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4-Cyanobenzaldehyde thiosemicarbazone

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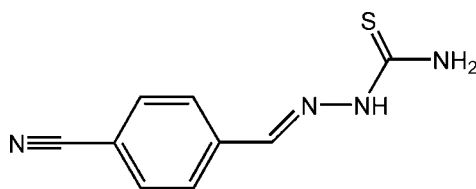
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 Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.055; wR factor = 0.109; data-to-parameter ratio = 18.2.

The molecule of the title compound, $\text{C}_9\text{H}_8\text{N}_4\text{S}$, adopts an *E* configuration about both the $\text{C}=\text{N}$ and $\text{C}-\text{NH}$ bonds. In the crystal structure, adjacent molecules are linked by intermolecular $\text{N}-\text{H}\cdots\text{S}$ hydrogen-bonding interactions, forming chains running parallel to the *b* axis.

Related literature

For a general background to thiosemicarbazone compounds, see: Casas *et al.* (2000); Tarafder *et al.* (2000); Deschamps *et al.* (2003); Liu *et al.* (1999); Wu *et al.* (2000). For reference structural data, see: Sutton (1965).



Experimental

Crystal data

 $\text{C}_9\text{H}_8\text{N}_4\text{S}$
 $M_r = 204.26$
 Monoclinic, $P2_1/c$
 $a = 12.284$ (6) Å

 $b = 8.209$ (4) Å
 $c = 10.058$ (3) Å
 $\beta = 92.20$ (3)°
 $V = 1013.5$ (8) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.28$ mm⁻¹
 $T = 291$ (2) K
 $0.25 \times 0.17 \times 0.15$ mm

Data collection

 Rigaku Mercury2 diffractometer
 Absorption correction: multi-scan
 (*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.94$, $T_{\max} = 0.96$

 10019 measured reflections
 2309 independent reflections
 1596 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.055$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.109$
 $S = 1.01$
 2309 reflections

 127 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.17$ e Å⁻³
 $\Delta\rho_{\min} = -0.19$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N2—H2A \cdots S1 ⁱ	0.86	2.50	3.355 (2)	171
N1—H1B \cdots S1 ⁱⁱ	0.86	2.63	3.399 (3)	150

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2264).

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supplementary materials

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4-Cyanobenzaldehyde thiosemicarbazone

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Comment

Thiosemicarbazones constitute an important class of N,S donors due to their propensity to react with a wide range of metals (Casas *et al.*, 2000). Schiff bases show potential as antimicrobial and anticancer agents (Tarafter *et al.*, 2000; Deschamps *et al.*, 2003) and so have biochemical and pharmacological applications. It has been postulated that extensive electron delocalization in the thiosemicarbazone moiety helps the free thiosemicarbazone ligands and their metal complexes to exhibit SHG (second harmonic generation) efficiency (Liu *et al.*, 1999; Wu *et al.*, 2000). As part of a research on non-linear optical materials, specifically thiosemicarbazones and their metal complexes, we report here the crystal structure of a new Schiff base compound derived from thiosemicarbazide and 4-cyanobenzaldehyde.

In the title compound (Fig. 1), the thiosemicarbazone moiety is nearly planar (maximum deviation 0.113 (2) Å for atom N2) and shows an *E* configuration about both the C1=N2 and C2=N3 bonds. The molecule is not strictly planar, the dihedral angle between the thiosemicarbazone moiety and the phenyl ring being 15.8 (6)°. The C—S bond distance of 1.689 (2) Å agrees well with similar bonds in related compounds, being intermediate between the value of 1.82 Å for a C—S single bond and 1.56 Å for a C=S double bond (Sutton, 1965). The C1—N2 bond distance (1.344 (3) Å) is indicative of some double-bond character, suggesting extensive electron delocalization in the whole molecule. The C1—N1 bond distance of 1.316 (3) Å is also indicative of some double-bond character. All the bond distances except for the C6—C9 bond length (1.447 (3) Å) fall within the normal range. In the crystal packing, adjacent molecules are linked by N—H···S hydrogen bonds (Table 1) to form chains running parallel to the *b* axis.

Experimental

The title compound was synthesized by refluxing 4-cyanobenzaldehyde (1.05 g, 8 mmol) and thiosemicarbazide (0.73 g, 8 mmol) in absolute ethanol (40 ml) for 6 h. After cooling to room temperature, the white solid formed was isolated and dried under vacuum (1.47 g, yield 90%). Single crystals suitable for X-ray structure analysis were obtained by slow evaporation of a methanol solution.

Refinement

H atoms were placed in calculated positions and refined using a riding model, with N—H = 0.86 Å, C—H = 0.93 Å and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{N})$.

Figures

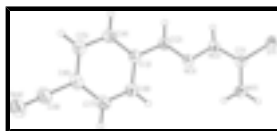


Fig. 1. The molecular structure of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

4-Cyanobenzaldehyde thiosemicarbazone

Crystal data

$C_9H_8N_4S$	$F_{000} = 424$
$M_r = 204.26$	$D_x = 1.339 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
Hall symbol: -P 2ybc	$\lambda = 0.71073 \text{ \AA}$
$a = 12.284 (6) \text{ \AA}$	Cell parameters from 1740 reflections
$b = 8.209 (4) \text{ \AA}$	$\theta = 2.5\text{--}27.5^\circ$
$c = 10.058 (3) \text{ \AA}$	$\mu = 0.28 \text{ mm}^{-1}$
$\beta = 92.20 (3)^\circ$	$T = 291 (2) \text{ K}$
$V = 1013.5 (8) \text{ \AA}^3$	Block, colourless
$Z = 4$	$0.25 \times 0.17 \times 0.15 \text{ mm}$

Data collection

Rigaku Mercury2 diffractometer	2309 independent reflections
Radiation source: fine-focus sealed tube	1596 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.055$
Detector resolution: $13.6612 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 27.5^\circ$
$T = 291(2) \text{ K}$	$\theta_{\text{min}} = 3.0^\circ$
CCD_Profile_fitting scans	$h = -15 \rightarrow 15$
Absorption correction: multi-scan (CrystalClear; Rigaku, 2005)	$k = -10 \rightarrow 10$
$T_{\text{min}} = 0.94, T_{\text{max}} = 0.96$	$l = -12 \rightarrow 13$
10019 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.055$	H-atom parameters constrained
$wR(F^2) = 0.109$	$w = 1/[\sigma^2(F_o^2) + (0.0258P)^2 + 0.6908P]$
$S = 1.01$	where $P = (F_o^2 + 2F_c^2)/3$
2309 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
127 parameters	$\Delta\rho_{\text{max}} = 0.17 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
	Extinction correction: none

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.07786 (19)	0.5792 (3)	0.6753 (2)	0.0446 (6)
C2	0.18757 (19)	0.2982 (3)	0.4587 (2)	0.0454 (6)
H2	0.1575	0.2048	0.4946	0.054*
C3	0.26310 (18)	0.2841 (3)	0.3506 (2)	0.0426 (6)
C4	0.30116 (19)	0.1304 (3)	0.3163 (2)	0.0482 (6)
H4	0.2748	0.0384	0.3583	0.058*
C5	0.3781 (2)	0.1135 (3)	0.2198 (2)	0.0532 (7)
H5	0.4029	0.0108	0.1964	0.064*
C6	0.4175 (2)	0.2517 (3)	0.1588 (2)	0.0509 (6)
C7	0.3777 (2)	0.4058 (3)	0.1891 (2)	0.0541 (7)
H7	0.4028	0.4973	0.1452	0.065*
C8	0.3008 (2)	0.4214 (3)	0.2846 (2)	0.0500 (6)
H8	0.2740	0.5239	0.3052	0.060*
C9	0.5021 (2)	0.2377 (4)	0.0632 (3)	0.0616 (7)
N1	0.1138 (2)	0.7144 (3)	0.6221 (2)	0.0717 (8)
H1A	0.1485	0.7106	0.5496	0.086*
H1B	0.1026	0.8065	0.6600	0.086*
N2	0.09749 (15)	0.4384 (2)	0.61235 (17)	0.0436 (5)
H2A	0.0694	0.3490	0.6396	0.052*
N3	0.16254 (15)	0.4379 (2)	0.50426 (18)	0.0441 (5)
N4	0.5709 (2)	0.2293 (3)	-0.0102 (3)	0.0853 (9)
S1	0.01195 (6)	0.57476 (8)	0.81966 (6)	0.0544 (2)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0526 (14)	0.0390 (12)	0.0423 (12)	0.0019 (12)	0.0033 (11)	0.0001 (11)
C2	0.0475 (14)	0.0477 (14)	0.0414 (13)	-0.0021 (12)	0.0063 (11)	-0.0010 (11)
C3	0.0399 (13)	0.0479 (14)	0.0402 (12)	-0.0015 (11)	0.0030 (10)	-0.0042 (10)
C4	0.0505 (14)	0.0477 (14)	0.0467 (13)	-0.0025 (12)	0.0053 (12)	-0.0032 (11)
C5	0.0533 (15)	0.0568 (17)	0.0498 (14)	0.0051 (13)	0.0050 (12)	-0.0093 (12)
C6	0.0463 (14)	0.0659 (17)	0.0406 (13)	0.0036 (14)	0.0050 (11)	-0.0039 (13)

supplementary materials

C7	0.0540 (15)	0.0593 (17)	0.0496 (14)	-0.0012 (14)	0.0094 (12)	0.0056 (13)
C8	0.0533 (15)	0.0469 (14)	0.0500 (14)	0.0026 (13)	0.0072 (11)	-0.0046 (12)
C9	0.0626 (17)	0.0696 (19)	0.0535 (15)	0.0057 (15)	0.0115 (14)	0.0018 (14)
N1	0.112 (2)	0.0411 (13)	0.0645 (15)	-0.0058 (13)	0.0407 (14)	-0.0043 (11)
N2	0.0546 (12)	0.0375 (11)	0.0396 (10)	0.0007 (10)	0.0111 (9)	-0.0008 (9)
N3	0.0492 (11)	0.0464 (12)	0.0372 (10)	0.0016 (10)	0.0068 (8)	-0.0027 (9)
N4	0.088 (2)	0.091 (2)	0.0797 (18)	0.0167 (17)	0.0398 (16)	0.0100 (16)
S1	0.0765 (5)	0.0431 (3)	0.0448 (3)	0.0083 (4)	0.0184 (3)	0.0010 (3)

Geometric parameters (Å, °)

C1—N1	1.316 (3)	C5—H5	0.9300
C1—N2	1.344 (3)	C6—C7	1.394 (4)
C1—S1	1.689 (2)	C6—C9	1.447 (3)
C2—N3	1.277 (3)	C7—C8	1.378 (3)
C2—C3	1.461 (3)	C7—H7	0.9300
C2—H2	0.9300	C8—H8	0.9300
C3—C4	1.394 (3)	C9—N4	1.146 (3)
C3—C8	1.396 (3)	N1—H1A	0.8600
C4—C5	1.387 (3)	N1—H1B	0.8600
C4—H4	0.9300	N2—N3	1.374 (2)
C5—C6	1.385 (4)	N2—H2A	0.8600
N1—C1—N2	117.7 (2)	C5—C6—C9	120.1 (3)
N1—C1—S1	123.15 (19)	C7—C6—C9	118.9 (2)
N2—C1—S1	119.15 (18)	C8—C7—C6	119.4 (2)
N3—C2—C3	120.5 (2)	C8—C7—H7	120.3
N3—C2—H2	119.8	C6—C7—H7	120.3
C3—C2—H2	119.8	C7—C8—C3	120.4 (2)
C4—C3—C8	119.5 (2)	C7—C8—H8	119.8
C4—C3—C2	119.0 (2)	C3—C8—H8	119.8
C8—C3—C2	121.4 (2)	N4—C9—C6	178.1 (3)
C5—C4—C3	120.5 (2)	C1—N1—H1A	120.0
C5—C4—H4	119.7	C1—N1—H1B	120.0
C3—C4—H4	119.7	H1A—N1—H1B	120.0
C6—C5—C4	119.1 (2)	C1—N2—N3	119.73 (19)
C6—C5—H5	120.4	C1—N2—H2A	120.1
C4—C5—H5	120.4	N3—N2—H2A	120.1
C5—C6—C7	121.0 (2)	C2—N3—N2	116.2 (2)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N2—H2A \cdots S1 ⁱ	0.86	2.50	3.355 (2)	171
N1—H1B \cdots S1 ⁱⁱ	0.86	2.63	3.399 (3)	150

Symmetry codes: (i) $-x, y-1/2, -z+3/2$; (ii) $-x, y+1/2, -z+3/2$.

Fig. 1

