(E)-1-(4-Chlorobenzylidene)thiosemi-carbazide

Aamer Saeed,[a]* Shams-ul Mahmood,[a] Michael Bolte,[b] Abdul Rauf[c] and Mohammad Subhan[d]

[a]Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan, [b]Institut für Anorganische Chemie, J. W. Goethe-Universität Frankfurt, Max-von-Laue-Strasse 7, 60438 Frankfurt/Main, Germany, [c]Department of Chemistry, Islamia Islamia College University, Peshawar, Pakistan, and [d]Department of Chemistry, Islamia University, Bahawalpur, Pakistan

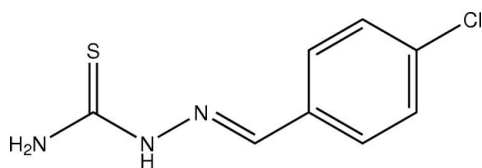Correspondence e-mail: aamersaeed@yahoo.com

In the crystal of the title compound, $C_8H_8ClN_3S$, molecules are connected by N—H$\cdots$S hydrogen bonds into strips parallel to the (112) planes and running along [1$\bar{1}$0]. One of the amino H atoms is not involved in a classical hydrogen bond. In addition, there is a rather short intermolecular Cl$\cdots$S distance of 3.3814 (5) Å.

Related literature

For background to Schiff bases, see: Mobinikhaledi et al. (2010); Hamaker et al. (2010); Mirkhani et al. (2010); Thangadurai et al. (2002). Ji & Lu (2010a,b); Lü et al. (2008). For a related structure, see: Zhang & Li (2008). For bioactivity, see: Chohan et al. (2004).

Experimental

Crystal data

$C_8H_8ClN_3S$	$b = 7.8329$ (7) Å
$M_r = 213.68$	$c = 11.2016$ (10) Å
Triclinic, $P\bar{1}$	$\alpha = 83.852$ (7)°
$a = 5.7611$ (5) Å	$\beta = 75.373$ (7)°
$\gamma = 76.353$ (7)°	$\mu = 0.58$ mm^{-1}
$V = 474.69$ (7) Å^3	$T = 173$ K
$Z = 2$	$0.38 \times 0.35 \times 0.27$ mm
Mo $K\alpha$ radiation	

Data collection

Stoe IPDS II two-circle diffractometer	8657 measured reflections
Absorption correction: multi-scan (MULABS; Spek, 2009; Blessing, 1995)	2179 independent reflections
	2054 reflections with $I > 2\sigma(I)$
$T_{min} = 0.811$, $T_{max} = 0.860$	$R_{int} = 0.055$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.079$	
$S = 1.10$	
2179 reflections	$\Delta\rho_{max} = 0.39$ e Å^{-3}
131 parameters	$\Delta\rho_{min} = -0.27$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$\cdots$S1^i	0.863 (19)	2.628 (19)	3.4288 (12)	154.7 (16)
N3—H3$A\cdots$S1^{ii}	0.877 (19)	2.65 (2)	3.5119 (12)	170.1 (17)

Symmetry codes: (i) $-x+3, -y+1, -z$; (ii) $-x+4, -y, -z$.

Data collection: X-AREA (Stoe & Cie, 2001); cell refinement: X-AREA; data reduction: X-AREA; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP (Sheldrick, 2008); software used to prepare material for publication: SHELXL97.

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supplementary materials

(*E*)-1-(4-Chlorobenzylidene)thiosemicarbazide

A. Saeed, S. Mahmood, M. Bolte, A. Rauf and M. Subhan

Comment

Schiff bases derived from semicarbazide and aromatic aldehydes are an important class of organic compounds because of their applications in many fields including inorganic, biological, and analytical chemistry (Mobinikhaledi *et al.*, 2010; Thangadurai *et al.*, 2002). Schiff bases are known to be versatile ligands in coordination chemistry (Ji & Lu, 2010*a*,2010*b*; Hamaker *et al.*, 2010; Mirkhani *et al.*, 2010). Shiff bases and their complexes are also important in material science applications like organic light emitting diodes (Lü *et al.*, 2008).

The title compound features an essentially planar molecule: the largest deviation of a torsion angle from 0 or 180Å is 13.02 (19)° for N1—C1—C11—C12. Bond lengths and angles do not show any unusual values. In the crystal, the molecules are connected by N—H⋯S hydrogen bonds into strips parallel to the (1 1 2) planes and running along [1 $\bar{1}$ 0]. One of the amino H atoms is not involved in a classical hydrogen bond. In addition there is a rather short intermolecular Cl⋯S^i distance of 3.3814 (5)Å (symmetry operator (i): *x* - 2, *y*, *z* + 1).

Experimental

Semicarbazide, 0.137 g (1 mmol) dissolved in 5 ml e thanol was added dropwise to a solution of 4-chlorobenzaldehyde, 0.122 g (1.1 mmol) in 10 ml e thanol at room temperature with continuous stirring. The reaction mixture was refluxed for 4 h and completion monitored by TLC. The reaction mixture was concentrated and the resulting product was separated. Colourless single crystals of the compound, suitable for X-ray crystallography, were grown by slow evaporation from a (2:1) ethyl acetate-ethanol solution. Anal.: calcd. for $C_8H_8N_3SCl$: C, 44.95; H, 3.74; N, 19.66; S, 14.98%; found: C, 45.01; H, 3.61; N, 19.81; S, 14.83%.

Refinement

H atoms bonded to N were freely refined. H atoms bonded to C were geometrically positioned and refined using a riding model with C—H = 0.95Å and U(H) set to $1.2U_{eq}(C)$.
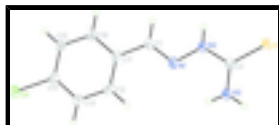
Figures

Fig. 1. Molecular structure of title compound. Displacement ellipsoids are drawn at the 50% probability level.
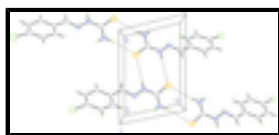

Fig. 2. Crystal packing with intermolecular hydrogen bonds indicated as dashed lines.

(*E*)-1-(4-Chlorobenzylidene)thiosemicarbazide

Crystal data

$C_8H_8ClN_3S$	$Z = 2$
$M_r = 213.68$	$F(000) = 220$
Triclinic, $P\bar{1}$	$D_x = 1.495$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.7611$ (5) Å	Cell parameters from 7492 reflections
$b = 7.8329$ (7) Å	$\theta = 3.4–27.8°$
$c = 11.2016$ (10) Å	$\mu = 0.58$ mm^{-1}
$\alpha = 83.852$ (7)°	$T = 173$ K
$\beta = 75.373$ (7)°	Block, colourless
$\gamma = 76.353$ (7)°	$0.38 \times 0.35 \times 0.27$ mm
$V = 474.69$ (7) Å^3	

Data collection

Stoe IPDS II two-circle diffractometer	2179 independent reflections
Radiation source: fine-focus sealed tube	2054 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.055$
ω scans	$\theta_{max} = 27.7°$, $\theta_{min} = 3.4°$
Absorption correction: multi-scan (*MULABS*; Spek, 2009; Blessing, 1995)	$h = -7\rightarrow7$
$T_{min} = 0.811$, $T_{max} = 0.860$	$k = -10\rightarrow10$
8657 measured reflections	$l = -14\rightarrow14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.029$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.079$	$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 0.1107P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.001$
2179 reflections	$\Delta\rho_{max} = 0.39$ e Å^{-3}
131 parameters	$\Delta\rho_{min} = -0.27$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.061 (7)

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.

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	$U_{iso}*/U_{eq}$
Cl1	0.16691 (5)	0.24404 (4)	0.64870 (3)	0.02702 (12)
S1	1.79101 (5)	0.26359 (4)	−0.06509 (3)	0.02625 (12)
N1	1.18834 (19)	0.23473 (14)	0.18778 (10)	0.0215 (2)
N2	1.35359 (19)	0.28547 (14)	0.08531 (10)	0.0220 (2)
H2	1.322 (3)	0.392 (3)	0.0550 (17)	0.033 (4)*
N3	1.6366 (2)	0.03361 (14)	0.11273 (11)	0.0256 (2)
H3A	1.787 (3)	−0.030 (3)	0.0942 (17)	0.037 (5)*
H3B	1.529 (4)	0.002 (2)	0.1674 (19)	0.037 (5)*
C1	0.9739 (2)	0.33723 (16)	0.20735 (11)	0.0206 (2)
H1	0.9408	0.4333	0.1503	0.025*
C2	1.5844 (2)	0.18669 (15)	0.05230 (11)	0.0200 (2)
C11	0.7791 (2)	0.30948 (15)	0.31550 (11)	0.0194 (2)
C12	0.8261 (2)	0.19449 (17)	0.41513 (12)	0.0258 (3)
H12	0.9887	0.1297	0.4129	0.031*
C13	0.6388 (2)	0.17389 (17)	0.51702 (12)	0.0275 (3)
H13	0.6721	0.0962	0.5847	0.033*
C14	0.4012 (2)	0.26838 (16)	0.51905 (11)	0.0209 (2)
C15	0.3492 (2)	0.38356 (16)	0.42174 (11)	0.0221 (2)
H15	0.1859	0.4470	0.4241	0.027*
C16	0.5394 (2)	0.40491 (16)	0.32075 (11)	0.0216 (2)
H16	0.5060	0.4855	0.2544	0.026*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.02137 (17)	0.02970 (19)	0.02380 (18)	−0.00376 (12)	0.00323 (12)	0.00098 (12)
S1	0.01985 (17)	0.02394 (18)	0.02535 (18)	0.00043 (12)	0.00505 (12)	0.00406 (12)
N1	0.0187 (5)	0.0228 (5)	0.0206 (5)	−0.0050 (4)	0.0009 (4)	−0.0024 (4)
N2	0.0171 (5)	0.0214 (5)	0.0217 (5)	−0.0008 (4)	0.0018 (4)	0.0005 (4)
N3	0.0193 (5)	0.0236 (5)	0.0260 (5)	0.0001 (4)	0.0024 (4)	0.0035 (4)
C1	0.0185 (5)	0.0218 (5)	0.0206 (5)	−0.0041 (4)	−0.0026 (4)	−0.0023 (4)
C2	0.0192 (5)	0.0212 (5)	0.0177 (5)	−0.0023 (4)	−0.0021 (4)	−0.0023 (4)

C11	0.0165 (5)	0.0190 (5)	0.0215 (6)	−0.0035 (4)	−0.0016 (4)	−0.0040 (4)
C12	0.0167 (5)	0.0248 (6)	0.0298 (6)	0.0024 (4)	−0.0023 (5)	0.0017 (5)
C13	0.0223 (6)	0.0259 (6)	0.0278 (6)	0.0011 (5)	−0.0031 (5)	0.0064 (5)
C14	0.0173 (5)	0.0216 (5)	0.0209 (5)	−0.0031 (4)	0.0003 (4)	−0.0032 (4)
C15	0.0148 (5)	0.0260 (6)	0.0233 (6)	−0.0005 (4)	−0.0034 (4)	−0.0027 (5)
C16	0.0183 (5)	0.0248 (6)	0.0201 (5)	−0.0016 (4)	−0.0047 (4)	−0.0010 (4)

Geometric parameters (Å, °)

Cl1—C14	1.7435 (12)	C11—C16	1.3967 (16)
S1—C2	1.6992 (12)	C11—C12	1.3972 (18)
N1—C1	1.2853 (16)	C12—C13	1.3835 (18)
N1—N2	1.3824 (14)	C12—H12	0.9500
N2—C2	1.3530 (15)	C13—C14	1.3898 (17)
N2—H2	0.863 (19)	C13—H13	0.9500
N3—C2	1.3211 (16)	C14—C15	1.3851 (17)
N3—H3A	0.877 (19)	C15—C16	1.3886 (17)
N3—H3B	0.82 (2)	C15—H15	0.9500
C1—C11	1.4648 (16)	C16—H16	0.9500
C1—H1	0.9500		
C1—N1—N2	114.01 (10)	C13—C12—C11	120.82 (11)
C2—N2—N1	120.12 (10)	C13—C12—H12	119.6
C2—N2—H2	119.3 (12)	C11—C12—H12	119.6
N1—N2—H2	118.7 (12)	C12—C13—C14	119.15 (12)
C2—N3—H3A	118.9 (13)	C12—C13—H13	120.4
C2—N3—H3B	119.0 (13)	C14—C13—H13	120.4
H3A—N3—H3B	122.1 (18)	C15—C14—C13	121.30 (11)
N1—C1—C11	121.62 (11)	C15—C14—Cl1	119.81 (9)
N1—C1—H1	119.2	C13—C14—Cl1	118.88 (10)
C11—C1—H1	119.2	C14—C15—C16	119.00 (11)
N3—C2—N2	117.92 (11)	C14—C15—H15	120.5
N3—C2—S1	123.29 (9)	C16—C15—H15	120.5
N2—C2—S1	118.78 (9)	C15—C16—C11	120.85 (11)
C16—C11—C12	118.86 (11)	C15—C16—H16	119.6
C16—C11—C1	118.86 (11)	C11—C16—H16	119.6
C12—C11—C1	122.26 (10)		
C1—N1—N2—C2	−178.33 (11)	C11—C12—C13—C14	0.5 (2)
N2—N1—C1—C11	−176.64 (10)	C12—C13—C14—C15	−0.6 (2)
N1—N2—C2—N3	6.86 (18)	C12—C13—C14—Cl1	−179.11 (10)
N1—N2—C2—S1	−173.83 (8)	C13—C14—C15—C16	−0.29 (19)
N1—C1—C11—C16	−168.81 (11)	Cl1—C14—C15—C16	178.22 (9)
N1—C1—C11—C12	13.02 (19)	C14—C15—C16—C11	1.31 (18)
C16—C11—C12—C13	0.53 (19)	C12—C11—C16—C15	−1.43 (18)
C1—C11—C12—C13	178.70 (12)	C1—C11—C16—C15	−179.66 (11)

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···S1[i]	0.863 (19)	2.628 (19)	3.4288 (12)	154.7 (16)

N3—H3A···S1[ii]	0.877 (19)	2.65 (2)	3.5119 (12)	170.1 (17)

Symmetry codes: (i) −*x*+3, −*y*+1, −*z*; (ii) −*x*+4, −*y*, −*z*.

Fig. 1

Fig. 2