

2-Methoxybenzaldehyde thiosemicarbazone

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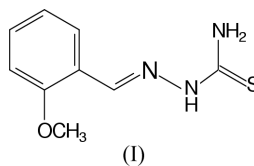
Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$
 R factor = 0.044
 wR factor = 0.126
Data-to-parameter ratio = 19.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title molecule, $\text{C}_9\text{H}_{11}\text{N}_3\text{OS}$, exhibits a *trans* conformation with respect to the phenyl ring and the thiosemicarbazone moiety. The dihedral angle between the thiosemicarbazone moiety and the phenyl ring is $4.68(5)^\circ$. In the solid state, inversion-related molecules exist as centrosymmetric $\text{N}-\text{H}\cdots\text{S}$ hydrogen-bonded dimers. Symmetry-related dimers are interlinked by $\text{N}-\text{H}\cdots\text{S}$ and $\text{N}-\text{H}\cdots\text{O}$ intermolecular hydrogen bonds, forming two-dimensional molecular networks parallel to the *ab* plane.

Comment

Thiosemicarbazones are derivatives of carbonyl compounds, exhibiting a wide range of biological activities (Shanmuga Sundara Raj *et al.*, 2000). There is considerable interest in the chemistry of Schiff base compounds containing N- and S-donors and of their metal complexes. This is due to their non-linear optical properties and chelating ability with transition metal ions (Ali & Tarafdar, 1977; Ali & Bose, 1984; Tian *et al.*, 1996). Antibacterial, antiviral and antitumour activities have been observed in N- and S-donor ligands, such as substituted thiosemicarbazides and thiosemicarbazones (Nandi *et al.*, 1984; French & Blanz, 1965, 1966; William, 1972). In this paper, we report the structure of 2-methoxybenzaldehyde thiosemicarbazone, (I).



The molecular structure of (I), with the atom-numbering scheme, is shown in Fig. 1. The bond distances agree well with the values reported for similar structures (Moers *et al.*, 1999; Nandi *et al.*, 1984; Shanmuga Sundara Raj *et al.*, 2000). The $\text{C}=\text{S}$ bond [$1.688(2)\text{ \AA}$] has a length intermediate between a single and double bond. The sum of the valence angles around atoms N1 and N2 indicate that these atoms are sp^2 hybridized. The exocyclic angles around atom C4 show considerable asymmetry, with the $\text{O1}-\text{C4}-\text{C5}$ angle [$123.9(2)^\circ$] being wider than $\text{O1}-\text{C4}-\text{C3}$ [$115.9(1)^\circ$], as observed in a related structure (Fun *et al.*, 1996). This may be due to the steric repulsion between the methyl group and the phenyl ring. The $\text{C9}-\text{O1}-\text{C4}-\text{C5}$ [$-14.1(3)^\circ$] and $\text{C9}-\text{O1}-\text{C4}-\text{C3}$ [$166.4(2)^\circ$] torsion angles indicate that the methoxy group is twisted away from the benzene plane. The $\text{S1}-\text{C1}-\text{N2}-\text{N3}$ [$-177.6(1)^\circ$] and $\text{N3}-\text{C2}-\text{C3}-\text{C4}$ [$-178.1(2)^\circ$] torsion

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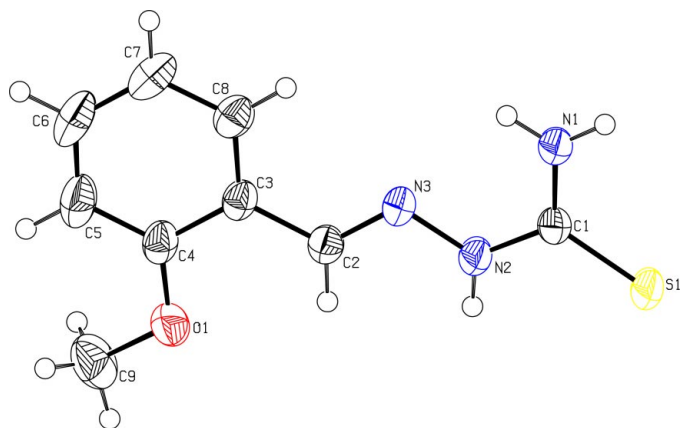


Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

angles indicate a *trans* conformation with respect to the thiosemicarbazone moiety and the phenyl ring. The *trans* conformation adopted by the side chain is evident from the values of the C1–N2–N3–C2 [172.8 (2)°], N2–N3–C2–C3 [–178.6 (1)°], N3–C2–C3–C4 [–178.1 (2)°] and C2–C3–C4–C5 [–178.4 (2)°] torsion angles. The thiosemicarbazone moiety forms a dihedral angle of 4.68 (5)° with the phenyl ring.

In the crystal, the molecules at (x, y, z) and $(-x, 1 - y, 1 - z)$ are linked by N–H···S hydrogen bonds involving the NH group, forming centrosymmetric dimeric units. Symmetry-related dimers are interlinked by N–H···S and N–H···O intermolecular hydrogen bonds involving the NH₂ group (Table 2), forming two-dimensional molecular networks parallel to the *ab* plane (Fig. 2). The N···S distances of 3.376 (1) and 3.398 (1) Å are close to the mean N···S distance reported for N–H···S hydrogen bonds by Srinivasan & Chacko (1967).

Experimental

2-Methoxybenzaldehyde and thiosemicarbazide, in almost equivalent quantities, with a few drops of HCl, yielded 2-methoxybenzaldehyde thiosemicarbazone. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from an acetone solution at room temperature.

Crystal data

| | |
|--|---------------------------------------|
| C ₉ H ₁₁ N ₃ OS | Mo K α radiation |
| $M_r = 209.27$ | Cell parameters from 6556 reflections |
| Orthorhombic, <i>Pbca</i> | $\theta = 2.8$ – 28.3° |
| $a = 13.5826$ (2) Å | $\mu = 0.28$ mm ⁻¹ |
| $b = 10.6063$ (2) Å | $T = 293$ (2) K |
| $c = 14.3260$ (3) Å | Block, colourless |
| $V = 2063.82$ (7) Å ³ | $0.48 \times 0.34 \times 0.20$ mm |
| $Z = 8$ | |
| $D_x = 1.347$ Mg m ⁻³ | |

Data collection

| | |
|--|--|
| Siemens SMART CCD area-detector diffractometer | 1742 reflections with $I > 2\sigma(I)$ |
| ω scans | $R_{\text{int}} = 0.079$ |
| Absorption correction: none | $\theta_{\text{max}} = 28.3^\circ$ |
| 13626 measured reflections | $h = -18 \rightarrow 17$ |
| 2547 independent reflections | $k = -14 \rightarrow 10$ |
| | $l = -19 \rightarrow 13$ |

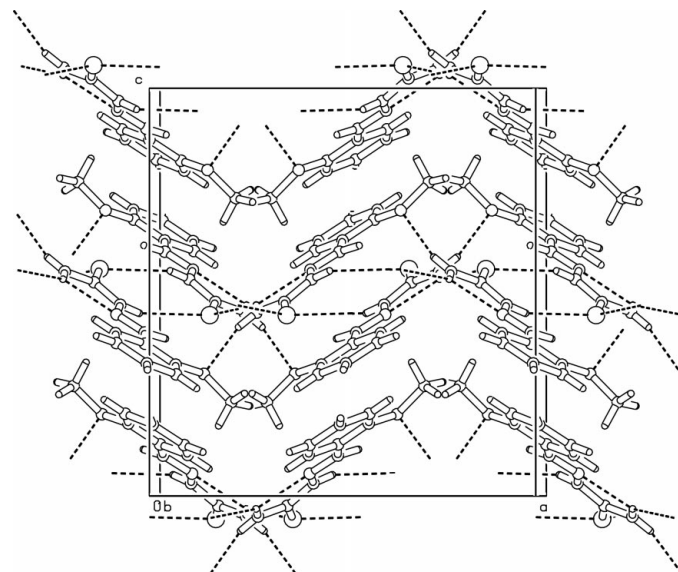


Figure 2
The packing of the title molecules, viewed down the *b* axis.

Refinement

| | |
|---------------------------------|---|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0674P)^2]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.044$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.126$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| $S = 0.98$ | $\Delta\rho_{\text{max}} = 0.32$ e Å ⁻³ |
| 2547 reflections | $\Delta\rho_{\text{min}} = -0.34$ e Å ⁻³ |
| 128 parameters | Extinction correction: <i>SHELXL97</i> |
| H-atom parameters constrained | Extinction coefficient: 0.0093 (15) |

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-------------|------------|-------------|------------|
| S1–C1 | 1.688 (2) | N2–C1 | 1.345 (2) |
| O1–C4 | 1.377 (2) | N2–N3 | 1.377 (2) |
| O1–C9 | 1.445 (2) | N3–C2 | 1.276 (2) |
| N1–C1 | 1.321 (2) | C2–C3 | 1.460 (2) |
| O1–C4–C5 | 123.9 (2) | O1–C4–C3 | 115.9 (1) |
| C1–N2–N3–C2 | 172.8 (2) | C9–O1–C4–C5 | –14.1 (3) |
| N3–N2–C1–S1 | –177.6 (1) | C9–O1–C4–C3 | 166.4 (2) |
| N2–N3–C2–C3 | –178.6 (1) | C2–C3–C4–C5 | –178.4 (2) |
| N3–C2–C3–C4 | –178.1 (2) | | |

Table 2

Hydrogen-bonding geometry (Å, °).

| <i>D</i> –H··· <i>A</i> | <i>D</i> –H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> –H··· <i>A</i> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| C2–H2A···O1 | 0.93 | 2.42 | 2.7427 (19) | 100 |
| N1–H1A···N3 | 0.86 | 2.29 | 2.6385 (19) | 105 |
| N1–H1B···O1 ⁱ | 0.86 | 2.19 | 3.0306 (18) | 166 |
| N1–H1A···S1 ⁱⁱ | 0.86 | 2.73 | 3.3982 (14) | 136 |
| N2–H2···S1 ⁱⁱⁱ | 0.86 | 2.58 | 3.3759 (14) | 154 |

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

All H atoms were positioned geometrically and were treated as riding on their parent C and N atoms, with C–H distances of 0.93 or 0.96 Å and N–H distances of 0.86 Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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