 (3)	0.042 (10)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0149 (4)	0.0241 (4)	0.0175 (3)	−0.0083 (3)	−0.0051 (3)	0.0033 (3)
O1	0.0222 (11)	0.0221 (12)	0.0140 (9)	−0.0081 (9)	−0.0089 (8)	0.0025 (8)
O2	0.0244 (11)	0.0202 (12)	0.0149 (9)	−0.0088 (9)	−0.0059 (8)	0.0047 (8)
N1	0.0114 (12)	0.0181 (13)	0.0148 (11)	−0.0035 (10)	−0.0038 (9)	−0.0007 (9)
N2	0.0153 (12)	0.0168 (13)	0.0158 (11)	−0.0060 (10)	−0.0056 (9)	0.0024 (9)
N3	0.0121 (11)	0.0136 (12)	0.0175 (11)	−0.0050 (9)	−0.0013 (9)	−0.0023 (9)
C1	0.0198 (15)	0.0231 (16)	0.0128 (12)	−0.0048 (12)	−0.0051 (11)	0.0015 (11)
C2	0.0137 (13)	0.0106 (14)	0.0155 (12)	−0.0011 (11)	−0.0032 (10)	−0.0022 (11)
C3	0.0136 (13)	0.0138 (14)	0.0147 (12)	−0.0019 (11)	−0.0053 (10)	−0.0025 (11)
C4	0.0134 (13)	0.0118 (14)	0.0153 (12)	−0.0008 (10)	−0.0034 (10)	−0.0038 (11)
C5	0.0137 (13)	0.0154 (15)	0.0133 (12)	0.0001 (11)	−0.0041 (10)	−0.0034 (11)
C6	0.0139 (13)	0.0162 (15)	0.0193 (13)	−0.0029 (11)	−0.0070 (10)	−0.0039 (11)
C7	0.0163 (14)	0.0102 (14)	0.0178 (13)	−0.0021 (11)	−0.0024 (10)	−0.0006 (11)
C8	0.0160 (14)	0.0144 (15)	0.0143 (12)	0.0006 (11)	−0.0050 (10)	−0.0023 (11)
C9	0.0158 (14)	0.0156 (15)	0.0140 (12)	−0.0021 (11)	−0.0059 (10)	−0.0031 (11)

Geometric parameters (Å, º)

S1—C2	1.695 (3)	C1—H1B	0.9800
O1—C5	1.367 (3)	C1—H1C	0.9800
O1—H1o	0.84 (3)	C3—C4	1.450 (4)
O2—C8	1.379 (3)	C3—H3	0.9500
O2—H2o	0.84 (3)	C4—C5	1.401 (4)
N1—C2	1.325 (3)	C4—C9	1.403 (3)
N1—C1	1.453 (3)	C5—C6	1.388 (4)
N1—H1n	0.84 (3)	C6—C7	1.393 (3)
N2—C2	1.349 (3)	C6—H6	0.9500
N2—N3	1.382 (3)	C7—C8	1.383 (4)
N2—H2n	0.84 (3)	C7—H7	0.9500
N3—C3	1.286 (3)	C8—C9	1.379 (4)

C1—H1A	0.9800	C9—H9	0.9500
C5—O1—H1O	110 (2)	C4—C3—H3	118.6
C8—O2—H2O	117 (3)	C5—C4—C9	118.9 (2)
C2—N1—C1	123.8 (2)	C5—C4—C3	123.2 (2)
C2—N1—H1N	117 (2)	C9—C4—C3	117.9 (2)
C1—N1—H1N	119 (2)	O1—C5—C6	117.7 (2)
C2—N2—N3	121.3 (2)	O1—C5—C4	122.3 (2)
C2—N2—H2N	122 (2)	C6—C5—C4	120.0 (2)
N3—N2—H2N	116 (2)	C5—C6—C7	120.1 (3)
C3—N3—N2	114.5 (2)	C5—C6—H6	120.0
N1—C1—H1A	109.5	C7—C6—H6	120.0
N1—C1—H1B	109.5	C8—C7—C6	120.3 (2)
H1A—C1—H1B	109.5	C8—C7—H7	119.9
N1—C1—H1C	109.5	C6—C7—H7	119.9
H1A—C1—H1C	109.5	O2—C8—C9	116.7 (2)
H1B—C1—H1C	109.5	O2—C8—C7	123.3 (2)
N1—C2—N2	118.2 (2)	C9—C8—C7	119.9 (2)
N1—C2—S1	123.80 (19)	C8—C9—C4	120.8 (2)
N2—C2—S1	118.0 (2)	C8—C9—H9	119.6
N3—C3—C4	122.7 (2)	C4—C9—H9	119.6
N3—C3—H3	118.6		
C2—N2—N3—C3	−175.1 (2)	C3—C4—C5—C6	−177.4 (2)
C1—N1—C2—N2	178.3 (2)	O1—C5—C6—C7	178.8 (2)
C1—N1—C2—S1	−2.5 (4)	C4—C5—C6—C7	−2.0 (4)
N3—N2—C2—N1	−11.0 (4)	C5—C6—C7—C8	1.1 (4)
N3—N2—C2—S1	169.69 (19)	C6—C7—C8—O2	179.7 (2)
N2—N3—C3—C4	177.5 (2)	C6—C7—C8—C9	0.2 (4)
N3—C3—C4—C5	−0.6 (4)	O2—C8—C9—C4	179.8 (2)
N3—C3—C4—C9	−179.5 (2)	C7—C8—C9—C4	−0.7 (4)
C9—C4—C5—O1	−179.3 (2)	C5—C4—C9—C8	−0.2 (4)
C3—C4—C5—O1	1.8 (4)	C3—C4—C9—C8	178.8 (2)
C9—C4—C5—C6	1.5 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*o*···N3	0.84 (3)	1.97 (2)	2.698 (3)	144 (3)
O2—H2*o*···S1^{i}	0.84 (3)	2.46 (2)	3.182 (2)	144 (3)
N2—H2*n*···O1^{ii}	0.84 (3)	2.47 (3)	3.111 (3)	134 (3)

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