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5-Chloro-2-hydroxybenzaldehyde 4-ethylthiosemicarbazone

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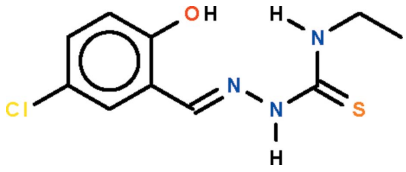
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.029; wR factor = 0.085; data-to-parameter ratio = 19.0.

In the title compound, $C_{10}H_{12}ClN_3OS$, the –C═N–N–C– chain bridging the ethylimino group and the benzene ring adopts an extended conformation with a C—N—N—C torsion angle of −171.98 (11)°. The imino H atom of the chain is a hydrogen-bond donor to the S atom of an inversion-related molecule, forming a supramolecular dimer. The hydroxy H atom is intramolecularly hydrogen bonded to the azomethine N atom.

Related literature

For the salicylaldehyde 4-methylthiosemicarbazone homolog, see: Vrdoljak *et al.* (2005).



Experimental

Crystal data

$C_{10}H_{12}ClN_3OS$
M_r = 257.74
Monoclinic, $C2/c$
a = 21.7956 (3) Å
b = 11.8536 (2) Å
c = 9.4155 (1) Å
β = 101.6870 (9)°
V = 2382.12 (6) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.48 mm^{-1}
T = 100 K
0.40 × 0.40 × 0.40 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.832, T_{max} = 0.832
11204 measured reflections
2985 independent reflections
2582 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.085
S = 1.02
2985 reflections
157 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1o···N1	0.84 (1)	1.92 (1)	2.670 (2)	149 (2)
N2—H2n···S1^{i}	0.87 (1)	2.48 (1)	3.308 (1)	159 (1)

Symmetry code: (i) $-x+\frac{3}{2}, -y+\frac{3}{2}, -z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); 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, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5210).

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supplementary materials

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5-Chloro-2-hydroxybenzaldehyde 4-ethylthiosemicarbazone

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Comment

Salicylaldehyde condenses with a large number of 4-alkyl/aryl-3-thiosemicarbazide to yield the corresponding thiosemicarbazone Schiff-bases. These compounds are used as chelating ligands to a range of metal ions. The semicarbazones, as exemplified by the salicylaldehyde 4-methyl-3-thiosemicarbazone homolog (Vrdoljak *et al.*, 2005), feature an N–H···S hydrogen bond that connects two molecules into a hydrogen-bonded dimer. In $C_{10}H_{12}ClN_3OS$, the –C═N–N–C– chain separating the double-bond S atom and the benzene ring adopts an extended zigzag conformation (Fig.1). The amino H atom of the chain is hydrogen-bond donor to the S atom of an inversion-related molecule to form a dimer. The H atom of the hydroxy unit is hydrogen bond donor to the azomethine N atom. The other amino H atom is only weakly involved in hydrogen bonding (Table 1).

Experimental

5-Chloro-2-hydroxybenzaldehyde (3.1 g, 20 mol) and of 4-ethyl-3-thiosemicarbazide (2.4 g, 20 mmol) were heated in ethanol (100 ml) for an hour. The solution was filtered and colorless crystals were obtained upon slow evaporation of the solvent.

Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.95 to 0.99 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) =1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for the others. The hydroxy and amino H atoms were located in a difference Fourier map, and were refined with distance restraints of O—H 0.84±0.01 and N—H 0.88±0.01 Å; their temperature factors were freely refined.

Figures

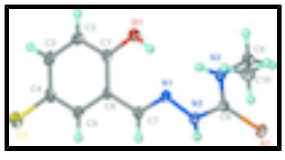

Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of $C_{10}H_{12}ClN_3OS$ at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

5-Chloro-2-hydroxybenzaldehyde 4-ethylthiosemicarbazone

Crystal data

$C_{10}H_{12}ClN_3OS$	$F(000)$ = 1072
M_r = 257.74	D_x = 1.437 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 6011 reflections

a = 21.7956 (3) Å	θ = 2.8–28.3°
b = 11.8536 (2) Å	μ = 0.48 mm^{-1}
c = 9.4155 (1) Å	T = 100 K
β = 101.6870 (9)°	Block, colorless
V = 2382.12 (6) Å^3	0.40 × 0.40 × 0.40 mm
Z = 8	

Data collection

Bruker SMART APEX diffractometer	2985 independent reflections
Radiation source: fine-focus sealed tube	2582 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.022
ω scans	θ_{max} = 28.4°, θ_{min} = 1.9°
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	h = −29→29
T_{min} = 0.832, T_{max} = 0.832	k = −15→15
11204 measured reflections	l = −12→12

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.029	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.085	H atoms treated by a mixture of independent and constrained refinement
S = 1.02	$w = 1/[\sigma^2(F_o^2) + (0.0483P)^2 + 1.7745P]$ where $P = (F_o^2 + 2F_c^2)/3$
2985 reflections	$(\Delta/\sigma)_{max}$ = 0.001
157 parameters	$\Delta\rho_{max}$ = 0.33 e Å^{-3}
3 restraints	$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.485785 (16)	0.65980 (4)	0.51634 (4)	0.03990 (13)
S1	0.835591 (14)	0.65767 (3)	−0.01381 (3)	0.01821 (10)
O1	0.75861 (4)	0.62629 (8)	0.57947 (10)	0.01950 (19)
N1	0.73919 (5)	0.61554 (8)	0.29057 (11)	0.0159 (2)
N2	0.75536 (5)	0.63100 (9)	0.15711 (11)	0.0167 (2)
N3	0.85219 (5)	0.55435 (9)	0.24435 (11)	0.0169 (2)
C1	0.69537 (6)	0.62896 (10)	0.56025 (13)	0.0160 (2)
C2	0.66935 (6)	0.63906 (10)	0.68348 (14)	0.0189 (2)
H2	0.6959	0.6406	0.7769	0.023*
C3	0.60511 (6)	0.64685 (11)	0.67054 (14)	0.0215 (3)
H3	0.5875	0.6549	0.7544	0.026*

C4	0.56661 (6)	0.64280 (12)	0.53368 (15)	0.0230 (3)
C5	0.59099 (6)	0.63056 (11)	0.41045 (14)	0.0203 (3)
H5	0.5638	0.6262	0.3180	0.024*
C6	0.65605 (5)	0.62453 (10)	0.42189 (13)	0.0160 (2)
C7	0.68017 (5)	0.62429 (10)	0.28864 (13)	0.0166 (2)
H7	0.6517	0.6307	0.1982	0.020*
C8	0.81461 (5)	0.61070 (10)	0.14031 (12)	0.0152 (2)
C9	0.91574 (5)	0.51980 (11)	0.23606 (13)	0.0199 (2)
H9A	0.9414	0.5132	0.3353	0.024*
H9B	0.9350	0.5783	0.1840	0.024*
C10	0.91595 (6)	0.40780 (12)	0.15821 (14)	0.0235 (3)
H10A	0.9591	0.3872	0.1542	0.035*
H10B	0.8911	0.4144	0.0594	0.035*
H10C	0.8977	0.3494	0.2107	0.035*
H1O	0.7673 (10)	0.6201 (18)	0.4975 (14)	0.057 (6)*
H2N	0.7319 (6)	0.6770 (11)	0.0975 (14)	0.017 (4)*
H3N	0.8351 (7)	0.5207 (13)	0.3075 (15)	0.026 (4)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.01591 (17)	0.0783 (3)	0.0285 (2)	0.00085 (16)	0.01169 (14)	0.00069 (17)
S1	0.01839 (16)	0.02150 (16)	0.01680 (15)	0.00297 (10)	0.00847 (12)	0.00232 (11)
O1	0.0152 (4)	0.0239 (5)	0.0195 (4)	0.0018 (3)	0.0039 (3)	0.0007 (4)
N1	0.0165 (5)	0.0162 (5)	0.0165 (5)	0.0003 (4)	0.0072 (4)	0.0002 (4)
N2	0.0151 (5)	0.0210 (5)	0.0152 (5)	0.0030 (4)	0.0061 (4)	0.0030 (4)
N3	0.0144 (4)	0.0207 (5)	0.0166 (5)	0.0012 (4)	0.0055 (4)	0.0015 (4)
C1	0.0163 (5)	0.0135 (5)	0.0189 (5)	0.0006 (4)	0.0054 (4)	0.0010 (4)
C2	0.0218 (6)	0.0191 (6)	0.0163 (5)	−0.0002 (4)	0.0047 (5)	−0.0004 (4)
C3	0.0241 (6)	0.0238 (6)	0.0193 (6)	−0.0001 (5)	0.0106 (5)	0.0001 (5)
C4	0.0152 (6)	0.0318 (7)	0.0241 (6)	−0.0007 (5)	0.0092 (5)	0.0011 (5)
C5	0.0172 (6)	0.0263 (6)	0.0183 (6)	−0.0019 (5)	0.0053 (5)	0.0013 (5)
C6	0.0163 (5)	0.0162 (5)	0.0170 (5)	−0.0007 (4)	0.0070 (4)	0.0003 (4)
C7	0.0164 (5)	0.0175 (5)	0.0167 (5)	−0.0009 (4)	0.0053 (4)	0.0006 (4)
C8	0.0148 (5)	0.0157 (5)	0.0159 (5)	−0.0010 (4)	0.0047 (4)	−0.0031 (4)
C9	0.0127 (5)	0.0251 (6)	0.0217 (6)	0.0022 (4)	0.0031 (4)	0.0000 (5)
C10	0.0185 (6)	0.0273 (7)	0.0248 (6)	0.0043 (5)	0.0046 (5)	−0.0015 (5)

Geometric parameters (Å, °)

Cl1—C4	1.7476 (13)	C2—H2	0.9500
S1—C8	1.7011 (12)	C3—C4	1.3889 (19)
O1—C1	1.3539 (14)	C3—H3	0.9500
O1—H1O	0.835 (9)	C4—C5	1.3782 (18)
N1—C7	1.2870 (15)	C5—C6	1.4020 (16)
N1—N2	1.3842 (13)	C5—H5	0.9500
N2—C8	1.3541 (14)	C6—C7	1.4552 (16)
N2—H2N	0.870 (9)	C7—H7	0.9500
N3—C8	1.3234 (15)	C9—C10	1.5169 (18)

N3—C9	1.4615 (14)	C9—H9A	0.9900
N3—H3N	0.860 (9)	C9—H9B	0.9900
C1—C2	1.3959 (17)	C10—H10A	0.9800
C1—C6	1.4078 (17)	C10—H10B	0.9800
C2—C3	1.3837 (17)	C10—H10C	0.9800
C1—O1—H1O	107.2 (15)	C6—C5—H5	120.1
C7—N1—N2	114.46 (10)	C5—C6—C1	119.07 (11)
C8—N2—N1	120.45 (10)	C5—C6—C7	118.05 (11)
C8—N2—H2N	119.1 (10)	C1—C6—C7	122.65 (11)
N1—N2—H2N	116.3 (10)	N1—C7—C6	121.50 (11)
C8—N3—C9	123.58 (10)	N1—C7—H7	119.2
C8—N3—H3N	117.1 (11)	C6—C7—H7	119.2
C9—N3—H3N	117.0 (11)	N3—C8—N2	117.72 (10)
O1—C1—C2	117.70 (11)	N3—C8—S1	124.30 (9)
O1—C1—C6	122.36 (11)	N2—C8—S1	117.97 (9)
C2—C1—C6	119.92 (11)	N3—C9—C10	111.51 (10)
C3—C2—C1	120.44 (12)	N3—C9—H9A	109.3
C3—C2—H2	119.8	C10—C9—H9A	109.3
C1—C2—H2	119.8	N3—C9—H9B	109.3
C2—C3—C4	119.33 (12)	C10—C9—H9B	109.3
C2—C3—H3	120.3	H9A—C9—H9B	108.0
C4—C3—H3	120.3	C9—C10—H10A	109.5
C5—C4—C3	121.41 (12)	C9—C10—H10B	109.5
C5—C4—Cl1	119.13 (10)	H10A—C10—H10B	109.5
C3—C4—Cl1	119.40 (10)	C9—C10—H10C	109.5
C4—C5—C6	119.81 (12)	H10A—C10—H10C	109.5
C4—C5—H5	120.1	H10B—C10—H10C	109.5
C7—N1—N2—C8	−171.98 (11)	C2—C1—C6—C5	0.09 (17)
O1—C1—C2—C3	177.38 (11)	O1—C1—C6—C7	−4.18 (17)
C6—C1—C2—C3	−1.19 (18)	C2—C1—C6—C7	174.32 (12)
C1—C2—C3—C4	0.97 (19)	N2—N1—C7—C6	−172.18 (10)
C2—C3—C4—C5	0.4 (2)	C5—C6—C7—N1	−177.90 (11)
C2—C3—C4—Cl1	−176.77 (10)	C1—C6—C7—N1	7.82 (18)
C3—C4—C5—C6	−1.5 (2)	C9—N3—C8—N2	175.63 (11)
Cl1—C4—C5—C6	175.68 (10)	C9—N3—C8—S1	−3.54 (17)
C4—C5—C6—C1	1.21 (18)	N1—N2—C8—N3	13.77 (17)
C4—C5—C6—C7	−173.28 (12)	N1—N2—C8—S1	−167.01 (8)
O1—C1—C6—C5	−178.40 (11)	C8—N3—C9—C10	−85.80 (14)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1o···N1	0.84 (1)	1.92 (1)	2.670 (2)	149 (2)
N2—H2n···S1^{i}	0.87 (1)	2.48 (1)	3.308 (1)	159 (1)

Symmetry codes: (i) −*x*+3/2, −*y*+3/2, −*z*.

Fig. 1