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4-Methylbenzenecarbothioamide

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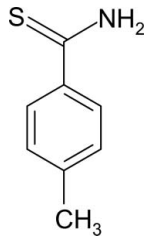
Key indicators: single-crystal X-ray study; T = 123 K; mean σ(C–C) = 0.002 Å; R factor = 0.034; wR factor = 0.089; data-to-parameter ratio = 16.1.

In the title molecule, C_8H_9NS, 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 N—H···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. Futhermore, 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.* (2009*a*,*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

C_8H_9NS
M_r = 151.22
Monoclinic, $P2_1/c$
a = 9.7341 (5) Å
b = 5.8391 (2) Å
c = 13.9055 (6) Å
β = 104.946 (3)°
V = 763.63 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.34 mm^{-1}
T = 123 K
0.10 × 0.06 × 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_{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···A	D—H	H···A	D···A	D—H···A
N1—H1B···S1^{i}	0.88	2.56	3.4178 (14)	166
N1—H1A···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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supporting information

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4-Methylbenzenecarbothioamide

Saqib Ali, Shahid Hameed, Ahmad Luqman, Tashfeen Akhtar and Masood Parvez

S1. 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.*, 2009*a*; 2009*b*; 2009*c*; 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.*, 2009*a*; 2009*b*; 2009*c*; 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.Futhermore, these hydrogen bonds build up chains parallel to the b axis.

S2. Experimental

4-Methylbenzonitrile (13.2 mmol) was added to a slurry of magnesium cholride 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.

S3. 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 1.2/1.5U_{eq}(N/C). The final difference map was essentially featurless.

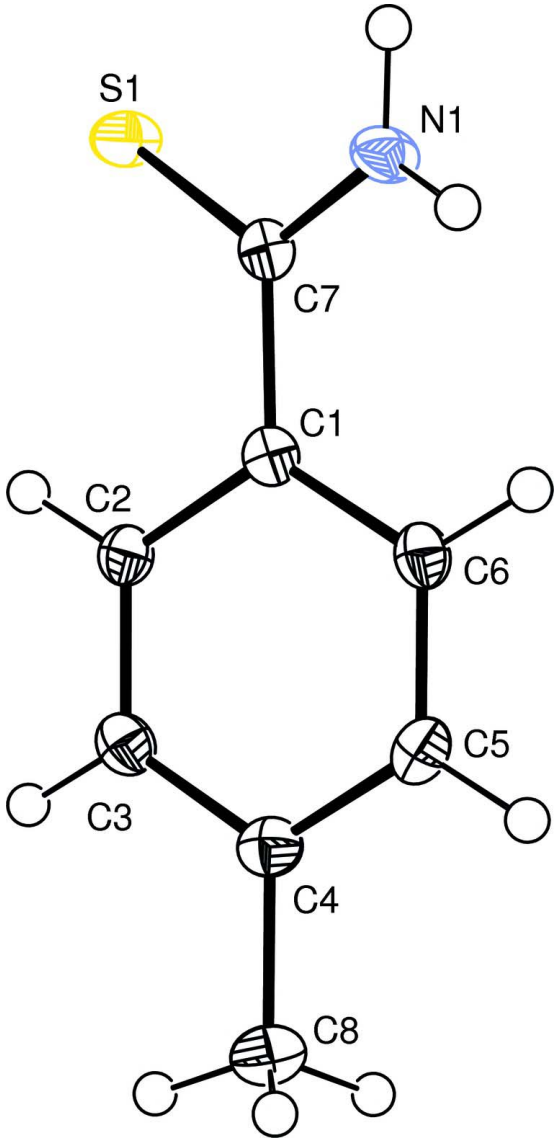

Figure 1

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.

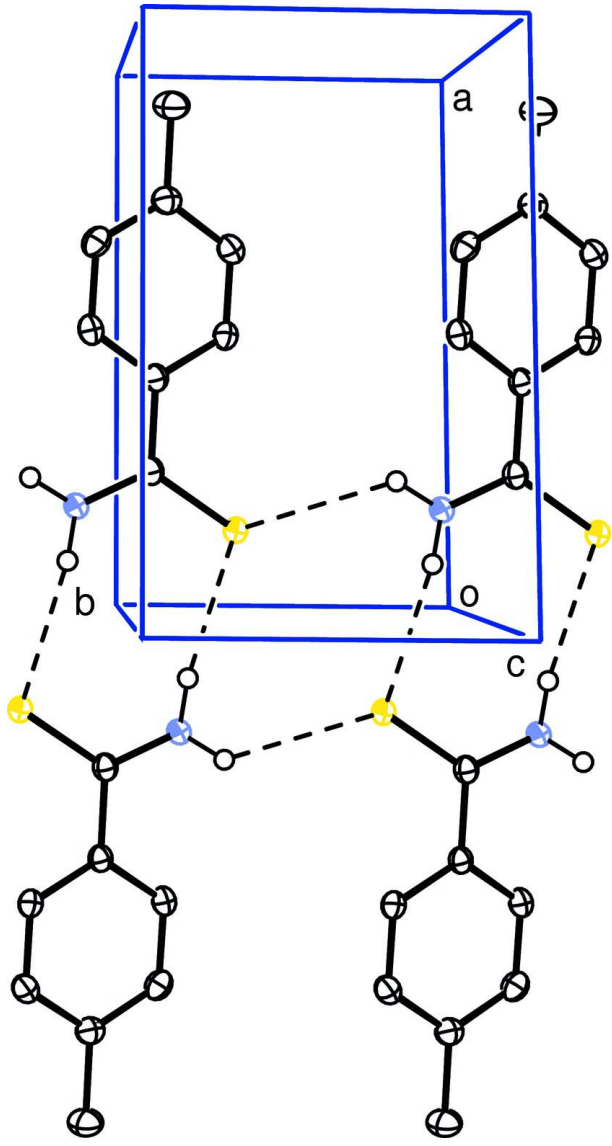

Figure 2

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) Å
b = 5.8391 (2) Å
c = 13.9055 (6) Å
β = 104.946 (3)°
V = 763.63 (6) Å^3
Z = 4
$F(000)$ = 320
D_x = 1.315 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1473 reflections
θ = 1.0–26.0°
μ = 0.34 mm^{-1}
T = 123 K
Block, yellow
0.10 × 0.06 × 0.06 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
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_{int} = 0.025
θ_{max} = 26.0°, θ_{min} = 3.8°
$h = -11 \rightarrow 11$
$k = -7 \rightarrow 7$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.089
S = 1.06
1482 reflections
92 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 0.5912P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{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)
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 (Å²)

	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 (Å, º)

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 (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···S1^{i}	0.88	2.56	3.4178 (14)	166
N1—H1*A*···S1^{ii}	0.88	2.75	3.3179 (15)	124

Symmetry codes: (i) −*x*, −*y*+1, −*z*; (ii) *x*, *y*−1, *z*.