Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

4-(Methylsulfanyl)benzaldehyde semicarbazone

B. K. Sarojini,[a] B. Narayana,[b] S. Bindya,[c] H. S. Yathirajan[c] and Michael Bolte[d]*

[a]Department of Chemistry, P. A. College of Engineering, Nadupadavu, Mangalore 574 153, India, [b]Department of Studies in Chemistry, Mangalore University, Mangalagangotri 574 199, India, [c]Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore 570 006, India, and [d]Institut für Anorganische Chemie, J. W. Goethe-Universität Frankfurt, Max-von-Laue-Strasse 7, 60438 Frankfurt/Main, Germany
Correspondence e-mail: bolte@chemie.uni-frankfurt.de

Received 11 May 2007; accepted 11 May 2007

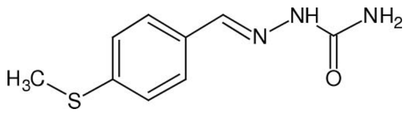
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; disorder in main residue; R factor = 0.054; wR factor = 0.168; data-to-parameter ratio = 14.2.

The crystal packing of the title compound, $C_9H_{11}N_3OS$, is stabilized by two N—H···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

$C_9H_{11}N_3OS$
M_r = 209.27
Monoclinic, $P2_1/c$
a = 15.1006 (19) Å
b = 5.3082 (7) Å
c = 13.0746 (17) Å
β = 107.494 (9)°
V = 999.5 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.29 mm^{-1}
T = 173 (2) K
0.48 × 0.45 × 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_{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^{-3}
$\Delta\rho_{min}$ = −0.66 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O1^{i}	0.881 (10)	2.016 (11)	2.886 (3)	169 (2)
N3—H3A···O1^{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*.

BKS thanks the AICTE, Government of India, for financial assistance through the Career Award for Young Teachers Scheme. SB thanks the University of Mysore for research facilities.

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

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Fichou, D., Watanabe, T., Takeda, T., Miyata, S., Goto, Y. & Nakayama, M. (1988). *Jpn. J. Appl. Phys.* **27**, 429–430.
Furniss, B. S., Hannaford, A. J., Smith, P. W. G. & Tatchell, A. R. (1989). *Vogel's Textbook of Practical Organic Chemistry*, 5th ed., p. 1258. London: Longman Group UK Ltd.
Goto, Y., Hayashi, A., Kimura, Y. & Nakayama, M. (1991). *J. Cryst. Growth*, **108**, 688–698.
Indira, J., Karat, P. P. & Sarojini, B. K. (2002). *J. Cryst. Growth*, **242**, 209–214.
Manivennan, S. & Dhanushkodi, S. (2003). *J. Cryst. Growth*, **257**, 305–308.
Naik, D. V. & Palenik, G. J. (1974). *Acta Cryst.* B**30**, 2396–2401.
Ramesh Babu, R., Vijayan, N., Gopalakrishnan, R. & Ramassamy, P. J. (2002). *J. Cryst. Growth*, **240**, 545–548.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Stoe & Cie (2001). *X-AREA*. Stoe & Cie, Darmstadt, Germany.
Tam, W., Guerin, B., Calabrese, J. C. & Stevenson, S. H. (1989). *Chem. Phys. Lett.* **154**, 93–96.
Vijayan, N., Ramesh Babu, R., Gopalakrishnan, R., Dhanushkodi, S. & Ramassamy, P. (2001). *J. Cryst. Growth*, **233**, 863–867.
Wang, J.-L., Jia, Y.-J. & Yu, M. (2004). *Acta Cryst.* E**60**, o662–o663.
Yathirajan, H. S., Bindya, S., Narayana, B., Sarojini, B. K. & Bolte, M. (2006). *Acta Cryst.* E**62**, o5925–o5926.

doi:10.1107/S1600536807023239

supplementary materials

Acta Cryst. (2007). E**63**, o2946 [**doi:10.1107/S1600536807023239**]

4-(Methylsulfanyl)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), $C_9H_{11}N_3OS$.

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 $C_9H_{11}N_3OS$: 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 $U_{iso}(H) = 1.2U_{eq}(C)$ or C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C_{methyl})$. 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

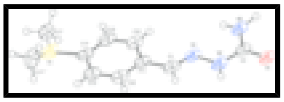


Fig. 1. Perspective view of (I); displacement ellipsoids are at the 50% probability level (arbitrary spheres for the H atoms). One site of the disordered methyl group is shown with dashed bonds.

4-(Methylthio)benzaldehyde semicarbazone

Crystal data

$C_9H_{11}N_3OS$	$F_{000} = 440$
$M_r = 209.27$	$D_x = 1.391$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 5218 reflections
$a = 15.1006$ (19) Å	$\theta = 3.3$–27.2°

$b = 5.3082\ (7)$ Å

$c = 13.0746\ (17)$ Å

$\beta = 107.494\ (9)$°

$V = 999.5\ (2)$ Å^3

$Z = 4$

$\mu = 0.29$ mm^{-1}

$T = 173\ (2)$ K

Block, colourless

0.48 × 0.45 × 0.43 mm

Data collection

Stoe IPDS II two-circle diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 173(2)$ K

ω 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 $I > 2\sigma(I)$

$R_{\text{int}} = 0.053$

$\theta_{\max} = 27.0$°

$\theta_{\min} = 2.8$°

$h = -19 \rightarrow 19$

$k = -6 \rightarrow 6$

$l = -14 \rightarrow 16$

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 $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.46$ e Å^{-3}

$\Delta\rho_{\min} = -0.66$ e Å^{-3}

Extinction correction: SHELXL (Sheldrick, 1997), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$	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 (Å^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)

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, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1^{i}	0.881 (10)	2.016 (11)	2.886 (3)	169 (2)
N3—H3A···O1^{ii}	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