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# Crystal structure of 1-(4-formylbenzylidene)-4-methylthiosemicarbazone

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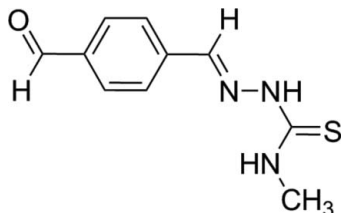
The structure of the title compound, C<sub>10</sub>H<sub>11</sub>N<sub>3</sub>OS, comprises an approximately planar molecule, with the r.m.s. deviation for the 15 non-H atoms being 0.089 Å. The conformation about the imine bond is *E* and an intramolecular N—H...N hydrogen bond is evident. Molecules are linked into a supramolecular chain along the *b* axis by N—H...S hydrogen bonds.

**Keywords:** crystal structure; thiosemicarbazone; thiourea; hydrogen bonding.

**CCDC reference:** 1014062

## 1. Related literature

For the synthesis of the title compound, see: Jagst *et al.* (2005). For biological properties, see: Serda *et al.* (2012). For supramolecular studies of thiosemicarbazones, see: Alonso *et al.* (2002).



## 2. Experimental

### 2.1. Crystal data

C<sub>10</sub>H<sub>11</sub>N<sub>3</sub>OS  
M<sub>r</sub> = 221.28

Orthorhombic, *Pbca*  
a = 13.1231 (3) Å

b = 8.8559 (2) Å  
c = 19.3702 (4) Å  
V = 2251.14 (9) Å<sup>3</sup>  
Z = 8

Cu Kα radiation  
μ = 2.38 mm<sup>-1</sup>  
T = 296 K  
0.14 × 0.13 × 0.05 mm

### 2.2. Data collection

Bruker CCD SMART 6000 diffractometer  
Absorption correction: multi-scan (SADABS; Bruker, 2007)  
T<sub>min</sub> = 0.730, T<sub>max</sub> = 0.898

22698 measured reflections  
1986 independent reflections  
1798 reflections with I > 2σ(I)  
R<sub>int</sub> = 0.046

### 2.3. Refinement

R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.034  
wR(F<sup>2</sup>) = 0.100  
S = 1.08  
1986 reflections  
145 parameters

H atoms treated by a mixture of independent and constrained refinement  
Δρ<sub>max</sub> = 0.21 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -0.16 e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N2—H2N...S1 <sup>i</sup>	0.902 (19)	2.53 (2)	3.4154 (14)	165.6 (16)
N1—H1...N3	0.84 (2)	2.238 (18)	2.6467 (18)	109.9 (15)
N1—H1...S1 <sup>ii</sup>	0.84 (2)	2.992 (19)	3.5401 (15)	124.6 (16)

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

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: *Mercury* (Bruno *et al.*, 2002); software used to prepare material for publication: *publCIF* (Westrip, 2010).

## Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: TK5328).

## References

- Alonso, R., Bermejo, E., Carballo, R., Castiñeiras, A. & Pérez, T. (2002). *J. Mol. Struct.* **606**, 155–173.  
 Bruker (2007). *SADABS*, *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* **B58**, 389–397.  
 Jagst, A., Sánchez, A., Vázquez-López, E. M. & Abram, U. (2005). *Inorg. Chem.* **44**, 5738–5744.  
 Serda, M., Mrozek-Wilczkiewicz, A., Jampilek, J., Pesko, M., Kralova, K., Vejsova, M., Musiol, R., Ratuszna, A. & Polanski, J. (2012). *Molecules*, **17**, 13483–13502.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

## supporting information

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## Crystal structure of 1-(4-formylbenzylidene)-4-methylthiosemicarbazone

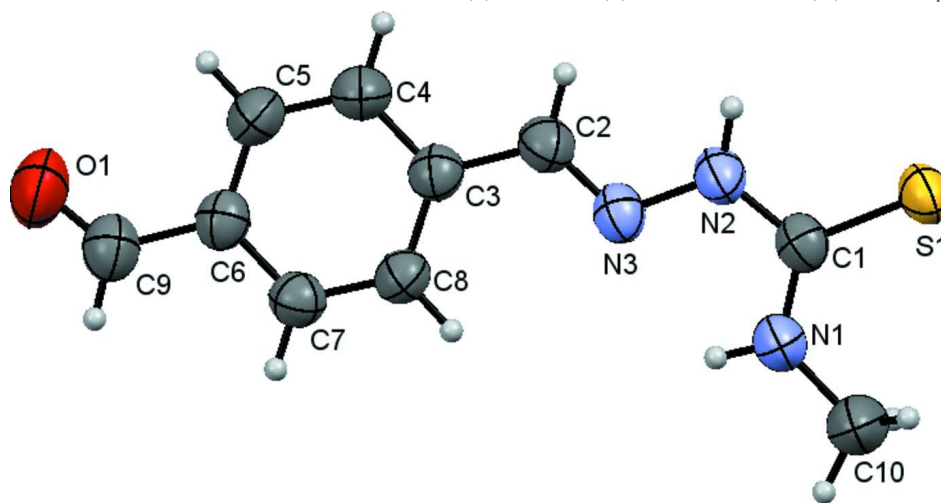
Arantxa Pino-Cuevas, Rosa Carballo and Ezequiel M. Vázquez-López

### S1. Synthesis and crystallization

A solution of 4-methyl-3-thiosemicarbazide (392 mg, 3.72 mmol) in water (50 mL) was slowly added at 50°C to a solution of terephthalaldehyde (500 mg, 3.73 mmol) in 100 mL water. Then the mixture was stirred at 50°C for 30 mins. Once cooled to room temperature, the yellow solid was filtered off and vacuum dried. Yellow single crystals suitable for X-ray diffraction were obtained by recrystallization from EtOH/H<sub>2</sub>O (1:1). Yield: 91%, M. pt: 213–216 °C. IR data (KBr, cm<sup>-1</sup>): 3368m, 3150m ν(N—H); 2838w, 2742w ν(C—H aldehyde); 1692 s ν(C=O); 1545 s, 1257m ν(C=N), 833m, 777w ν(C=S). <sup>1</sup>H NMR data (DMSO-d<sub>6</sub>, ppm): 11.72 (s, 1H, N(2)—H); 10.03 (s, 1H, C(1)—H); 8.69 (s, 1H, N(2)—H); 8.11 (s, 1H, C(8)—H); 8.04 (d, 2H, J = 8.1 Hz, C(3,7)-H); 7.94 (d, 2H, J = 8.1 Hz, C(4,6)-H); 3.04 (s, 3H, C(10)—H).

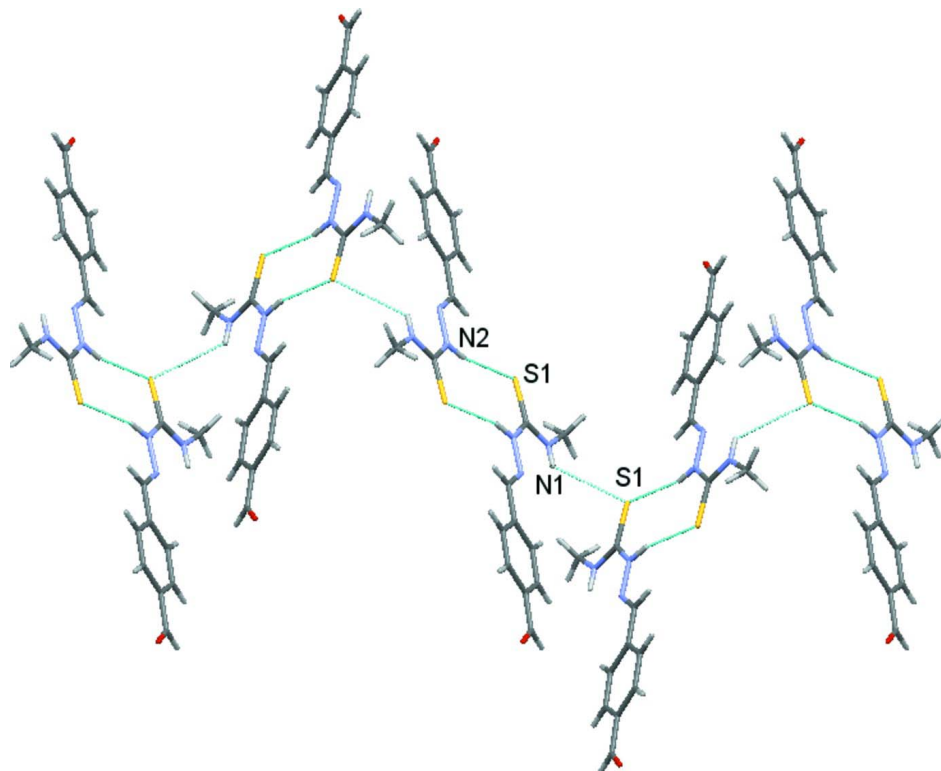
### S2. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H = 0.95–0.99 Å) and were included in the refinement in the riding model approximation, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The N-bound H-atoms were located in a difference Fourier map but were refined with distance restraints N—H = 0.84 (1) and 0.90 (1) Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ .



**Figure 1**

The molecular structure of the title compound showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

**Figure 2**

View of supramolecular chain formed by N—H...S interactions (dashed lines).

### 1-[(4-formylbenzylidene)amino]-3-methylthiourea

#### Crystal data

$C_{10}H_{11}N_3OS$

$M_r = 221.28$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 13.1231 (3) \text{ \AA}$

$b = 8.8559 (2) \text{ \AA}$

$c = 19.3702 (4) \text{ \AA}$

$V = 2251.14 (9) \text{ \AA}^3$

$Z = 8$

$F(000) = 928$

$D_x = 1.306 \text{ Mg m}^{-3}$

Cu  $K\alpha$  radiation,  $\lambda = 1.54178 \text{ \AA}$

Cell parameters from 9894 reflections

$\theta = 4.6\text{--}66.6^\circ$

$\mu = 2.38 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Plate, yellow

$0.14 \times 0.13 \times 0.05 \text{ mm}$

#### Data collection

Bruker CCD SMART 6000  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2007)

$T_{\min} = 0.730$ ,  $T_{\max} = 0.898$

22698 measured reflections

1986 independent reflections

1798 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.046$

$\theta_{\max} = 66.6^\circ$ ,  $\theta_{\min} = 4.6^\circ$

$h = -15 \rightarrow 15$

$k = -10 \rightarrow 10$

$l = -22 \rightarrow 22$

Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.100$   
 $S = 1.08$   
 1986 reflections  
 145 parameters  
 0 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0559P)^2 + 0.3598P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.16 \text{ e } \text{\AA}^{-3}$

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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.90393 (3)	1.04683 (4)	0.40705 (2)	0.06222 (18)
O1	0.88220 (12)	-0.01792 (18)	0.72752 (8)	0.0921 (5)
N1	0.81376 (12)	0.78044 (16)	0.39148 (7)	0.0655 (4)
C1	0.87314 (11)	0.86850 (16)	0.42864 (8)	0.0517 (3)
N2	0.90945 (10)	0.81086 (15)	0.48868 (7)	0.0579 (3)
C2	0.92328 (12)	0.62083 (19)	0.56504 (9)	0.0605 (4)
H2	0.9617	0.6879	0.5913	0.073*
N3	0.88781 (9)	0.66473 (14)	0.50704 (7)	0.0542 (3)
C3	0.90556 (11)	0.46928 (19)	0.59137 (8)	0.0536 (4)
C4	0.93836 (15)	0.43343 (19)	0.65777 (9)	0.0678 (4)
H4	0.9707	0.5066	0.6844	0.081*
C5	0.92354 (14)	0.2913 (2)	0.68448 (9)	0.0675 (4)
H5	0.9454	0.2692	0.7290	0.081*
C6	0.87602 (11)	0.18070 (18)	0.64526 (8)	0.0554 (4)
C7	0.84324 (11)	0.21631 (18)	0.57902 (8)	0.0558 (4)
H7	0.8112	0.1429	0.5524	0.067*
C8	0.85745 (11)	0.35836 (17)	0.55224 (8)	0.0543 (4)
H8	0.8349	0.3805	0.5079	0.065*
C9	0.86069 (14)	0.0265 (2)	0.67155 (10)	0.0678 (4)
H9	0.8313	-0.0428	0.6415	0.081*
C10	0.76953 (19)	0.8229 (2)	0.32581 (10)	0.0924 (7)
H10A	0.7165	0.8957	0.3332	0.139*
H10B	0.7415	0.7351	0.3038	0.139*
H10C	0.8213	0.8660	0.2968	0.139*

H2N	0.9542 (15)	0.865 (2)	0.5138 (9)	0.075 (5)*
H1	0.8010 (15)	0.695 (2)	0.4085 (9)	0.073 (6)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0655 (3)	0.0429 (3)	0.0782 (3)	-0.00218 (15)	-0.01004 (18)	0.00628 (16)
O1	0.1022 (10)	0.0890 (10)	0.0851 (9)	0.0013 (8)	-0.0037 (8)	0.0320 (8)
N1	0.0797 (9)	0.0507 (8)	0.0662 (8)	-0.0120 (7)	-0.0135 (7)	0.0075 (6)
C1	0.0458 (7)	0.0469 (8)	0.0622 (8)	0.0028 (6)	0.0023 (6)	0.0008 (6)
N2	0.0550 (7)	0.0479 (7)	0.0707 (8)	-0.0065 (5)	-0.0097 (6)	0.0089 (6)
C2	0.0566 (8)	0.0555 (9)	0.0693 (9)	-0.0066 (7)	-0.0097 (7)	0.0047 (7)
N3	0.0477 (6)	0.0487 (7)	0.0663 (8)	-0.0014 (5)	-0.0001 (5)	0.0069 (6)
C3	0.0468 (8)	0.0555 (10)	0.0585 (9)	0.0000 (6)	-0.0032 (6)	0.0047 (6)
C4	0.0759 (11)	0.0641 (10)	0.0635 (9)	-0.0119 (8)	-0.0176 (8)	0.0023 (7)
C5	0.0763 (10)	0.0707 (11)	0.0555 (9)	-0.0044 (8)	-0.0131 (8)	0.0106 (8)
C6	0.0504 (8)	0.0573 (9)	0.0585 (8)	0.0032 (6)	0.0018 (6)	0.0059 (7)
C7	0.0539 (8)	0.0544 (9)	0.0590 (8)	-0.0013 (6)	-0.0037 (6)	-0.0017 (7)
C8	0.0536 (8)	0.0564 (9)	0.0531 (7)	0.0013 (6)	-0.0071 (6)	0.0040 (6)
C9	0.0656 (10)	0.0653 (10)	0.0724 (10)	0.0035 (8)	0.0001 (8)	0.0122 (8)
C10	0.1231 (18)	0.0784 (12)	0.0756 (11)	-0.0277 (12)	-0.0324 (12)	0.0131 (10)

*Geometric parameters (Å, °)*

S1—C1	1.6829 (15)	C3—C8	1.392 (2)
O1—C9	1.187 (2)	C3—C4	1.393 (2)
N1—C1	1.317 (2)	C4—C5	1.375 (2)
N1—C10	1.448 (2)	C5—C6	1.388 (2)
C1—N2	1.356 (2)	C6—C7	1.390 (2)
N2—N3	1.3718 (18)	C6—C9	1.471 (2)
C2—N3	1.277 (2)	C7—C8	1.373 (2)
C2—C3	1.454 (2)		
C1—N1—C10	124.33 (15)	C4—C3—C2	118.99 (15)
N1—C1—N2	116.98 (14)	C5—C4—C3	120.82 (15)
N1—C1—S1	124.20 (12)	C4—C5—C6	120.26 (15)
N2—C1—S1	118.81 (12)	C5—C6—C7	118.98 (15)
C1—N2—N3	120.30 (13)	C5—C6—C9	121.80 (15)
N3—C2—C3	122.09 (15)	C7—C6—C9	119.21 (15)
C2—N3—N2	116.10 (13)	C8—C7—C6	120.97 (15)
C8—C3—C4	118.82 (15)	C7—C8—C3	120.15 (14)
C8—C3—C2	122.19 (14)	O1—C9—C6	126.24 (19)

*Hydrogen-bond geometry (Å, °)*

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2N $\cdots$ S1 <sup>i</sup>	0.902 (19)	2.53 (2)	3.4154 (14)	165.6 (16)

N1—H1…N3	0.84 (2)	2.238 (18)	2.6467 (18)	109.9 (15)
N1—H1…S1 <sup>ii</sup>	0.84 (2)	2.992 (19)	3.5401 (15)	124.6 (16)

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