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N-Benzoylthiourea

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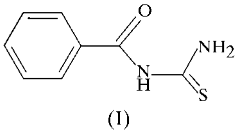
In the title compound, $C_8H_8N_2OS$, strong intramolecular N—H···O hydrogen bonds [N···O = 2.669 (3) and 2.618 (3) Å] form almost planar six-membered rings and enforce the conformation of the molecule. Two kinds of intermolecular N—H···S hydrogen bonds [N···S = 3.309 (3)–3.456 (2) Å] between two symmetry-independent molecules form consecutive dimers that expand in ribbons along the [100] direction.

Comment

Thiourea derivatives can be regarded as model compounds for different intra- and intermolecular interactions involving S atoms. In the literature, there are only a few structural reports describing these compounds, perhaps due to the reported difficulties in preparing crystals for X-ray diffraction studies (Shanmuga Sundara Raj *et al.*, 1999). Therefore, we have carried out the X-ray structural study of a simple thiourea derivative, *viz.* *N*-benzoyl-thiourea, (I). The main goal of this study was to identify the patterns created by the intermolecular N—H···S interactions.



(I)

The asymmetric part of the unit cell of (I) contains two molecules, hereinafter referred to as molecules *A* and *B*. The bond lengths and angles of these symmetry-independent molecules are quite similar (Table 1). The normal probability plot analysis (Abrahams & Keve, 1971; International Tables for X-ray Crystallography, 1974, Vol. IV, pp. 293–309) shows that the differences are of a statistical rather than systematic nature; the correlation coefficients between experimental and theoretical distributions are 0.97 for bond lengths and 0.94 for bond angles. In fact, there is an approximate pseudo-centre of symmetry between molecules *A* and *B*. Taking into account only C–CO–thiourea fragments, the coordinates of this pseudo-centre are [0.704 (6), 0.78 (2), 0.502 (7)]. The benzene rings deviate considerably from this approximate symmetry, the dihedral angle between the least-squares plane of the ring and the plane through the three atoms C11, O11 and N11 being 42.9 (1)° in molecule *A* and 33.0 (1)° in molecule *B*.

The C1/C11/O11/N11 and thiourea fragments are almost ideally planar, with the maximum deviations from the least-squares planes not exceeding 0.012 (2) Å. The dihedral angles between these planes are also small, *viz.* 7.3 (1)° in *A* and 2.1 (2)° in *B*. This almost coplanar conformation is enforced by a strong intramolecular N12—H···O11 hydrogen bond that closes an almost planar six-membered ring [maximum deviations of 0.051 (6) and 0.015 (8) Å for molecules *A* and *B*, respectively]. The significantly more folded conformation of molecule *A* correlates well with the lengths of the intramolecular hydrogen bonds (Table 2). A similar conformation was found in a closely related compound, *N*-(4-methylbenzoyl)-thiourea, (II) (Reinke, 2001). In (II), the dihedral angle between two planar fragments is 5.8°, and the hydrogen bonds also have an intermediate length, with an N···O distance of 2.640 Å. Additional arguments for the decisive role of this hydrogen bond in the determination of molecular conformation can be obtained by an examination of the May 2002 release of the Cambridge Structural Database (Allen, 2002). For 28 fragments with primary and secondary N12 groups, the mean value of the improper OC···CN torsion angle is 3 (2)° [for (I), this angle is 7.0 (2)° in molecule *A* and 1.0 (2)° in *B*, and for (II), it is 3.5°], while for 26 compounds with tertiary groups, the mean value of this angle is 51 (7)° (after the removal of two outliers).

The pattern of bond lengths and angles in (I) is quite typical. Both C═O and C═S bonds have double-bond char-

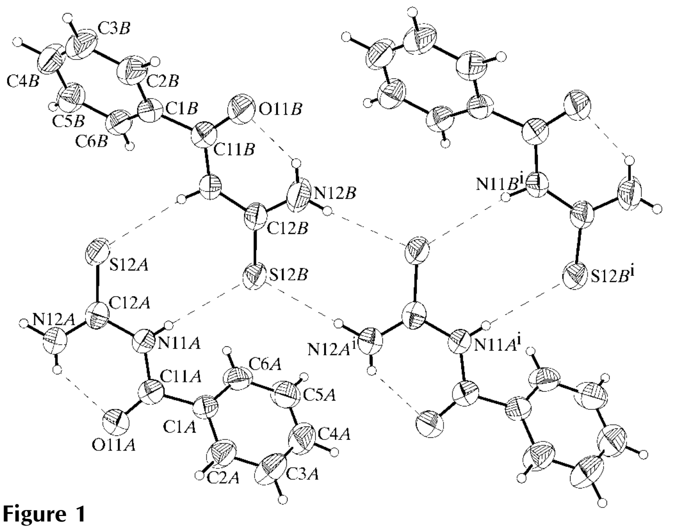


Figure 1
A fragment of the hydrogen-bonded ribbon of molecules *A* and *B* of (I), together with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, H atoms are shown as small spheres of arbitrary radii and hydrogen bonds are shown with dashed lines [symmetry code: (i) 1 + *x*, *y*, *z*].

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acter, and the C—N bonds in the thiourea fragment are significantly different. The C—NH$_2$ bond is remarkably short; indeed it is one of the shortest C—N bonds found in thiourea derivatives.

The crystal packing in (I) is governed by two kinds of strong N—H···S hydrogen bonds (Table 2 and Fig. 1) which form pseudo-centrosymmetric dimers of molecules *A* and *B*. These hydrogen bonds connect the molecules into ribbons along the [100] direction, and these hydrophilic hydrogen-bonded channels are surrounded by the hydrophobic surface of the phenyl rings. Interestingly, the true centre of symmetry is not utilized in creating the main structural pattern; instead, the structure uses two different molecules connected by approximate centres of symmetry. The molecule of (II) also crystallizes in the triclinic space group $P\overline{1}$, but with $Z = 2$, and a similar packing is created by means of exact centres of symmetry. However, in that case, one of the N—H···S intermolecular hydrogen bonds is much longer than the other (3.711 Å).

Experimental

N-Benzoylthiourea was prepared by a modification of the method previously described by Klayman *et al.* (1972). Benzoyl chloride was added to a solution of potassium thiocyanate in warm anhydrous acetone, and the resulting mixture was refluxed. Potassium chloride, which precipitated as a fine powder, was removed by filtration and a concentrated aqueous ammonia solution was added to the filtrate. The resulting mixture was evaporated to dryness using a rotatory evaporator and the residue was extracted with ethanol. Colourless crystals of (I) were obtained by slow evaporation from a methanol solution.

Crystal data

$C_8H_8N_2OS$
$M_r = 180.22$
Triclinic, $P\overline{1}$
$a = 8.2300\ (16)$ Å
$b = 9.3410\ (18)$ Å
$c = 12.594\ (3)$ Å
$\alpha = 73.91\ (3)^\circ$
$\beta = 88.14\ (3)^\circ$
$\gamma = 70.80\ (3)^\circ$
$V = 876.7\ (4)$ Å^3

$Z = 4$
$D_x = 1.365$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 5$–26°
$\mu = 0.32$ mm^{-1}
$T = 293\ (2)$ K
Plate, colourless
$0.30 \times 0.15 \times 0.10$ mm

Table 1
Selected geometric parameters (Å, °).

S12*A*—C12*A*	1.678 (2)	S12*B*—C12*B*	1.679 (2)
O11*A*—C11*A*	1.220 (2)	O11*B*—C11*B*	1.220 (3)
N11*A*—C11*A*	1.376 (3)	N11*B*—C11*B*	1.382 (3)
N11*A*—C12*A*	1.377 (3)	N11*B*—C12*B*	1.374 (3)
N12*A*—C12*A*	1.303 (3)	N12*B*—C12*B*	1.295 (3)
S12*A*—C12*A*—N11*A*	118.70 (17)	S12*B*—C12*B*—N11*B*	120.50 (16)
S12*A*—C12*A*—N12*A*	122.97 (18)	S12B—C12*B*—N12*B*	122.19 (18)
N11*A*—C12*A*—N12*A*	118.3 (2)	N11*B*—C12*B*—N12*B*	117.3 (2)
C11*A*—N11*A*—C12*A*	128.0 (2)	C11*B*—N11*B*—C12*B*	127.72 (19)
C6*A*—C1*A*—C11*A*—O11*A*	135.1 (2)		
C6*B*—C1*B*—C11*B*—O11*B*	145.3 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11*A*—H11*A*···S12*B*	0.791 (19)	2.60 (2)	3.391 (2)	175.0 (19)
N12*A*—H121···O11*A*	0.77 (2)	2.06 (2)	2.669 (3)	136 (2)
N11*B*—H11*B*···S12*A*	0.850 (19)	2.606 (19)	3.442 (2)	168.2 (17)
N12*B*—H124···O11*B*	0.84 (3)	1.92 (3)	2.618 (3)	140 (3)
N12*B*—H123···S12*A*^{i}	0.83 (3)	2.49 (3)	3.309 (3)	170 (2)
N12*A*—H122···S12*B*^{ii}	0.93 (3)	2.55 (3)	3.456 (2)	167 (2)

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

Data collection

Kuma KM-4 four-circle diffractometer
$\omega/2\theta$ scans
3276 measured reflections
3067 independent reflections
1929 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$

$\theta_{\rm max} = 25.1^\circ$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 10$
$l = -14 \rightarrow 14$
3 standard reflections every 100 reflections intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.071$
$S = 1.00$
3067 reflections
282 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.01P)^2 + 0.30P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.009$
$\Delta\rho_{\rm max} = 0.15$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.024 (2)

Data collection: *KM*-4 *Software* (Kuma, 1992); cell refinement: *KM*-4 *Software*; data reduction: *KM*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1152). Services for accessing these data are described at the back of the journal.

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