organic compounds

1-(2,6-Dimethylphenyl)thiourea

B. K. Sarojini,[a] B. Narayana,[b] K. Sunil,[b] 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
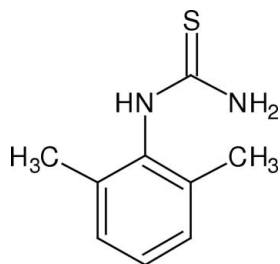
Correspondence e-mail: bolte@chemie.uni-frankfurt.de

The geometric parameters of the title compound, $C_9H_{12}N_2S$, are in the usual ranges. The thiourea group is almost perpendicular to the aromatic ring [dihedral angle = 80.75 (7)°]. The crystal packing is stabilized by N—H···S hydrogen bonds linking the molecules into layers perpendicular to the c axis. Only two of the three amino H atoms are involved in hydrogen bonding.

Related literature

For related structures, see: Usman *et al.* (2002); Zhang *et al.* (2003); Dege *et al.* (2005). For related literature, see: Ren *et al.* (2004); Rodriguez-Fernandez *et al.* (2005); Zhou *et al.* (2003); Stankovic & Vukovic (1996); Trochimczuk & Kolarz *et al.* (2000); Castro *et al.* (2003); Kearney *et al.* (1998); Nie *et al.* (2004).

Experimental

Crystal data

$C_9H_{12}N_2S$
$M_r = 180.27$
Monoclinic, $P2_1/n$
$a = 9.8715$ (13) Å
$b = 8.3940$ (7) Å
$c = 11.8276$ (16) Å
$\beta = 91.557$ (11)°

$V = 979.7$ (2) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.28$ mm^{-1}
$T = 173$ (2) K
$0.29 \times 0.28 \times 0.25$ mm

Data collection

Stoe IPDS II two-circle diffractometer
Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)
$T_{min} = 0.934$, $T_{max} = 0.944$

6116 measured reflections
1830 independent reflections
1598 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.087$
$S = 1.04$
1830 reflections
124 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···S1^i	0.88 (2)	2.56 (2)	3.4302 (14)	172.6 (16)
N2—H2B···S1^{ii}	0.91 (2)	2.42 (2)	3.3073 (15)	164.8 (19)

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

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) and *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97*.

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supplementary materials

1-(2,6-Dimethylphenyl)thiourea

B. K. Sarojini, B. Narayana, K. Sunil, H. S. Yathirajan and M. Bolte

Comment

Thiourea and its derivatives have been the focus of attention in recent years in view of their interesting physicochemical properties and broad range of applications in several chemical disciplines. Certain thiourea molecules have antiviral activity and might be characterized as prospective inhibitors of many enzymes, particularly, HIV-1 reverse transcriptase As antibacterial and antifungal agents, they have been used in agriculture In technical applications dithioamide compounds are known to be prospective nonlinear optical materials corrosion inhibitors for copper and iron in acidic media and functionalization agents for production of chemically modified resins. Thiourea derivatives have been also reported as potential receptors and ionophores for heavy metal cations building blocks in the synthesis of heterocyclic compounds. Finally, the strong hydrogen-bonding donor capability of the –N(H)—C(=S)—N(H)- group has been widely exploited in supramolecular chemistry, where it has been used as a building block for anion receptors A new thiourea, $C_9H_{12}N_2S$ was synthesized and its crystal structure is reported.

Geometric parameters of the title compound (Fig. 1) are in the usual ranges. The thio-urea moiety is almost perpendicular to the aromatic ring [dihedral angle 80.75 (7)°]. The crystal packing is stabilized by N—H···S hydrogen bonds linking the molecules into layers perpendicular to the *c* axis (Fig.2). Only two of the three amino H atoms are involved in hydrogen bonding.

Experimental

2,6-dimethylaniline (0.983 g, 0.0081 mol) was refluxed with potassium thiocyanate (1.4 g, 0.0142 mol) in 20 ml of water and 1.6 ml of conc. HCl for 3 h. The reaction mixture was then cooled to room temperature and stirred overnight. The precipitated product was then filtered, washed with water, dried and recrystallized from acetone (m.p.: 453–455 K). Analysis for $C_9H_{12}N_2S$: Found (Calculated): C: 59.92 (59.96); H: 6.74 (6.71); N: 15.49 (15.54): S: 17.83% (17.79%).

Refinement

H atoms were found in a difference map, but those bonded to C were refined using a riding model with C—H = 0.95Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for $C_{aromatic}$ and C—H = 0.98Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for C_{methyl}. The methyl group was allowed to rotate but not to tip. The H atoms bonded to N were freely refined.
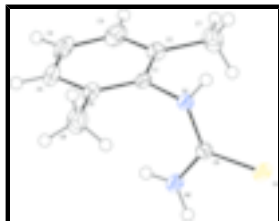
Figures

Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level.
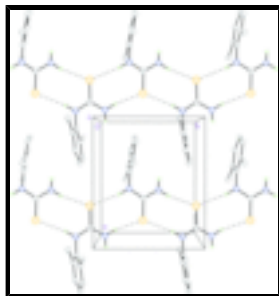

Fig. 2. Packing diagram of the title compound with view along the c axis. H atoms bonded to C omitted. Hydrogen bonds shown as dashed lines.

1-(2,6-Dimethylphenyl)thiourea

Crystal data

$C_9H_{12}N_2S$	$F_{000} = 384$
$M_r = 180.27$	$D_x = 1.222$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 6186 reflections
$a = 9.8715$ (13) Å	$\theta = 3.6–25.8º$
$b = 8.3940$ (7) Å	$\mu = 0.28$ mm^{-1}
$c = 11.8276$ (16) Å	$T = 173$ (2) K
$\beta = 91.557$ (11)º	Block, colourless
$V = 979.7$ (2) Å^3	$0.29 \times 0.28 \times 0.25$ mm
$Z = 4$	

Data collection

Stoe IPDS II two-circle diffractometer	1830 independent reflections
Radiation source: fine-focus sealed tube	1598 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.034$
$T = 173(2)$ K	$\theta_{max} = 25.6º$
ω scans	$\theta_{min} = 3.6º$
Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)	$h = -11 \rightarrow 11$
$T_{min} = 0.934$, $T_{max} = 0.944$	$k = -10 \rightarrow 9$
6116 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.033$	$w = 1/[\sigma^2(F_o{}^2) + (0.0421P)^2 + 0.4733P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2) = 0.087$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.04$	$\Delta\rho_{max} = 0.24$ e Å^{-3}
1830 reflections	$\Delta\rho_{min} = -0.27$ e Å^{-3}
124 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.032 (3)
Secondary atom site location: difference Fourier map	

Special details

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_{iso}*/U_{eq}
S1	0.80471 (4)	0.44604 (5)	0.77764 (4)	0.02740 (17)
N1	0.55700 (12)	0.31654 (16)	0.75999 (11)	0.0199 (3)
H1	0.6001 (18)	0.226 (2)	0.7519 (15)	0.029 (5)*
N2	0.56619 (14)	0.58952 (16)	0.77011 (13)	0.0252 (3)
H2A	0.480 (2)	0.596 (2)	0.7641 (17)	0.034 (5)*
H2B	0.613 (2)	0.683 (3)	0.7684 (19)	0.047 (6)*
C1	0.41512 (14)	0.32335 (17)	0.72473 (13)	0.0192 (3)
C2	0.38282 (16)	0.31028 (19)	0.60910 (14)	0.0237 (3)
C3	0.24801 (17)	0.3325 (2)	0.57317 (15)	0.0314 (4)
H3	0.2237	0.3227	0.4952	0.038*
C4	0.14901 (16)	0.3689 (2)	0.65092 (16)	0.0330 (4)
H4	0.0583	0.3879	0.6255	0.040*
C5	0.18274 (16)	0.3775 (2)	0.76508 (15)	0.0303 (4)
H5	0.1141	0.4005	0.8174	0.036*
C6	0.31617 (15)	0.35293 (19)	0.80533 (13)	0.0243 (4)

C7	0.49229 (18)	0.2749 (2)	0.52544 (14)	0.0358 (4)
H7A	0.5599	0.3603	0.5281	0.054*
H7B	0.4518	0.2681	0.4490	0.054*
H7C	0.5360	0.1734	0.5450	0.054*
C8	0.35129 (19)	0.3592 (3)	0.93045 (15)	0.0388 (5)
H8A	0.3435	0.2523	0.9629	0.058*
H8B	0.2888	0.4316	0.9679	0.058*
H8C	0.4444	0.3979	0.9417	0.058*
C9	0.63163 (14)	0.45104 (17)	0.76801 (12)	0.0178 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0138 (2)	0.0166 (2)	0.0516 (3)	0.00035 (14)	−0.00217 (16)	−0.00235 (17)
N1	0.0160 (6)	0.0153 (6)	0.0284 (7)	0.0002 (5)	0.0000 (5)	−0.0009 (5)
N2	0.0149 (7)	0.0157 (7)	0.0451 (9)	0.0000 (5)	0.0010 (6)	−0.0005 (6)
C1	0.0163 (7)	0.0142 (7)	0.0270 (8)	−0.0025 (6)	0.0005 (6)	−0.0001 (6)
C2	0.0231 (8)	0.0212 (8)	0.0268 (8)	−0.0022 (6)	0.0017 (6)	−0.0008 (6)
C3	0.0268 (9)	0.0389 (10)	0.0282 (9)	−0.0052 (7)	−0.0061 (7)	0.0008 (7)
C4	0.0159 (8)	0.0361 (10)	0.0469 (10)	−0.0038 (7)	−0.0030 (7)	0.0046 (8)
C5	0.0183 (8)	0.0327 (9)	0.0403 (10)	−0.0048 (7)	0.0082 (7)	−0.0014 (8)
C6	0.0209 (8)	0.0235 (8)	0.0286 (8)	−0.0064 (6)	0.0045 (6)	−0.0020 (7)
C7	0.0335 (9)	0.0483 (11)	0.0259 (9)	0.0028 (8)	0.0052 (7)	−0.0047 (8)
C8	0.0334 (10)	0.0561 (13)	0.0273 (9)	−0.0071 (9)	0.0077 (7)	−0.0045 (9)
C9	0.0180 (7)	0.0172 (7)	0.0183 (7)	−0.0006 (6)	0.0013 (5)	0.0004 (6)

Geometric parameters (Å, °)

S1—C9	1.7098 (15)	C3—H3	0.9500
N1—C9	1.3500 (19)	C4—C5	1.384 (3)
N1—C1	1.4516 (19)	C4—H4	0.9500
N1—H1	0.88 (2)	C5—C6	1.404 (2)
N2—C9	1.330 (2)	C5—H5	0.9500
N2—H2A	0.86 (2)	C6—C8	1.512 (2)
N2—H2B	0.91 (2)	C7—H7A	0.9800
C1—C2	1.400 (2)	C7—H7B	0.9800
C1—C6	1.405 (2)	C7—H7C	0.9800
C2—C3	1.399 (2)	C8—H8A	0.9800
C2—C7	1.514 (2)	C8—H8B	0.9800
C3—C4	1.394 (2)	C8—H8C	0.9800
C9—N1—C1	120.51 (13)	C6—C5—H5	119.3
C9—N1—H1	117.9 (12)	C5—C6—C1	117.32 (15)
C1—N1—H1	118.0 (12)	C5—C6—C8	121.00 (14)
C9—N2—H2A	122.3 (14)	C1—C6—C8	121.67 (15)
C9—N2—H2B	120.4 (14)	C2—C7—H7A	109.5
H2A—N2—H2B	117 (2)	C2—C7—H7B	109.5
C2—C1—C6	122.17 (14)	H7A—C7—H7B	109.5
C2—C1—N1	118.03 (13)	C2—C7—H7C	109.5

C6—C1—N1	119.67 (14)	H7A—C7—H7C	109.5
C3—C2—C1	118.42 (14)	H7B—C7—H7C	109.5
C3—C2—C7	121.17 (15)	C6—C8—H8A	109.5
C1—C2—C7	120.40 (14)	C6—C8—H8B	109.5
C4—C3—C2	120.47 (16)	H8A—C8—H8B	109.5
C4—C3—H3	119.8	C6—C8—H8C	109.5
C2—C3—H3	119.8	H8A—C8—H8C	109.5
C5—C4—C3	120.05 (15)	H8B—C8—H8C	109.5
C5—C4—H4	120.0	N2—C9—N1	117.89 (13)
C3—C4—H4	120.0	N2—C9—S1	120.33 (12)
C4—C5—C6	121.47 (15)	N1—C9—S1	121.77 (11)
C4—C5—H5	119.3		
C9—N1—C1—C2	90.37 (18)	C3—C4—C5—C6	1.1 (3)
C9—N1—C1—C6	−85.50 (18)	C4—C5—C6—C1	1.6 (2)
C6—C1—C2—C3	2.0 (2)	C4—C5—C6—C8	−178.72 (17)
N1—C1—C2—C3	−173.73 (14)	C2—C1—C6—C5	−3.2 (2)
C6—C1—C2—C7	−178.72 (15)	N1—C1—C6—C5	172.46 (14)
N1—C1—C2—C7	5.5 (2)	C2—C1—C6—C8	177.13 (16)
C1—C2—C3—C4	0.9 (3)	N1—C1—C6—C8	−7.2 (2)
C7—C2—C3—C4	−178.39 (17)	C1—N1—C9—N2	16.1 (2)
C2—C3—C4—C5	−2.4 (3)	C1—N1—C9—S1	−164.98 (11)

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯S1[i]	0.88 (2)	2.56 (2)	3.4302 (14)	172.6 (16)
N2—H2B⋯S1[ii]	0.91 (2)	2.42 (2)	3.3073 (15)	164.8 (19)

Symmetry codes: (i) −x+3/2, y−1/2, −z+3/2; (ii) −x+3/2, y+1/2, −z+3/2.

Fig. 1

Fig. 2