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## Structure Reports

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## 4-Methylbenzaldehyde thiosemi-carbazone

Jian Zhang, Hao Geng, Ling-hua Zhuang and Guo-wei Wang\*

Department of Light Chemical Engineering, College of Food Science and Light Engineering, Nanjing University of Technology, Nanjing 210009, People's Republic of China

Correspondence e-mail: kingwell2004@sina.com.cn

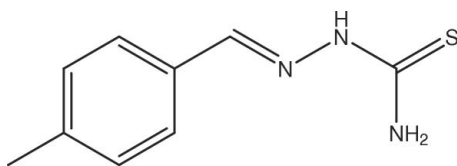
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.052;  $wR$  factor = 0.146; data-to-parameter ratio = 15.8.

The title compound,  $\text{C}_9\text{H}_{11}\text{N}_3\text{S}$ , was prepared by reacting 4-methylbenzaldehyde with thiosemicarbazide. An intramolecular  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bond helps to establish the observed molecular conformation. The crystal packing is realized by intermolecular  $\text{N}-\text{H}\cdots\text{S}$  hydrogen bonds.

## Related literature

For general background to thiosemicarbazone compounds, see: Casas *et al.* (2000); Tarafder *et al.* (2000); Ferrari *et al.* (2000); Deschamps *et al.* (2003); Maccioni *et al.* (2003); Chimenti *et al.* (2007); Zhang *et al.* (2009). For bond-length data, see: Allen *et al.* (1987).



## Experimental

## Crystal data

$\text{C}_9\text{H}_{11}\text{N}_3\text{S}$   
 $M_r = 193.27$   
 Monoclinic,  $P2_1/c$   
 $a = 13.234$  (3) Å  
 $b = 8.221$  (2) Å  
 $c = 10.311$  (2) Å  
 $\beta = 111.15$  (3)°

$V = 1046.2$  (4) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.27$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.30 \times 0.20 \times 0.10$  mm

## Data collection

Enraf–Nonius CAD-4 diffractometer  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{\min} = 0.924$ ,  $T_{\max} = 0.974$   
 1982 measured reflections

1898 independent reflections  
 1322 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.032$   
 3 standard reflections every 200 reflections  
 intensity decay: 9%

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$   
 $wR(F^2) = 0.146$   
 $S = 1.00$   
 1988 reflections

120 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.26$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.20$  e Å<sup>-3</sup>

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H2A}\cdots\text{S}^{\text{i}}$	0.86	2.54	3.389 (3)	168
$\text{N3}-\text{H3B}\cdots\text{S}^{\text{ii}}$	0.86	2.61	3.395 (3)	153
$\text{N3}-\text{H3A}\cdots\text{N1}$	0.86	2.29	2.641 (4)	105

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); 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: IM2136).

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## supporting information

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## 4-Methylbenzaldehyde thiosemicarbazone

Jian Zhang, Hao Geng, Ling-hua Zhuang and Guo-wei Wang

### S1. Comment

Thiosemicarbazones constitute an important class of N,S donor ligands due to their ability to react with a wide range of metals (Casas *et al.*, 2000). Thiosemicarbazones exhibit various biological activities and have therefore attracted considerable pharmaceutical interest (Maccioni *et al.*, 2003; Ferrari *et al.*, 2000). They have been evaluated as antiviral, antibacterial and anticancer therapeutics. Thiosemicarbazones belong to a large group of thiourea derivatives, whose biological activities are a function of the parent aldehyde or ketone moiety (Chimenti *et al.*, 2007). Schiff bases in general show potential as antimicrobial and anticancer agents (Tarafder *et al.*, 2000; Deschamps *et al.*, 2003) and have therefore envisaged biochemical and pharmacological applications. We are focusing our synthetic and structural studies on new products of thiazole Schiff bases from thiosemicarbazones (Zhang *et al.*, 2009). We herein report the crystal structure of the title compound (I).

The atom-numbering scheme of (I) is shown in Fig.1, and all bond lengths are within normal ranges (Allen *et al.*, 1987).

The sulfur atom and the hydrazine nitrogen N1 are in *trans* position with respect to the C9–N2 bond. The molecular conformation is determined by a strong intramolecular hydrogen bond N3–H3A···N1(2.641 (3) Å).

The planar phenyl ring A (C2/C3/C4/C5/C6/C7, r.m.s. deviation 0.0115 (1) Å) and the pseudo five-membered ring B(N1/N2/C9/N3/H3A, r.m.s. deviation 0.035 (1) Å) that is formed by the N3–H3A···N1 hydrogen bond enclose a dihedral angle of 14 (1)°. The dihedral angle between the thiourea group (N1/N2/C9/S) and the phenyl ring measures to 17 (2)°.

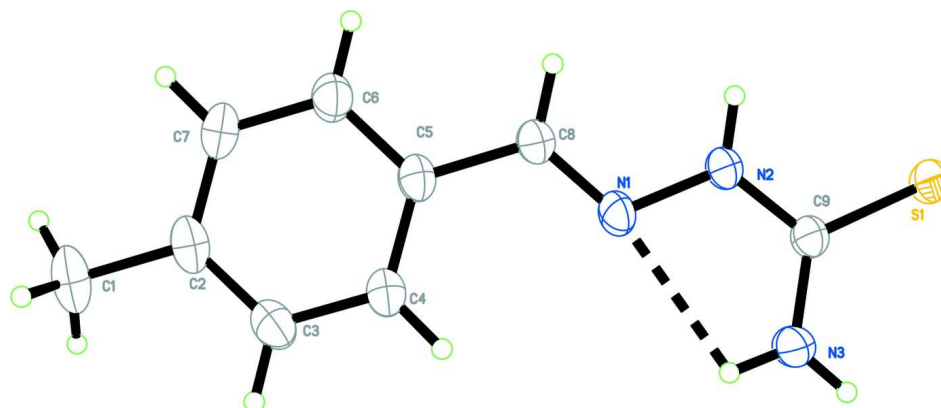
The crystal packing is realized by intermolecular N–H···S hydrogen bonds (Table 1, Fig. 1 and Fig.2).

### S2. Experimental

A mixture of 4-methyl-benzaldehyde (1.20 g, 0.01 mol) and hydrazinecarbothioamide (0.91 g, 0.01 mol) in 20 ml of absolute methanol was refluxed for about 3 h. After cooling, the precipitated solid separated was filtered and recrystallized from ethyl acetate. Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of ethyl acetate at room temperature. <sup>1</sup>H NMR (DMSO, δ, p.p.m.) 11.39 (s, 1 H), 8.17 (s, 1 H), 8.02 (s, 2 H), 7.42 (m, 1 H), 7.30 (t, 2 H), 6.99 (t, 1 H), 1.79 (t, 3 H).

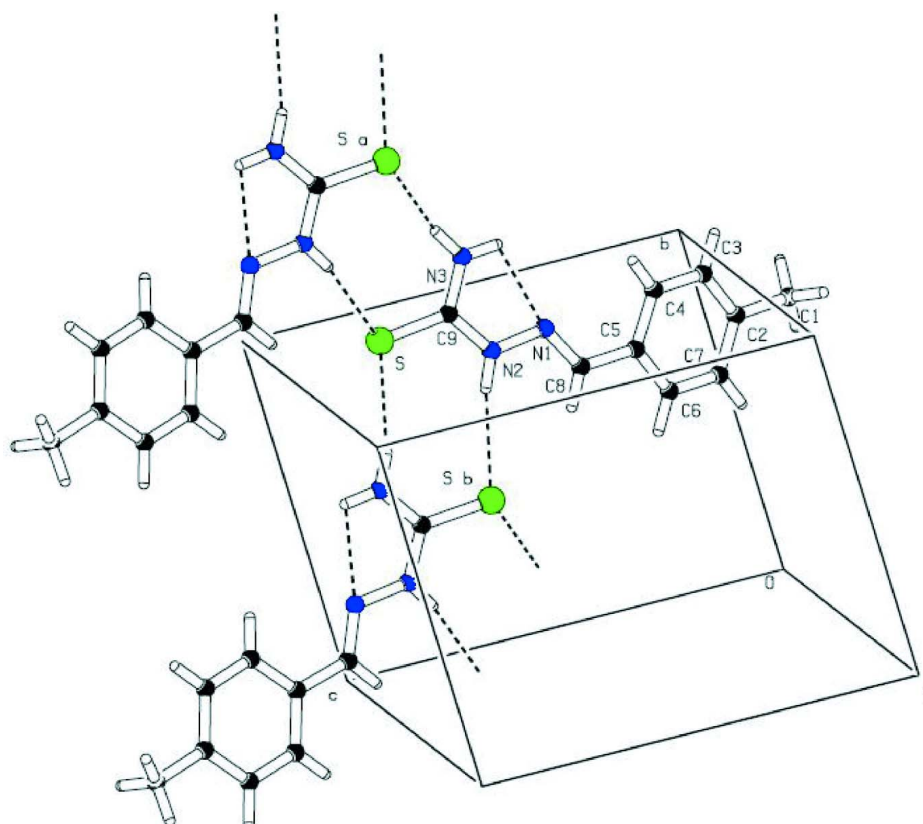
### S3. Refinement

All H atoms were positioned geometrically, with C–H = 0.93 Å and N–H = 0.86 Å, and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$ , where  $x = 1.5$  for methyl H and  $x = 1.2$  for methylene H atoms.



**Figure 1**

Molecular structure of (I) showing the atom-numbering scheme and 30% displacement ellipsoids. The intramolecular hydrogen bond is shown as dashed lines.



**Figure 2**

Crystal packing of (I). Hydrogen bonds are drawn as dashed lines.

#### 4-Methylbenzaldehyde thiosemicarbazone

##### Crystal data

$C_9H_{11}N_3S$

$M_r = 193.27$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P 2_1/c$

$a = 13.234 (3) \text{ \AA}$

$b = 8.221 (2) \text{ \AA}$

$c = 10.311 (2) \text{ \AA}$   
 $\beta = 111.15 (3)^\circ$   
 $V = 1046.2 (4) \text{ \AA}^3$   
 $Z = 4$   
 $F(000) = 408$   
 $D_x = 1.227 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 27 reflections  
 $\theta = 1-25^\circ$   
 $\mu = 0.27 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
 Block, colorless  
 $0.30 \times 0.20 \times 0.10 \text{ mm}$

*Data collection*

Enraf-Nonius CAD-4  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 $\omega/2\theta$  scans  
 Absorption correction:  $\psi$  scan  
 (North *et al.*, 1968)  
 $T_{\min} = 0.924$ ,  $T_{\max} = 0.974$   
 1982 measured reflections

1898 independent reflections  
 1322 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.032$   
 $\theta_{\max} = 25.3^\circ$ ,  $\theta_{\min} = 1.7^\circ$   
 $h = -15 \rightarrow 0$   
 $k = 0 \rightarrow 9$   
 $l = -11 \rightarrow 12$   
 3 standard reflections every 200 reflections  
 intensity decay: 9%

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.052$   
 $wR(F^2) = 0.146$   
 $S = 1.00$   
 1898 reflections  
 120 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-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 0.38P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.26 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.20 \text{ e \AA}^{-3}$   
 Extinction correction: *SHELXL97* (Sheldrick,  
 2008),  $F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.034 (4)

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

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
S	0.48277 (7)	0.09017 (9)	0.81196 (7)	0.0534 (3)
N1	0.34064 (18)	-0.0455 (3)	0.4236 (2)	0.0438 (6)
C1	-0.0005 (3)	-0.2600 (6)	-0.1894 (3)	0.0788 (12)
H1B	-0.0374	-0.3614	-0.1934	0.118*
H1C	0.0324	-0.2593	-0.2585	0.118*
H1D	-0.0514	-0.1721	-0.2067	0.118*
N2	0.40264 (19)	-0.0458 (3)	0.5647 (2)	0.0456 (6)

H2A	0.4275	-0.1358	0.6065	0.055*
C2	0.0863 (3)	-0.2397 (5)	-0.0467 (3)	0.0560 (9)
N3	0.3955 (2)	0.2299 (3)	0.5633 (3)	0.0630 (8)
H3A	0.3650	0.2263	0.4743	0.076*
H3B	0.4078	0.3222	0.6054	0.076*
C3	0.1264 (3)	-0.0877 (4)	0.0043 (3)	0.0614 (9)
H3C	0.1006	0.0034	-0.0513	0.074*
C4	0.2041 (3)	-0.0681 (4)	0.1365 (3)	0.0553 (8)
H4A	0.2302	0.0352	0.1678	0.066*
C5	0.2429 (2)	-0.2018 (4)	0.2222 (3)	0.0445 (7)
C6	0.2060 (2)	-0.3553 (4)	0.1705 (3)	0.0521 (8)
H6A	0.2329	-0.4465	0.2255	0.063*
C7	0.1289 (3)	-0.3741 (4)	0.0370 (3)	0.0565 (9)
H7A	0.1056	-0.4779	0.0036	0.068*
C8	0.3157 (2)	-0.1842 (4)	0.3664 (3)	0.0452 (7)
H8A	0.3446	-0.2770	0.4180	0.054*
C9	0.4235 (2)	0.0939 (3)	0.6353 (3)	0.0420 (7)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S	0.0798 (6)	0.0472 (5)	0.0282 (4)	-0.0056 (4)	0.0134 (4)	-0.0039 (3)
N1	0.0512 (15)	0.0501 (15)	0.0282 (11)	-0.0033 (11)	0.0121 (10)	-0.0016 (10)
C1	0.071 (2)	0.116 (3)	0.0399 (18)	-0.014 (2)	0.0086 (17)	-0.015 (2)
N2	0.0603 (16)	0.0443 (14)	0.0268 (11)	-0.0011 (12)	0.0094 (11)	-0.0010 (10)
C2	0.0497 (19)	0.081 (2)	0.0362 (16)	-0.0065 (17)	0.0143 (14)	-0.0080 (16)
N3	0.100 (2)	0.0425 (15)	0.0339 (13)	0.0016 (14)	0.0082 (14)	-0.0005 (11)
C3	0.068 (2)	0.067 (2)	0.0419 (17)	-0.0007 (18)	0.0119 (16)	0.0070 (16)
C4	0.064 (2)	0.055 (2)	0.0386 (16)	-0.0061 (16)	0.0082 (14)	-0.0039 (14)
C5	0.0452 (17)	0.0530 (18)	0.0342 (14)	-0.0006 (14)	0.0131 (12)	-0.0056 (13)
C6	0.0556 (19)	0.0562 (19)	0.0423 (17)	-0.0015 (15)	0.0151 (14)	-0.0060 (15)
C7	0.057 (2)	0.066 (2)	0.0451 (17)	-0.0113 (16)	0.0169 (15)	-0.0190 (16)
C8	0.0516 (18)	0.0476 (18)	0.0332 (14)	0.0002 (14)	0.0115 (13)	-0.0019 (13)
C9	0.0492 (17)	0.0438 (16)	0.0320 (14)	-0.0015 (13)	0.0135 (12)	-0.0018 (13)

*Geometric parameters (Å, °)*

S—C9	1.704 (3)	N3—H3A	0.8600
N1—C8	1.271 (4)	N3—H3B	0.8600
N1—N2	1.389 (3)	C3—C4	1.390 (4)
C1—C2	1.514 (4)	C3—H3C	0.9300
C1—H1B	0.9600	C4—C5	1.387 (4)
C1—H1C	0.9600	C4—H4A	0.9300
C1—H1D	0.9600	C5—C6	1.388 (4)
N2—C9	1.334 (3)	C5—C8	1.458 (4)
N2—H2A	0.8600	C6—C7	1.395 (4)
C2—C3	1.385 (5)	C6—H6A	0.9300
C2—C7	1.390 (5)	C7—H7A	0.9300

N3—C9	1.319 (3)	C8—H8A	0.9300
C8—N1—N2	116.1 (2)	C5—C4—C3	120.4 (3)
C2—C1—H1B	109.5	C5—C4—H4A	119.8
C2—C1—H1C	109.5	C3—C4—H4A	119.8
H1B—C1—H1C	109.5	C4—C5—C6	118.5 (3)
C2—C1—H1D	109.5	C4—C5—C8	121.9 (3)
H1B—C1—H1D	109.5	C6—C5—C8	119.5 (3)
H1C—C1—H1D	109.5	C5—C6—C7	120.7 (3)
C9—N2—N1	119.9 (2)	C5—C6—H6A	119.7
C9—N2—H2A	120.1	C7—C6—H6A	119.7
N1—N2—H2A	120.1	C2—C7—C6	120.8 (3)
C3—C2—C7	117.9 (3)	C2—C7—H7A	119.6
C3—C2—C1	121.4 (3)	C6—C7—H7A	119.6
C7—C2—C1	120.8 (3)	N1—C8—C5	121.8 (3)
C9—N3—H3A	120.0	N1—C8—H8A	119.1
C9—N3—H3B	120.0	C5—C8—H8A	119.1
H3A—N3—H3B	120.0	N3—C9—N2	117.5 (2)
C2—C3—C4	121.6 (3)	N3—C9—S	123.0 (2)
C2—C3—H3C	119.2	N2—C9—S	119.5 (2)
C4—C3—H3C	119.2		
C8—N1—N2—C9	-173.6 (3)	C3—C2—C7—C6	2.8 (5)
C7—C2—C3—C4	-2.1 (5)	C1—C2—C7—C6	-177.7 (3)
C1—C2—C3—C4	178.4 (3)	C5—C6—C7—C2	-0.8 (5)
C2—C3—C4—C5	-0.7 (5)	N2—N1—C8—C5	174.4 (2)
C3—C4—C5—C6	2.8 (5)	C4—C5—C8—N1	5.3 (5)
C3—C4—C5—C8	-173.4 (3)	C6—C5—C8—N1	-170.9 (3)
C4—C5—C6—C7	-2.0 (5)	N1—N2—C9—N3	-8.5 (4)
C8—C5—C6—C7	174.2 (3)	N1—N2—C9—S	170.71 (19)

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3A $\cdots$ N1	0.86	2.29	2.641 (4)	105
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