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# The influence of the type of halogen substituent and its position on the molecular conformation, intermolecular interactions and crystal packing for a series of 1-benzoyl-3-(halogenophenyl)thioureas

Damian Rosiak, Andrzej Okuniewski\* and Jarosław Chojnacki

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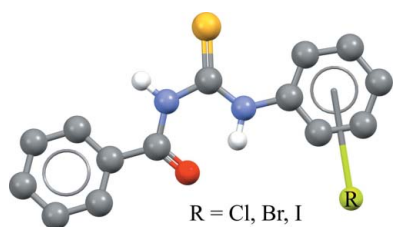
Department of Inorganic Chemistry, Chemical Faculty, Gdańsk University of Technology, G. Narutowicza 11/12, 80-233 Gdańsk, Poland. \*Correspondence e-mail: andrzej.okuniewski@pg.edu.pl

By the reaction of benzoyl chloride, potassium isothiocyanate and the appropriate halogenoaniline, *i.e.* 2/3/4-(bromo/iodo)aniline, we have obtained five new 1-benzoyl-3-(halogenophenyl)thioureas, namely, 1-benzoyl-3-(2-bromophenyl)thiourea and 1-benzoyl-3-(3-bromophenyl)thiourea,  $C_{14}H_{11}BrN_2OS$ , and 1-benzoyl-3-(2-iodophenyl)thiourea, 1-benzoyl-3-(3-iodophenyl)thiourea and 1-benzoyl-3-(4-iodophenyl)thiourea,  $C_{14}H_{11}IN_2OS$ . Structural and conformational features of the compounds have been analyzed using X-ray diffraction and theoretical calculations. The novel compounds were characterized by solid-state IR and  $^1H/^{13}C$  NMR spectroscopy. The conformations and intermolecular interactions, such as hydrogen bonds,  $\pi$ - $\pi$  and  $S(6) \cdots \pi$  stacking, and  $X \cdots O$  ( $X = I$  or  $Br$ ),  $I \cdots S$  and  $I \cdots \pi$ , have been examined and rationalized, together with four analogous compounds described previously in the literature. The set of nine compounds was chosen to examine how a change of the halogen atom and its position on the phenyl ring affects the molecular and crystal structures.

## 1. Introduction

The understanding, prediction and possibility of crystal structure control at the supramolecular level are the main goals of crystal engineering. In our research, we have investigated benzoylthioureas, which are compounds with a wide range of applications. Possessing a thiocarbonyl group, 1-acylthioureas easily form coordination complexes with soft Lewis acids, such as mercury (Estévez-Hernández *et al.*, 2015; Okuniewski *et al.*, 2015; Rosiak *et al.*, 2018a; Hu *et al.*, 2016) or copper (Wang *et al.*, 2017) ions. Due to the simultaneous presence of the carbonyl group and the thiourea core, they have interesting coordination properties which enable various chemical and biochemical applications. Ruthenium complexes are very effective catalysts (Correa *et al.*, 2015), platinum complexes exhibit antimalarial activity (Egan *et al.*, 2004) and some complexes were reported to exhibit anti-HIV properties (Sivan *et al.*, 2013). Uncomplexed thioureas exhibit antibacterial and antifungal activity (Cunha *et al.*, 2007; Saeed *et al.*, 2008, 2010, 2011).

The simultaneous presence of sulfur and oxygen electron-pair donors (and potential nitrogen donors upon deprotonation; Rosiak *et al.*, 2018b) causes the versatility in the behaviour of acylthioureas as building blocks of crystal frameworks. Because of the partial double-bond character of the C–N bonds in (thio)ureas, S, U, M and Z conformational isomers can be distinguished, depending on the mutual position of the carbonyl and thiocarbonyl groups (Woldu & Dillen, 2008). The shape of the letter reflects the position of the C=O



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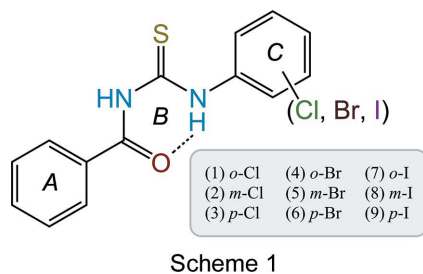
**Table 1**  
Substituents and references for the compounds under consideration.

Compound	Substituent and position in ring C	Reference [CSD refcode]
(1)	2-Cl	Yusof & Yamin (2004) [IZAMIF]
(2)	3-Cl	Khawar Rauf <i>et al.</i> (2006) [MEGNIW]
(3)	4-Cl	Rauf <i>et al.</i> (2006) [VEGMEA]
(4)	2-Br	This work
(5)	3-Br	This work
(6)	4-Br	Yamin & Yusof (2003) [GUWFIN]
(7)	2-I	This work
(8)	3-I	This work
(9)	4-I	This work

and C=S double bonds relative to the vertically drawn N—H bond, while the C=O group is placed on the left-hand side.

In monosubstituted acylthioureas, the molecules are usually stabilized by an intramolecular N—H...O hydrogen bond and the molecule adopts an S-shape conformation and a six-membered pseudo-ring is formed (Okuniewski *et al.*, 2012, 2017). Moreover, the molecules in the crystalline state are often stabilized by intermolecular N—H...O/S and C—H...O/S hydrogen bonds. Because of mesomeric effects, the acylthiourea core tends to be essentially planar. The *S*(6) hydrogen-bond ring motif (Etter, 1990) is quasi-aromatic and can interact with aromatic rings in a stacking manner (Okuniewski *et al.*, 2017; Saeed *et al.*, 2016). The incorporation of other functional groups affects the crystal structures and intra/intermolecular interactions. In this study, we were interested mainly in the role of noncovalent halogen bonding and stacking effects.

We have obtained five new 1-benzoyl-3-(halogenophenyl)thioureas, namely, 1-benzoyl-3-(2-bromophenyl)thiourea, (4), 1-benzoyl-3-(3-bromophenyl)thiourea, (5), 1-benzoyl-3-(2-iodophenyl)thiourea, (7), 1-benzoyl-3-(3-iodophenyl)thiourea, (8), and 1-benzoyl-3-(4-iodophenyl)thiourea, (9) (Scheme 1). These compounds are presented along with four analogous compounds described previously in the literature, namely, 1-benzoyl-3-(2-chlorophenyl)thiourea, (1), 1-benzoyl-3-(3-chlorophenyl)thiourea, (2), 1-benzoyl-3-(4-chlorophenyl)thiourea, (3), and 1-benzoyl-3-(4-bromophenyl)thiourea, (6) (Table 1).



## 2. Experimental

Melting points were measured on an SMP30 (Stuart, Stone, UK) and were uncorrected. The solid-state IR spectra were measured using a Nicolet iS50 FT-IR spectrometer equipped with a Specac Quest single-reflection diamond attenuated total reflectance (ATR) accessory controlled by *Omnice* com-

puter software in the range 4000–400 cm<sup>-1</sup>. The NMR spectra were measured with a Bruker Avance III HD 400 MHz spectrometer (USA) with a TXI <sup>1</sup>H/<sup>13</sup>C/<sup>31</sup>P probe.

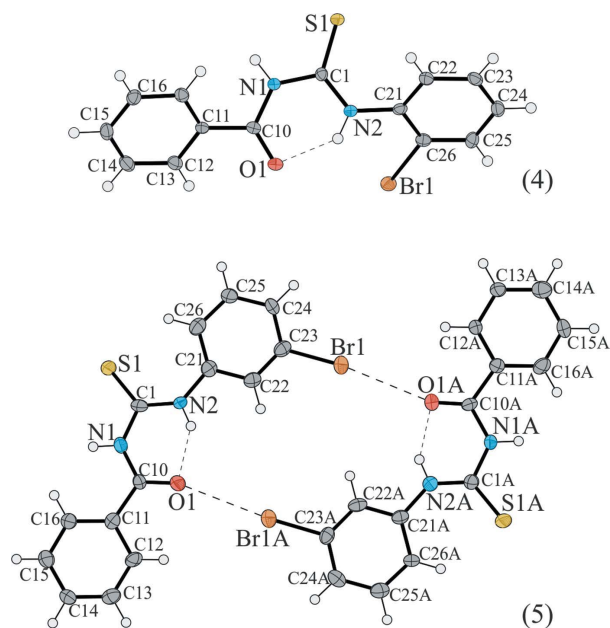
A search of the Cambridge Structural Database (CSD, Version 5.41, May 2020 update; Groom *et al.*, 2016) was made for benzoylthiourea derivatives with rings A and C being C<sub>6</sub> aromatic rings (212 hits) and benzoylthiourea derivatives monosubstituted in the C ring in the *ortho* position (9 hits), the *meta* position (4 hits) and the *para* position (17 hits).

### 2.1. Synthesis and crystallization

All the title compounds were synthesized as described in the literature (Okuniewski *et al.*, 2017). Potassium thiocyanate (92 mmol, 9.56 g) and dry acetone (60 ml) were placed in a two-necked flask. Benzoyl chloride (80 mmol, 9.30 ml) in acetone (40 ml) was added through a dropping funnel with stirring. After the addition was complete, the mixture was refluxed for an additional 15 min and then 80 mmol of the relevant amine [*i.e.* 2/3/4-(bromo/iodo)aniline] in acetone (40 ml) was added through a dropping funnel. The contents were poured carefully into cold water (500 ml) with stirring. In all cases, the resulting precipitate was filtered off using a Büchner funnel. Single crystals suitable for X-ray diffraction analysis were isolated by recrystallization from acetone. For atom and compound numbering, see Figs. 1 and 2 and Table 2. Analytical data for the obtained products are presented in the following section.

### 2.2. Analytical data

For (4), 1-benzoyl-3-(2-bromophenyl)thiourea: yield = 94%; *T*<sub>mp</sub> = 134 (1) °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 12.63 (s,



**Figure 1**  
The molecular structures of the novel 1-benzoyl-3-(bromophenyl)thioureas. Displacement ellipsoids are drawn at the 50% probability level.

**Table 2**  
Experimental details.

Experiments were carried out with Mo  $K\alpha$  radiation using a Stoe IPDS 2T diffractometer. Absorption was corrected for by Gaussian integration [X-RED32 (Stoe & Cie, 2009), analogous to Coppens (1970)]. H-atom parameters were constrained.

	(4)	(5)	(7)	(8)	(9)
<b>Crystal data</b>					
Chemical formula	C <sub>14</sub> H <sub>11</sub> BrN <sub>2</sub> OS	C <sub>14</sub> H <sub>11</sub> BrN <sub>2</sub> OS	C <sub>14</sub> H <sub>11</sub> IN <sub>2</sub> OS	C <sub>14</sub> H <sub>11</sub> IN <sub>2</sub> OS	C <sub>14</sub> H <sub>11</sub> IN <sub>2</sub> OS
$M_r$	335.23	335.22	382.21	382.21	382.21
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $Pc$	Triclinic, $P\bar{1}$	Monoclinic, $Pc$	Triclinic, $P\bar{1}$
Temperature (K)	120	125	125	125	120
$a, b, c$ (Å)	3.9592 (4), 15.142 (2), 22.250 (2)	4.6404 (7), 15.017 (2), 19.074 (3)	6.2410 (7), 7.2420 (8), 16.709 (2)	4.5639 (5), 15.375 (3), 19.355 (2)	4.4279 (5), 13.0767 (14), 13.4410 (14)
$\alpha, \beta, \gamma$ (°)	90, 95.183 (8), 90	90, 91.052 (12), 90	84.408 (9), 89.142 (9), 65.933 (8)	90, 91.404 (9), 90	61.622 (7), 86.203 (9), 85.241 (9)
$V$ (Å <sup>3</sup> )	1328.4 (3)	1329.0 (3)	686.02 (14)	1357.7 (3)	682.06 (13)
$Z$	4	4	2	4	2
$\mu$ (mm <sup>-1</sup> )	3.24	3.24	2.48	2.51	2.49
Crystal size (mm)	0.76 × 0.05 × 0.03	0.68 × 0.05 × 0.04	0.38 × 0.36 × 0.20	0.7 × 0.08 × 0.05	0.33 × 0.08 × 0.05
<b>Data collection</b>					
$T_{\min}, T_{\max}$	0.379, 0.892	0.354, 0.875	0.405, 0.644	0.393, 0.885	0.734, 0.932
No. of measured, independent and observed reflections [ $I > 2\sigma(I)$ ]	7908, 3566, 2917	15213, 4537, 4294	7847, 3616, 3508	13551, 5820, 5398	9681, 3617, 3348
$R_{\text{int}}$	0.057	0.087	0.026	0.070	0.020
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.682	0.617	0.682	0.650	0.682
<b>Refinement</b>					
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.049, 0.145, 1.07	0.066, 0.183, 1.02	0.028, 0.072, 1.07	0.054, 0.148, 1.07	0.021, 0.054, 1.05
No. of reflections	3530	4909	3616	5820	3617
No. of parameters	172	343	172	343	172
No. of restraints	0	2	0	2	0
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	1.06, -1.48	1.97, -0.65	0.70, -0.94	1.24, -1.28	0.80, -0.39
Absolute structure	–	Flack (1983), 2288 Friedel pairs	–	Flack (1983), 2156 Friedel pairs	–
Absolute structure parameter	–	0.01 (2)	–	0.30 (4)	–

Computer programs: X-AREA (Stoe & Cie, 2009), X-RED32 (Stoe & Cie, 2009), SHELXT (Sheldrick, 2015a), SHELXL2018 (Sheldrick, 2015b) and OLEX2 (Dolomanov *et al.*, 2009).

1H), 9.25 (*s*, 1H), 8.41–6.97 (*m*, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  179.03, 166.74, 136.48, 133.84, 132.97, 131.48, 129.23, 128.29, 127.66, 127.58, 127.17, 118.69.

For (5), 1-benzoyl-3-(3-bromophenyl)thiourea: yield = 84%;  $T_{\text{mp}} = 130$  (1) °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  12.67 (*s*, 1H), 9.21 (*s*, 1H), 8.17–7.09 (*m*, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  178.41, 167.12, 138.85, 133.90, 131.40, 130.14, 129.80, 129.25, 127.61, 126.89, 122.66, 122.27.

For (7), 1-benzoyl-3-(2-iodophenyl)thiourea: yield = 70%;  $T_{\text{mp}} = 144$  (1) °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  12.38 (*s*, 1H), 9.24 (*s*, 1H), 8.23–6.82 (*m*, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  179.67, 166.72, 139.81, 139.47, 133.86, 131.51, 129.25, 129.00, 128.62, 127.94, 127.66, 95.55.

For (8), 1-benzoyl-3-(3-iodophenyl)thiourea: yield = 95%;  $T_{\text{mp}} = 172$  (1) °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  12.64 (*s*, 1H), 9.11 (*s*, 1H), 8.32–6.99 (*m*, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  178.40, 167.00, 138.69, 135.83, 133.93, 132.69, 131.45, 130.29, 129.31, 127.53, 123.38, 93.57.

For (9), 1-benzoyl-3-(4-iodophenyl)thiourea: yield = 99%;  $T_{\text{mp}} = 154$  (1) °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  12.64 (*s*, 1H), 9.12 (*s*, 1H), 8.08–7.07 (*m*, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$

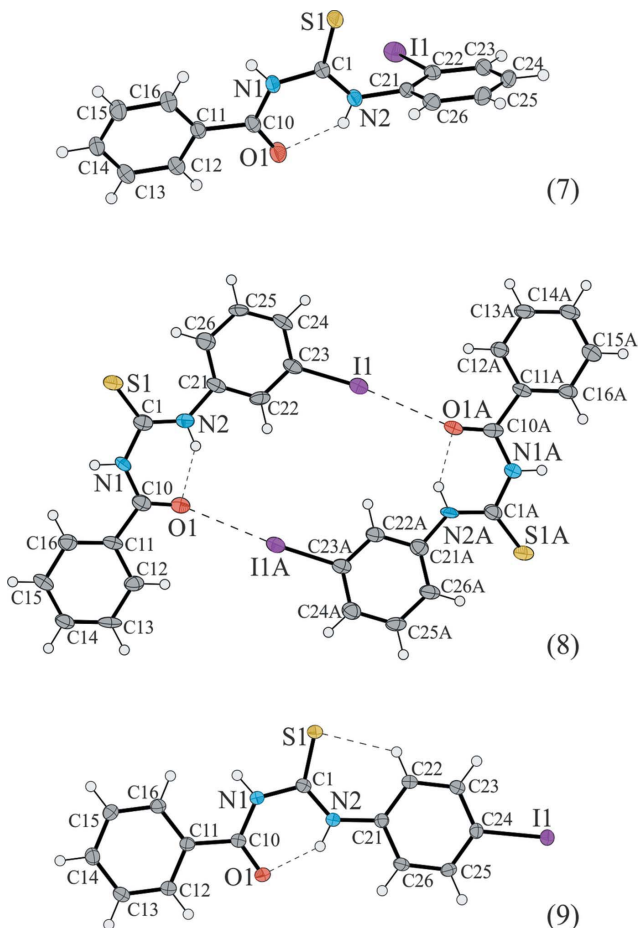
178.20, 167.01, 137.97, 137.37, 133.92, 131.46, 129.30, 127.52, 125.73, 91.22.

### 2.3. Refinement

Crystal data, data collection and structure refinement details for (4), (5) and (7)–(9) are summarized in Table 2. H atoms were placed at calculated positions (C–H = 0.95 Å and N–H = 0.88 Å) and treated as riding on their parent atoms, with  $U_{\text{iso}}(\text{H})$  values set at 1.2–1.5 $U_{\text{eq}}(\text{C})$  or 1.2 $U_{\text{eq}}(\text{N})$ .

## 3. Results and discussion

To investigate the molecular geometry of 3-aryl-substituted derivatives of 1-arylothioureas, we defined the dihedral angles  $\varphi_1$  and  $\varphi_2$  (Fig. 3, top), which measure the inclination of the aromatic rings with respect to the main thiourea core. Our analysis of the CSD shows how the position of the ring substituents affects the mutual arrangement of the aromatic rings (Fig. 3, bottom). We found that the presence of a hydrogen-bond acceptor (F or OR;  $R = \text{H}$  or Me) in the *ortho*



**Figure 2**  
The molecular structures of the novel 1-benzoyl-3-(iodophenyl)thiureas. Displacement ellipsoids are drawn at the 50% probability level.

**Table 3**  
Parameters of halogen bonding in structures (5)–(8).

Type C=E...X	Angle C=E...X (°)	Distance E...X (Å)	Structure
C10=O1...Br1A	153.9 (7)	3.071 (8)	(5)
C10A=O1A...Br1	155.3 (8)	3.088 (8)	(5)
C10=O1...I1A	154.0 (8)	3.121 (8)	(8)
C10A=O1A...I1A	155.3 (8)	3.137 (9)	(8)
C1=S1...I1	109.97 (9)	3.7333 (8)	(7)

Type X...X

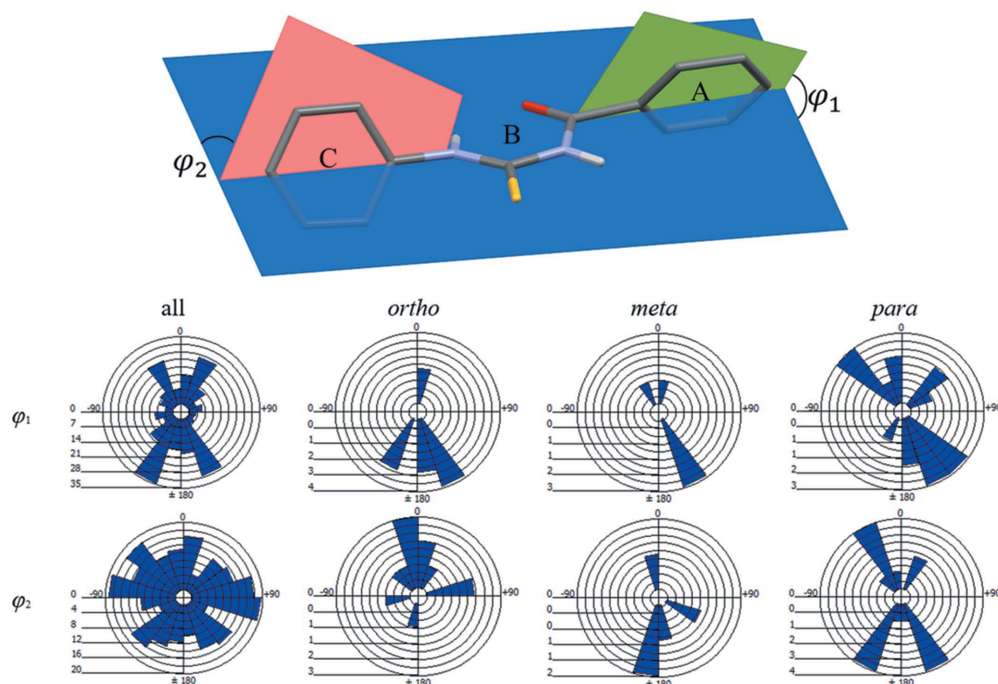
C1—Br1...Br1 <sup>i</sup>	156.22 (7)	3.8829 (8)	(6)
C1—Br1...Br1 <sup>ii</sup>	88.74 (7)	3.8829 (8)	(6)

Notes: E = O or S. Symmetry codes: (i)  $-x, y - \frac{1}{2}, -z + \frac{5}{2}$ ; (ii)  $-x, y + \frac{1}{2}, -z + \frac{5}{2}$ .

position of ring A or C may induce the formation of intramolecular hydrogen bonds and the planarity of the molecule. When these substituents are larger, the whole molecule is twisted and the dihedral angle can even reach a value close to orthogonal. In cases with substituents in the *meta* and *para* positions, the systems are more planar, with a slightly tilted geometry, with torsion angles in the range 15–45° preferred. The lack of information on some bromo and all iodo derivatives (presumably forming the strongest halogen bonds) encouraged us to investigate how the heaviest halides change the way 1-benzoylthiourea molecules pack in their crystals.

### 3.1. Isostructurality

The *meta*-substituted compounds (5) and (8) (Br and I, respectively) are isostructural. The parameter of unit-cell identity  $\Pi = 0.041$  (Fábián & Kálmán, 1999), while the parameter of isostructurality  $I' = 0.70$  (Kubicki & Szafranski, 1998).



**Figure 3**  
(Top) Definition of the auxiliary dihedral angles  $\varphi_1$  and  $\varphi_2$ , together with the notation of aromatic rings A and C, and pseudo-ring B [S(6) motif]. (Bottom) Circular histograms with values of the  $\varphi_1$  and  $\varphi_2$  angles for the benzoylthiourea derivatives deposited in the CSD.

**Table 4**  
Parameters of stacking interactions in the investigated structures.

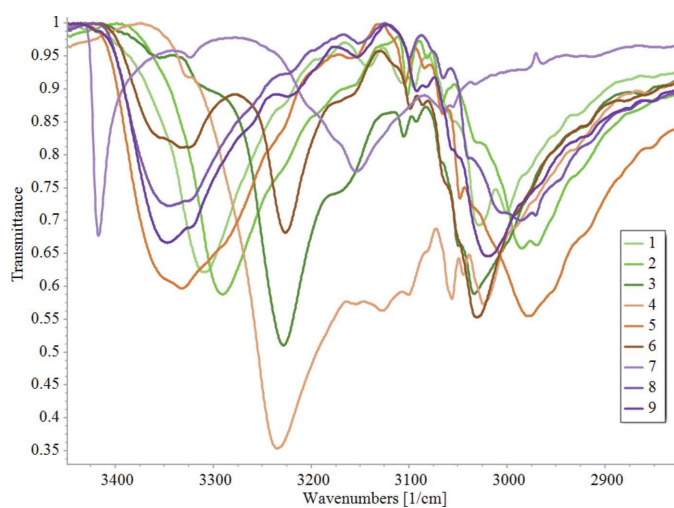
The fourth column lists the inter-centroid ( $Cg \cdots Cg$ ) distances. For ring 2, the symmetry operation applied to move ring 2 from the asymmetric unit to the correct position to interact is given. Subscript *A* denotes the next independent molecule in the asymmetric unit.

Structure	Ring 1	Ring 2	$Cg1 \cdots Cg2$ (Å)	Dihedral angle between rings 1 and 2 (°)	Slippage (Å)
(1)	B	$A(x, -y + \frac{1}{2}, z + \frac{1}{2})$	3.4092 (13)	1.28 (8)	
	B	$C(x, -y + \frac{1}{2}, z - \frac{1}{2})$	3.6302 (16)	15.12 (6)	
(2)	B	$A(x, y + 1, z)$	3.7423 (12)	17.73 (5)	
	B	$C(x, y - 1, z)$	3.2584 (10)	2.77 (5)	
(3)	B	$A(x - 1, y, z)$	3.834 (2)	8.15 (7)	
	B	$C(x + 1, y, z)$	3.274 (3)	8.78 (6)	
(4)	A	$A(x + 1, y, z)$	3.9592 (4)	0	1.804
	B	$B(x + 1, y, z)$			
	C	$C(x + 1, y, z)$			
(5)	B	$A(x + 1, y, z)$	3.668 (6)	4.1 (4)	
	B	$C(x - 1, y, z)$	3.501 (6)	1.6 (4)	
	$B_A$	$A_A(x + 1, y, z)$	3.492 (6)	3.8 (4)	
	$B_A$	$C_A(x - 1, y, z)$	3.709 (6)	9.0 (4)	
(7)	B	$A(-x + 1, -y + 1, -z + 1)$	3.646	4.11	
	C	$C(-x + 1, -y + 1, -z)$	3.836	0	2.16
(8)	B	$A(x - 1, y, z)$	3.687	10.28	
	B	$C(x + 1, y, z)$	3.552	13.07	
	$B_A$	$A_A(x + 1, y, z)$	3.772	13.20	
	$B_A$	$C_A(x - 1, y, z)$	3.551	13.80	
(9)	B	$A(x + 1, y, z)$	3.734	5.70	
	B	$C(x - 1, y, z)$	3.620	2.39	

The asymmetric units of these compounds consist of two molecules that are related by a noncrystallographic centre of symmetry. In both molecules, the position of the halogen atom is antiperiplanar to the thiocarbonyl group.

### 3.2. Hydrogen bonding

In each of the title benzoylthioureas, the molecules form cyclic intramolecular  $N-H \cdots O$  hydrogen bonds, so-called



**Figure 4**  
Superposition of the FT-IR spectra of (1)–(9) in the range 3500–2800  $\text{cm}^{-1}$ , corresponding to the vibration of the  $N-H$  amide bond. Note the sharp absorption band for (7) at 3417  $\text{cm}^{-1}$ .

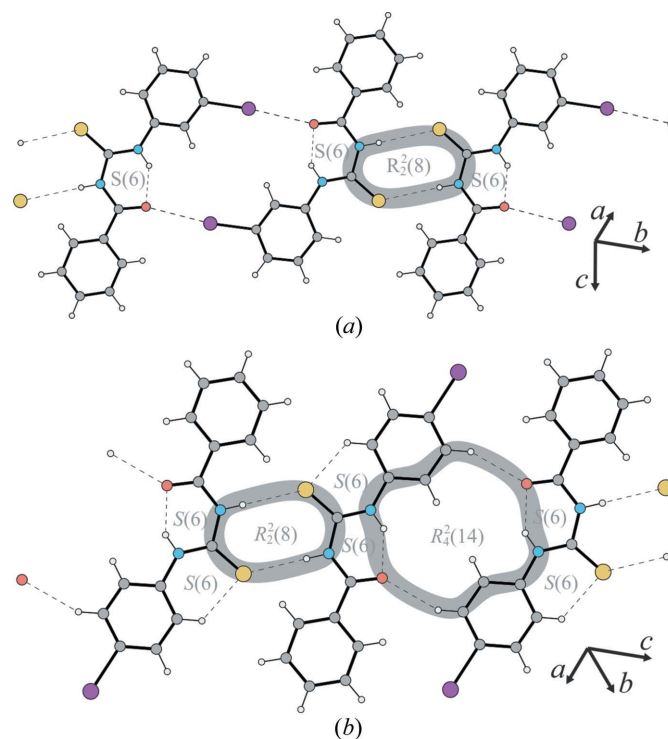
$S(6)$  motifs (Etter, 1990), stabilizing the *S* conformation. Moreover, in almost all cases [except for (7)], the molecules interact *via*  $N-H \cdots S$  hydrogen bonds, usually forming  $R_2^2(8)$  ring motifs, often centrosymmetric. In contrast, the molecules of (7) form  $I \cdots S$  halogen bonds. Differences in the FT-IR spectra are also noticeable. For compound (7), a sharp peak due to the  $N-H$  stretching can be seen at 3417  $\text{cm}^{-1}$ , while in other cases these peaks are wide, confirming their contribution to intermolecular interactions (Fig. 4). In the case of (9), due to the planarity of the molecule, weak intramolecular  $C-H \cdots S$  hydrogen bonds, forming an  $S(6)$  ring, can be observed. Weak intermolecular  $C-H \cdots O$  interactions forming centrosymmetric  $R_4^2(14)$  motifs are also present.

### 3.3. Halogen bonding

The numerical data for the halogen-bond interactions are presented in Table 3. Because no significant halogen bonding can be found in (4) and (9), they are absent from this table.

The most important intermolecular interactions in isostructural (5) and (8) are  $N-H \cdots S$  hydrogen bonds and mixed  $C-Br/I \cdots O=C$  halogen-chalcogen interactions, which can be classified as type I according to Corpinot & Bučar (2018) (the  $C=O1 \cdots X$  angle is greater than 150°; see Table 3). The alternating occurrence of these interactions results in the formation of chains (see Fig. 5a).

A mixed halogen-chalcogen interaction between iodine and sulfur is found in (7). The  $C=S \cdots I$  contact is bent and can be classified as type II (Corpinot & Bučar, 2018; see Fig. 6 and Table 3). It links the molecules along the  $[\bar{1}10]$  direction, so



**Figure 5**  
The main interactions in (a) (8) and (b) (9), forming ring motifs. The resulting hydrogen/halogen-bonded pairs are then linked by analogous interactions to form chains.

Table 5

The values of dihedral angles  $\varphi_1$  and  $\varphi_2$  (for definition, see Fig. 3).

Structure	(1)	(4)	(7)	(2)	(5)	(8)	(3)	(6)	(9)
Substitution of ring C	2-Cl	2-Br	2-I	3-Cl	3-Br	3-I	4-Cl	4-Br	4-I
$\varphi_1$ (°)	15.83	40.34	7.78	22.12	10.21; 14.15	10.28; 13.20	36.81	30.01	11.59
$\varphi_2$ (°)	23.51	45.26	73.05	4.23	15.44; 15.39	13.07; 13.80	10.36	21.06	13.09

that they form rack-type layers parallel to the (001) plane. In our previous work (Rosiak *et al.*, 2018b), we showed that this compound in reaction with CuI undergoes dehalogenation and cyclization to form *N*-(benzo[*d*]thiazol-2-yl)benzamide. It then serves as an *N*-donor ligand stabilizing quadruple CuI chains.

In the case of (9), I atoms do not participate in specific halogen-bond interactions (Fig. 5b); instead they interact with aromatic rings yielding I $\cdots\pi$  contacts. The distance (*d*) between the I atom and the centroid of ring C is 3.824 Å.

However, in the case of (6), the molecules are connected by Br $\cdots$ Br interactions, forming a herringbone pattern, which can be classified as type II (see Fig. 7 and Table 3). Equal distances are due to the generation of both equivalent Br1 atoms by the screw axes with opposite shift vectors, *i.e.*  $\frac{1}{2}b$  and  $-\frac{1}{2}b$ . This implies that the infinite pattern has subperiodic symmetry of the screw-axis symmetry involved (rod group  $\mathcal{A}112_1$ ).

### 3.4. Stacking

Table 4 summarizes data on the stacking interactions. As no such interactions are found in (6), it is absent from this table.

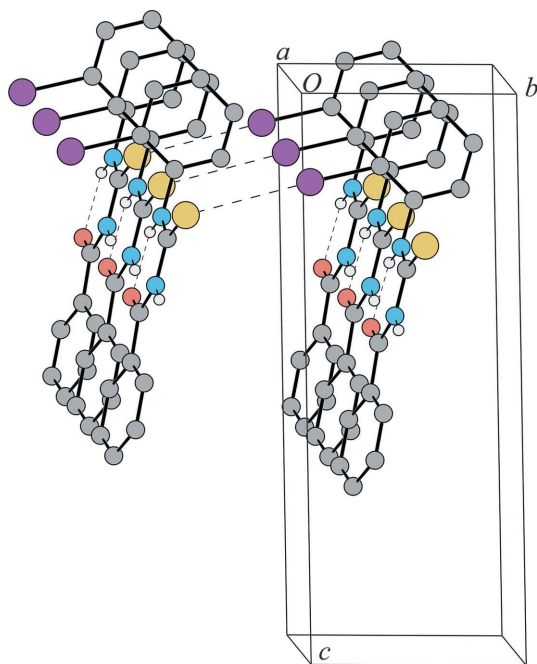


Figure 6

Depiction of the I $\cdots$ S contacts found in (7) that form chains propagating along the  $[110]$  direction.

In the case of (1), the molecules are antiparallel. The positions of subsequent molecules of the stack are generated

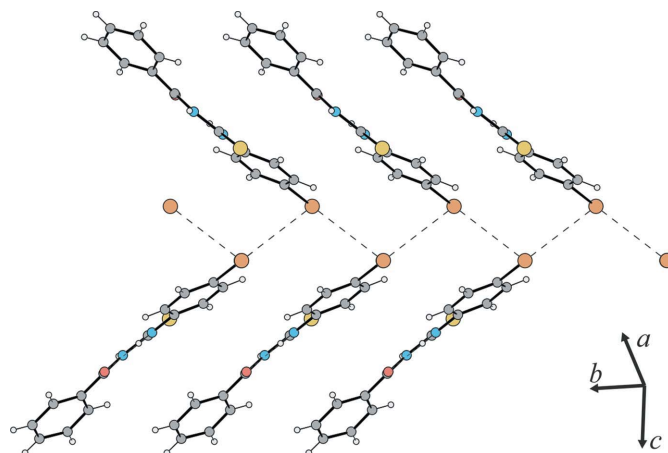


Figure 7

The herringbone pattern found in the structure of (6) in a projection perpendicular to the screw axis.

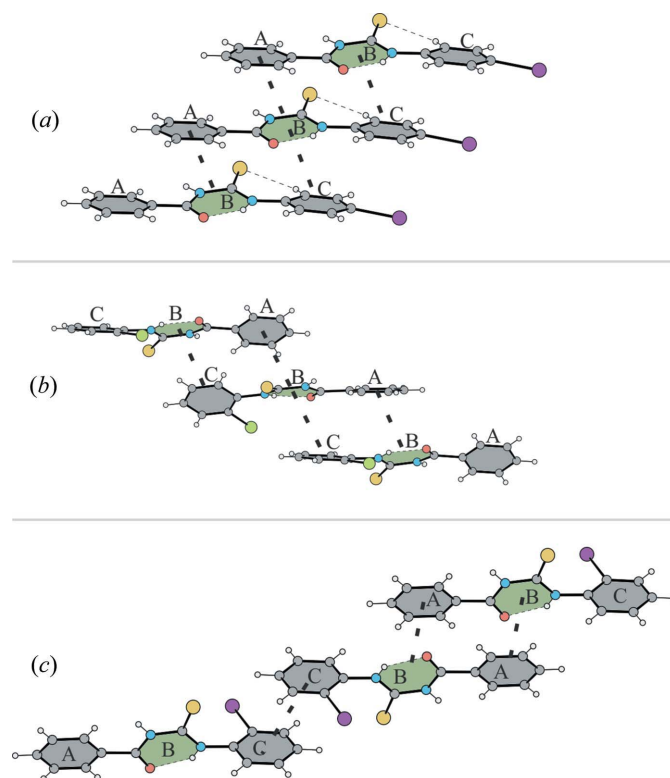
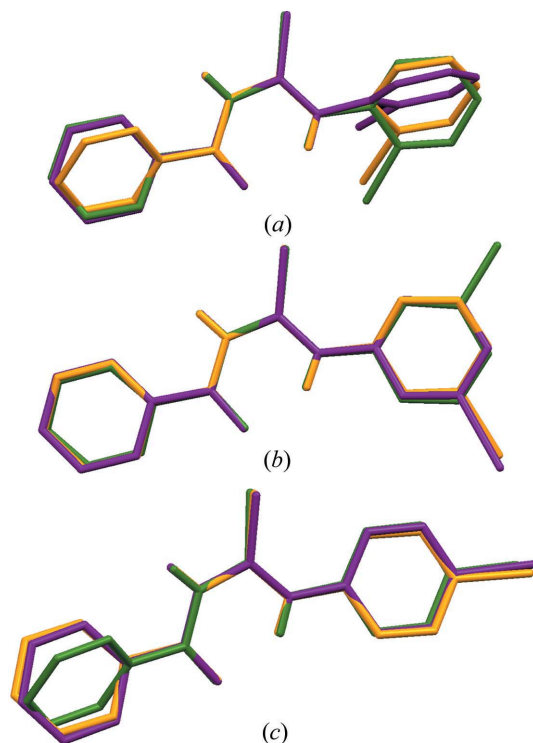


Figure 8

Stacking motifs that can be found in (a) (2)–(5), (8) and (9), (b) (1) and (c) (7).



**Figure 9**  
Overlays of molecules of 1-benzoyl-3-(halogenophenyl)thioureas from the discussed structures (this study or CSD structures; see Table 1) for (a) *ortho*, (b) *meta* and (c) *para* isomers. Colour codes: Cl is green, Br orange and I purple. Fitting was based on the central S(6) pseudo-ring (see Fig. 2). C–H hydrogens have been omitted for clarity.

by the glide plane (symmetry operation:  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ) (see Fig. 8b).

Despite some differences, compounds (2)–(5), (8) and (9) form a characteristic motif of stacking interactions in which the molecules stack up on top of each other and are slightly shifted (see Table 4). The positions of subsequent molecules of the stack are generated by translation (see Fig. 8a). The cyclic hydrogen-bonded motif *S*(6) (ring *B*) is often employed in such interactions, similar to our previous research (Okuniewski *et al.*, 2017).

Due to the twist of ring *C* relative to the flat fragment formed by the *A* and *B* rings [benzoyl and *S*(6) motifs], molecules of (7) form *A*···*B* stacking interactions and separate stacking interactions between adjacent iodobenzene rings. These interactions cause the formation of chains (Fig. 8c).

### 3.5. Conformational analysis

The conformational differences between (1)–(9) can be seen in the superposition of the *ortho*-, *meta*- and *para*-substituted derivatives (Fig. 9). The values of  $\varphi_1$  and  $\varphi_2$  are summarized in Table 5.

Additionally, we have calculated the potential energy plots obtained by the optimization of the structures of (1)–(9) with the C1–N2–C21–C26 torsion angles ( $\varphi_2$ ) set to values in the 0–360° range. A detailed description of the procedure can be found in the caption of Fig. 10. The plots for the *meta* and *para*

derivatives are very similar. When the molecule is flat ( $\varphi_2 = 0, 180$  and  $360^\circ$ ), then the energy minimum is reached. On the other hand, when rings *B* and *C* rings are perpendicular ( $\varphi_2 = 90$  and  $270^\circ$ ), the molecule has maximum energy due to weak orbital overlap and blocked electron-density delocalization. As can be seen in the magnification, the difference between the energies of the *meta* and *para* isomers is greater the larger the halogen atom.

For the *ortho* derivatives, there are two energetic minima: for (1) at  $5/355^\circ$ , for (4) at  $30/330^\circ$  and for (7) at  $45/315^\circ$ . The larger the halogen atom, the more tilted the phenyl ring and the energy minimum is at higher values of the  $\varphi_2$  torsion angle as expected. Due to the close position and overlapping of Cl/Br/I and S atoms, the energy rises significantly in the range  $170$ – $190^\circ$ . The calculated values of the energy minimum do not exactly correspond to the values of  $\varphi_2$  in the structures extracted from the crystallographic data, due to additional interactions occurring in the crystal lattice.

In contrast to simple diphenylthiourea, in all of the title compounds, the thiocarbonyl group is significantly tilted. Due to steric hindrance, the tilt is in the opposite direction to that of the nearby phenyl substituent. This can be quantified in terms of the valence angles. For the title compounds, the smaller S=C–N valence angles are in the  $116$ – $119^\circ$  range, while the larger angles are in the  $125$ – $129^\circ$  range. On the other hand, in simple diphenylthiourea, the angles are approximately equal to  $120$ – $123^\circ$  (depending on the polymorph).

## 4. Conclusions

During this study, we performed an analysis of the influence of the position of the ring substituent on the dihedral angles between the rings in substituted 1-benzoylthioureas deposited in the CSD. It turns out that when the substituent is in the *meta* or *para* position, then its effect on the twist of the molecule is small. On the other hand, when the substituent is in an *ortho* position, then two kinds of effects can occur. If the substituent is small and can act as a hydrogen-bond acceptor (*e.g.* F or OR; *R* = H or Me), then it can support the planarity of the system, but for larger substituents (*e.g.* I or Ph), the molecule is twisted and the dihedral angle can even reach a value close to  $90^\circ$ .

For the compounds presented in this article, the carbonyl and thiourea groups are almost coplanar and the conformation adopted by the C=S and C=O groups is antiperiplanar; an *S* conformation according to Woldu & Dillen (2008). This is reinforced by an intramolecular N–H···O hydrogen bond, forming an *S*(6) motif. In the solid state, molecules in the crystal are usually connected by intermolecular N–H···S=C hydrogen bonds, forming centrosymmetric  $R_2^2(8)$  motifs, or by N–H···O=C and N–H···S=C hydrogen bonds, forming  $R_2^2(6)$  hydrogen-bonded rings.

As anticipated, the presence of a halogen atom as a substituent affects the crystal packing due to the formation of halogen bonds. Halogen-substituted 1-benzoylthioureas readily form interactions between the halogen atom (with an electron hole, Lewis acid) and the carbonyl/thiocarbonyl



groups (Lewis base). These interactions are of similar importance to hydrogen bonds. In the case of (7), we found the formation of  $C=S \cdots I$  interactions instead of the  $C=S \cdots H-N$  interactions observed in all other cases. Interactions between two halogen atoms are only found in the case of (6). The  $Br \cdots Br$  contacts form supramolecular herringbone motifs. Additionally, some  $I \cdots \pi$  interactions can be found in (9) thus hindering the usual stacking interactions.

Due to the presence of intramolecular  $N-H \cdots O$  hydrogen bonds forming  $S(6)$  quasi-aromatic pseudo-rings, 1-acylthio-ureas readily form intermolecular stacking-like interactions with other rings. The most common layer interaction motif is a parallel displacement where molecules forming stacks are related by a simple translation.

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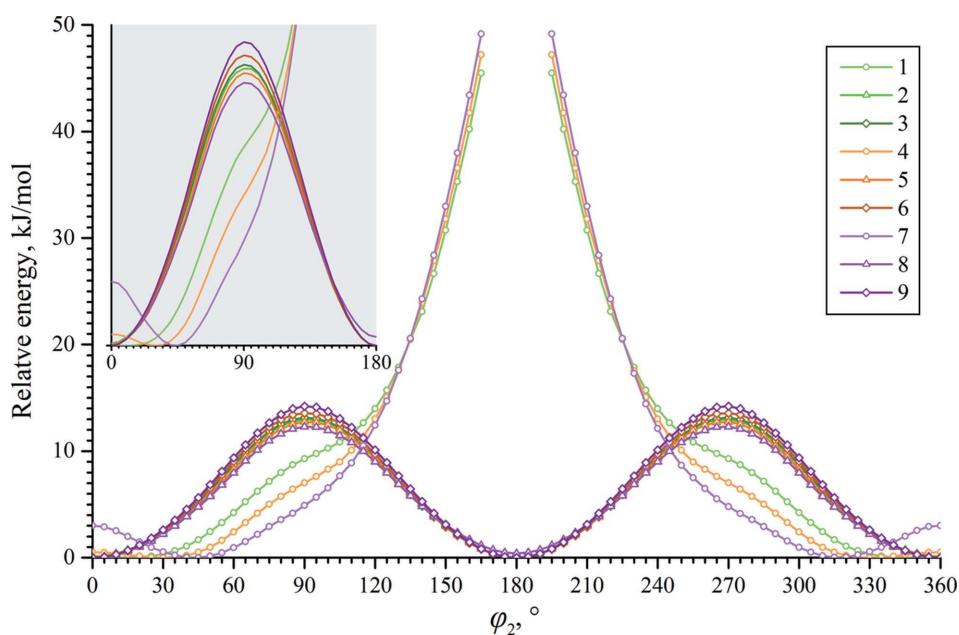


Figure 10

The potential energy plots obtained by optimization of the structures of (1)–(9), with the  $C1-N2-C21-C26$  torsion angles ( $\varphi_2$ ) set to values in the  $0-360^\circ$  range. The  $\varphi_2$  angles were modified with  $+5$  and  $-5^\circ$  steps and the resulting energies were averaged. Calculations were performed in *GAUSSIAN09* (Frisch *et al.*, 2009) at the B3LYP/LanL2DZ level of theory. For compounds with an *ortho* substituent, data points in the range  $170-190^\circ$  were excluded, as the energy rises drastically and the calculations were unstable because of close  $Cl/Br/I \cdots S$  contacts. The inset shows the  $0-180^\circ$  fragment without data points for clarity.

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## supporting information

*Acta Cryst.* (2021). C77, 11-19 [https://doi.org/10.1107/S2053229620015594]

## The influence of the type of halogen substituent and its position on the molecular conformation, intermolecular interactions and crystal packing for a series of 1-benzoyl-3-(halogenophenyl)thioureas

**Damian Rosiak, Andrzej Okuniewski and Jarosław Chojnacki**

### Computing details

For all structures, data collection: *X-AREA* (Stoe & Cie, 2009); cell refinement: *X-AREA* (Stoe & Cie, 2009); data reduction: *X-RED32* (Stoe & Cie, 2009); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

### 1-Benzoyl-3-(2-iodophenyl)thiourea (7)

#### Crystal data

C<sub>14</sub>H<sub>11</sub>IN<sub>2</sub>OS

*M<sub>r</sub>* = 382.21

Triclinic, *P* $\bar{1}$

*a* = 6.2410 (7) Å

*b* = 7.2420 (8) Å

*c* = 16.709 (2) Å

$\alpha$  = 84.408 (9)°

$\beta$  = 89.142 (9)°

$\gamma$  = 65.933 (8)°

*V* = 686.02 (14) Å<sup>3</sup>

*Z* = 2

*F*(000) = 372

*D<sub>x</sub>* = 1.850 Mg m<sup>-3</sup>

Mo *K* $\alpha$  radiation,  $\lambda$  = 0.71073 Å

Cell parameters from 15454 reflections

$\theta$  = 5.0–58.9°

$\mu$  = 2.48 mm<sup>-1</sup>

*T* = 125 K

Needle, colourless

0.38 × 0.36 × 0.20 mm

#### Data collection

Stoe IPDS 2T

diffractometer

Detector resolution: 6.67 pixels mm<sup>-1</sup>

rotation method,  $\omega$  scans

Absorption correction: integration

[*X-RED32* (Stoe & Cie, 2009), by Gaussian

integration, analogous to Coppens (1970)]

*T<sub>min</sub>* = 0.405, *T<sub>max</sub>* = 0.644

7847 measured reflections

3616 independent reflections

3508 reflections with *I* > 2 $\sigma$ (*I*)

*R<sub>int</sub>* = 0.026

$\theta_{\max}$  = 29.0°,  $\theta_{\min}$  = 2.5°

*h* = -8→8

*k* = -9→9

*l* = -22→22

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.028

*wR*(*F*<sup>2</sup>) = 0.072

*S* = 1.07

3616 reflections

172 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 0.7088P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.70 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.94 \text{ e } \text{\AA}^{-3}$$

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.90242 (2)	0.02230 (2)	0.15049 (2)	0.03196 (7)
S1	0.15430 (10)	0.46926 (10)	0.22234 (3)	0.03037 (13)
O1	0.7747 (3)	0.2798 (3)	0.39791 (9)	0.0285 (3)
N2	0.6016 (3)	0.4070 (3)	0.24851 (10)	0.0211 (3)
H2	0.723735	0.364016	0.281876	0.025*
N1	0.3991 (3)	0.3503 (3)	0.35827 (10)	0.0220 (3)
H1	0.265397	0.351322	0.376215	0.026*
C26	0.7606 (3)	0.3342 (3)	0.11447 (12)	0.0228 (4)
C22	0.5295 (4)	0.6780 (4)	0.14173 (13)	0.0261 (4)
H22	0.440446	0.772704	0.177811	0.031*
C11	0.5187 (4)	0.2440 (3)	0.49911 (11)	0.0210 (4)
C21	0.6289 (3)	0.4723 (3)	0.16703 (11)	0.0207 (4)
C1	0.4010 (3)	0.4079 (3)	0.27636 (12)	0.0208 (3)
C10	0.5784 (4)	0.2919 (3)	0.41490 (12)	0.0210 (3)
C12	0.7032 (4)	0.1607 (4)	0.55539 (13)	0.0282 (4)
H12	0.858015	0.137499	0.539275	0.034*
C25	0.7944 (4)	0.4025 (4)	0.03653 (13)	0.0298 (5)
H25	0.886598	0.308343	0.000756	0.036*
C23	0.5600 (4)	0.7459 (4)	0.06345 (14)	0.0326 (5)
H23	0.489514	0.886869	0.045740	0.039*
C16	0.2916 (4)	0.2777 (3)	0.52341 (13)	0.0261 (4)
H16	0.164269	0.333137	0.485342	0.031*
C24	0.6928 (4)	0.6084 (5)	0.01139 (14)	0.0342 (5)
H24	0.714536	0.655435	-0.041909	0.041*
C13	0.6637 (5)	0.1113 (4)	0.63477 (14)	0.0340 (5)
H13	0.791269	0.052973	0.672691	0.041*
C14	0.4383 (5)	0.1469 (4)	0.65881 (13)	0.0309 (5)
H14	0.410940	0.114186	0.713373	0.037*
C15	0.2522 (4)	0.2301 (4)	0.60339 (14)	0.0301 (4)
H15	0.097554	0.254730	0.620068	0.036*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
I1	0.02866 (9)	0.03127 (10)	0.03389 (10)	-0.00873 (7)	0.00216 (6)	-0.00997 (6)
S1	0.0253 (2)	0.0501 (3)	0.0197 (2)	-0.0211 (2)	-0.00379 (18)	0.0045 (2)

O1	0.0241 (7)	0.0369 (9)	0.0218 (7)	-0.0112 (6)	-0.0010 (5)	0.0036 (6)
N2	0.0195 (7)	0.0264 (8)	0.0163 (7)	-0.0087 (6)	-0.0008 (6)	0.0002 (6)
N1	0.0230 (8)	0.0279 (8)	0.0155 (7)	-0.0114 (7)	0.0003 (6)	0.0006 (6)
C26	0.0178 (8)	0.0339 (10)	0.0198 (9)	-0.0136 (8)	-0.0008 (6)	-0.0030 (7)
C22	0.0273 (10)	0.0285 (10)	0.0241 (9)	-0.0138 (8)	-0.0048 (7)	0.0015 (8)
C11	0.0282 (9)	0.0187 (8)	0.0165 (8)	-0.0100 (7)	-0.0006 (7)	-0.0008 (6)
C21	0.0197 (8)	0.0295 (10)	0.0158 (8)	-0.0135 (7)	-0.0012 (6)	0.0007 (7)
C1	0.0229 (9)	0.0226 (9)	0.0172 (8)	-0.0098 (7)	-0.0002 (6)	-0.0009 (6)
C10	0.0255 (9)	0.0187 (8)	0.0172 (8)	-0.0078 (7)	-0.0017 (7)	0.0001 (6)
C12	0.0314 (10)	0.0358 (11)	0.0203 (9)	-0.0173 (9)	-0.0037 (8)	0.0020 (8)
C25	0.0218 (9)	0.0546 (14)	0.0197 (9)	-0.0220 (10)	0.0034 (7)	-0.0057 (9)
C23	0.0348 (11)	0.0409 (13)	0.0278 (11)	-0.0243 (10)	-0.0088 (9)	0.0124 (9)
C16	0.0272 (10)	0.0264 (10)	0.0210 (9)	-0.0077 (8)	0.0014 (7)	-0.0003 (7)
C24	0.0299 (11)	0.0612 (16)	0.0210 (9)	-0.0306 (11)	-0.0028 (8)	0.0070 (10)
C13	0.0422 (13)	0.0455 (14)	0.0192 (9)	-0.0242 (11)	-0.0079 (9)	0.0043 (9)
C14	0.0464 (13)	0.0365 (12)	0.0176 (9)	-0.0254 (11)	0.0011 (8)	-0.0002 (8)
C15	0.0357 (11)	0.0344 (11)	0.0224 (10)	-0.0161 (10)	0.0070 (8)	-0.0053 (8)

*Geometric parameters (Å, °)*

I1—C26	2.090 (2)	C11—C16	1.397 (3)
S1—C1	1.670 (2)	C12—H12	0.9500
O1—C10	1.224 (3)	C12—C13	1.385 (3)
N2—H2	0.8800	C25—H25	0.9500
N2—C21	1.428 (2)	C25—C24	1.385 (4)
N2—C1	1.326 (3)	C23—H23	0.9500
N1—H1	0.8800	C23—C24	1.381 (4)
N1—C1	1.393 (2)	C16—H16	0.9500
N1—C10	1.376 (3)	C16—C15	1.391 (3)
C26—C21	1.388 (3)	C24—H24	0.9500
C26—C25	1.392 (3)	C13—H13	0.9500
C22—H22	0.9500	C13—C14	1.384 (4)
C22—C21	1.384 (3)	C14—H14	0.9500
C22—C23	1.390 (3)	C14—C15	1.386 (3)
C11—C10	1.494 (3)	C15—H15	0.9500
C11—C12	1.389 (3)		
C21—N2—H2	118.4	C11—C12—H12	119.7
C1—N2—H2	118.4	C13—C12—C11	120.6 (2)
C1—N2—C21	123.21 (17)	C13—C12—H12	119.7
C1—N1—H1	115.7	C26—C25—H25	120.2
C10—N1—H1	115.7	C24—C25—C26	119.6 (2)
C10—N1—C1	128.69 (17)	C24—C25—H25	120.2
C21—C26—I1	120.46 (15)	C22—C23—H23	120.0
C21—C26—C25	120.1 (2)	C24—C23—C22	120.0 (2)
C25—C26—I1	119.44 (17)	C24—C23—H23	120.0
C21—C22—H22	120.0	C11—C16—H16	120.0
C21—C22—C23	119.9 (2)	C15—C16—C11	119.9 (2)

C23—C22—H22	120.0	C15—C16—H16	120.0
C12—C11—C10	116.82 (19)	C25—C24—H24	119.8
C12—C11—C16	119.26 (19)	C23—C24—C25	120.3 (2)
C16—C11—C10	123.92 (18)	C23—C24—H24	119.8
C26—C21—N2	121.15 (19)	C12—C13—H13	120.0
C22—C21—N2	118.82 (19)	C14—C13—C12	120.0 (2)
C22—C21—C26	119.98 (19)	C14—C13—H13	120.0
N2—C1—S1	126.10 (15)	C13—C14—H14	120.0
N2—C1—N1	116.28 (17)	C13—C14—C15	120.1 (2)
N1—C1—S1	117.62 (15)	C15—C14—H14	120.0
O1—C10—N1	122.48 (18)	C16—C15—H15	119.9
O1—C10—C11	121.69 (18)	C14—C15—C16	120.1 (2)
N1—C10—C11	115.83 (18)	C14—C15—H15	119.9

## Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H2···O1	0.88	1.97	2.659 (2)	135

## 1-Benzoyl-3-(3-iodophenyl)thiourea (8)

## Crystal data

C<sub>14</sub>H<sub>11</sub>IN<sub>2</sub>OS  
*M<sub>r</sub>* = 382.21  
 Monoclinic, *Pc*  
*a* = 4.5639 (5) Å  
*b* = 15.375 (3) Å  
*c* = 19.355 (2) Å  
 $\beta$  = 91.404 (9)°  
*V* = 1357.7 (3) Å<sup>3</sup>  
*Z* = 4

*F*(000) = 744  
*D<sub>x</sub>* = 1.870 Mg m<sup>-3</sup>  
 Mo *K*α radiation,  $\lambda$  = 0.71073 Å  
 Cell parameters from 2158 reflections  
 $\theta$  = 2.5–29.4°  
 $\mu$  = 2.51 mm<sup>-1</sup>  
*T* = 125 K  
 Needle, colourless  
 0.7 × 0.08 × 0.05 mm

## Data collection

Stoe\_IPDS\_2T  
 diffractometer  
 Radiation source: microfocus sealed X-ray tube,  
 GeniX Mo, 0.05 × 0.05 mm<sup>2</sup>  
 Parabolic x-ray mirror monochromator  
 Detector resolution: 6.67 pixels mm<sup>-1</sup>  
 rotation method scans  
 Absorption correction: integration  
 [X-RED32 (Stoe & Cie, 2009), by Gaussian  
 integration, analogous to Coppens (1970)]

*T*<sub>min</sub> = 0.393, *T*<sub>max</sub> = 0.885  
 13551 measured reflections  
 5820 independent reflections  
 5398 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.070  
 $\theta$ <sub>max</sub> = 27.5°,  $\theta$ <sub>min</sub> = 2.5°  
*h* = -5→5  
*k* = -19→19  
*l* = -25→23

## Refinement

Refinement on *F*<sup>2</sup>  
 Least-squares matrix: full  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.054  
*wR*(*F*<sup>2</sup>) = 0.148  
*S* = 1.07  
 5820 reflections  
 343 parameters

2 restraints  
 Primary atom site location: dual  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.1066P)^2 + 0.9908P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 1.24 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.27 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack (1983), 2156 Friedel  
pairs  
Absolute structure parameter: 0.30 (4)

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
IIA	0.87867 (10)	0.35387 (4)	0.39772 (4)	0.0328 (2)
II	0.14942 (12)	0.40415 (4)	0.61116 (4)	0.0338 (2)
S1	0.7822 (7)	-0.05110 (18)	0.57618 (16)	0.0368 (6)
S1A	0.1700 (7)	0.80028 (19)	0.41313 (17)	0.0393 (7)
O1A	-0.1126 (19)	0.5770 (6)	0.5497 (4)	0.0330 (17)
O1	1.123 (2)	0.1767 (5)	0.4527 (4)	0.0341 (17)
N2A	0.189 (2)	0.6285 (7)	0.4449 (5)	0.0280 (19)
H2A	0.124794	0.589646	0.474320	0.034*
C12	1.478 (3)	0.1371 (8)	0.3423 (6)	0.030 (2)
H12	1.395714	0.193753	0.345652	0.036*
N2	0.794 (2)	0.1221 (7)	0.5524 (5)	0.0288 (19)
H2	0.868530	0.162280	0.525647	0.035*
N1	1.101 (2)	0.0358 (6)	0.4888 (5)	0.0282 (18)
H1	1.179490	-0.015895	0.482922	0.034*
N1A	-0.130 (2)	0.7143 (6)	0.5053 (5)	0.0306 (18)
H1A	-0.220421	0.764534	0.508664	0.037*
C25A	0.666 (3)	0.5976 (7)	0.2925 (6)	0.032 (2)
H25A	0.717177	0.625646	0.250752	0.038*
C23	0.299 (2)	0.2779 (7)	0.6325 (6)	0.029 (2)
C21	0.591 (2)	0.1540 (7)	0.6007 (6)	0.027 (2)
C22	0.494 (2)	0.2395 (7)	0.5876 (6)	0.029 (2)
H22	0.560848	0.270554	0.548633	0.035*
C24A	0.788 (3)	0.5167 (8)	0.3096 (7)	0.033 (2)
H24A	0.923610	0.489731	0.279989	0.040*
C10	1.201 (3)	0.1003 (8)	0.4464 (6)	0.029 (2)
C22A	0.508 (2)	0.5159 (7)	0.4143 (6)	0.027 (2)
H22A	0.453406	0.487322	0.455542	0.033*
C26A	0.468 (3)	0.6375 (9)	0.3372 (7)	0.032 (3)
H26A	0.387924	0.692794	0.325606	0.039*
C1	0.891 (2)	0.0417 (7)	0.5403 (6)	0.028 (2)
C11A	-0.418 (2)	0.6775 (7)	0.6071 (6)	0.026 (2)
C14	1.788 (2)	0.0358 (8)	0.2847 (6)	0.032 (2)
H14	1.919888	0.023232	0.248821	0.038*
C23A	0.707 (2)	0.4762 (7)	0.3703 (5)	0.027 (2)
C13	1.660 (3)	0.1178 (9)	0.2890 (6)	0.033 (2)
H13	1.698782	0.160457	0.254936	0.040*

C11	1.411 (3)	0.0736 (7)	0.3919 (6)	0.027 (2)
C21A	0.388 (3)	0.5969 (6)	0.3980 (6)	0.029 (2)
C16A	-0.573 (2)	0.7558 (7)	0.6067 (6)	0.031 (2)
H16A	-0.549717	0.795796	0.569802	0.037*
C24	0.199 (3)	0.2334 (8)	0.6895 (6)	0.033 (2)
H24	0.065033	0.259819	0.719880	0.039*
C15	1.722 (3)	-0.0272 (8)	0.3328 (6)	0.035 (2)
H15	1.803195	-0.083840	0.328833	0.042*
C25	0.300 (3)	0.1495 (7)	0.7013 (6)	0.032 (2)
H25	0.236230	0.118764	0.740804	0.039*
C15A	-0.760 (2)	0.7754 (8)	0.6592 (6)	0.032 (2)
H15A	-0.866389	0.828518	0.658524	0.038*
C13A	-0.635 (3)	0.6399 (8)	0.7136 (7)	0.034 (3)
H13A	-0.658159	0.599928	0.750468	0.041*
C14A	-0.792 (3)	0.7163 (8)	0.7139 (6)	0.034 (2)
H14A	-0.919502	0.728911	0.750532	0.041*
C16	1.538 (3)	-0.0082 (7)	0.3870 (6)	0.032 (2)
H16	1.499738	-0.051296	0.420745	0.038*
C10A	-0.210 (3)	0.6517 (7)	0.5523 (6)	0.030 (2)
C12A	-0.447 (3)	0.6194 (9)	0.6618 (6)	0.030 (2)
H12A	-0.338093	0.566679	0.663213	0.036*
C1A	0.078 (2)	0.7089 (7)	0.4525 (6)	0.029 (2)
C26	0.492 (3)	0.1092 (9)	0.6568 (7)	0.033 (3)
H26	0.554691	0.051109	0.665226	0.039*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
I1A	0.0339 (4)	0.0383 (3)	0.0266 (4)	0.0024 (3)	0.0080 (3)	-0.0009 (3)
I1	0.0359 (4)	0.0374 (3)	0.0285 (4)	0.0035 (3)	0.0086 (3)	0.0000 (3)
S1	0.0428 (15)	0.0374 (13)	0.0310 (14)	0.0015 (11)	0.0172 (12)	0.0045 (10)
S1A	0.0478 (17)	0.0380 (14)	0.0330 (15)	0.0021 (11)	0.0180 (13)	0.0066 (11)
O1A	0.035 (4)	0.040 (4)	0.025 (4)	0.003 (3)	0.009 (3)	0.003 (3)
O1	0.041 (5)	0.036 (4)	0.026 (4)	0.002 (4)	0.006 (3)	0.001 (3)
N2A	0.023 (4)	0.041 (5)	0.021 (5)	0.004 (4)	0.008 (4)	0.006 (4)
C12	0.025 (6)	0.039 (6)	0.027 (6)	-0.002 (4)	0.007 (4)	0.004 (4)
N2	0.029 (5)	0.035 (5)	0.022 (4)	0.004 (4)	0.009 (4)	0.005 (4)
N1	0.029 (4)	0.032 (4)	0.024 (4)	0.004 (3)	0.008 (4)	-0.001 (3)
N1A	0.033 (5)	0.034 (4)	0.025 (4)	0.002 (3)	0.010 (4)	0.004 (4)
C25A	0.037 (6)	0.043 (6)	0.017 (5)	-0.001 (4)	0.006 (5)	0.001 (4)
C23	0.029 (5)	0.034 (5)	0.025 (5)	-0.003 (4)	0.003 (4)	0.001 (4)
C21	0.020 (5)	0.043 (5)	0.018 (5)	0.003 (4)	0.004 (4)	-0.002 (4)
C22	0.030 (5)	0.040 (5)	0.018 (5)	0.001 (4)	0.004 (4)	0.002 (4)
C24A	0.028 (5)	0.039 (6)	0.032 (6)	0.002 (4)	0.005 (4)	0.004 (4)
C10	0.022 (5)	0.041 (6)	0.024 (5)	-0.003 (4)	-0.002 (4)	-0.001 (4)
C22A	0.021 (5)	0.033 (5)	0.028 (5)	0.000 (4)	0.006 (4)	0.002 (4)
C26A	0.023 (6)	0.048 (7)	0.027 (6)	0.001 (4)	0.005 (5)	0.008 (5)
C1	0.025 (5)	0.040 (5)	0.020 (5)	-0.002 (4)	0.000 (4)	0.000 (4)





C11A	0.023 (5)	0.035 (5)	0.021 (5)	-0.001 (4)	0.002 (4)	-0.002 (4)
C14	0.026 (5)	0.047 (6)	0.022 (5)	0.000 (4)	0.007 (4)	0.002 (4)
C23A	0.023 (5)	0.039 (5)	0.019 (5)	0.000 (4)	0.003 (4)	-0.002 (4)
C13	0.032 (6)	0.045 (6)	0.023 (6)	-0.009 (5)	0.006 (4)	0.009 (5)
C11	0.022 (5)	0.036 (4)	0.023 (5)	-0.005 (4)	0.006 (4)	0.000 (4)
C21A	0.032 (5)	0.036 (5)	0.018 (5)	0.000 (5)	0.007 (4)	-0.002 (5)
C16A	0.022 (5)	0.042 (6)	0.029 (6)	0.002 (4)	0.005 (4)	0.004 (4)
C24	0.034 (6)	0.044 (6)	0.021 (5)	0.002 (4)	0.009 (4)	-0.001 (4)
C15	0.040 (6)	0.039 (6)	0.026 (6)	0.003 (5)	0.007 (5)	-0.003 (4)
C25	0.045 (7)	0.040 (6)	0.012 (5)	0.003 (4)	0.009 (5)	0.008 (4)
C15A	0.030 (5)	0.041 (5)	0.025 (5)	0.001 (4)	0.009 (4)	-0.004 (4)
C13A	0.032 (6)	0.042 (6)	0.028 (6)	-0.001 (4)	0.002 (5)	0.004 (4)
C14A	0.029 (6)	0.044 (6)	0.029 (6)	0.000 (4)	0.004 (4)	0.000 (4)
C16	0.035 (6)	0.035 (5)	0.026 (5)	-0.001 (4)	0.005 (4)	0.002 (4)
C10A	0.025 (5)	0.039 (6)	0.025 (5)	-0.005 (4)	0.008 (4)	0.002 (4)
C12A	0.025 (6)	0.041 (6)	0.024 (5)	0.001 (5)	0.009 (4)	0.005 (5)
C1A	0.025 (5)	0.037 (5)	0.025 (5)	0.001 (4)	0.007 (4)	-0.004 (4)
C26	0.029 (6)	0.045 (6)	0.023 (6)	0.003 (5)	-0.002 (5)	0.003 (5)

*Geometric parameters (Å, °)*

I1A—C23A	2.101 (11)	C21—C22	1.408 (16)
I1—C23	2.095 (11)	C21—C26	1.373 (17)
S1—C1	1.668 (11)	C24A—C23A	1.389 (15)
S1A—C1A	1.658 (11)	C10—C11	1.501 (16)
O1A—C10A	1.232 (15)	C22A—C23A	1.399 (14)
O1—C10	1.233 (15)	C22A—C21A	1.392 (15)
N2A—C21A	1.388 (14)	C26A—C21A	1.389 (17)
N2A—C1A	1.345 (15)	C11A—C16A	1.397 (15)
C12—C13	1.374 (17)	C11A—C10A	1.494 (15)
C12—C11	1.408 (16)	C11A—C12A	1.394 (16)
N2—C21	1.420 (14)	C14—C13	1.393 (18)
N2—C1	1.335 (16)	C14—C15	1.382 (16)
N1—C10	1.371 (14)	C11—C16	1.391 (16)
N1—C1	1.403 (14)	C16A—C15A	1.376 (15)
N1A—C10A	1.380 (14)	C24—C25	1.388 (16)
N1A—C1A	1.414 (13)	C15—C16	1.390 (15)
C25A—C24A	1.399 (17)	C25—C26	1.390 (18)
C25A—C26A	1.406 (18)	C15A—C14A	1.405 (17)
C23—C22	1.389 (15)	C13A—C14A	1.374 (17)
C23—C24	1.385 (15)	C13A—C12A	1.374 (17)
C1A—N2A—C21A	130.3 (10)	C24A—C23A—I1A	120.6 (8)
C13—C12—C11	120.4 (11)	C24A—C23A—C22A	120.6 (10)
C1—N2—C21	131.3 (11)	C22A—C23A—I1A	118.8 (8)
C10—N1—C1	128.3 (9)	C12—C13—C14	120.3 (10)
C10A—N1A—C1A	129.0 (9)	C12—C11—C10	116.2 (11)
C24A—C25A—C26A	120.0 (11)	C16—C11—C12	118.9 (11)

C22—C23—I1	118.8 (8)	C16—C11—C10	124.9 (11)
C24—C23—I1	120.1 (8)	N2A—C21A—C22A	115.1 (10)
C24—C23—C22	121.1 (10)	N2A—C21A—C26A	125.9 (10)
C22—C21—N2	114.4 (10)	C26A—C21A—C22A	119.0 (11)
C26—C21—N2	125.4 (11)	C15A—C16A—C11A	120.5 (11)
C26—C21—C22	120.2 (11)	C23—C24—C25	118.4 (10)
C23—C22—C21	119.2 (10)	C14—C15—C16	120.4 (11)
C23A—C24A—C25A	119.1 (11)	C24—C25—C26	121.6 (10)
O1—C10—N1	122.0 (11)	C16A—C15A—C14A	119.4 (11)
O1—C10—C11	121.3 (11)	C12A—C13A—C14A	122.3 (12)
N1—C10—C11	116.7 (10)	C13A—C14A—C15A	119.1 (11)
C21A—C22A—C23A	120.6 (10)	C15—C16—C11	120.2 (11)
C21A—C26A—C25A	120.7 (11)	O1A—C10A—N1A	121.4 (10)
N2—C1—S1	127.9 (9)	O1A—C10A—C11A	120.8 (10)
N2—C1—N1	114.8 (9)	N1A—C10A—C11A	117.8 (10)
N1—C1—S1	117.2 (8)	C13A—C12A—C11A	118.7 (12)
C16A—C11A—C10A	123.8 (10)	N2A—C1A—S1A	129.0 (9)
C12A—C11A—C16A	120.0 (11)	N2A—C1A—N1A	113.2 (10)
C12A—C11A—C10A	116.3 (10)	N1A—C1A—S1A	117.6 (8)
C15—C14—C13	119.7 (10)	C21—C26—C25	119.4 (12)

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N2A—H2A...O1A	0.88	1.85	2.602 (13)	142
N2—H2...O1	0.88	1.86	2.614 (13)	142
N1—H1...S1A <sup>i</sup>	0.88	3.13	3.922 (10)	150
N1A—H1A...S1 <sup>ii</sup>	0.88	3.12	3.884 (10)	146

Symmetry codes: (i)  $x+1, y-1, z$ ; (ii)  $x-1, y+1, z$ .**1-Benzoyl-3-(4-iodophenyl)thiourea (9)***Crystal data*

C<sub>14</sub>H<sub>11</sub>IN<sub>2</sub>OS  
*M<sub>r</sub>* = 382.21  
 Triclinic, *P* $\bar{1}$   
*a* = 4.4279 (5) Å  
*b* = 13.0767 (14) Å  
*c* = 13.4410 (14) Å  
 $\alpha$  = 61.622 (7)°  
 $\beta$  = 86.203 (9)°  
 $\gamma$  = 85.241 (9)°  
*V* = 682.06 (13) Å<sup>3</sup>

*Z* = 2  
*F*(000) = 372  
*D<sub>x</sub>* = 1.861 Mg m<sup>-3</sup>  
 Mo *K* $\alpha$  radiation,  $\lambda$  = 0.71073 Å  
 Cell parameters from 17633 reflections  
 $\theta$  = 3.0–29.6°  
 $\mu$  = 2.49 mm<sup>-1</sup>  
*T* = 120 K  
 Needle, colourless  
 0.33 × 0.08 × 0.05 mm

*Data collection*

Stoe IPDS 2T  
 diffractometer  
 Detector resolution: 6.67 pixels mm<sup>-1</sup>  
 rotation method scans

Absorption correction: integration  
 [X-RED32 (Stoe & Cie, 2009), by Gaussian  
 integration, analogous to Coppens (1970)]  
*T<sub>min</sub>* = 0.734, *T<sub>max</sub>* = 0.932  
 9681 measured reflections

3617 independent reflections  
 3348 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.020$   
 $\theta_{\text{max}} = 29.0^\circ$ ,  $\theta_{\text{min}} = 3.0^\circ$

$h = -6 \rightarrow 5$   
 $k = -17 \rightarrow 17$   
 $l = -18 \rightarrow 18$

Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.021$   
 $wR(F^2) = 0.054$   
 $S = 1.05$   
 3617 reflections  
 172 parameters  
 0 restraints

Hydrogen site location: inferred from neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 0.1682P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.002$   
 $\Delta\rho_{\text{max}} = 0.80 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.39 \text{ e } \text{\AA}^{-3}$

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 ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
II	1.54166 (3)	0.97722 (2)	0.30315 (2)	0.02325 (5)
S1	0.69441 (13)	0.63634 (4)	0.85377 (4)	0.02636 (10)
O1	0.4225 (3)	0.43021 (12)	0.68414 (11)	0.0242 (3)
N2	0.7238 (4)	0.60053 (13)	0.67111 (13)	0.0195 (3)
H2	0.659541	0.556723	0.644375	0.023*
N1	0.4100 (4)	0.48760 (13)	0.82067 (13)	0.0198 (3)
H1	0.322999	0.474879	0.886008	0.024*
C24	1.2997 (4)	0.84543 (15)	0.43373 (15)	0.0191 (3)
C21	0.9269 (4)	0.68403 (15)	0.59760 (14)	0.0176 (3)
C23	1.1904 (4)	0.86015 (16)	0.52524 (16)	0.0221 (3)
H23	1.243847	0.925496	0.531840	0.026*
C22	1.0024 (4)	0.77975 (16)	0.60781 (16)	0.0220 (3)
H22	0.926668	0.790207	0.670373	0.026*
C11	0.1253 (4)	0.32291 (15)	0.85074 (14)	0.0178 (3)
C12	0.0857 (4)	0.23904 (16)	0.81704 (16)	0.0214 (3)
H12	0.183570	0.245258	0.749489	0.026*
C1	0.6126 (4)	0.57668 (15)	0.77422 (15)	0.0195 (3)
C25	1.2329 (4)	0.74801 (16)	0.42476 (15)	0.0212 (3)
H25	1.314542	0.736362	0.363510	0.025*
C26	1.0454 (4)	0.66836 (16)	0.50665 (15)	0.0209 (3)
H26	0.996650	0.602062	0.500796	0.025*
C10	0.3288 (4)	0.41730 (15)	0.77783 (15)	0.0182 (3)
C14	-0.2385 (5)	0.13765 (17)	0.98032 (16)	0.0239 (4)
H14	-0.361951	0.074328	1.024676	0.029*
C16	-0.0220 (4)	0.31351 (16)	0.94942 (15)	0.0216 (3)
H16	0.000485	0.370853	0.972299	0.026*

C15	-0.2017 (5)	0.22064 (17)	1.01444 (16)	0.0241 (4)
H15	-0.299221	0.213934	1.082217	0.029*
C13	-0.0951 (5)	0.14698 (17)	0.88137 (17)	0.0246 (4)
H13	-0.121186	0.090296	0.857955	0.030*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
I1	0.02755 (7)	0.02270 (7)	0.01967 (7)	-0.00760 (4)	0.00314 (4)	-0.00969 (5)
S1	0.0372 (3)	0.0277 (2)	0.0205 (2)	-0.01240 (19)	0.00619 (18)	-0.01575 (18)
O1	0.0316 (7)	0.0244 (6)	0.0199 (6)	-0.0064 (5)	0.0042 (5)	-0.0129 (5)
N2	0.0220 (7)	0.0199 (7)	0.0195 (7)	-0.0042 (6)	0.0020 (6)	-0.0115 (6)
N1	0.0218 (7)	0.0211 (7)	0.0199 (7)	-0.0045 (6)	0.0037 (6)	-0.0124 (6)
C24	0.0196 (8)	0.0181 (7)	0.0178 (7)	-0.0028 (6)	0.0003 (6)	-0.0069 (6)
C21	0.0185 (8)	0.0172 (7)	0.0169 (7)	-0.0004 (6)	-0.0008 (6)	-0.0079 (6)
C23	0.0272 (9)	0.0208 (8)	0.0215 (8)	-0.0047 (7)	0.0007 (7)	-0.0123 (7)
C22	0.0262 (9)	0.0219 (8)	0.0222 (8)	-0.0039 (7)	0.0031 (7)	-0.0139 (7)
C11	0.0188 (8)	0.0179 (7)	0.0175 (7)	0.0002 (6)	-0.0022 (6)	-0.0090 (6)
C12	0.0232 (8)	0.0229 (8)	0.0207 (8)	-0.0030 (7)	-0.0002 (6)	-0.0122 (7)
C1	0.0206 (8)	0.0184 (7)	0.0211 (8)	-0.0008 (6)	-0.0008 (6)	-0.0107 (6)
C25	0.0258 (9)	0.0220 (8)	0.0183 (8)	-0.0015 (7)	0.0018 (6)	-0.0118 (7)
C26	0.0264 (9)	0.0189 (8)	0.0213 (8)	-0.0022 (7)	0.0000 (7)	-0.0126 (7)
C10	0.0192 (8)	0.0179 (7)	0.0189 (7)	-0.0001 (6)	-0.0013 (6)	-0.0099 (6)
C14	0.0255 (9)	0.0211 (8)	0.0229 (8)	-0.0052 (7)	0.0007 (7)	-0.0082 (7)
C16	0.0269 (9)	0.0206 (8)	0.0185 (8)	-0.0025 (7)	-0.0001 (7)	-0.0102 (7)
C15	0.0286 (9)	0.0238 (8)	0.0194 (8)	-0.0037 (7)	0.0026 (7)	-0.0100 (7)
C13	0.0297 (10)	0.0223 (8)	0.0261 (9)	-0.0050 (7)	-0.0001 (7)	-0.0144 (7)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

I1—C24	2.0930 (18)	C11—C12	1.398 (2)
S1—C1	1.6656 (19)	C11—C10	1.488 (2)
O1—C10	1.236 (2)	C11—C16	1.394 (2)
N2—H2	0.8800	C12—H12	0.9500
N2—C21	1.413 (2)	C12—C13	1.384 (3)
N2—C1	1.336 (2)	C25—H25	0.9500
N1—H1	0.8800	C25—C26	1.385 (3)
N1—C1	1.400 (2)	C26—H26	0.9500
N1—C10	1.375 (2)	C14—H14	0.9500
C24—C23	1.384 (2)	C14—C15	1.388 (3)
C24—C25	1.392 (3)	C14—C13	1.391 (3)
C21—C22	1.392 (2)	C16—H16	0.9500
C21—C26	1.395 (2)	C16—C15	1.389 (3)
C23—H23	0.9500	C15—H15	0.9500
C23—C22	1.394 (3)	C13—H13	0.9500
C22—H22	0.9500		
C21—N2—H2	114.5	N2—C1—S1	128.09 (15)

C1—N2—H2	114.5	N2—C1—N1	114.60 (16)
C1—N2—C21	131.06 (16)	N1—C1—S1	117.28 (13)
C1—N1—H1	115.7	C24—C25—H25	120.6
C10—N1—H1	115.7	C26—C25—C24	118.89 (16)
C10—N1—C1	128.66 (15)	C26—C25—H25	120.6
C23—C24—H1	119.07 (13)	C21—C26—H26	119.5
C23—C24—C25	120.57 (17)	C25—C26—C21	121.00 (16)
C25—C24—H1	120.23 (13)	C25—C26—H26	119.5
C22—C21—N2	124.91 (16)	O1—C10—N1	122.06 (17)
C22—C21—C26	119.73 (17)	O1—C10—C11	121.19 (16)
C26—C21—N2	115.30 (15)	N1—C10—C11	116.74 (15)
C24—C23—H23	119.8	C15—C14—H14	119.9
C24—C23—C22	120.46 (17)	C15—C14—C13	120.15 (18)
C22—C23—H23	119.8	C13—C14—H14	119.9
C21—C22—C23	119.28 (17)	C11—C16—H16	119.9
C21—C22—H22	120.4	C15—C16—C11	120.28 (17)
C23—C22—H22	120.4	C15—C16—H16	119.9
C12—C11—C10	116.82 (16)	C14—C15—C16	119.97 (17)
C16—C11—C12	119.22 (17)	C14—C15—H15	120.0
C16—C11—C10	123.95 (16)	C16—C15—H15	120.0
C11—C12—H12	119.8	C12—C13—C14	119.86 (18)
C13—C12—C11	120.50 (17)	C12—C13—H13	120.1
C13—C12—H12	119.8	C14—C13—H13	120.1

*Hydrogen-bond geometry* (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2...O1	0.88	1.87	2.620 (2)	142
N1—H1...S1 <sup>i</sup>	0.88	3.08	3.8864 (17)	153
C22—H22...S1	0.95	2.54	3.200 (2)	126

Symmetry code: (i)  $-x+1, -y+1, -z+2$ .**1-Benzoyl-3-(2-bromophenyl)thiourea (4)***Crystal data*C<sub>14</sub>H<sub>11</sub>BrN<sub>2</sub>OS*M<sub>r</sub>* = 335.23Monoclinic, *P*2<sub>1</sub>/*n**a* = 3.9592 (4) Å*b* = 15.142 (2) Å*c* = 22.250 (2) Å $\beta$  = 95.183 (8)°*V* = 1328.4 (3) Å<sup>3</sup>*Z* = 4*F*(000) = 672*D<sub>x</sub>* = 1.676 Mg m<sup>-3</sup>Mo *K*α radiation,  $\lambda$  = 0.71073 Å

Cell parameters from 7760 reflections

 $\theta$  = 2.7–29.7° $\mu$  = 3.24 mm<sup>-1</sup>*T* = 120 K

Needle, colourless

0.76 × 0.05 × 0.03 mm

*Data collection*

Stoe IPDS 2T diffractometer	$T_{\min} = 0.379$ , $T_{\max} = 0.892$ 7908 measured reflections
Radiation source: GeniX Mo, 0.05 x 0.05 mm <sup>2</sup> microfocus, GeniX Mo, 0.05 x 0.05 mm <sup>2</sup>	3566 independent reflections 2917 reflections with $I \geq 2\sigma(I)$
Parabolic x-ray mirror monochromator	$R_{\text{int}} = 0.057$
Detector resolution: 6.67 pixels mm <sup>-1</sup>	$\theta_{\max} = 29.0^\circ$ , $\theta_{\min} = 2.7^\circ$
rotation method, $\omega$ scans	$h = -5 \rightarrow 4$
Absorption correction: integration	$k = -20 \rightarrow 20$
[X-RED32 (Stoe & Cie, 2009), by Gaussian integration, analogous to Coppens (1970)]	$l = -30 \rightarrow 28$

*Refinement*

Refinement on $F^2$	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0967P)^2 + 0.6126P]$
$wR(F^2) = 0.145$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{\max} = 0.001$
3530 reflections	$\Delta\rho_{\max} = 1.06 \text{ e } \text{\AA}^{-3}$
172 parameters	$\Delta\rho_{\min} = -1.47 \text{ e } \text{\AA}^{-3}$
0 restraints	
Primary atom site location: dual	

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.83362 (8)	0.34433 (2)	0.77092 (2)	0.01943 (14)
S1	0.6259 (2)	0.54961 (5)	0.58644 (4)	0.01665 (18)
O1	0.2706 (9)	0.27419 (16)	0.62856 (12)	0.0297 (6)
N1	0.3562 (7)	0.39130 (16)	0.56653 (12)	0.0161 (5)
H1	0.353938	0.406926	0.528399	0.019*
N2	0.4080 (8)	0.43571 (16)	0.66660 (13)	0.0173 (5)
H2	0.329777	0.382603	0.673484	0.021*
C26	0.6616 (8)	0.46142 (19)	0.76882 (15)	0.0162 (6)
C21	0.4747 (8)	0.49224 (19)	0.71708 (14)	0.0154 (6)
C23	0.3934 (9)	0.6301 (2)	0.76853 (16)	0.0189 (6)
H23	0.297239	0.687607	0.768823	0.023*
C25	0.7230 (8)	0.5146 (2)	0.81993 (15)	0.0190 (6)
H25	0.853494	0.492943	0.854762	0.023*
C22	0.3352 (8)	0.5774 (2)	0.71732 (15)	0.0175 (6)
H22	0.201802	0.598914	0.682784	0.021*
C1	0.4536 (8)	0.45618 (19)	0.60940 (14)	0.0140 (5)
C11	0.1546 (8)	0.25167 (18)	0.52290 (14)	0.0160 (6)
C14	-0.0510 (9)	0.1466 (2)	0.42403 (17)	0.0221 (7)
H14	-0.119601	0.110393	0.390232	0.026*
C24	0.5898 (9)	0.5998 (2)	0.81905 (16)	0.0201 (6)

H24	0.633754	0.637177	0.853146	0.024*
C16	-0.0313 (8)	0.2886 (2)	0.47280 (15)	0.0171 (6)
H16	-0.084947	0.349728	0.472294	0.021*
C12	0.2344 (9)	0.16178 (19)	0.52423 (16)	0.0192 (6)
H12	0.353727	0.136073	0.558862	0.023*
C10	0.2633 (9)	0.30534 (19)	0.57767 (15)	0.0185 (6)
C13	0.1350 (9)	0.1106 (2)	0.47352 (17)	0.0227 (7)
H13	0.196328	0.049976	0.473065	0.027*
C15	-0.1383 (9)	0.2354 (2)	0.42343 (15)	0.0201 (6)
H15	-0.269855	0.259882	0.389659	0.024*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.0214 (2)	0.01716 (18)	0.0198 (2)	0.00371 (10)	0.00254 (13)	0.00192 (10)
S1	0.0205 (4)	0.0149 (3)	0.0147 (4)	-0.0040 (2)	0.0020 (3)	0.0016 (2)
O1	0.0553 (19)	0.0163 (11)	0.0179 (12)	-0.0079 (11)	0.0043 (12)	0.0027 (9)
N1	0.0226 (13)	0.0130 (10)	0.0129 (12)	-0.0018 (9)	0.0018 (10)	0.0009 (9)
N2	0.0244 (13)	0.0139 (10)	0.0137 (12)	-0.0035 (9)	0.0030 (11)	0.0014 (9)
C26	0.0136 (12)	0.0163 (12)	0.0188 (15)	-0.0009 (10)	0.0021 (12)	0.0022 (11)
C21	0.0163 (13)	0.0159 (12)	0.0147 (14)	-0.0013 (10)	0.0050 (11)	0.0027 (10)
C23	0.0203 (14)	0.0141 (13)	0.0232 (16)	-0.0032 (11)	0.0072 (13)	-0.0003 (11)
C25	0.0185 (14)	0.0229 (14)	0.0151 (14)	-0.0017 (11)	-0.0005 (12)	-0.0023 (11)
C22	0.0187 (14)	0.0157 (12)	0.0183 (14)	-0.0028 (10)	0.0034 (12)	0.0007 (11)
C1	0.0141 (12)	0.0142 (12)	0.0136 (13)	0.0004 (9)	-0.0002 (11)	-0.0005 (10)
C11	0.0201 (13)	0.0134 (12)	0.0152 (14)	-0.0039 (10)	0.0047 (12)	0.0007 (10)
C14	0.0232 (16)	0.0233 (15)	0.0204 (16)	-0.0073 (12)	0.0053 (14)	-0.0074 (12)
C24	0.0225 (15)	0.0187 (13)	0.0197 (15)	-0.0029 (11)	0.0057 (13)	-0.0048 (11)
C16	0.0157 (13)	0.0170 (12)	0.0188 (15)	-0.0023 (10)	0.0024 (12)	-0.0007 (11)
C12	0.0220 (15)	0.0155 (13)	0.0197 (16)	0.0003 (10)	0.0001 (13)	0.0010 (11)
C10	0.0251 (15)	0.0133 (13)	0.0173 (15)	-0.0019 (10)	0.0023 (13)	0.0019 (10)
C13	0.0262 (16)	0.0158 (13)	0.0268 (17)	-0.0019 (12)	0.0058 (14)	-0.0029 (12)
C15	0.0207 (15)	0.0229 (14)	0.0164 (15)	-0.0030 (11)	0.0003 (12)	-0.0006 (11)

*Geometric parameters (Å, °)*

Br1—C26	1.898 (3)	C25—C24	1.394 (5)
S1—C1	1.671 (3)	C22—H22	0.9500
O1—C10	1.225 (4)	C11—C16	1.396 (5)
N1—H1	0.8800	C11—C12	1.397 (4)
N1—C1	1.399 (4)	C11—C10	1.495 (4)
N1—C10	1.381 (4)	C14—H14	0.9500
N2—H2	0.8800	C14—C13	1.380 (6)
N2—C21	1.418 (4)	C14—C15	1.389 (5)
N2—C1	1.338 (4)	C24—H24	0.9500
C26—C21	1.392 (5)	C16—H16	0.9500
C26—C25	1.396 (4)	C16—C15	1.396 (5)
C21—C22	1.402 (4)	C12—H12	0.9500

C23—H23	0.9500	C12—C13	1.396 (5)
C23—C22	1.394 (5)	C13—H13	0.9500
C23—C24	1.386 (5)	C15—H15	0.9500
C25—H25	0.9500		
C1—N1—H1	116.5	C16—C11—C12	120.6 (3)
C10—N1—H1	116.5	C16—C11—C10	121.7 (3)
C10—N1—C1	126.9 (3)	C12—C11—C10	117.7 (3)
C21—N2—H2	117.2	C13—C14—H14	119.9
C1—N2—H2	117.2	C13—C14—C15	120.3 (3)
C1—N2—C21	125.6 (3)	C15—C14—H14	119.9
C21—C26—Br1	119.8 (2)	C23—C24—C25	120.2 (3)
C21—C26—C25	121.4 (3)	C23—C24—H24	119.9
C25—C26—Br1	118.9 (2)	C25—C24—H24	119.9
C26—C21—N2	120.0 (3)	C11—C16—H16	120.1
C26—C21—C22	119.0 (3)	C11—C16—C15	119.9 (3)
C22—C21—N2	120.8 (3)	C15—C16—H16	120.1
C22—C23—H23	119.6	C11—C12—H12	120.8
C24—C23—H23	119.6	C13—C12—C11	118.5 (3)
C24—C23—C22	120.8 (3)	C13—C12—H12	120.8
C26—C25—H25	120.5	O1—C10—N1	123.0 (3)
C24—C25—C26	119.0 (3)	O1—C10—C11	121.7 (3)
C24—C25—H25	120.5	N1—C10—C11	115.3 (3)
C21—C22—H22	120.2	C14—C13—C12	121.1 (3)
C23—C22—C21	119.6 (3)	C14—C13—H13	119.4
C23—C22—H22	120.2	C12—C13—H13	119.4
N1—C1—S1	118.8 (2)	C14—C15—C16	119.6 (3)
N2—C1—S1	125.5 (2)	C14—C15—H15	120.2
N2—C1—N1	115.7 (3)	C16—C15—H15	120.2

*Hydrogen-bond geometry* (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...S1 <sup>i</sup>	0.88	2.65	3.526 (3)	177
N2—H2...O1	0.88	1.93	2.629 (4)	136

Symmetry code: (i)  $-x+1, -y+1, -z+1$ .**1-Benzoyl-3-(3-bromophenyl)thiourea (5)***Crystal data*

C<sub>14</sub>H<sub>11</sub>BrN<sub>2</sub>OS  
*M<sub>r</sub>* = 335.22  
 Monoclinic, *Pc*  
*a* = 4.6404 (7) Å  
*b* = 15.017 (2) Å  
*c* = 19.074 (3) Å  
 $\beta$  = 91.052 (12)°  
*V* = 1329.0 (3) Å<sup>3</sup>  
*Z* = 4

*F*(000) = 672  
*D<sub>x</sub>* = 1.675 Mg m<sup>-3</sup>  
 Mo *K* $\alpha$  radiation,  $\lambda$  = 0.71073 Å  
 Cell parameters from 6776 reflections  
 $\theta$  = 2.5–29.4°  
 $\mu$  = 3.24 mm<sup>-1</sup>  
*T* = 125 K  
 Needle, colourless  
 0.68 × 0.05 × 0.04 mm



Data collection

Stoe IPDS 2T diffractometer	$T_{\min} = 0.354$ , $T_{\max} = 0.875$
Radiation source: GeniX Mo, 0.05 x 0.05 mm <sup>2</sup> microfocus, GeniX Mo, 0.05 x 0.05 mm <sup>2</sup>	15213 measured reflections 4537 independent reflections
Parabolic x-ray mirror monochromator	4294 reflections with $I > 2\sigma(I)$
Detector resolution: 6.67 pixels mm <sup>-1</sup>	$R_{\text{int}} = 0.087$
rotation method, $\omega$ scans	$\theta_{\max} = 26.0^\circ$ , $\theta_{\min} = 2.5^\circ$
Absorption correction: integration [X-RED32 (Stoe & Cie, 2009), by Gaussian integration, analogous to Coppens (1970)]	$h = -5 \rightarrow 5$ $k = -18 \rightarrow 18$ $l = -23 \rightarrow 23$

Refinement

Refinement on $F^2$	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.066$	$w = 1/[\sigma^2(F_o^2) + (0.1436P)^2]$
$wR(F^2) = 0.183$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\max} < 0.001$
4909 reflections	$\Delta\rho_{\max} = 1.97 \text{ e } \text{\AA}^{-3}$
343 parameters	$\Delta\rho_{\min} = -0.65 \text{ e } \text{\AA}^{-3}$
2 restraints	Absolute structure: Flack (1983), 2288 Friedel pairs
Primary atom site location: dual	Absolute structure parameter: 0.01 (2)

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 ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1A	0.1216 (2)	0.36015 (7)	0.60049 (6)	0.0339 (3)
Br1	0.8472 (2)	0.39778 (7)	0.38804 (7)	0.0363 (3)
S1	0.2193 (7)	-0.05182 (18)	0.42320 (16)	0.0331 (6)
S1A	0.8356 (7)	0.7992 (2)	0.58713 (17)	0.0372 (7)
O1A	1.1114 (18)	0.5705 (5)	0.4491 (4)	0.0292 (17)
O1	-0.1229 (18)	0.1826 (5)	0.5461 (4)	0.0288 (17)
N2	0.201 (2)	0.1267 (7)	0.4461 (5)	0.0238 (19)
H2	0.116675	0.168717	0.470412	0.029*
N2A	0.814 (2)	0.6247 (7)	0.5548 (5)	0.027 (2)
H2A	0.886318	0.584080	0.526870	0.032*
N1A	1.130 (2)	0.7115 (6)	0.4936 (5)	0.0257 (18)
H1A	1.221915	0.762601	0.490681	0.031*
N1	-0.099 (2)	0.0382 (6)	0.5108 (5)	0.0253 (18)
H1	-0.172561	-0.015048	0.517202	0.030*
C12	-0.484 (3)	0.1445 (8)	0.6559 (7)	0.030 (3)
H12	-0.404248	0.202517	0.652126	0.036*
C10	-0.204 (2)	0.1046 (7)	0.5528 (6)	0.022 (2)
C1	0.111 (2)	0.0441 (7)	0.4592 (6)	0.026 (2)

C22A	0.527 (3)	0.6346 (8)	0.6633 (6)	0.027 (2)
H22A	0.609316	0.690436	0.675859	0.032*
C24	0.806 (3)	0.2363 (8)	0.3099 (6)	0.029 (2)
H24	0.940707	0.263197	0.279534	0.035*
C11A	1.418 (2)	0.6723 (7)	0.3926 (5)	0.022 (2)
C23A	0.331 (3)	0.5941 (9)	0.7058 (6)	0.033 (3)
H23A	0.278747	0.622390	0.748276	0.039*
C26	0.510 (2)	0.2446 (7)	0.4119 (6)	0.025 (2)
H26	0.441157	0.277844	0.450456	0.030*
C21	0.410 (3)	0.1569 (8)	0.3993 (6)	0.028 (2)
C25	0.707 (3)	0.2807 (8)	0.3680 (6)	0.029 (2)
C26A	0.485 (2)	0.5093 (8)	0.5829 (6)	0.026 (2)
H26A	0.539187	0.479402	0.541306	0.031*
C13A	1.635 (3)	0.6325 (7)	0.2841 (6)	0.028 (2)
H13A	1.656135	0.591839	0.246407	0.033*
C11	-0.413 (2)	0.0790 (7)	0.6073 (6)	0.023 (2)
C23	0.702 (3)	0.1510 (8)	0.2973 (6)	0.031 (2)
H23	0.768490	0.119194	0.257672	0.037*
C13	-0.667 (3)	0.1251 (9)	0.7088 (6)	0.031 (2)
H13	-0.711529	0.169799	0.742179	0.037*
C21A	0.606 (3)	0.5914 (7)	0.6007 (6)	0.025 (2)
C10A	1.206 (3)	0.6462 (7)	0.4466 (6)	0.024 (2)
C16	-0.535 (3)	-0.0054 (8)	0.6132 (6)	0.027 (2)
H16	-0.488645	-0.050385	0.580284	0.033*
C1A	0.922 (2)	0.7045 (7)	0.5458 (6)	0.025 (2)
C24A	0.205 (2)	0.5125 (8)	0.6881 (6)	0.028 (2)
H24A	0.067460	0.485458	0.717769	0.034*
C14A	1.792 (3)	0.7102 (9)	0.2849 (7)	0.034 (3)
H14A	1.921841	0.722651	0.248208	0.041*
C22	0.504 (3)	0.1106 (8)	0.3413 (7)	0.030 (3)
H22	0.434508	0.052300	0.331595	0.036*
C25A	0.285 (2)	0.4723 (7)	0.6266 (6)	0.027 (2)
C12A	1.447 (3)	0.6125 (8)	0.3374 (7)	0.027 (2)
H12A	1.339264	0.558708	0.336270	0.033*
C14	-0.790 (2)	0.0423 (8)	0.7147 (6)	0.027 (2)
H14	-0.919974	0.030087	0.751344	0.032*
C15	-0.722 (3)	-0.0239 (8)	0.6663 (6)	0.031 (2)
H15	-0.804361	-0.081564	0.670121	0.037*
C15A	1.760 (3)	0.7709 (8)	0.3398 (6)	0.031 (2)
H15A	1.865168	0.825140	0.340197	0.037*
C16A	1.574 (3)	0.7518 (8)	0.3932 (6)	0.029 (2)
H16A	1.552695	0.792864	0.430674	0.035*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1A	0.0415 (6)	0.0233 (6)	0.0370 (6)	-0.0043 (5)	0.0063 (4)	0.0017 (5)
Br1	0.0474 (7)	0.0215 (6)	0.0404 (6)	-0.0066 (5)	0.0091 (5)	0.0002 (5)

S1	0.0476 (17)	0.0193 (12)	0.0329 (14)	-0.0021 (11)	0.0147 (12)	-0.0033 (10)
S1A	0.0550 (19)	0.0226 (13)	0.0347 (14)	-0.0013 (13)	0.0202 (13)	-0.0072 (11)
O1A	0.037 (4)	0.022 (4)	0.029 (4)	-0.007 (3)	0.005 (3)	-0.001 (3)
O1	0.037 (4)	0.020 (4)	0.029 (4)	-0.001 (3)	0.006 (3)	0.001 (3)
N2	0.030 (5)	0.021 (4)	0.021 (4)	-0.001 (4)	0.005 (4)	-0.005 (4)
N2A	0.029 (5)	0.024 (4)	0.028 (5)	-0.001 (4)	0.006 (4)	-0.004 (4)
N1A	0.029 (5)	0.020 (4)	0.029 (4)	-0.005 (4)	0.008 (4)	-0.002 (4)
N1	0.027 (4)	0.019 (4)	0.030 (5)	-0.003 (4)	0.006 (4)	0.002 (4)
C12	0.033 (6)	0.026 (6)	0.030 (6)	0.007 (5)	0.005 (5)	-0.004 (5)
C10	0.020 (5)	0.022 (6)	0.024 (5)	-0.003 (4)	0.000 (4)	0.000 (4)
C1	0.030 (5)	0.025 (5)	0.023 (5)	0.001 (4)	0.003 (4)	0.001 (4)
C22A	0.033 (6)	0.029 (6)	0.020 (5)	-0.004 (4)	0.007 (4)	-0.003 (4)
C24	0.034 (6)	0.028 (6)	0.027 (5)	-0.006 (5)	0.006 (4)	0.006 (4)
C11A	0.024 (5)	0.020 (5)	0.023 (5)	0.003 (4)	0.002 (4)	-0.001 (4)
C23A	0.036 (6)	0.036 (7)	0.026 (6)	0.006 (5)	-0.003 (5)	-0.004 (4)
C26	0.029 (5)	0.018 (5)	0.028 (5)	0.009 (4)	0.002 (4)	0.001 (4)
C21	0.031 (6)	0.026 (5)	0.026 (5)	0.003 (4)	-0.001 (4)	0.002 (4)
C25	0.036 (6)	0.024 (5)	0.028 (5)	0.008 (5)	-0.001 (5)	-0.004 (4)
C26A	0.030 (6)	0.028 (5)	0.020 (5)	0.007 (4)	0.004 (4)	-0.003 (4)
C13A	0.031 (6)	0.024 (5)	0.029 (6)	0.001 (4)	0.007 (5)	-0.005 (4)
C11	0.019 (5)	0.022 (4)	0.029 (5)	0.002 (4)	-0.003 (4)	-0.001 (4)
C23	0.040 (7)	0.028 (6)	0.025 (5)	-0.003 (5)	0.005 (5)	0.000 (4)
C13	0.030 (6)	0.033 (6)	0.030 (6)	0.001 (5)	0.004 (5)	-0.009 (5)
C21A	0.027 (5)	0.023 (5)	0.023 (5)	0.005 (5)	0.001 (4)	0.000 (4)
C10A	0.028 (5)	0.023 (6)	0.020 (5)	0.001 (4)	0.004 (4)	-0.004 (4)
C16	0.033 (6)	0.024 (5)	0.026 (5)	0.000 (4)	0.004 (4)	-0.001 (4)
C1A	0.026 (5)	0.023 (5)	0.027 (5)	-0.002 (4)	-0.002 (4)	-0.002 (4)
C24A	0.027 (5)	0.027 (5)	0.030 (6)	0.000 (4)	0.004 (4)	0.010 (4)
C14A	0.028 (6)	0.041 (7)	0.033 (6)	0.000 (5)	0.001 (4)	-0.002 (5)
C22	0.036 (7)	0.022 (6)	0.033 (6)	0.000 (4)	-0.001 (5)	-0.003 (4)
C25A	0.033 (6)	0.017 (5)	0.030 (6)	0.003 (4)	-0.003 (5)	0.000 (4)
C12A	0.028 (6)	0.023 (6)	0.031 (6)	-0.008 (4)	0.008 (4)	-0.003 (5)
C14	0.023 (5)	0.033 (6)	0.024 (5)	0.000 (4)	0.003 (4)	0.002 (4)
C15	0.036 (6)	0.026 (5)	0.030 (6)	-0.004 (4)	0.003 (5)	0.003 (4)
C15A	0.034 (6)	0.026 (5)	0.034 (6)	-0.008 (4)	0.003 (5)	0.002 (5)
C16A	0.031 (6)	0.022 (5)	0.036 (6)	0.005 (4)	0.001 (5)	-0.006 (4)

*Geometric parameters (Å, °)*

Br1A—C25A	1.909 (11)	C23A—H23A	0.9500
Br1—C25	1.911 (12)	C23A—C24A	1.396 (18)
S1—C1	1.678 (12)	C26—H26	0.9500
S1A—C1A	1.678 (11)	C26—C21	1.416 (16)
O1A—C10A	1.219 (14)	C26—C25	1.362 (18)
O1—C10	1.238 (14)	C21—C22	1.383 (19)
N2—H2	0.8800	C26A—H26A	0.9500
N2—C1	1.334 (15)	C26A—C21A	1.395 (16)
N2—C21	1.406 (17)	C26A—C25A	1.375 (17)

N2A—H2A	0.8800	C13A—H13A	0.9500
N2A—C21A	1.408 (17)	C13A—C14A	1.376 (17)
N2A—C1A	1.311 (15)	C13A—C12A	1.384 (18)
N1A—H1A	0.8800	C11—C16	1.393 (16)
N1A—C10A	1.379 (14)	C23—H23	0.9500
N1A—C1A	1.405 (15)	C23—C22	1.40 (2)
N1—H1	0.8800	C13—H13	0.9500
N1—C10	1.374 (15)	C13—C14	1.373 (18)
N1—C1	1.398 (15)	C16—H16	0.9500
C12—H12	0.9500	C16—C15	1.374 (17)
C12—C11	1.396 (16)	C24A—H24A	0.9500
C12—C13	1.36 (2)	C24A—C25A	1.378 (17)
C10—C11	1.483 (17)	C14A—H14A	0.9500
C22A—H22A	0.9500	C14A—C15A	1.399 (18)
C22A—C23A	1.37 (2)	C22—H22	0.9500
C22A—C21A	1.412 (17)	C12A—H12A	0.9500
C24—H24	0.9500	C14—H14	0.9500
C24—C25	1.380 (17)	C14—C15	1.396 (17)
C24—C23	1.388 (17)	C15—H15	0.9500
C11A—C10A	1.490 (16)	C15A—H15A	0.9500
C11A—C12A	1.392 (17)	C15A—C16A	1.375 (18)
C11A—C16A	1.398 (16)	C16A—H16A	0.9500
C1—N2—H2	115.0	C12—C11—C10	116.6 (11)
C1—N2—C21	130.0 (11)	C16—C11—C12	119.0 (12)
C21—N2—H2	115.0	C16—C11—C10	124.4 (10)
C21A—N2A—H2A	113.8	C24—C23—H23	119.1
C1A—N2A—H2A	113.8	C24—C23—C22	121.8 (12)
C1A—N2A—C21A	132.3 (10)	C22—C23—H23	119.1
C10A—N1A—H1A	116.7	C12—C13—H13	119.4
C10A—N1A—C1A	126.5 (9)	C12—C13—C14	121.2 (11)
C1A—N1A—H1A	116.7	C14—C13—H13	119.4
C10—N1—H1	115.7	N2A—C21A—C22A	123.6 (10)
C10—N1—C1	128.6 (9)	C26A—C21A—N2A	116.2 (10)
C1—N1—H1	115.7	C26A—C21A—C22A	120.2 (12)
C11—C12—H12	120.0	O1A—C10A—N1A	122.8 (11)
C13—C12—H12	120.0	O1A—C10A—C11A	121.0 (10)
C13—C12—C11	120.0 (12)	N1A—C10A—C11A	116.2 (9)
O1—C10—N1	120.9 (11)	C11—C16—H16	119.7
O1—C10—C11	121.4 (10)	C15—C16—C11	120.5 (11)
N1—C10—C11	117.7 (9)	C15—C16—H16	119.7
N2—C1—S1	128.6 (10)	N2A—C1A—S1A	128.2 (10)
N2—C1—N1	114.6 (10)	N2A—C1A—N1A	115.4 (10)
N1—C1—S1	116.8 (8)	N1A—C1A—S1A	116.3 (8)
C23A—C22A—H22A	120.7	C23A—C24A—H24A	120.9
C23A—C22A—C21A	118.7 (11)	C25A—C24A—C23A	118.1 (11)
C21A—C22A—H22A	120.7	C25A—C24A—H24A	120.9
C25—C24—H24	121.1	C13A—C14A—H14A	120.1



C25—C24—C23	117.8 (11)	C13A—C14A—C15A	119.8 (12)
C23—C24—H24	121.1	C15A—C14A—H14A	120.1
C12A—C11A—C10A	115.3 (10)	C21—C22—C23	118.9 (11)
C12A—C11A—C16A	120.0 (11)	C21—C22—H22	120.6
C16A—C11A—C10A	124.6 (10)	C23—C22—H22	120.6
C22A—C23A—H23A	119.1	C26A—C25A—Br1A	117.9 (8)
C22A—C23A—C24A	121.8 (12)	C26A—C25A—C24A	122.3 (11)
C24A—C23A—H23A	119.1	C24A—C25A—Br1A	119.8 (9)
C21—C26—H26	120.4	C11A—C12A—H12A	120.5
C25—C26—H26	120.4	C13A—C12A—C11A	119.1 (11)
C25—C26—C21	119.2 (11)	C13A—C12A—H12A	120.5
N2—C21—C26	114.9 (10)	C13—C14—H14	120.3
C22—C21—N2	125.2 (11)	C13—C14—C15	119.5 (11)
C22—C21—C26	119.8 (12)	C15—C14—H14	120.3
C24—C25—Br1	119.2 (9)	C16—C15—C14	119.7 (11)
C26—C25—Br1	118.2 (9)	C16—C15—H15	120.1
C26—C25—C24	122.5 (11)	C14—C15—H15	120.1
C21A—C26A—H26A	120.6	C14A—C15A—H15A	120.1
C25A—C26A—H26A	120.6	C16A—C15A—C14A	119.8 (11)
C25A—C26A—C21A	118.9 (10)	C16A—C15A—H15A	120.1
C14A—C13A—H13A	119.4	C11A—C16A—H16A	119.9
C14A—C13A—C12A	121.1 (11)	C15A—C16A—C11A	120.2 (10)
C12A—C13A—H13A	119.4	C15A—C16A—H16A	119.9

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2 $\cdots$ O1	0.88	1.85	2.590 (13)	141
N2A—H2A $\cdots$ O1A	0.88	1.84	2.595 (14)	142
N1A—H1A $\cdots$ S1 <sup>i</sup>	0.88	3.07	3.825 (9)	145
N1—H1 $\cdots$ S1A <sup>ii</sup>	0.88	3.09	3.888 (10)	151

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