

C6—C7—C8	122.6 (2)	C12—C13—C14	121.9 (2)
C9—C8—C7	116.2 (2)	C12—C13—C15	122.7 (2)
C9—C8—C18	125.0 (2)	C14—C13—C15	115.4 (2)
C7—C8—C18	118.7 (2)	O7—C16—C17	110.2 (1)
O1—C9—C8	116.0 (2)	O7—C16—C19	108.0 (2)
O1—C9—C10	120.5 (2)	C17—C16—C19	110.7 (2)
C8—C9—C10	123.5 (2)	O7—C16—C20	104.7 (2)
C9—C10—C5	117.6 (2)	C17—C16—C20	111.5 (2)
C9—C10—C4	120.3 (2)	C19—C16—C20	111.5 (2)
C5—C10—C4	122.1 (2)	C18—C17—C16	122.1 (2)
C6'—C1'—C2'	118.5 (2)	C17—C18—C8	119.5 (2)

For both compounds, data collection: *MSC/AFC* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structures: *SHELXL86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1170). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-Benzoyl-3-(4-nitrophenyl)thiourea

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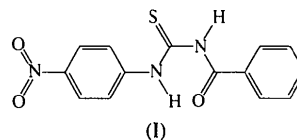
(Received 19 October 1995; accepted 22 January 1996)

Abstract

In the molecules of the title compound, C₁₄H₁₁N₃O₃S, there is an intramolecular N—H···O hydrogen bond [2.635 (3) Å] between the amide N and benzoyl O atoms which completes a nearly planar six-membered ring in the central part of the molecule. The benzene rings of the benzoyl and nitrophenyl moieties form angles of 30.5 (4) and 35.7 (4)°, respectively, with the plane of this hydrogen-bonded ring. In the crystal, molecules are connected into infinite zigzag chains by N—H···O bonds and these chains are linked across centres of symmetry by weak N—H···S interactions, thus forming a two-dimensional network. Van der Waals interactions between layers lead to a crystal structure with one very short axis (4 Å).

Comment

During our systematic search for non-linear optical organic crystals having a short cut-off wavelength, we isolated the title compound, (I).



Since we do not have access to the Cambridge Structural Database (Allen *et al.*, 1979), a literature search was carried out on compounds of the type R¹C₆H₄—CO—NH—CS—NH—C₆H₄R². The structure determination of one similar compound was found with R¹ = Cl and R² = H (Dago, Simonov, Pobedimskaya, Martin & Masias, 1988), which has bond lengths and angles in close agreement with those of the present determination. An N(2)—H···O(1) intramolecular hydrogen bond [2.635 (3) Å] completes an almost planar six-membered ring with atoms C(1), N(1) and C(8); the maximum deviation from the best plane of the five non-H atoms is 0.014 (2) Å and the S atom is 0.104 (2) Å out of the plane (Fig. 1). The NO₂ group is twisted by 10.0 (4)° from the plane of the benzene ring to which it is attached.

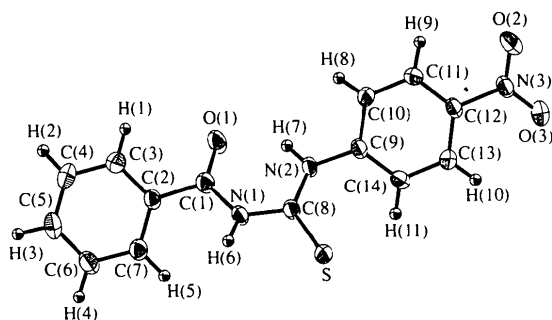


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

Intermolecular hydrogen bond distances and other weak intermolecular interactions are given in Table 2. The last four given appear to be weak interactions between C_{sp^2} —H and either a nitro or benzoyl O atom (Krishnamohan Sharma & Desiraju, 1994).

Experimental

The synthesis of the title compound was carried out by the addition of 6 ml benzoyl chloride to a solution of 6 g KSCN in 50 ml dry acetone. After removal of the residue, the filtrate was added to a solution of 7 g *p*-nitroaniline in 50 ml dry acetone and the resulting solution stirred at 333 K for 2 h. The product was recrystallized three times from acetone.

Crystal data

$C_{14}H_{11}N_3O_3S$

$M_r = 301.32$

Monoclinic

$P2_1/c$

$a = 4.098(3) \text{ \AA}$

$b = 25.665(2) \text{ \AA}$

$c = 12.989(3) \text{ \AA}$

$\beta = 97.22(5)^\circ$

$V = 1355.5(10) \text{ \AA}^3$

$Z = 4$

$D_x = 1.476 \text{ Mg m}^{-3}$

D_m not measured

Data collection

Rigaku AFC-7R diffractometer

ω - 2θ scans

Absorption correction:

empirical via ψ scans

(North, Phillips &

Mathews, 1968)

$T_{\min} = 0.980$, $T_{\max} =$

1.000

2804 measured reflections

2445 independent reflections

Refinement

Refinement on F

$R = 0.034$

$wR = 0.044$

Mo $K\alpha$ radiation

$\lambda = 0.7107 \text{ \AA}$

Cell parameters from 20 reflections

$\theta = 23.27$ – 26.28°

$\mu = 0.2530 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Prismatic

$0.30 \times 0.20 \times 0.20 \text{ mm}$

Colourless

1736 observed reflections

$[I > 3\sigma(I)]$

$R_{\text{int}} = 0.016$

$\theta_{\text{max}} = 25^\circ$

$h = 0 \rightarrow 4$

$k = 0 \rightarrow 9$

$l = -13 \rightarrow 10$

3 standard reflections

monitored every 200

reflections

intensity decay: 0.60%

$(\Delta/\sigma)_{\text{max}} = 0.029$

$\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$

$S = 1.630$

1736 reflections

234 parameters

H atoms refined isotropically

$w = 1/[\sigma^2(F)]$

Extinction correction: none

Atomic scattering factors

from Cromer & Waber

(1974)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
S	0.6926 (2)	0.03651 (2)	0.37744 (5)	0.0381
O(1)	0.7966 (6)	0.16027 (7)	0.6290 (1)	0.0627
O(2)	0.2445 (5)	0.26697 (8)	0.0273 (2)	0.0691
O(3)	-0.0982 (6)	0.20465 (8)	-0.0046 (2)	0.0697
N(1)	0.8241 (5)	0.07875 (8)	0.5619 (1)	0.0392
N(2)	0.5964 (6)	0.13534 (8)	0.4345 (2)	0.0405
N(3)	0.1235 (5)	0.22620 (8)	0.0511 (2)	0.0430
C(1)	0.8694 (6)	0.11427 (10)	0.6421 (2)	0.0410
C(2)	1.0177 (6)	0.09400 (9)	0.7445 (2)	0.0339
C(3)	1.2056 (7)	0.1281 (1)	0.8109 (2)	0.0451
C(4)	1.3456 (7)	0.1115 (1)	0.9075 (2)	0.0512
C(5)	1.2976 (7)	0.0615 (1)	0.9385 (2)	0.0499
C(6)	1.1077 (7)	0.0275 (1)	0.8739 (2)	0.0471
C(7)	0.9686 (6)	0.04345 (10)	0.7767 (2)	0.0378
C(8)	0.6970 (6)	0.08651 (9)	0.4585 (2)	0.0331
C(9)	0.4766 (6)	0.15577 (9)	0.3360 (2)	0.0337
C(10)	0.5718 (7)	0.20637 (9)	0.3143 (2)	0.0394
C(11)	0.4606 (6)	0.22932 (10)	0.2206 (2)	0.0381
C(12)	0.2494 (6)	0.20184 (9)	0.1499 (2)	0.0339
C(13)	0.1473 (6)	0.15191 (10)	0.1706 (2)	0.0388
C(14)	0.2624 (6)	0.12906 (10)	0.2640 (2)	0.0383

Table 2. Selected geometric parameters (\AA , $^\circ$)

S—C(8)	1.658 (2)	N(1)—C(8)	1.393 (3)
O(1)—C(1)	1.224 (3)	N(2)—C(8)	1.344 (3)
O(2)—N(3)	1.214 (3)	N(2)—C(9)	1.413 (3)
O(3)—N(3)	1.220 (3)	N(3)—C(12)	1.463 (3)
N(1)—C(1)	1.379 (3)	C(1)—C(2)	1.485 (3)
C(1)—N(1)—C(8)	129.2 (2)	C(1)—C(2)—C(7)	122.7 (2)
C(8)—N(2)—C(9)	128.1 (2)	S—C(8)—N(1)	118.3 (2)
O(2)—N(3)—O(3)	122.5 (2)	S—C(8)—N(2)	126.6 (2)
O(2)—N(3)—C(12)	118.8 (2)	N(1)—C(8)—N(2)	115.0 (2)
O(3)—N(3)—C(12)	118.7 (2)	N(2)—C(9)—C(10)	117.0 (2)
O(1)—C(1)—N(1)	121.7 (2)	N(2)—C(9)—C(14)	123.2 (2)
O(1)—C(1)—C(2)	121.8 (2)	N(3)—C(12)—C(11)	119.3 (2)
N(1)—C(1)—C(2)	116.5 (2)	N(3)—C(12)—C(13)	118.9 (2)
C(1)—C(2)—C(3)	117.9 (2)		
N(2)···O(1)	2.635 (3)	C(4)···O(3 ⁱⁱ)	3.294 (4)
N(1)···S	3.592 (2)	C(4)···O(3 ^v)	3.400 (4)
N(2)···O(2 ⁱⁱ)	3.202 (3)	C(11)···O(1 ^{vi})	3.428 (3)
C(7)···S ⁱ	3.294 (3)	C(10)···O(3 ^{vii})	3.432 (3)
C(7)···S ⁱⁱⁱ	3.768 (3)		

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

The weighting scheme was based on counting statistics and includes a factor P of 0.03 to downweight the intense reflections.

Data collection: *MSCI/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCI/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985, 1992). Program(s) used to solve structure: *SAPI91* (Fan, 1991) and expanded using Fourier techniques (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN LS*. Software used to prepare material for publication: *TEXSAN FINISH*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: HA1152). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C52, 1718–1719

5-Ethylamino-3-*p*-tolyl-1 λ^4 ,2,4-thiaselenazol-1-ylum Bromide: a New Heteroaromatic System

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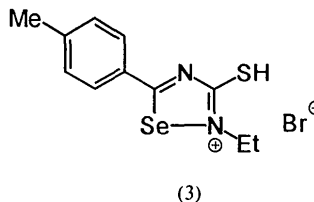
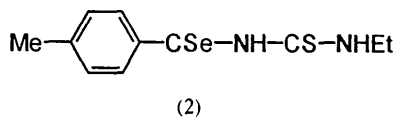
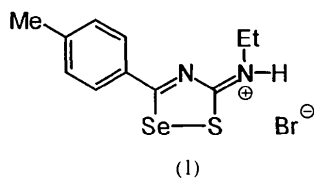
(Received 24 July 1995; accepted 22 December 1995)

Abstract

In the title compound, C₁₁H₁₃N₂SSe⁺.Br⁻, the Se—S bond length is 2.189 (2) Å and the C(2)—Se and C(1)—S bond lengths are 1.890 (3) and 1.765 (3) Å, respectively. The C(2)—Se—S and C(1)—S—Se bond angles are 89.36 (10) and 93.36 (11)°, respectively. In the planar heterocyclic ring, π -electron delocalization extends over the exocyclic N(2) atom.

Comment

The structure determination of the title compound, (1), obtained by intramolecular oxidative coupling of compound (2) with bromine (Lai, 1992), was undertaken in order to confirm that Se—S coupling had indeed occurred in (2), rather than Se—N coupling which would lead to the isomeric salt (3).



The cation in (1) is a derivative of the 1 λ^4 ,2,4-thiaselenazol-1-ylum cation, a new heteroaromatic system whose derivatives we are employing in a new synthesis of hypervalent heterocyclic compounds, in particular 1,6,6a λ^4 -triheterapentalenes (Lai, 1992). A feature of these hypervalent interactions is a correlation between the bond lengths within the three-heteroatom system. The length of the Se—S bond [2.189 (2) Å] is almost the same as the accepted covalent Se—S bond length [2.195 (15) Å; Allen *et al.*, 1987]. This indicates the absence of any significant three-centre bonding involving Se, S and Br. This is also confirmed by the long S...Br distance (3.558 Å), despite the near linearity of the system, with an angle of 178.7° at S. The C(2)—Se and

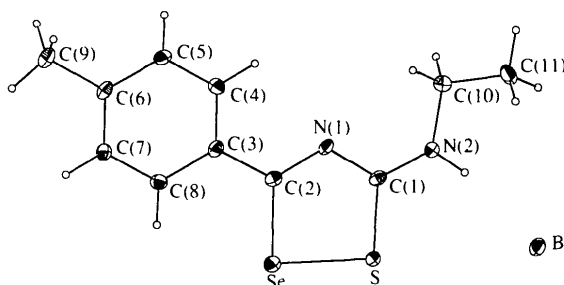


Fig. 1. ORTEP (Johnson, 1976) diagram of the title compound with the atomic labelling scheme. Displacement ellipsoids are shown at the 50% probability level.