

## 4-(Methylsulfanyl)benzaldehyde semicarbazone

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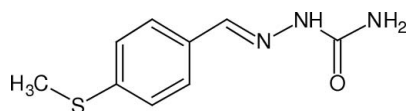
Key indicators: single-crystal X-ray study;  $T = 173$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å; disorder in main residue;  $R$  factor = 0.054;  $wR$  factor = 0.168; data-to-parameter ratio = 14.2.

The crystal packing of the title compound,  $\text{C}_9\text{H}_{11}\text{N}_3\text{OS}$ , is stabilized by two  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds. One of the amino H atoms is not involved in a classical hydrogen bond. The methyl group is disordered over two positions with almost equal occupancies.

### Related literature

For related structures, see: acetone semicarbazone and benzaldehyde semicarbazone (Naik & Palenik, 1974); 3,4-methylenedioxybenzaldehyde semicarbazone (Wang *et al.*, 2004); 4-(methylsulfanyl)benzaldehyde thiosemicarbazone (Yathirajan *et al.*, 2006).

For related literature, see: Fichou *et al.* (1988); Furniss *et al.* (1989); Goto *et al.* (1991); Tam *et al.* (1989); Indira *et al.* (2002); Vijayan *et al.* (2001); Ramesh Babu *et al.* (2002); Manivennan & Dhanushkodi (2003).



### Experimental

#### Crystal data

$\text{C}_9\text{H}_{11}\text{N}_3\text{OS}$   
 $M_r = 209.27$   
 Monoclinic,  $P2_1/c$   
 $a = 15.1006$  (19) Å  
 $b = 5.3082$  (7) Å  
 $c = 13.0746$  (17) Å  
 $\beta = 107.494$  (9)°

$V = 999.5$  (2) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.29$  mm<sup>-1</sup>  
 $T = 173$  (2) K  
 $0.48 \times 0.45 \times 0.43$  mm

#### Data collection

Stoe IPDS II two-circle diffractometer  
 Absorption correction: multi-scan [*MULABS* (Spek, 2003; Blessing, 1995)]  
 $T_{\min} = 0.872$ ,  $T_{\max} = 0.884$   
 7445 measured reflections  
 2162 independent reflections  
 1678 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.053$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.168$   
 $S = 1.09$   
 2162 reflections  
 152 parameters  
 3 restraints  
 H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.46$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.66$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H2}\cdots\text{O1}^{\text{i}}$	0.881 (10)	2.016 (11)	2.886 (3)	169 (2)
$\text{N3}-\text{H3A}\cdots\text{O1}^{\text{ii}}$	0.886 (10)	2.025 (12)	2.904 (3)	171 (4)

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

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2410).

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**supplementary materials**

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#### 4-(Methylsulfonyl)benzaldehyde semicarbazone

B. K. Sarojini, B. Narayana, S. Bindya, H. S. Yathirajan and M. Bolte

##### Comment

NLO materials play an important role in the field of fibre optic communications and optical signal processing. In the last two decades, extensive research has shown that organic crystals can exhibit nonlinear optical efficiencies which are two orders of magnitude higher than those of inorganic materials. Thiosemicarbazones (TSCs) of aromatic aldehydes and ketones are widely known as carcinostatic and antimicrobial agents. Semicarbazones of substituted benzaldehydes and acetophenones were reported to be some of the potential organic NLO materials. In the present paper, we report the crystal structure of title compound, (I), C<sub>9</sub>H<sub>11</sub>N<sub>3</sub>OS.

##### Experimental

The title compound was synthesized according to the literature method (Furnis *et al.*, 1989) with a yield of 80% and purified by recrystallization from ethanol. Crystals of (I) were grown from DMF solution by slow evaporation (m.p. 423–425 K). Analysis for C<sub>9</sub>H<sub>11</sub>N<sub>3</sub>OS: Found (Calculated): C 51.55 (51.65); H 5.28 (5.30); N 20.15% (20.08%).

##### Refinement

The H atoms were found in a difference map, but those bonded to C were refined using a riding model with C—H = 0.95 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or C—H = 0.98 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$ . The H atoms bonded to N were refined with an N—H distance restraint of 0.88 (1) Å. The methyl group is disordered over two sites with occupation factors of 0.505 (6) and 0.495 (6).

##### Figures

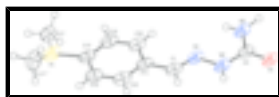


Fig. 1. Perspective view of (I); displacement ellipsoids are at the 50% probability level (arbitrary spheres for the H atoms). One site of the disordered methyl group is shown with dashed bonds.

#### 4-(Methylthio)benzaldehyde semicarbazone

##### Crystal data

C<sub>9</sub>H<sub>11</sub>N<sub>3</sub>OS

$M_r = 209.27$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 15.1006$  (19) Å

$F_{000} = 440$

$D_x = 1.391$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 5218 reflections

$\theta = 3.3\text{--}27.2^\circ$

# supplementary materials

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$b = 5.3082 (7) \text{ \AA}$   
 $c = 13.0746 (17) \text{ \AA}$   
 $\beta = 107.494 (9)^\circ$   
 $V = 999.5 (2) \text{ \AA}^3$   
 $Z = 4$

$\mu = 0.29 \text{ mm}^{-1}$   
 $T = 173 (2) \text{ K}$   
Block, colourless  
 $0.48 \times 0.45 \times 0.43 \text{ mm}$

## Data collection

Stoe IPDS II two-circle diffractometer  
Radiation source: fine-focus sealed tube  
Monochromator: graphite  
 $T = 173(2) \text{ K}$   
 $\omega$  scans  
Absorption correction: multi-scan [MULABS (Spek, 2003; Blessing, 1995)]  
 $T_{\min} = 0.872$ ,  $T_{\max} = 0.884$   
7445 measured reflections

2162 independent reflections  
1678 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.053$   
 $\theta_{\max} = 27.0^\circ$   
 $\theta_{\min} = 2.8^\circ$   
 $h = -19 \rightarrow 19$   
 $k = -6 \rightarrow 6$   
 $l = -14 \rightarrow 16$

## Refinement

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.168$   
 $S = 1.09$   
2162 reflections  
152 parameters  
3 restraints  
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map  
Hydrogen site location: difference Fourier map  
H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0852P)^2 + 0.4974P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.46 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.66 \text{ e \AA}^{-3}$   
Extinction correction: SHELXL (Sheldrick, 1997),  
 $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
Extinction coefficient: 0.087 (13)

## Special details

### Experimental ;

**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  $F^2 > 2\sigma(F^2)$  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	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N2	0.08441 (13)	-0.2424 (3)	0.53704 (18)	0.0462 (5)	
H2	0.0655 (18)	-0.359 (4)	0.4872 (17)	0.051 (7)*	
S1	0.42858 (5)	0.66516 (12)	0.32545 (8)	0.0703 (4)	
O1	0.00019 (11)	-0.4136 (3)	0.63569 (15)	0.0487 (5)	
N1	0.13881 (12)	-0.0461 (3)	0.52048 (17)	0.0439 (5)	
N3	0.07342 (13)	-0.0387 (4)	0.68943 (18)	0.0478 (5)	
H3A	0.049 (2)	-0.017 (7)	0.7422 (19)	0.075 (10)*	
H3B	0.1089 (17)	0.078 (4)	0.675 (2)	0.057 (8)*	
C1	0.15927 (14)	-0.0536 (4)	0.4320 (2)	0.0440 (6)	
H1	0.1340	-0.1846	0.3823	0.053*	
C2	0.04991 (14)	-0.2357 (4)	0.62250 (19)	0.0426 (6)	
C11	0.22026 (14)	0.1332 (4)	0.4052 (2)	0.0424 (5)	
C12	0.24456 (15)	0.1058 (4)	0.3108 (2)	0.0477 (6)	
H12	0.2182	-0.0281	0.2631	0.057*	
C13	0.30620 (15)	0.2693 (5)	0.2850 (2)	0.0478 (6)	
H13	0.3216	0.2469	0.2203	0.057*	
C14	0.34570 (14)	0.4670 (4)	0.3542 (2)	0.0451 (6)	
C15	0.32039 (15)	0.4988 (4)	0.4481 (2)	0.0482 (6)	
H15	0.3461	0.6340	0.4953	0.058*	
C16	0.25829 (16)	0.3356 (4)	0.4730 (2)	0.0466 (6)	
H16	0.2413	0.3611	0.5366	0.056*	
C17	0.4761 (3)	0.8650 (9)	0.4225 (4)	0.0513 (14)	0.495 (6)
H17A	0.5225	0.9672	0.4026	0.077*	0.495 (6)
H17B	0.5063	0.7718	0.4885	0.077*	0.495 (6)
H17C	0.4280	0.9752	0.4342	0.077*	0.495 (6)
C17'	0.4006 (4)	0.6638 (12)	0.1996 (5)	0.0642 (17)	0.505 (6)
H17D	0.3337	0.6944	0.1701	0.096*	0.505 (6)
H17E	0.4158	0.4998	0.1749	0.096*	0.505 (6)
H17F	0.4347	0.7965	0.1754	0.096*	0.505 (6)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N2	0.0425 (9)	0.0279 (9)	0.0604 (12)	-0.0064 (7)	0.0039 (9)	-0.0055 (8)
S1	0.0441 (4)	0.0384 (4)	0.1218 (8)	-0.0049 (2)	0.0148 (4)	0.0032 (3)
O1	0.0434 (8)	0.0270 (7)	0.0686 (12)	-0.0057 (6)	0.0062 (7)	-0.0010 (7)
N1	0.0352 (9)	0.0267 (9)	0.0601 (13)	-0.0011 (7)	-0.0002 (8)	-0.0003 (8)
N3	0.0440 (10)	0.0299 (9)	0.0614 (13)	-0.0066 (8)	0.0036 (9)	-0.0039 (9)
C1	0.0347 (10)	0.0293 (10)	0.0572 (14)	0.0016 (8)	-0.0027 (9)	-0.0030 (9)
C2	0.0327 (10)	0.0267 (9)	0.0575 (14)	0.0025 (8)	-0.0029 (9)	0.0019 (9)
C11	0.0318 (9)	0.0286 (10)	0.0562 (14)	0.0048 (7)	-0.0027 (9)	0.0006 (9)
C12	0.0373 (10)	0.0354 (11)	0.0584 (15)	0.0020 (8)	-0.0036 (10)	-0.0072 (10)
C13	0.0415 (11)	0.0406 (12)	0.0540 (14)	0.0052 (9)	0.0031 (10)	-0.0035 (10)
C14	0.0363 (10)	0.0293 (10)	0.0611 (15)	0.0067 (8)	0.0018 (9)	0.0008 (9)

## supplementary materials

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C15	0.0452 (11)	0.0290 (10)	0.0605 (15)	-0.0003 (9)	0.0009 (10)	-0.0058 (9)
C16	0.0423 (11)	0.0322 (11)	0.0562 (14)	0.0010 (8)	0.0012 (10)	-0.0008 (9)
C17	0.036 (2)	0.043 (3)	0.068 (3)	-0.0043 (18)	0.005 (2)	0.007 (2)
C17'	0.054 (3)	0.070 (4)	0.064 (4)	-0.014 (3)	0.011 (2)	0.012 (3)

### *Geometric parameters (Å, °)*

N2—C2	1.368 (3)	C12—C13	1.386 (4)
N2—N1	1.384 (3)	C12—H12	0.9500
N2—H2	0.881 (10)	C13—C14	1.397 (3)
S1—C17'	1.571 (6)	C13—H13	0.9500
S1—C17	1.644 (5)	C14—C15	1.401 (4)
S1—C14	1.760 (2)	C15—C16	1.385 (3)
O1—C2	1.250 (3)	C15—H15	0.9500
N1—C1	1.285 (3)	C16—H16	0.9500
N3—C2	1.341 (3)	C17—H17A	0.9800
N3—H3A	0.886 (10)	C17—H17B	0.9800
N3—H3B	0.875 (10)	C17—H17C	0.9800
C1—C11	1.466 (3)	C17'—H17D	0.9800
C1—H1	0.9500	C17'—H17E	0.9800
C11—C12	1.397 (4)	C17'—H17F	0.9800
C11—C16	1.402 (3)		
C2—N2—N1	119.86 (19)	C12—C13—C14	120.0 (2)
C2—N2—H2	120.2 (19)	C12—C13—H13	120.0
N1—N2—H2	119.3 (19)	C14—C13—H13	120.0
C17'—S1—C17	136.8 (3)	C13—C14—C15	118.8 (2)
C17'—S1—C14	103.7 (2)	C13—C14—S1	120.2 (2)
C17—S1—C14	113.2 (2)	C15—C14—S1	120.93 (17)
C1—N1—N2	115.62 (19)	C16—C15—C14	120.8 (2)
C2—N3—H3A	121 (2)	C16—C15—H15	119.6
C2—N3—H3B	118 (2)	C14—C15—H15	119.6
H3A—N3—H3B	121 (3)	C15—C16—C11	120.5 (3)
N1—C1—C11	122.2 (2)	C15—C16—H16	119.7
N1—C1—H1	118.9	C11—C16—H16	119.7
C11—C1—H1	118.9	S1—C17—H17A	109.5
O1—C2—N3	123.5 (2)	S1—C17—H17B	109.5
O1—C2—N2	119.0 (2)	S1—C17—H17C	109.5
N3—C2—N2	117.5 (2)	S1—C17'—H17D	109.5
C12—C11—C16	118.2 (2)	S1—C17'—H17E	109.5
C12—C11—C1	119.5 (2)	H17D—C17'—H17E	109.5
C16—C11—C1	122.3 (2)	S1—C17'—H17F	109.5
C13—C12—C11	121.6 (2)	H17D—C17'—H17F	109.5
C13—C12—H12	119.2	H17E—C17'—H17F	109.5
C11—C12—H12	119.2		
C2—N2—N1—C1	-172.28 (18)	C12—C13—C14—S1	176.68 (16)
N2—N1—C1—C11	-176.76 (17)	C17'—S1—C14—C13	29.8 (3)
N1—N2—C2—O1	179.36 (18)	C17—S1—C14—C13	-173.2 (2)
N1—N2—C2—N3	-2.1 (3)	C17'—S1—C14—C15	-152.3 (3)
N1—C1—C11—C12	175.99 (19)	C17—S1—C14—C15	4.7 (3)

N1—C1—C11—C16	-1.7 (3)	C13—C14—C15—C16	0.9 (3)
C16—C11—C12—C13	1.5 (3)	S1—C14—C15—C16	-177.06 (16)
C1—C11—C12—C13	-176.25 (19)	C14—C15—C16—C11	0.7 (3)
C11—C12—C13—C14	0.1 (3)	C12—C11—C16—C15	-1.9 (3)
C12—C13—C14—C15	-1.3 (3)	C1—C11—C16—C15	175.80 (19)

*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—H2 $\cdots$ O1 <sup>i</sup>	0.881 (10)	2.016 (11)	2.886 (3)	169 (2)
N3—H3A $\cdots$ O1 <sup>ii</sup>	0.886 (10)	2.025 (12)	2.904 (3)	171 (4)

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

Fig. 1

