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Key indicators

Single-crystal X-ray study
 $T = 173$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.031
 wR factor = 0.084
 Data-to-parameter ratio = 22.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

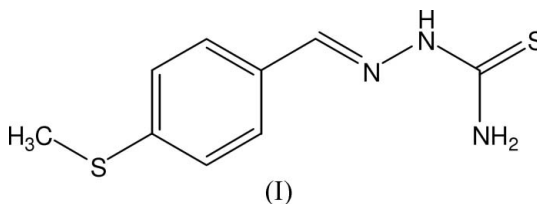
4-(Methylsulfonyl)benzaldehyde thiosemicarbazone

The title compound, $\text{C}_9\text{H}_{11}\text{N}_3\text{S}_2$, crystallizes with two molecules in the asymmetric unit, which differ mainly in the degree of planarity. The $\text{C}=\text{N}$ double bonds are *trans* configured. Geometric parameters are in the usual ranges. The crystal structure is characterized by $\text{N}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds.

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Comment

Thiosemicarbazones (TSCs) of aromatic aldehydes and ketones are widely known as carcinostatic and antimicrobial agents. It has been found that silyl-substituted furfural TSCs possess neurotropic activity (Lukevics *et al.*, 1993). TSCs of arylidene and aryl aldehydes and ketones have shown anti-convulsant activity in maximal electroshock seizure tests (Dimmock *et al.*, 1986, 1990, 1991). In view of the importance of thiosemicarbazones, a new thiosemicarbazone, (I), has been prepared and its crystal structure is reported here.



A perspective view of (I) is shown in Fig. 1. Bond lengths and angles can be regarded as normal (Cambridge Structural Database, Version 5.27, November 2005 updated August 2006; *MOGUL* Version 1.1; Allen, 2002). The $\text{C}=\text{N}$ double bonds are *trans* configured. Whereas one molecule (labelled with suffix *A*) is essentially planar (r.m.s. deviation = 0.062 Å for all non-H atoms) the other one deviates markedly from planarity (r.m.s. deviation = 0.262 Å for all non-H atoms). The methylsulfonyl residues are coplanar with the benzene rings (Table 1). The thiosemicarbazone units are planar (r.m.s. deviation = 0.036 Å for the non-planar molecule and 0.014 Å for molecule *A*), but they form different dihedral angles with the benzene ring, *viz.* 25.19 (4)° for the non-planar molecule and 7.32 (6)° for molecule *A*. Both molecules show an intramolecular $\text{N}-\text{H}\cdots\text{N}$ contact and two $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds (Table 2). It is remarkable that only the thiocarbonyl S atom acts as an acceptor for hydrogen bonds, while the methylsulfonyl S atom is not involved in hydrogen bonds.

Experimental

A mixture of 4-methylsulfonylbenzaldehyde (1.52 g, 0.01 mol) and thiosemicarbazide (0.91 g, 0.01 mol) in ethanol (15 ml) was refluxed

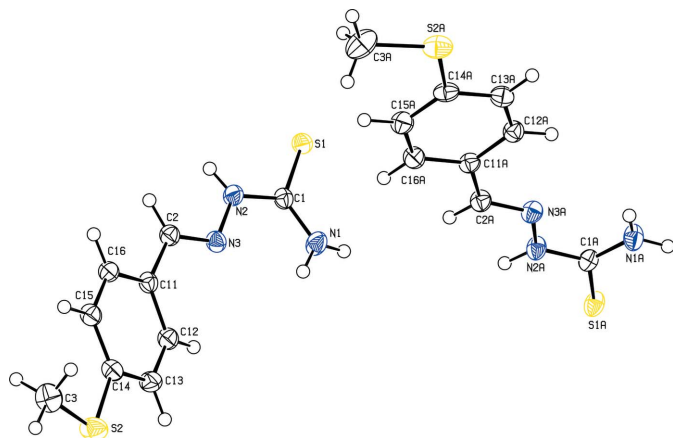


Figure 1
Perspective view of the two molecules in the asymmetric unit of the title compound with the atom numbering; displacement ellipsoids are drawn at the 50% probability level.

for 3 h on a water bath. The precipitated solid was filtered, washed with water, dried and recrystallized from acetone (yield: 81%; m.p. 463–465 K). Analysis (%) found (calculated) for $C_9H_{11}N_3S_2$: C 47.84 (47.97), H 4.85 (4.92), N 18.54 (18.65), S 28.38 (28.46).

Crystal data

$C_9H_{11}N_3S_2$ $V = 1089.76 (10) \text{ \AA}^3$
 $M_r = 225.33$ $Z = 4$
 Triclinic, $P\bar{1}$ $D_x = 1.373 \text{ Mg m}^{-3}$
 $a = 8.2052 (4) \text{ \AA}$ Mo $K\alpha$ radiation
 $b = 9.1947 (5) \text{ \AA}$ $\mu = 0.45 \text{ mm}^{-1}$
 $c = 15.5994 (8) \text{ \AA}$ $T = 173 (2) \text{ K}$
 $\alpha = 106.558 (5)^\circ$ Block, light orange
 $\beta = 97.573 (3)^\circ$ $0.38 \times 0.36 \times 0.33 \text{ mm}$
 $\gamma = 100.110 (4)^\circ$

Data collection

Stoe IPDS-II two-circle diffractometer 36432 measured reflections
 6421 independent reflections
 ω scans 6026 reflections with $I > 2\sigma(I)$
 Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995) $R_{int} = 0.041$
 $T_{min} = 0.847$, $T_{max} = 0.865$ $\theta_{max} = 30.2^\circ$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 0.3428P]$
 $R[F^2 > 2\sigma(F^2)] = 0.031$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.084$ $(\Delta/\sigma)_{max} = 0.001$
 $S = 1.06$ $\Delta\rho_{max} = 0.38 \text{ e \AA}^{-3}$
 6421 reflections $\Delta\rho_{min} = -0.28 \text{ e \AA}^{-3}$
 280 parameters Extinction correction: *SHELXL97*
 H atoms treated by a mixture of independent and constrained refinement Extinction coefficient: 0.048 (3)

Table 1
Selected torsion angles ($^\circ$).

C3–S2–C14–C15	5.08 (12)	C3A–S2A–C14A–C15A	7.41 (12)
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Table 2
Hydrogen-bond geometry (\AA , $^\circ$).

D–H...A	D–H	H...A	D...A	D–H...A
N1–H1A...S1 ⁱ	0.873 (17)	2.459 (17)	3.3254 (11)	172.1 (15)
N1–H1B...N3	0.875 (17)	2.266 (16)	2.6364 (13)	105.4 (12)
N2–H2...S1A ⁱ	0.854 (17)	2.555 (18)	3.3412 (10)	153.5 (15)
N1A–H1C...S1A ⁱⁱ	0.869 (19)	2.604 (19)	3.4707 (11)	174.7 (17)
N2A–H2A...S1 ⁱ	0.906 (17)	2.454 (17)	3.3499 (10)	169.8 (14)
N1A–H1D...N3A	0.852 (17)	2.302 (16)	2.6440 (14)	104.2 (13)

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

H atoms were found in a difference map. Those bonded to carbon were refined using a riding model, with C–H = 0.95 Å for aromatic and C–H = 0.98 Å for methyl groups. $U_{iso}(H)$ values were set at $1.2U_{eq}(C)$ [$1.5U_{eq}(\text{methyl C})$]. In addition, the methyl groups were allowed to rotate but not to tip. H atoms bonded to N were freely refined.

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* and *PLATON*.

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