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2,4-Dihydroxybenzaldehyde 4-methylthiosemicarbazone

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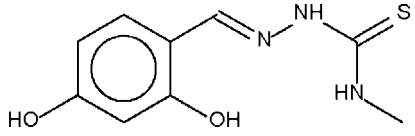
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.004 Å; R factor = 0.038; wR factor = 0.109; data-to-parameter ratio = 13.9.

The approximately planar molecule of the title compound, $C_9H_{11}N_3O_2S$, is linked to adjacent molecules by O—H···S hydrogen bonds to form a zigzag chain. Adjacent chains are consolidated by N—H···O hydrogen bonds into a two-dimensional array. An intramolecular O—H···N link is also present.

Related literature

For the structure of isomeric 2,5-dihydroxybenzaldehyde 4-methylthiosemicarbazone, see: Tan *et al.* (2008).



Experimental

Crystal data

$C_9H_{11}N_3O_2S$
M_r = 225.27
Monoclinic, *Cc*
a = 18.0046 (6) Å
b = 4.6436 (1) Å
c = 12.2842 (4) Å
β = 106.695 (2)°
V = 983.74 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 100 (2) K
0.09 × 0.06 × 0.03 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.973, T_{max} = 0.991
4390 measured reflections
2128 independent reflections
1925 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.109
S = 1.11
2128 reflections
153 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Absolute structure: Flack (1983), with 814 Friedel pairs
Flack parameter: 0.00 (1)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···N1	0.84 (1)	1.93 (3)	2.694 (3)	151 (6)
O2—H2O···S1^{i}	0.84 (1)	2.54 (1)	3.365 (2)	170 (4)
N2—H2N···O1^{ii}	0.87 (1)	2.11 (1)	2.950 (4)	162 (3)

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

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).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2316).

References

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supporting information

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2,4-Dihydroxybenzaldehyde 4-methylthiosemicarbazone

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S1. Comment

In continuation of on-going studies into the structural chemistry of thiosemicarbazones (Tan *et al.*, 2008), the title compound (I) was investigated. Molecule (I), Fig. 1, is essentially planar and is consolidated into a 2-D array by a combination of N-H···O and O-H···S hydrogen bonding contacts, Table 1.

S2. Experimental

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

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 with distance retraints of O–H = 0.84±0.01 and N–H = 0.88±0.01 Å; their temperature factors were freely refined.

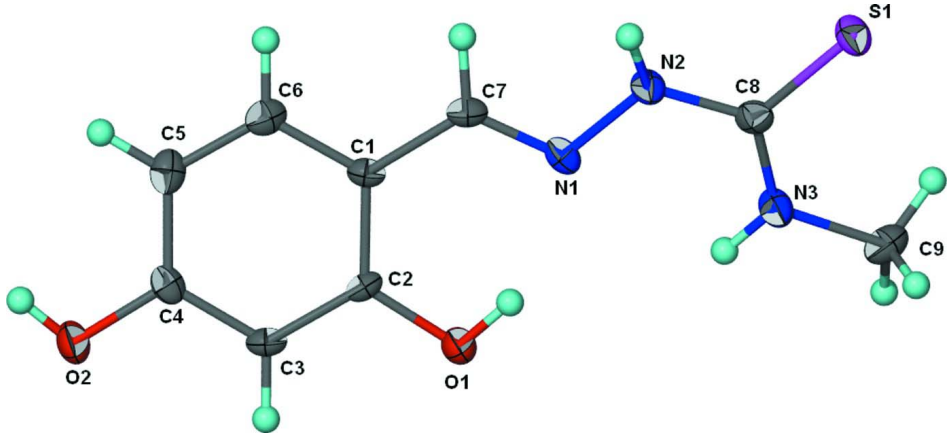

Figure 1

Thermal ellipsoid (Barbour, 2001) plot of (I) drawn at the 70% probability level. Hydrogen atoms are drawn as spheres of arbitrary radii.

2,4-Dihydroxybenzaldehyde 4-methylthiosemicarbazone

Crystal data

$C_9H_{11}N_3O_2S$
M_r = 225.27

Monoclinic, *Cc*
Hall symbol: C -2yc

a = 18.0046 (6) Å
b = 4.6436 (1) Å
c = 12.2842 (4) Å
β = 106.695 (2)°
V = 983.74 (5) Å^3
Z = 4
F(000) = 472
D_x = 1.521 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1090 reflections
θ = 2.4–24.9°
μ = 0.31 mm^{-1}
T = 100 K
Prims, yellow
0.09 × 0.06 × 0.03 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} = 0.973, T_{max} = 0.991

4390 measured reflections
2128 independent reflections
1925 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 27.5°, θ_{min} = 2.4°
h = −23→22
k = −6→6
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.109
S = 1.11
2128 reflections
153 parameters
6 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
$w = 1/[\sigma^2(F_o^2) + (0.0598P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Absolute structure: Flack (1983), 814 Friedel pairs
Absolute structure parameter: 0.00 (1)

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.

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

	x	y	z	U_{iso}*/U_{eq}
S1	0.50003 (5)	0.63599 (16)	0.50001 (6)	0.01776 (19)
O1	0.65168 (12)	−0.1181 (5)	0.93136 (19)	0.0174 (5)
O2	0.84529 (13)	−0.8242 (5)	1.05294 (19)	0.0198 (5)
N1	0.63927 (15)	0.1424 (5)	0.7309 (2)	0.0144 (5)
N2	0.60440 (15)	0.2962 (6)	0.6322 (2)	0.0147 (5)
N3	0.53164 (15)	0.5567 (6)	0.7241 (2)	0.0166 (6)
C1	0.73692 (17)	−0.2114 (7)	0.8141 (2)	0.0128 (6)
C2	0.71210 (17)	−0.2660 (7)	0.9113 (2)	0.0122 (6)
C3	0.74812 (18)	−0.4725 (7)	0.9891 (3)	0.0141 (6)
H3	0.7300	−0.5117	1.0530	0.017*
C4	0.81112 (16)	−0.6232 (6)	0.9739 (2)	0.0142 (6)

C5	0.83798 (18)	−0.5674 (7)	0.8800 (3)	0.0174 (7)
H5	0.8815	−0.6688	0.8704	0.021*
C6	0.80096 (17)	−0.3645 (7)	0.8017 (3)	0.0159 (7)
H6	0.8192	−0.3274	0.7378	0.019*
C7	0.69685 (17)	−0.0131 (7)	0.7250 (2)	0.0142 (6)
H7	0.7142	0.0020	0.6590	0.017*
C8	0.54711 (17)	0.4887 (7)	0.6279 (3)	0.0149 (6)
C9	0.47552 (19)	0.7743 (8)	0.7317 (3)	0.0206 (7)
H9A	0.4879	0.8460	0.8099	0.031*
H9B	0.4234	0.6899	0.7100	0.031*
H9C	0.4773	0.9340	0.6804	0.031*
H1O	0.633 (3)	−0.017 (11)	0.874 (3)	0.08 (2)*
H2O	0.8796 (19)	−0.909 (8)	1.032 (4)	0.038 (13)*
H2N	0.6097 (19)	0.218 (7)	0.5703 (17)	0.011 (8)*
H3N	0.5552 (19)	0.476 (7)	0.7898 (17)	0.018 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0196 (4)	0.0180 (4)	0.0138 (3)	0.0027 (4)	0.0018 (3)	0.0021 (4)
O1	0.0193 (13)	0.0174 (12)	0.0159 (11)	0.0038 (9)	0.0059 (9)	0.0029 (10)
O2	0.0216 (12)	0.0196 (13)	0.0171 (12)	0.0069 (10)	0.0037 (9)	0.0040 (9)
N1	0.0159 (13)	0.0126 (13)	0.0125 (12)	−0.0018 (11)	0.0008 (10)	0.0013 (10)
N2	0.0176 (13)	0.0163 (13)	0.0097 (13)	0.0024 (11)	0.0030 (10)	−0.0001 (11)
N3	0.0195 (14)	0.0144 (13)	0.0152 (13)	0.0023 (11)	0.0037 (10)	0.0014 (10)
C1	0.0153 (14)	0.0135 (15)	0.0103 (14)	−0.0029 (12)	0.0048 (11)	−0.0005 (12)
C2	0.0105 (14)	0.0147 (15)	0.0129 (15)	−0.0017 (12)	0.0056 (11)	−0.0034 (12)
C3	0.0162 (15)	0.0159 (16)	0.0120 (15)	−0.0032 (12)	0.0069 (12)	−0.0012 (11)
C4	0.0148 (16)	0.0139 (14)	0.0113 (14)	−0.0007 (12)	−0.0006 (12)	0.0000 (12)
C5	0.0155 (16)	0.0163 (16)	0.0180 (17)	0.0012 (12)	0.0010 (12)	−0.0031 (12)
C6	0.0121 (15)	0.0214 (18)	0.0134 (15)	−0.0031 (14)	0.0023 (12)	−0.0033 (13)
C7	0.0157 (16)	0.0164 (16)	0.0117 (15)	−0.0035 (13)	0.0058 (12)	−0.0016 (12)
C8	0.0154 (15)	0.0127 (15)	0.0175 (16)	−0.0031 (12)	0.0064 (12)	0.0002 (12)
C9	0.0169 (16)	0.0266 (19)	0.0201 (17)	0.0003 (13)	0.0079 (13)	−0.0038 (13)

Geometric parameters (Å, º)

S1—C8	1.699 (3)	C1—C2	1.413 (4)
O1—C2	1.367 (4)	C1—C7	1.454 (4)
O1—H1O	0.838 (10)	C2—C3	1.378 (4)
O2—C4	1.360 (4)	C3—C4	1.391 (4)
O2—H2O	0.836 (10)	C3—H3	0.9500
N1—C7	1.283 (4)	C4—C5	1.397 (4)
N1—N2	1.392 (3)	C5—C6	1.374 (4)
N2—C8	1.354 (4)	C5—H5	0.9500
N2—H2N	0.871 (10)	C6—H6	0.9500
N3—C8	1.328 (4)	C7—H7	0.9500
N3—C9	1.451 (4)	C9—H9A	0.9800

N3—H3N	0.880 (10)	C9—H9B	0.9800
C1—C6	1.400 (4)	C9—H9C	0.9800
C2—O1—H1O	106 (4)	C3—C4—C5	120.5 (3)
C4—O2—H2O	109 (3)	C6—C5—C4	119.5 (3)
C7—N1—N2	114.1 (3)	C6—C5—H5	120.3
C8—N2—N1	121.4 (3)	C4—C5—H5	120.3
C8—N2—H2N	121 (2)	C5—C6—C1	121.4 (3)
N1—N2—H2N	114 (2)	C5—C6—H6	119.3
C8—N3—C9	123.4 (3)	C1—C6—H6	119.3
C8—N3—H3N	123 (3)	N1—C7—C1	123.2 (3)
C9—N3—H3N	114 (3)	N1—C7—H7	118.4
C6—C1—C2	118.1 (3)	C1—C7—H7	118.4
C6—C1—C7	119.1 (3)	N3—C8—N2	118.3 (3)
C2—C1—C7	122.8 (3)	N3—C8—S1	123.4 (2)
O1—C2—C3	117.7 (3)	N2—C8—S1	118.3 (2)
O1—C2—C1	121.6 (3)	N3—C9—H9A	109.5
C3—C2—C1	120.8 (3)	N3—C9—H9B	109.5
C2—C3—C4	119.8 (3)	H9A—C9—H9B	109.5
C2—C3—H3	120.1	N3—C9—H9C	109.5
C4—C3—H3	120.1	H9A—C9—H9C	109.5
O2—C4—C3	117.9 (3)	H9B—C9—H9C	109.5
O2—C4—C5	121.6 (3)		
C7—N1—N2—C8	−174.4 (3)	C4—C5—C6—C1	0.2 (5)
C6—C1—C2—O1	177.7 (3)	C2—C1—C6—C5	1.4 (4)
C7—C1—C2—O1	−4.9 (4)	C7—C1—C6—C5	−176.0 (3)
C6—C1—C2—C3	−2.5 (4)	N2—N1—C7—C1	−174.0 (3)
C7—C1—C2—C3	174.8 (3)	C6—C1—C7—N1	−177.7 (3)
O1—C2—C3—C4	−178.3 (3)	C2—C1—C7—N1	5.0 (5)
C1—C2—C3—C4	1.9 (5)	C9—N3—C8—N2	175.6 (3)
C2—C3—C4—O2	179.7 (3)	C9—N3—C8—S1	−3.1 (4)
C2—C3—C4—C5	−0.2 (5)	N1—N2—C8—N3	8.8 (4)
O2—C4—C5—C6	179.3 (3)	N1—N2—C8—S1	−172.5 (2)
C3—C4—C5—C6	−0.9 (5)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···N1	0.84 (1)	1.93 (3)	2.694 (3)	151 (6)
O2—H2*O*···S1^{i}	0.84 (1)	2.54 (1)	3.365 (2)	170 (4)
N2—H2*N*···O1^{ii}	0.87 (1)	2.11 (1)	2.950 (4)	162 (3)

Symmetry codes: (i) *x*+1/2, −*y*−1/2, *z*+1/2; (ii) *x*, −*y*, *z*−1/2.