organic compounds

2-Hydroxy-5-nitrobenzaldehyde thio-semicarbazone

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The molecule of the title compound, $C_8H_8N_4O_3S$, is planar. Adjacent molecules are linked through O—H⋯S, N—H⋯S and N—H⋯O hydrogen bonds into a three-dimensional network.

Related literature

For the structure of 2-hydroxybenzaldehyde thiosemicarbazone, see: Chattopadhyay *et al.* (1988).
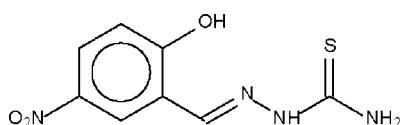
Experimental

Crystal data

$C_8H_8N_4O_3S$
$M_r = 240.24$
Monoclinic, $P2_1/n$
$a = 12.6157$ (3) Å
$b = 5.4815$ (2) Å
$c = 14.2397$ (2) Å
$\beta = 94.039$ (2)°

$V = 982.27$ (5) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.33$ mm^{-1}
$T = 100$ (2) K
$0.49 \times 0.01 \times 0.01$ mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.856$, $T_{max} = 0.997$

9462 measured reflections
2247 independent reflections
1725 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.111$
$S = 1.04$
2247 reflections
161 parameters
8 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯S1[i]	0.84 (1)	2.34 (1)	3.175 (2)	170 (3)
N3—H31⋯S1[ii]	0.85 (1)	2.50 (1)	3.337 (2)	167 (2)
N4—H41⋯O2[iii]	0.85 (1)	2.14 (1)	2.987 (2)	172 (3)
N4—H42⋯O3[iv]	0.85 (1)	2.31 (2)	3.044 (2)	144 (2)

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{5}{2}, z+\frac{1}{2}$; (ii) $-x+1, -y+3, -z+1$; (iii) $-x+\frac{3}{2}, y+\frac{3}{2}, -z+\frac{1}{2}$; (iv) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

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).

References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chattopadhyay, D., Mazumdar, S. K., Banerjee, T., Ghosh, S. & Mak, T. C. W. (1988). *Acta Cryst.* C**44**, 1025–1028.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
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supplementary materials

2-Hydroxy-5-nitrobenzaldehyde thiosemicarbazone

A. A. Alhadi, H. M. Ali, S. Puvaneswary, W. T. Robinson and **S. W. Ng**

Comment

Salicylaldehyde thiosemicarbazone uses its 2-hydroxy group to form an intramolecular hydrogen bond (Chattopadhyay *et al.*, 1988). In the present compound, the electron-withdrawing nitro group that is *para* to the hydroxy group renders the hydroxy group much more acidic, so that the compound (Scheme) is able to use the hydroxy group to form a hydrogen bond to an adjacent molecule instead (Fig. 1).

Experimental

The Schiff base was prepared by refluxing thiosemicarbazide (0.30 g, 3.3 mmol) and 5-nitro-2-hydroxybenzaldehyde (0.55 g, 3.3 mmol) in ethanol for 2 h. The product was recrystallized from ethanol.

Refinement

Nitrogen- and oxygen-bound hydrogen atoms were refined with a distance restraint of N—H and O—H 0.85 (1) Å. Their temperature factors were freely refined. The carbon-bound ones were placed in geometric positions with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures
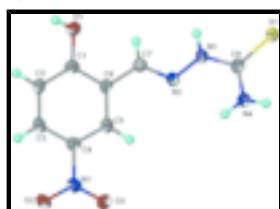
Fig. 1. Molecular structure of title compound with the atom numbering scheme (Barbour, 2001). Displacement ellipsoids are drawn at 50% probability level. H atoms are presented as a small spheres of arbitrary radius.

2-Hydroxy-5-nitrobenzaldehyde thiosemicarbazone

Crystal data

$C_8H_8N_4O_3S$	$F_{000} = 496$
$M_r = 240.24$	$D_x = 1.625$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 2540 reflections
$a = 12.6157$ (3) Å	θ = 2.2–29.5º
$b = 5.4815$ (2) Å	μ = 0.33 mm^{-1}
$c = 14.2397$ (2) Å	$T = 100$ (2) K

β = 94.039 (2)º

V = 982.27 (5) Å^3

Z = 4

Block, yellow

0.49 × 0.01 × 0.01 mm

Data collection

Bruker SMART APEX diffractometer	2247 independent reflections
Radiation source: fine-focus sealed tube	1725 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.037
T = 100(2) K	θ_{max} = 27.5º
ω scans	θ_{min} = 2.1º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −16→15
T_{min} = 0.856, T_{max} = 0.997	k = −5→7
9462 measured reflections	l = −18→18

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.039	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.111	$w = 1/[\sigma^2(F_o^2) + (0.0616P)^2 + 0.4126P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.04	$(\Delta/\sigma)_{max}$ = 0.001
2247 reflections	$\Delta\rho_{max}$ = 0.47 e Å^{-3}
161 parameters	$\Delta\rho_{min}$ = −0.23 e Å^{-3}
8 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}

S1	0.45571 (4)	1.58779 (11)	0.35227 (3)	0.02368 (17)
O1	0.78686 (12)	0.8925 (3)	0.67628 (10)	0.0271 (4)
O2	0.92212 (11)	0.0797 (3)	0.40282 (10)	0.0258 (3)
O3	0.82499 (11)	0.3034 (3)	0.30592 (9)	0.0243 (3)
N1	0.86480 (13)	0.2593 (3)	0.38518 (11)	0.0200 (4)
N2	0.64392 (12)	1.0445 (3)	0.42660 (11)	0.0179 (4)
N3	0.56870 (13)	1.2266 (3)	0.42711 (11)	0.0199 (4)
N4	0.57458 (14)	1.2637 (4)	0.26788 (12)	0.0222 (4)
C1	0.80683 (15)	0.7307 (4)	0.60870 (13)	0.0201 (4)
C2	0.87612 (16)	0.5353 (4)	0.62369 (13)	0.0215 (4)
H2	0.9106	0.5093	0.6843	0.026*
C3	0.89488 (15)	0.3793 (4)	0.55093 (13)	0.0211 (4)
H3	0.9414	0.2440	0.5609	0.025*
C4	0.84439 (15)	0.4236 (4)	0.46231 (13)	0.0185 (4)
C5	0.77372 (15)	0.6132 (4)	0.44565 (13)	0.0180 (4)
H5	0.7398	0.6378	0.3847	0.022*
C6	0.75301 (14)	0.7676 (4)	0.51947 (13)	0.0179 (4)
C7	0.67610 (15)	0.9650 (4)	0.50831 (13)	0.0197 (4)
H7	0.6492	1.0363	0.5626	0.024*
C8	0.53819 (15)	1.3452 (4)	0.34732 (13)	0.0195 (4)
H1	0.8337 (17)	0.880 (5)	0.7212 (14)	0.044 (8)*
H31	0.5515 (19)	1.281 (5)	0.4800 (11)	0.036 (7)*
H41	0.570 (2)	1.360 (4)	0.2208 (13)	0.038 (7)*
H42	0.6185 (16)	1.145 (3)	0.2711 (17)	0.030 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0247 (3)	0.0265 (3)	0.0193 (2)	0.0085 (2)	−0.00213 (18)	−0.0004 (2)
O1	0.0303 (8)	0.0290 (9)	0.0209 (7)	0.0072 (7)	−0.0059 (6)	−0.0041 (6)
O2	0.0268 (8)	0.0220 (8)	0.0287 (7)	0.0074 (7)	0.0022 (6)	−0.0008 (6)
O3	0.0268 (8)	0.0259 (9)	0.0200 (7)	0.0004 (7)	0.0016 (6)	0.0007 (6)
N1	0.0181 (8)	0.0185 (9)	0.0239 (8)	−0.0036 (7)	0.0047 (6)	0.0002 (7)
N2	0.0152 (8)	0.0175 (9)	0.0210 (7)	0.0005 (7)	0.0014 (6)	0.0008 (6)
N3	0.0201 (8)	0.0220 (10)	0.0174 (8)	0.0051 (7)	0.0008 (6)	0.0007 (7)
N4	0.0249 (9)	0.0228 (10)	0.0191 (8)	0.0049 (8)	0.0019 (7)	0.0015 (7)
C1	0.0201 (10)	0.0204 (11)	0.0200 (9)	−0.0020 (9)	0.0024 (7)	−0.0005 (8)
C2	0.0197 (10)	0.0242 (12)	0.0200 (9)	0.0011 (9)	−0.0029 (7)	0.0025 (8)
C3	0.0178 (10)	0.0198 (11)	0.0254 (10)	0.0022 (8)	−0.0001 (7)	0.0037 (8)
C4	0.0158 (9)	0.0175 (10)	0.0224 (9)	−0.0035 (8)	0.0029 (7)	−0.0005 (8)
C5	0.0155 (9)	0.0187 (11)	0.0198 (9)	−0.0028 (8)	0.0012 (7)	0.0043 (7)
C6	0.0149 (9)	0.0189 (11)	0.0199 (9)	−0.0013 (8)	0.0012 (7)	0.0023 (8)
C7	0.0188 (10)	0.0205 (11)	0.0198 (9)	0.0007 (8)	0.0015 (7)	−0.0010 (8)
C8	0.0166 (9)	0.0208 (11)	0.0207 (9)	−0.0024 (8)	−0.0016 (7)	0.0009 (8)

Geometric parameters (Å, °)

S1—C8	1.693 (2)	N4—H42	0.852 (10)
O1—C1	1.345 (2)	C1—C2	1.390 (3)

O1—H1	0.842 (10)	C1—C6	1.412 (2)
O2—N1	1.237 (2)	C2—C3	1.377 (3)
O3—N1	1.227 (2)	C2—H2	0.9500
N1—C4	1.457 (3)	C3—C4	1.394 (3)
N2—C7	1.281 (2)	C3—H3	0.9500
N2—N3	1.378 (2)	C4—C5	1.379 (3)
N3—C8	1.342 (2)	C5—C6	1.389 (3)
N3—H31	0.852 (10)	C5—H5	0.9500
N4—C8	1.328 (3)	C6—C7	1.455 (3)
N4—H41	0.853 (10)	C7—H7	0.9500
C1—O1—H1	109 (2)	C2—C3—H3	120.6
O3—N1—O2	122.64 (17)	C4—C3—H3	120.6
O3—N1—C4	119.27 (17)	C5—C4—C3	122.38 (19)
O2—N1—C4	118.09 (16)	C5—C4—N1	118.87 (17)
C7—N2—N3	114.57 (16)	C3—C4—N1	118.73 (18)
C8—N3—N2	120.22 (16)	C4—C5—C6	118.88 (17)
C8—N3—H31	120.1 (18)	C4—C5—H5	120.6
N2—N3—H31	118.6 (18)	C6—C5—H5	120.6
C8—N4—H41	116.8 (18)	C5—C6—C1	119.31 (18)
C8—N4—H42	118.3 (17)	C5—C6—C7	122.03 (17)
H41—N4—H42	122 (2)	C1—C6—C7	118.65 (18)
O1—C1—C2	123.07 (17)	N2—C7—C6	121.22 (18)
O1—C1—C6	116.53 (18)	N2—C7—H7	119.4
C2—C1—C6	120.40 (18)	C6—C7—H7	119.4
C3—C2—C1	120.18 (18)	N4—C8—N3	117.54 (19)
C3—C2—H2	119.9	N4—C8—S1	123.38 (15)
C1—C2—H2	119.9	N3—C8—S1	119.07 (15)
C2—C3—C4	118.77 (19)		

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···S1^i	0.84 (1)	2.34 (1)	3.175 (2)	170 (3)
N3—H31···S1^{ii}	0.85 (1)	2.50 (1)	3.337 (2)	167 (2)
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Symmetry codes: (i) $x+1/2$, $−y+5/2$, $z+1/2$; (ii) $−x+1$, $−y+3$, $−z+1$; (iii) $−x+3/2$, $y+3/2$, $−z+1/2$; (iv) $−x+3/2$, $y+1/2$, $−z+1/2$.

Fig. 1