Acta Cryst. (1999). C**55**, 1318–1320

N—H···S hydrogen bonding in *N*-benzoyl-*N*′-methyl-*N*′-phenylthiourea and *N*-benzoyl-*N*′-(3,4-dimethylphenyl)thiourea

S. Shanmuga Sundara Raj,[a] K. Puviarasan,[b]
D. Velmurugan,[b] G. Jayanthi[c] and Hoong-Kun Fun[a]

[a]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia,* [b]*Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai 600 025, India, and* [c]*Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India. E-mail: velu@cyberspace.org*

(*Received 26 January 1999; accepted 26 April 1999*)

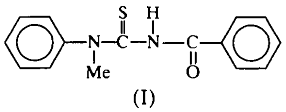
Abstract

In the title compounds, $C_{15}H_{14}N_2OS$ and $C_{16}H_{16}N_2OS$, the C=S bond distances are 1.670 (2) and 1.667 (2) Å, respectively. The molecules are packed in a centrosymmetric manner by forming a two-dimensional array through N—H···S hydrogen bonding.

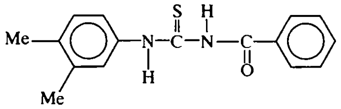
Comment

There are very few structure reports exclusively concerning substituted-thiourea derivatives, which may be due to the difficulty in preparing crystals for X-ray diffraction studies. These thiourea derivatives have applications as rubber accelerators and as intermediate materials in dye preparation, and are very useful agrochemical intermediates (Ramadas *et al.*, 1993). Recently, these derivatives were found to possess non-linear optical properties. We are particularly interested in the molecular structures and the N—H···S-type hydrogen bonding of these derivatives.

The structures of *N*-benzoyl-*N*′-methyl-*N*′-phenylthiourea, (I), and *N*-benzoyl-*N*′-(3,4-dimethylphenyl)thiourea, (II), have been determined. The crystal structure of (I) is composed of discrete molecules (Fig. 1), the bond lengths and angles being quite typical for thiourea compounds found in the Cambridge Structural Database (Allen & Kennard, 1993; Fletcher *et al.*, 1996; Ramnathan, Sivakumar, Subramanian, Janarthanan *et al.*, 1996; Ramnathan, Sivakumar, Subramanian, Meerarani *et al.*, 1996).



(I)



(II)

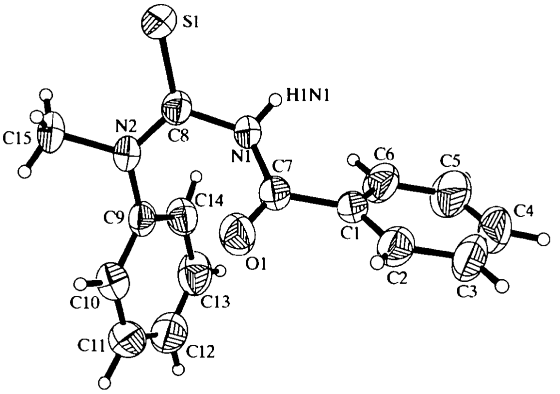


Fig. 1. Plot (*SHELXTL*; Sheldrick, 1997) of compound (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

The short C—S distance [1.670 (2) Å] clearly shows its double-bond character and is very close to the unweighted mean value of 1.681 Å for the C=S distance in thioureas (Allen *et al.*, 1992). This may be influenced by the nature of the substituent group and in particular by its ability to participate in π-conjugation.

The methyl group and the S atom are *cis* with respect to the N2—C8 bond [torsion angle −4.3 (2)°]. The C9-phenyl and the benzoyl groups are *trans* to S with respect to the C—N thiourea bonds, which favours dimer formation through an almost linear [174 (2)°] N—H···S intermolecular hydrogen bond. The steric interaction between the C9–C14 ring and the C15 methyl group at N2 is avoided by a twist of −57.8 (2)° between them.

The S1 atom is 0.036 (1) Å out of the plane of the N—C—N thiourea bridge. The dihedral angle formed by the benzoyl and the thiourea bridge is 80.8 (1)°, and the C9-phenyl ring makes a dihedral angle of 57.8 (1)° with the thiourea bridge. The distance between the centroids of the C1–C6 phenyl ring [$Cg1\cdots Cg1(-x-1, 2-y, -z)$] is 4.31 Å and the perpendicular distance between the rings is 3.47 Å. The structure is stabilized by van der Waals interactions.

The bond lengths and angles of (II) are comparable with the values in the literature (Zhang *et al.*, 1996; Cao *et al.*, 1996). The dimethylphenyl moiety is *cis* and the benzoyl group *trans* to S with respect to the C—N thiourea bonds, as observed in most substituted-thiourea derivatives. This is in contrast to the structure of 1,3-bis(3,4-dichlorophenyl)thiourea (Stankovic & Andreetti, 1978) where the conformation is *cis–cis*. The *trans–cis* conformation favours dimer formation among the molecules. The intramolecular N—H···O hydrogen bonding between the amide-N and benzoyl-O atoms completes a nearly planar six-membered ring in the central part of the molecule. This group makes dihedral angles of 24.7 (1) and 43.4 (1)° with the benzoyl and dimethylphenyl rings, respectively. The maximum deviation from the best plane of the five non-H atoms is 0.026 (2) Å for C7, and the S atom lies almost in the plane of the ring [deviation 0.055 (1) Å].

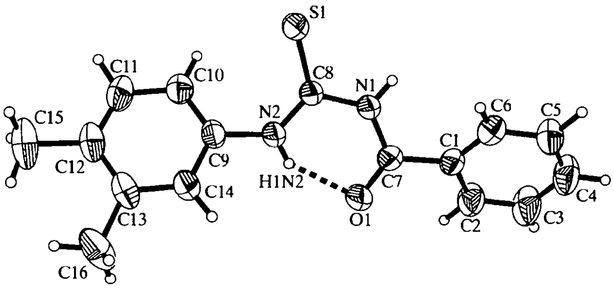


Fig. 2. Plot (*SHELXTL*; Sheldrick, 1997) of compound (II) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

The molecules are packed in a centrosymmetric manner through weak N1—H···S1 hydrogen bonding. The molecules exist as dimers and the crystal lattice consists of parallel layers of these dimers. The C10 atom is involved in weak C—H···S hydrogen bonding with the S1 atom.

Experimental

For the preparation of (I), a solution of *N*-methylaniline (5.4 ml, 0.05 mol) in acetone (15 ml) was added dropwise with stirring to a solution of benzoyl isothiocyanate (0.05 mol) in acetone. The reaction mixture was heated under reflux for 30 min, after which time the solvent was evaporated and the residue poured onto ice. The isolated solid was dried to give compound (I) [yield 11.6 g (86%); m.p. 400–402 K]. For the preparation of (II), a solution of 3,4-dimethylaniline (6.05 g, 0.05 mol) in acetone (15 ml) was added dropwise with stirring to a freshly prepared acetone solution of benzoyl isothiocyanate (0.05 mol) (prepared from NH_4SCN and benzoyl chloride). Following the addition, the mixture was heated under reflux for 30 min and poured onto crushed ice with vigorous stirring. The isolated solid was filtered, washed with water and dried to give compound (II) [yield 13.7 g (97%); m.p. 407–408 K].

Compound (I)

Crystal data

$C_{15}H_{14}N_2OS$
M_r = 270.34
Triclinic
$P\overline{1}$
a = 8.4551 (2) Å
b = 8.9044 (2) Å
c = 10.7293 (3) Å
α = 91.142 (1)°
β = 107.437 (1)°
γ = 113.035 (1)°
V = 700.50 (3) Å^3
Z = 2
D_x = 1.282 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 8192 reflections
θ = 2.01–28.29°
μ = 0.224 mm^{-1}
T = 293 (2) K
Block
0.48 × 0.34 × 0.20 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.900, $T_{\max}$ = 0.957
5735 measured reflections
3325 independent reflections

2219 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.049
$\theta_{\max}$ = 28.32°
$h = -9 \rightarrow 11$
$k = -10 \rightarrow 11$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.104
S = 0.925
3325 reflections
229 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001

$\Delta\rho_{\max}$ = 0.276 e Å^{-3}
$\Delta\rho_{\min}$ = −0.279 e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1997)
Extinction coefficient: 0.016 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (I)*

S1—C8	1.670 (2)	N2—C8	1.331 (2)
O1—C7	1.2101 (2)	N2—C9	1.442 (2)
N1—C8	1.404 (2)	N2—C15	1.473 (2)
C7—N1—C8	123.5 (1)	O1—C7—C1	122.6 (2)
C8—N2—C9	123.9 (1)	N2—C8—N1	116.9 (1)

Table 2. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N1···S1$^{\rm i}$	0.83 (2)	2.65 (2)	3.473 (1)	174 (2)

Symmetry code: (i) $-x, 2-y, -z$.

Compound (II)

Crystal data

$C_{16}H_{16}N_2OS$
M_r = 284.37
Monoclinic
$P2_1/c$
a = 5.4664 (1) Å
b = 28.0208 (4) Å
c = 9.8585 (1) Å
β = 94.262 (1)°
V = 1505.88 (4) Å^3
Z = 4
D_x = 1.254 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 8192 reflections
θ = 1.45–28.33°
μ = 0.212 mm^{-1}
T = 293 (2) K
Plate
0.44 × 0.42 × 0.08 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.913$, $T_{max} = 0.983$
11 799 measured reflections
3688 independent reflections
2555 reflections with $I > 2\sigma(I)$
$R_{int} = 0.072$
$\theta_{max} = 28.28°$
$h = -7 \rightarrow 7$
$k = -22 \rightarrow 37$
$l = -13 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.165$
$S = 1.056$
3688 reflections
221 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0958P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.314$ e Å^{-3}
$\Delta\rho_{min} = -0.396$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

S1—C8	1.667 (2)	N1—C8	1.391 (2)
O1—C7	1.233 (2)	N2—C8	1.330 (2)
N1—C7	1.380 (2)	N2—C9	1.423 (2)
C7—N1—C8	128.2 (2)	O1—C7—C1	121.7 (2)
C8—N2—C9	127.9 (2)	N2—C8—N1	115.6 (2)

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1N2···O1	0.80 (2)	1.92 (2)	2.619 (2)	145 (2)
C10—H10···S1	0.95 (2)	2.85 (2)	3.253 (2)	107 (2)
N1—H1N1···S1^{i}	0.83 (2)	2.70 (2)	3.501 (2)	163 (3)

Symmetry code: (i) $1 - x, 1 - y, 2 - z$.

For both compounds, data collection: *SMART* (Siemens, 1996*a*); cell refinement: *SAINT* (Siemens, 1996*b*); data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 190-9609-2801. SSSR thanks the Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1414). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1992). *International Tables for Crystallography*, Vol. C, edited by A. J. C. Wilson, pp. 685–706. Dordrecht: Kluwer Academic Publishers.

Cao, Y. & Zha, O.-B., Zhang, Y.-Q. & Zhang, O.-C. (1996). *Acta Cryst.* C**52**, 1772–1774.

Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Ramadas, K., Srinivasan, N. & Janarthanan, N. (1993). *Tetrahedron Lett.* **34**, 6447–6450.

Ramnathan, A., Sivakumar, K., Subramanian, K., Janarthanan, N., Ramadas, K. & Fun, H.-K. (1996). *Acta Cryst.* C**52**, 134–136.

Ramnathan, A., Sivakumar, K., Subramanian, K., Meerarani, D., Ramadas, K. & Fun, H.-K. (1996). *Acta Cryst.* C**52**, 139–142.

Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction of Area Detector Data.* University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXTL Software Reference Manual.* Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1996*a*). *SMART Software Reference Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1996*b*). *SAINT Software Reference Manual.* Version 4. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Stankovic, S. & Andreetti, G. D. (1978). *Acta Cryst.* B**34**, 3787–3790.

Zhang, O.-C., Zhang, Y.-Q., Cao, Y. & Zha, O.-B. (1996). *Acta Cryst.* C**52**, 1716–1718.

Acta Cryst. (1999). C**55**, 1320–1322

The first mixed iodide–dithiocarbamate complex of selenium(II): *catena*-poly[[(di-*n*-propyldithiocarbamato-*S*,*S*′)selenium(II)]-*μ*-iodo]

S. Rajashree,[a] R. Krishna Kumar,[a] G. Aravamudan,[a] M. R. Udupa,[a] Kandasamy Sivakumar[b]† and Hoong-Kun Fun[b]

[a]*Department of Chemistry, Indian Institute of Technology, Chennai 600 036, India, and* [b]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: kramanat@unity.ncsu.edu*

(*Received 16 September 1998; accepted 10 March 1999*)

Abstract

The title compound, $[SeI(C_7H_{14}NS_2)]_n$, was prepared by the oxidative displacement of one of the dithiocarbamates in bis(di-*n*-propyldithiocarbamato)selenium(II) using iodine. This complex has a polymeric structure, with the central Se atoms bridged by the iodine ions. The geometry around each Se atom is planar trapezoidal (SeS_2I_2), with Se—I distances of 3.124 (2) and 3.232 (1) Å. This is the first example of a mixed iodide–dithiocarbamate complex of selenium(II).

---

† On leave from the Department of Physics, Anna University, Chennai 600 052, India.