

4-Methylbenzenecarbothioamide

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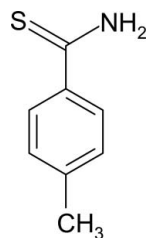
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Key indicators: single-crystal X-ray study; $T = 123$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.034; wR factor = 0.089; data-to-parameter ratio = 16.1.

In the title molecule, $\text{C}_8\text{H}_9\text{NS}$, the mean plane of the carbothioamide group is twisted slightly with respect to the mean plane of the benzene ring, making a dihedral angle of 17.03 (10)°. The crystal structure is stabilized by intermolecular $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds, resulting in the formation of eight-membered rings lying about inversion centers and representing $R_2^2(8)$ and $R_4^2(8)$ motifs. Furthermore, these hydrogen bonds build up chains parallel to the b axis.

Related literature

For the use of thioamides as intermediates in the synthesis of various heterocyclic compounds, see: Zahid *et al.* (2009). For the uses of thioamides, see: Lebana *et al.* (2008). For the biological activity of thioamides, see: Jagodzinski (2003); Klimesova *et al.* (1999). For related structures, see: Khan *et al.* (2009a,b,c); Jian *et al.* (2006); Ali *et al.* (2010). For graph-set notation, see: Etter *et al.* (1990); Bernstein *et al.* (1994).



Experimental

Crystal data

$\text{C}_8\text{H}_9\text{NS}$
 $M_r = 151.22$
 Monoclinic, $P2_1/c$
 $a = 9.7341$ (5) Å

$b = 5.8391$ (2) Å
 $c = 13.9055$ (6) Å
 $\beta = 104.946$ (3)°
 $V = 763.63$ (6) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.34$ mm⁻¹

$T = 123$ K
 $0.10 \times 0.06 \times 0.06$ mm

Data collection

Nonius KappaCCD diffractometer
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1997)
 $T_{\min} = 0.967$, $T_{\max} = 0.980$

2741 measured reflections
 1482 independent reflections
 1399 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.089$
 $S = 1.06$
 1482 reflections

92 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.27$ e Å⁻³
 $\Delta\rho_{\min} = -0.24$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1B}\cdots\text{S1}^i$	0.88	2.56	3.4178 (14)	166
$\text{N1}-\text{H1A}\cdots\text{S1}^{ii}$	0.88	2.75	3.3179 (15)	124

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

Data collection: COLLECT (Hooft, 1998); cell refinement: DENZO (Otwinowski & Minor, 1997); data reduction: SCALEPACK (Otwinowski & Minor, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2557).

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supplementary materials

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4-Methylbenzenecarbothioamide

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Comment

Thioamides are not only used as intermediates in the synthesis of various heterocyclic compounds (Zahid *et al.*, 2009), they are important biologically active agents (Jagodzinski, 2003; Klimesova *et al.*, 1999). In addition, they are important ligands in the field of coordination chemistry (Lebana *et al.*, 2008). In continuation to our work on thioamides (Khan *et al.*, 2009a; 2009b; 2009c; Ali *et al.*, 2010), we have synthesized 4-methylbenzenecarbothioamide, (I). In this article we report the crystal structure of the title compound.

In the title molecule (Fig. 1), the bond distances and angles agree with the corresponding bond distances and angles reported in closely related compounds (Khan *et al.*, 2009a; 2009b; 2009c; Jian *et al.*, 2006; Ali *et al.*, 2010). In the title compound, the mean-plane of the carbothioamide group (S1/N1/C7) is slightly twisted with respect to the mean-plane of the phenyl ring (C1–C6), making a dihedral angle of 17.03 (10)°.

The structure is stabilized by intermolecular N—H···S hydrogen bonds resulting in the formation of eight membered rings lying about inversion centers (Tab. 1 and Fig. 2). In the graph set notation (Etter *et al.*, 1990; Bernstein *et al.*, 1994) the hydrogen bonded rings may be best described as representing $R_2^2(8)$ and $R_4^2(8)$ motifs. Furthermore, these hydrogen bonds build up chains parallel to the b axis.

Experimental

4-Methylbenzonitrile (13.2 mmol) was added to a slurry of magnesium chloride hexahydrate (13.2 mmol) and sodium hydrogen sulphide hydrate (70%, 26.4 mmol) in dimethylformamide (35 ml) and the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was poured into water (100 ml) and the resulting precipitates were collected by filtration. The product obtained was resuspended in 1 N HCl (50 ml), stirred for another 25 min, the precipitated solid filtered and washed with water. Recrystallization of the product from chloroform afforded the crystals of the title compound suitable for X-ray analysis.

Refinement

Though all the H atoms could be distinguished in the difference Fourier map the H-atoms were included at geometrically idealized positions and refined in riding-model approximation with N—H = 0.88 Å and C—H = 0.95 and 0.98 Å for aryl and methyl H-atoms, respectively. The $U_{iso}(H)$ were allowed at 1.2/1.5 $U_{eq}(N/C)$. The final difference map was essentially featureless.

Figures

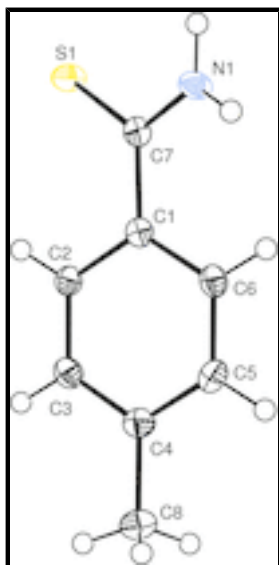


Fig. 1. Molecular view of title compound with the atom labeling scheme. Ellipsoids are drawn at the 50% probability level. H atoms are represented as small sphere of arbitrary radii.

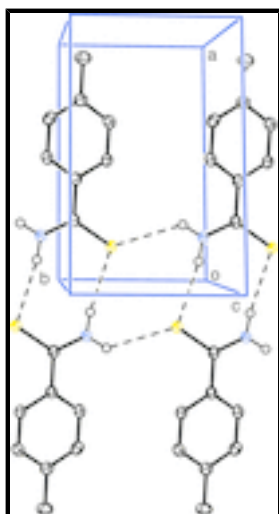


Fig. 2. A part of the unit cell showing the N-H...S hydrogen bonds as dashed lines. H-atoms not involved in H-bonds have been excluded for clarity.

4-Methylbenzenecarbothioamide

Crystal data

C_8H_9NS

$M_r = 151.22$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 9.7341\ (5)\ \text{\AA}$

$b = 5.8391\ (2)\ \text{\AA}$

$c = 13.9055\ (6)\ \text{\AA}$

$\beta = 104.946\ (3)^\circ$

$V = 763.63\ (6)\ \text{\AA}^3$

$F(000) = 320$

$D_x = 1.315\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1473 reflections

$\theta = 1.0\text{--}26.0^\circ$

$\mu = 0.34\ \text{mm}^{-1}$

$T = 123\ \text{K}$

Block, yellow

$0.10 \times 0.06 \times 0.06\ \text{mm}$

Z = 4

Data collection

Nonius KappaCCD diffractometer	1482 independent reflections
Radiation source: fine-focus sealed tube graphite	1399 reflections with $I > 2\sigma(I)$
ω and ϕ scans	$R_{\text{int}} = 0.025$
Absorption correction: multi-scan (SORTAV; Blessing, 1997)	$\theta_{\text{max}} = 26.0^\circ$, $\theta_{\text{min}} = 3.8^\circ$
$T_{\text{min}} = 0.967$, $T_{\text{max}} = 0.980$	$h = -11 \rightarrow 11$
2741 measured reflections	$k = -7 \rightarrow 7$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.034$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.089$	H-atom parameters constrained
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 0.5912P]$
1482 reflections	where $P = (F_o^2 + 2F_c^2)/3$
92 parameters	$(\Delta/\sigma)_{\text{max}} < 0.001$
0 restraints	$\Delta\rho_{\text{max}} = 0.27 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.24 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.15464 (4)	0.79266 (7)	0.03136 (3)	0.02316 (16)
N1	0.19369 (15)	0.3538 (2)	0.06514 (10)	0.0219 (3)
H1A	0.2463	0.2313	0.0844	0.026*
H1B	0.1007	0.3410	0.0440	0.026*
C1	0.41221 (16)	0.5673 (3)	0.10461 (11)	0.0168 (3)
C2	0.48580 (17)	0.7599 (3)	0.08529 (11)	0.0189 (3)
H2	0.4344	0.8849	0.0496	0.023*
C3	0.63277 (18)	0.7714 (3)	0.11743 (12)	0.0207 (4)
H3	0.6805	0.9045	0.1037	0.025*
C4	0.71154 (17)	0.5908 (3)	0.16965 (11)	0.0203 (4)
C5	0.63795 (18)	0.3995 (3)	0.19021 (11)	0.0211 (4)

supplementary materials

H5	0.6897	0.2753	0.2264	0.025*
C6	0.49105 (17)	0.3872 (3)	0.15894 (11)	0.0196 (3)
H6	0.4433	0.2557	0.1744	0.023*
C7	0.25443 (17)	0.5571 (3)	0.06803 (11)	0.0177 (3)
C8	0.87114 (18)	0.6011 (3)	0.20278 (13)	0.0280 (4)
H8A	0.9033	0.7532	0.1883	0.042*
H8B	0.9114	0.4848	0.1671	0.042*
H8C	0.9028	0.5719	0.2745	0.042*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0174 (2)	0.0146 (2)	0.0353 (3)	0.00051 (14)	0.00272 (18)	0.00029 (16)
N1	0.0160 (7)	0.0155 (7)	0.0332 (8)	-0.0010 (6)	0.0045 (6)	0.0019 (6)
C1	0.0192 (8)	0.0154 (8)	0.0163 (7)	-0.0005 (6)	0.0055 (6)	-0.0017 (6)
C2	0.0205 (8)	0.0156 (7)	0.0204 (7)	0.0009 (6)	0.0050 (6)	0.0019 (6)
C3	0.0215 (8)	0.0192 (8)	0.0221 (8)	-0.0032 (6)	0.0066 (6)	-0.0004 (6)
C4	0.0193 (8)	0.0229 (8)	0.0182 (7)	0.0001 (6)	0.0041 (6)	-0.0033 (6)
C5	0.0240 (8)	0.0203 (8)	0.0180 (7)	0.0042 (6)	0.0037 (6)	0.0024 (6)
C6	0.0234 (8)	0.0158 (8)	0.0202 (7)	-0.0018 (6)	0.0068 (6)	0.0009 (6)
C7	0.0204 (8)	0.0161 (8)	0.0170 (7)	-0.0007 (6)	0.0057 (6)	-0.0007 (6)
C8	0.0194 (9)	0.0328 (10)	0.0299 (9)	0.0000 (7)	0.0026 (7)	0.0007 (8)

Geometric parameters (\AA , $^\circ$)

S1—C7	1.6852 (16)	C3—H3	0.9500
N1—C7	1.322 (2)	C4—C5	1.396 (2)
N1—H1A	0.8800	C4—C8	1.503 (2)
N1—H1B	0.8800	C5—C6	1.385 (2)
C1—C2	1.396 (2)	C5—H5	0.9500
C1—C6	1.403 (2)	C6—H6	0.9500
C1—C7	1.489 (2)	C8—H8A	0.9800
C2—C3	1.386 (2)	C8—H8B	0.9800
C2—H2	0.9500	C8—H8C	0.9800
C3—C4	1.393 (2)		
C7—N1—H1A	120.0	C6—C5—C4	121.35 (15)
C7—N1—H1B	120.0	C6—C5—H5	119.3
H1A—N1—H1B	120.0	C4—C5—H5	119.3
C2—C1—C6	118.11 (15)	C5—C6—C1	120.48 (15)
C2—C1—C7	120.12 (14)	C5—C6—H6	119.8
C6—C1—C7	121.77 (14)	C1—C6—H6	119.8
C3—C2—C1	121.02 (15)	N1—C7—C1	117.39 (14)
C3—C2—H2	119.5	N1—C7—S1	120.35 (12)
C1—C2—H2	119.5	C1—C7—S1	122.26 (12)
C2—C3—C4	120.99 (15)	C4—C8—H8A	109.5
C2—C3—H3	119.5	C4—C8—H8B	109.5
C4—C3—H3	119.5	H8A—C8—H8B	109.5
C3—C4—C5	118.04 (15)	C4—C8—H8C	109.5

C3—C4—C8	121.05 (15)	H8A—C8—H8C	109.5
C5—C4—C8	120.91 (15)	H8B—C8—H8C	109.5
C6—C1—C2—C3	1.0 (2)	C4—C5—C6—C1	0.6 (2)
C7—C1—C2—C3	-179.07 (14)	C2—C1—C6—C5	-1.4 (2)
C1—C2—C3—C4	0.3 (2)	C7—C1—C6—C5	178.65 (14)
C2—C3—C4—C5	-1.1 (2)	C2—C1—C7—N1	162.91 (15)
C2—C3—C4—C8	178.76 (15)	C6—C1—C7—N1	-17.2 (2)
C3—C4—C5—C6	0.7 (2)	C2—C1—C7—S1	-17.1 (2)
C8—C4—C5—C6	-179.18 (15)	C6—C1—C7—S1	162.78 (12)

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

<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>
N1—H1B \cdots S1 ⁱ	0.88	2.56	3.4178 (14)	166
N1—H1A \cdots S1 ⁱⁱ	0.88	2.75	3.3179 (15)	124

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

Fig. 1

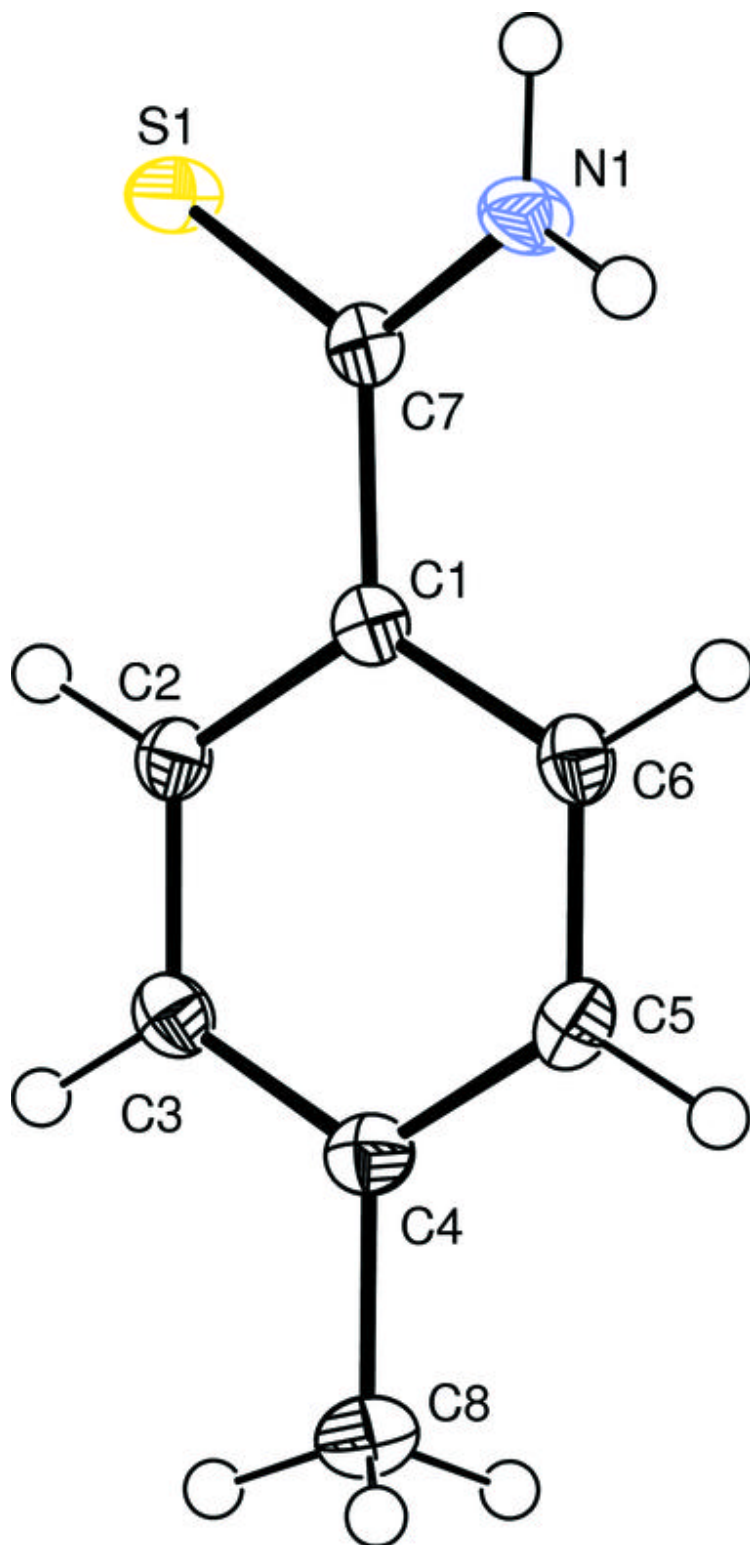


Fig. 2

