Acta Cryst E STRUCTURE REPORTS

OPEN ACCESS

ISSN 1600-5368

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

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

Departamento de Química Inorgánica, Facultade de Química, Edificio de Ciencias Experimentais, Universidade de Vigo, E-36310 Vigo, Galicia, Spain. *Correspondence e-mail: ezequiel@uvigo.es

Received 11 July 2014; accepted 15 July 2014

Edited by E. R. T. Tiekink, University of Malaya, Malaysia

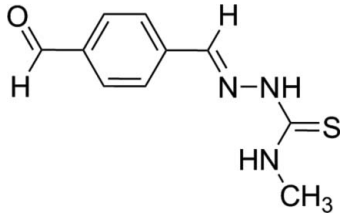
The structure of the title compound, $C_{10}H_{11}N_3OS$, comprises an approximately planar molecule, with the r.m.s. deviation for the 15 non-H atoms being 0.089 Å. The conformation about the imine bond is *E* and an intramolecular N—H···N hydrogen bond is evident. Molecules are linked into a supramolecular 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

$C_{10}H_{11}N_3OS$
M_r = 221.28
Orthorhombic, *Pbca*
a = 13.1231 (3) Å
b = 8.8559 (2) Å
c = 19.3702 (4) Å
V = 2251.14 (9) Å^3
Z = 8
Cu *K*α radiation
μ = 2.38 mm^{-1}
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_{min} = 0.730, T_{max} = 0.898
22698 measured reflections
1986 independent reflections
1798 reflections with $I > 2\sigma(I)$
R_{int} = 0.046

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.100
S = 1.08
1986 reflections
145 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2N···S1^{i}	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^{ii}	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

This research was supported by the European Rural Development Fund and the Spanish Ministry of Education and Science through Project CTQ2010–19386/BQU.

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.* B**58**, 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.* A**64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2014). E**70**, o926 [doi:10.1107/S1600536814016407]

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

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

S1. Chemical context

S2. Structural commentary

S3. 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 terephthaldicarboxaldehyde (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_2O (1:1). Yield: 91%, M. pt: 213-216 °C. IR data (KBr, cm^{-1}): 3368m, 3150m *v*(N—H); 2838w, 2742w *v*(C—H aldehyde); 1692 s *v*(C═O); 1545 s, 1257m *v*(C═N), 833m, 777w *v*(C═S). ^{1}H NMR data (DMSO-d_6, 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).

S4. 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_{iso}(H) = 1.2U_{eq}(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_{iso}(H) = 1.2U_{eq}(N).

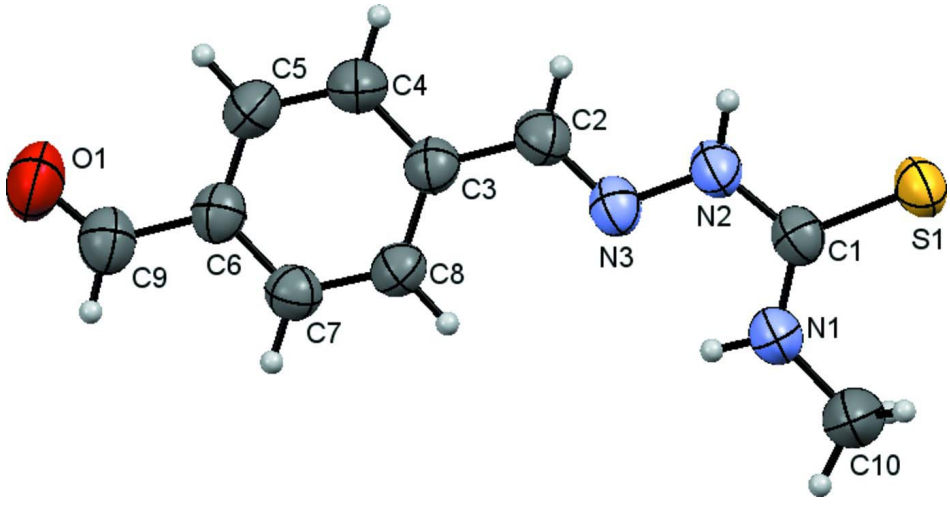


Figure 1

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

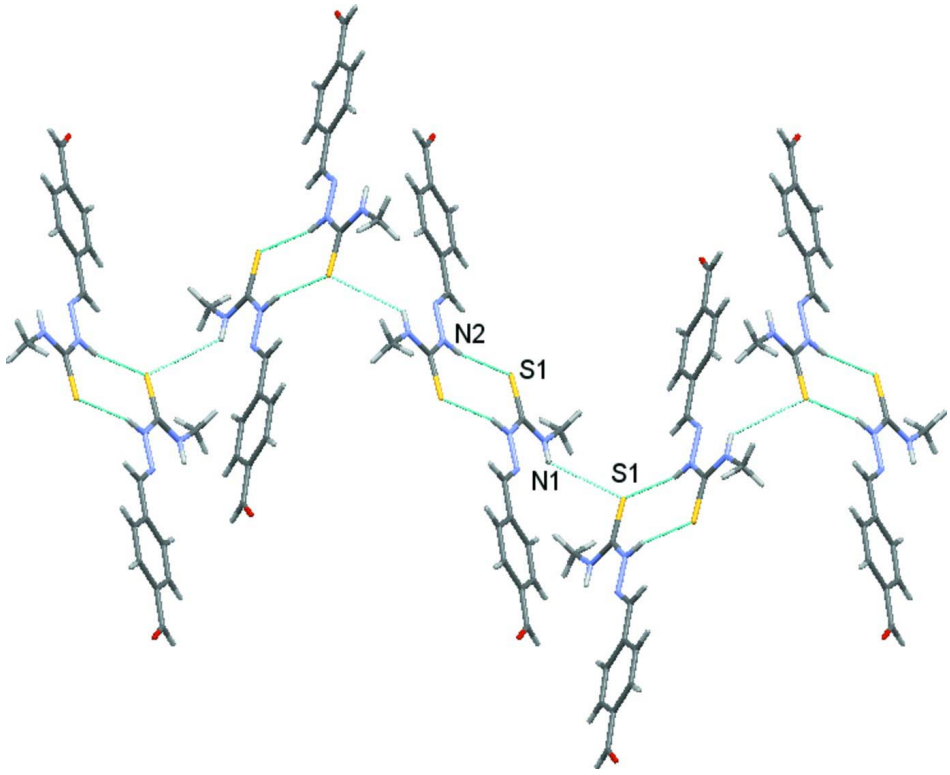


Figure 2

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) Å
$b = 8.8559$ (2) Å
$c = 19.3702$ (4) Å
$V = 2251.14$ (9) Å^3
$Z = 8$

$F(000) = 928$
$D_x = 1.306$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Cell parameters from 9894 reflections
$\theta = 4.6$–$66.6°$
$\mu = 2.38$ mm^{-1}
$T = 296$ K
Plate, yellow
0.14 × 0.13 × 0.05 mm

Data collection

Bruker CCD SMART 6000 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω 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 $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 66.6°$, $\theta_{min} = 4.6°$
$h = -15 \rightarrow 15$
$k = -10 \rightarrow 10$
$l = -22 \rightarrow 22$

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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{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 (Å²)

	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, º)

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, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*N*···S1^{i}	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^{ii}	0.84 (2)	2.992 (19)	3.5401 (15)	124.6 (16)

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