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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

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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.*, 2018*a*; 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.*, 2018*b*) 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

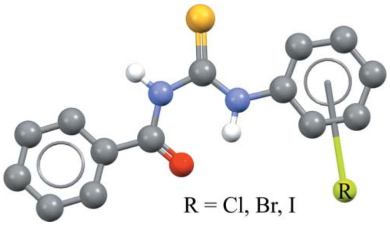


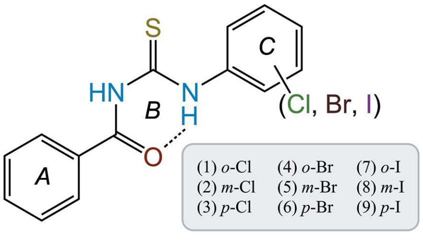
**Table 1**
Substituents and references for the compounds under consideration.

| Compound | Substituent and position in ring *C* | Reference [CSD refcode] |
|---|---|---|
| (1) | 2-Cl | Yusof & Yamin (2004) [IZAMIF] |
| (2) | 3-Cl | Khawar Rauf *et al.* (2006) [MEGNIW] |
| (3) | 4-Cl | Rauf *et al.* (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).



Scheme 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 *Omnic* computer software in the range 4000–400 cm$^{-1}$. The NMR spectra were measured with a Bruker Avance III HD 400 MHz spectrometer (USA) with a TXI $^{1}$H/$^{13}$C/$^{31}$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 $C_6$ 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%; $T_{\rm mp}$ = 134 (1) °C; $^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.63 (*s*,

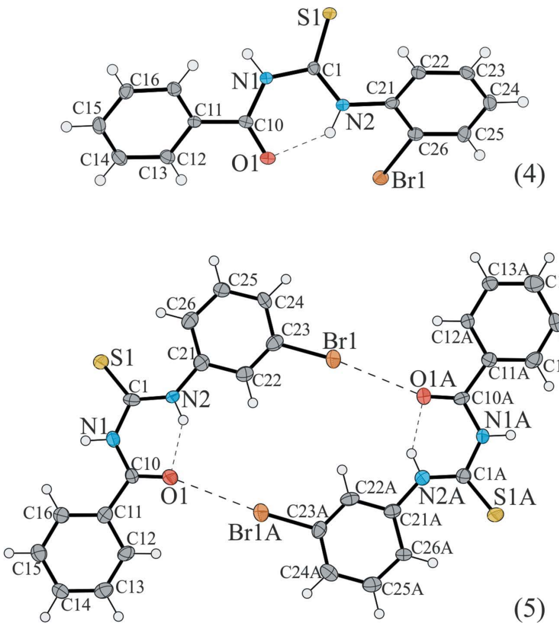


**Figure 1**
The molecular structures of the novel 1-benzoyl-3-(bromophenyl)thioureas. Displacement ellipsoids are drawn at the 50% probability level.

**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) |
|---|---|---|---|---|---|
| Crystal data | | | | | |
| Chemical formula | $C_{14}H_{11}BrN_2OS$ | $C_{14}H_{11}BrN_2OS$ | $C_{14}H_{11}IN_2OS$ | $C_{14}H_{11}IN_2OS$ | $C_{14}H_{11}IN_2OS$ |
| $M_r$ | 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$^3$) | 1328.4 (3) | 1329.0 (3) | 686.02 (14) | 1357.7 (3) | 682.06 (13) |
| $Z$ | 4 | 4 | 2 | 4 | 2 |
| $\mu$ (mm$^{-1}$) | 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 |
| Data collection | | | | | |
| $T_{min}$, $T_{max}$ | 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 |
| $R_{int}$ | 0.057 | 0.087 | 0.026 | 0.070 | 0.020 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.682 | 0.617 | 0.682 | 0.650 | 0.682 |
| Refinement | | | | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 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 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 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, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

1H), 9.25 (*s*, 1H), 8.41–6.97 (*m*, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 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%; $T_{mp}$ = 130 (1) °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 12.67 (*s*, 1H), 9.21 (*s*, 1H), 8.17–7.09 (*m*, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 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%; $T_{mp}$ = 144 (1) °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 12.38 (*s*, 1H), 9.24 (*s*, 1H), 8.23–6.82 (*m*, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 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%; $T_{mp}$ = 172 (1) °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 12.64 (*s*, 1H), 9.11 (*s*, 1H), 8.32–6.99 (*m*, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 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%; $T_{mp}$ = 154 (1) °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 12.64 (*s*, 1H), 9.12 (*s*, 1H), 8.08–7.07 (*m*, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 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 $U_{iso}$(H) values set at 1.2–1.5$U_{eq}$(C) or 1.2$U_{eq}$(N).

## 3. Results and discussion

To investigate the molecular geometry of 3-aryl-substituted derivatives of 1-aroylthioureas, 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 O*R*; *R* = H or Me) in the *ortho*

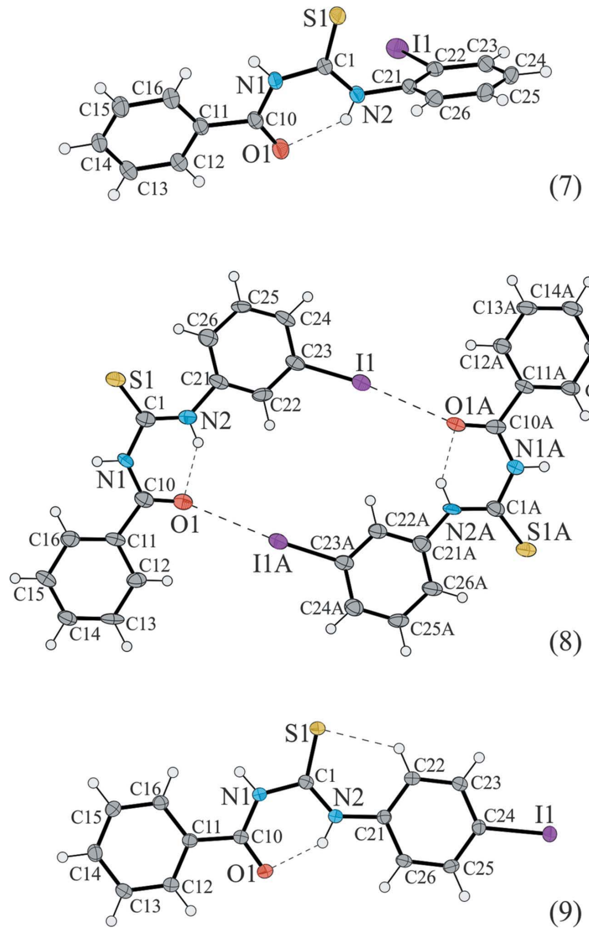


**Figure 2**
The molecular structures of the novel 1-benzoyl-3-(iodophenyl)thioureas. Displacement ellipsoids are drawn at the 50% probability level.

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

| Type $C{=}E\cdots X$ | Angle $C{=}E\cdots X$ (°) | Distance $E\cdots X$ (Å) | Structure |
|---|---|---|---|
| $C10{=}O1\cdots Br1A$ | 153.9 (7) | 3.071 (8) | (5) |
| $C10A{=}O1A\cdots Br1$ | 155.3 (8) | 3.088 (8) | (5) |
| $C10{=}O1\cdots I1A$ | 154.0 (8) | 3.121 (8) | (8) |
| $C10A{=}O1A\cdots I1A$ | 155.3 (8) | 3.137 (9) | (8) |
| $C1{=}S1\cdots I1$ | 109.97 (9) | 3.7333 (8) | (7) |
| Type $X\cdots X$ | | | |
| $C1-Br1\cdots Br1^{i}$ | 156.22 (7) | 3.8829 (8) | (6) |
| $C1-Br1\cdots Br1^{ii}$ | 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 Π = 0.041 (Fábián & Kálmán, 1999), while the parameter of isostructurality $I' = 0.70$ (Kubicki & Szafrański, 1998).

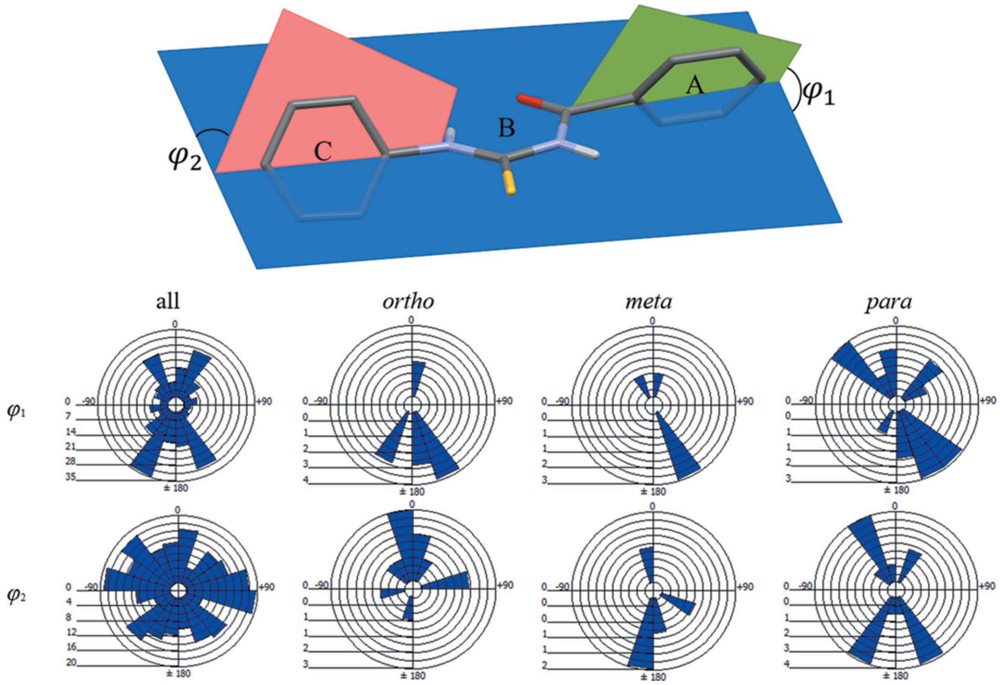


**Figure 3**
(Top) Definition of the auxiliary dihedral angles $\varphi_1$ and $\varphi_2$, together with the notation of aromatic rings *A* and *C*, and pseudo-ring *B* [*S*(6) motif]. (Bottom) Circular histograms with values of the $\varphi_1$ and $\varphi_2$ angles for the benzoylthiourea derivatives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

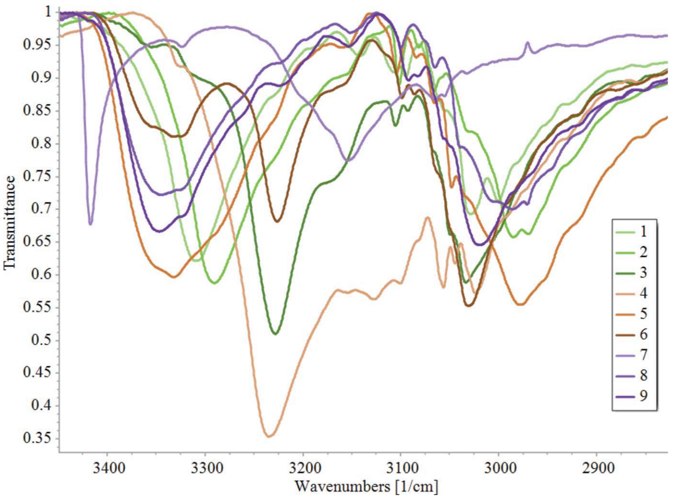


**Figure 4**
Superposition of the FT–IR spectra of (1)–(9) in the range 3500–2800 cm$^{-1}$, corresponding to the vibration of the N—H amide bond. Note the sharp absorption band for (7) at 3417 cm$^{-1}$.

### 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. 5*a*).

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 [$\overline{1}$10] direction, so

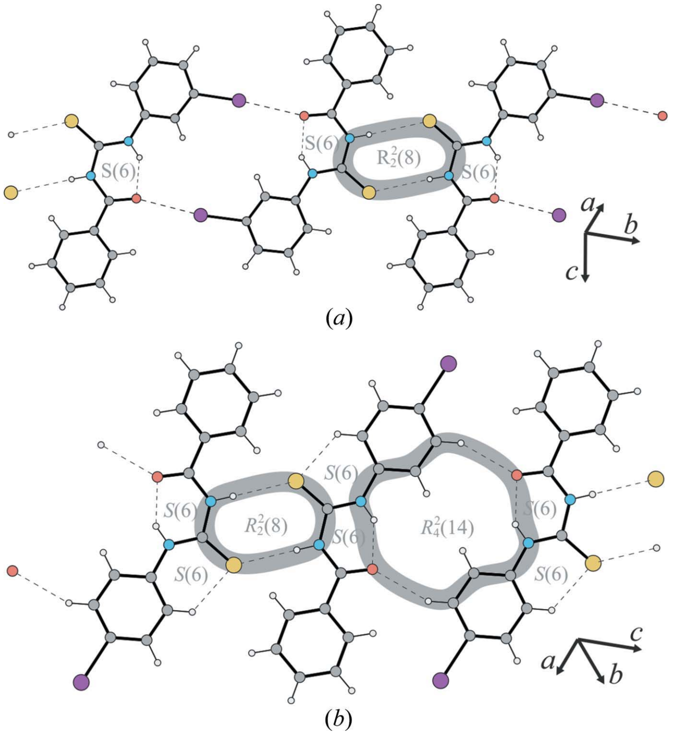


**Figure 5**
The main interactions in (*a*) (8) and (*b*) (9), forming ring motifs. The resulting hydrogen/halogen-bonded pairs are then linked by analogous interactions to form chains.

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**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.*, 2018*b*), 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. 5*b*); 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 $\not{p}112_1$).

### 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.

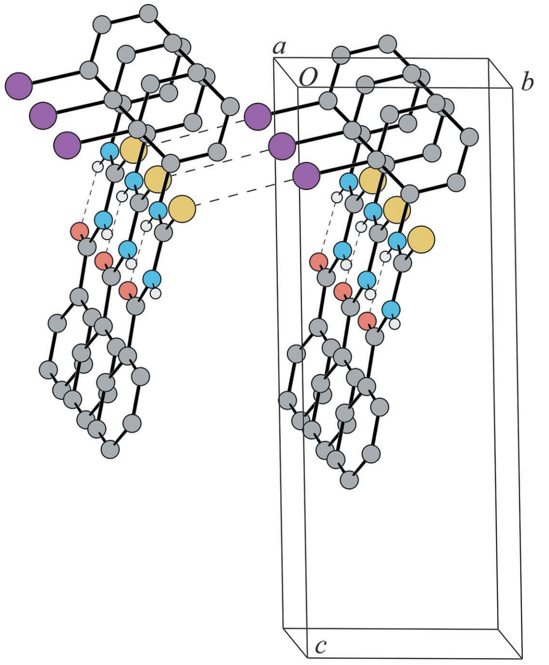

**Figure 6**
Depiction of the I$\cdots$S contacts found in (7) that form chains propagating along the $[\bar{1}10]$ direction.

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

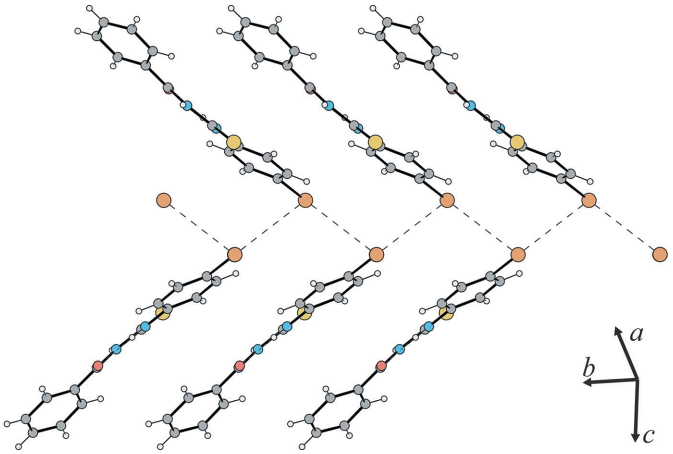

**Figure 7**
The herringbone pattern found in the structure of (6) in a projection perpendicular to the screw axis.

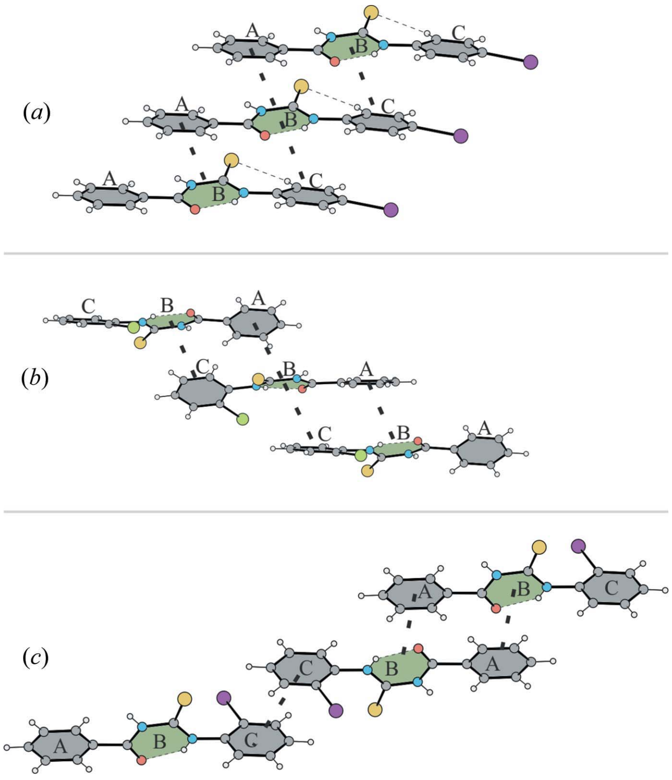

**Figure 8**
Stacking motifs that can be found in (*a*) (2)–(5), (8) and (9), (*b*) (1) and (*c*) (7).

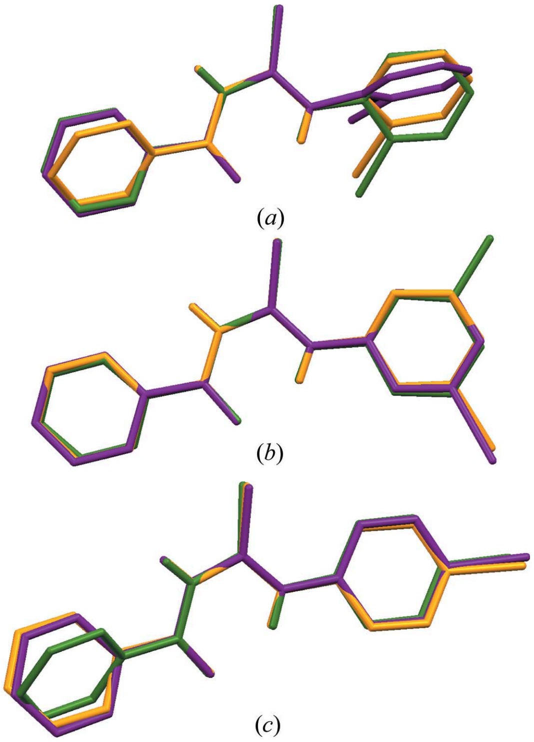

**Figure 9**
Overlays of molecules of 1-benzoyl-3-(halogenophenyl)thioureas from the discussed structures (this study or CSD structures; see Table 1) for (*a*) *ortho*, (*b*) *meta* and (*c*) *para* isomers. Colour codes: Cl is green, Br orange and I purple. Fitting was based on the central *S*(6) pseudo-ring (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. 8*b*).

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. 8*a*). 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 $A\cdots B$ stacking interactions and separate stacking interactions between adjacent iodobenzene rings. These interactions cause the formation of chains (Fig. 8*c*).

### 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°), then the energy minimum is reached. On the other hand, when rings *B* and *C* rings are perpendicular ($\varphi_2$ = 90 and 270°), 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°, for (4) at 30/330° and for (7) at 45/315°. 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°. 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° range, while the larger angles are in the 125–129° range. On the other hand, in simple diphenylthiourea, the angles are approximately equal to 120–123° (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 O*R*; *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°.

For the compounds presented in ths 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···I interactions instead of the C═S···H—N interactions observed in all other cases. Interactions between two halogen atoms are only found in the case of (6). The Br···Br contacts form supramolecular herringbone motifs. Additionally, some I···$\pi$ interactions can be found in (9) thus hindering the usual stacking interactions.

Due to the presence of intramolecular N—H···O hydrogen bonds forming *S*(6) quasi-aromatic pseudo-rings, 1-acylthioureas 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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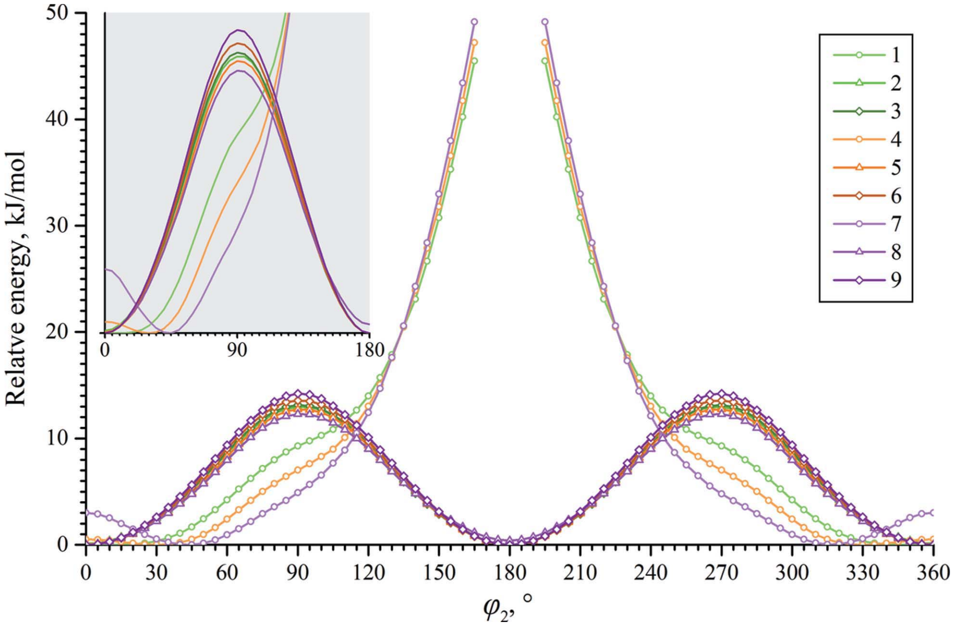

**Figure 10**
The potential energy plots obtained by optimization of the structures of (1)–(9), with the C1—N2—C21—C26 torsion angles ($\varphi_2$) set to values in the 0–360° range. The $\varphi_2$ angles were modified with +5 and −5° steps and the resulting energies were averaged. Calculations were 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° were excluded, as the energy rises drastically and the calculations were unstable because of close Cl/Br/I···S contacts. The inset shows the 0–180° fragment without data points for clarity.

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# supporting information

*Acta Cryst.* (2021). C**77**, 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, 2015*a*); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015*b*); 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*

$C_{14}H_{11}IN_2OS$
$M_r = 382.21$
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$^3$

$Z = 2$
$F(000) = 372$
$D_x = 1.850$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 15454 reflections
$\theta = 5.0$–$58.9$°
$\mu = 2.48$ mm$^{-1}$
$T = 125$ K
Needle, colourless
0.38 × 0.36 × 0.20 mm

### *Data collection*

Stoe IPDS 2T
diffractometer
Detector resolution: 6.67 pixels mm$^{-1}$
rotation method, $\omega$ scans
Absorption correction: integration
[X-RED32 (Stoe & Cie, 2009), by Gaussian integration, analogous to Coppens (1970)]
$T_{min} = 0.405$, $T_{max} = 0.644$

7847 measured reflections
3616 independent reflections
3508 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 29.0$°, $\theta_{min} = 2.5$°
$h = -8 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -22 \rightarrow 22$

### *Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.072$
$S = 1.07$
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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.70$ e Å$^{-3}$
$\Delta\rho_{min} = -0.94$ e Å$^{-3}$

*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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| 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 (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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, º)*

| | | | |
|---|---|---|---|
| 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, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2···O1 | 0.88 | 1.97 | 2.659 (2) | 135 |

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

### *Crystal data*

$C_{14}H_{11}IN_2OS$
$M_r = 382.21$
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$^3$
$Z = 4$
$F(000) = 744$
$D_x = 1.870$ Mg m$^{-3}$
Mo *Kα* radiation, $\lambda = 0.71073$ Å
Cell parameters from 2158 reflections
$\theta = 2.5$–29.4°
$\mu = 2.51$ mm$^{-1}$
$T = 125$ 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 x 0.05 mm2
Parabolic x-ray mirror monochromator
Detector resolution: 6.67 pixels mm$^{-1}$
rotation method scans
Absorption correction: integration [X-RED32 (Stoe & Cie, 2009), by Gaussian integration, analogous to Coppens (1970)]
$T_{\min} = 0.393$, $T_{\max} = 0.885$
13551 measured reflections
5820 independent reflections
5398 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.070$
$\theta_{\max} = 27.5°$, $\theta_{\min} = 2.5°$
$h = -5 \rightarrow 5$
$k = -19 \rightarrow 19$
$l = -25 \rightarrow 23$

### *Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.148$
$S = 1.07$
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 $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.24$ e Å$^{-3}$
$\Delta\rho_{\min} = -1.27$ e Å$^{-3}$

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 (Å²)*

| | *x* | *y* | *z* | $U_{\rm iso}$*/$U_{\rm eq}$ |
|---|---|---|---|---|
| I1A | 0.87867 (10) | 0.35387 (4) | 0.39772 (4) | 0.0328 (2) |
| I1 | 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 (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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, º)*

| | | | |
|---|---|---|---|
| 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, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2*A*—H2*A*···O1*A* | 0.88 | 1.85 | 2.602 (13) | 142 |
| N2—H2···O1 | 0.88 | 1.86 | 2.614 (13) | 142 |
| N1—H1···S1*A*$^{\text{i}}$ | 0.88 | 3.13 | 3.922 (10) | 150 |
| N1*A*—H1*A*···S1$^{\text{ii}}$ | 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*

$C_{14}H_{11}IN_2OS$
$M_r = 382.21$
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$^3$

$Z = 2$
$F(000) = 372$
$D_x = 1.861$ Mg m$^{-3}$
Mo *Kα* radiation, $\lambda = 0.71073$ Å
Cell parameters from 17633 reflections
$\theta = 3.0–29.6$°
$\mu = 2.49$ mm$^{-1}$
$T = 120$ K
Needle, colourless
0.33 × 0.08 × 0.05 mm

*Data collection*

Stoe IPDS 2T diffractometer
Detector resolution: 6.67 pixels mm$^{-1}$
rotation method scans

Absorption correction: integration [X-RED32 (Stoe & Cie, 2009), by Gaussian integration, analogous to Coppens (1970)]
$T_{\min} = 0.734$, $T_{\max} = 0.932$
9681 measured reflections

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

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

*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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} = 0.002$
$\Delta\rho_{\text{max}} = 0.80$ e Å$^{-3}$
$\Delta\rho_{\text{min}} = -0.39$ e Å$^{-3}$

*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 (Å²)*

| | $x$ | $y$ | $z$ | $U_{\text{iso}}$*/$U_{\text{eq}}$ |
|---|---|---|---|---|
| I1 | 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 (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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 (Å, º)*

| | | | |
|---|---|---|---|
| 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—I1 | 119.07 (13) | C21—C26—H26 | 119.5 |
| C23—C24—C25 | 120.57 (17) | C25—C26—C21 | 121.00 (16) |
| C25—C24—I1 | 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, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2···O1 | 0.88 | 1.87 | 2.620 (2) | 142 |
| N1—H1···S1$^{i}$ | 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*

$C_{14}H_{11}BrN_2OS$
$M_r = 335.23$
Monoclinic, $P2_1/n$
$a = 3.9592$ (4) Å
$b = 15.142$ (2) Å
$c = 22.250$ (2) Å
$\beta = 95.183$ (8)°
$V = 1328.4$ (3) Å$^3$
$Z = 4$

$F(000) = 672$
$D_x = 1.676$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7760 reflections
$\theta = 2.7–29.7°$
$\mu = 3.24$ mm$^{-1}$
$T = 120$ K
Needle, colourless
0.76 × 0.05 × 0.03 mm

*Data collection*

Stoe IPDS 2T
diffractometer
Radiation source: GeniX Mo, 0.05 x 0.05 mm2
microfocus, GeniX Mo, 0.05 x 0.05 mm2
Parabolic x-ray mirror monochromator
Detector resolution: 6.67 pixels mm$^{-1}$
rotation method, $\omega$ scans
Absorption correction: integration
[X-RED32 (Stoe & Cie, 2009), by Gaussian integration, analogous to Coppens (1970)]

$T_{\min} = 0.379$, $T_{\max} = 0.892$
7908 measured reflections
3566 independent reflections
2917 reflections with $I \geq 2u(I)$
$R_{\text{int}} = 0.057$
$\theta_{\max} = 29.0°$, $\theta_{\min} = 2.7°$
$h = -5 \rightarrow 4$
$k = -20 \rightarrow 20$
$l = -30 \rightarrow 28$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.145$
$S = 1.07$
3530 reflections
172 parameters
0 restraints
Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0967P)^2 + 0.6126P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.06$ e Å$^{-3}$
$\Delta\rho_{\min} = -1.47$ e Å$^{-3}$

*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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{\text{iso}}$*/$U_{\text{eq}}$ |
|---|---|---|---|---|
| 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$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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, º)*

| | | | |
|---|---|---|---|
| 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, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···S1$^{i}$ | 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*

$C_{14}H_{11}BrN_2OS$
$M_r = 335.22$
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$^3$
$Z = 4$

$F(000) = 672$
$D_x = 1.675$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6776 reflections
$\theta = 2.5$–29.4°
$\mu = 3.24$ mm$^{-1}$
$T = 125$ K
Needle, colourless
0.68 × 0.05 × 0.04 mm

*Data collection*

Stoe IPDS 2T
diffractometer
Radiation source: GeniX Mo, 0.05 x 0.05 mm2
microfocus, GeniX Mo, 0.05 x 0.05 mm2
Parabolic x-ray mirror monochromator
Detector resolution: 6.67 pixels mm$^{-1}$
rotation method, $\omega$ scans
Absorption correction: integration
[X-RED32 (Stoe & Cie, 2009), by Gaussian integration, analogous to Coppens (1970)]

$T_{\min} = 0.354$, $T_{\max} = 0.875$
15213 measured reflections
4537 independent reflections
4294 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.087$
$\theta_{\max} = 26.0°$, $\theta_{\min} = 2.5°$
$h = -5 \rightarrow 5$
$k = -18 \rightarrow 18$
$l = -23 \rightarrow 23$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.183$
$S = 1.02$
4909 reflections
343 parameters
2 restraints
Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1436P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.97$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.65$ e Å$^{-3}$
Absolute structure: Flack (1983), 2288 Friedel pairs
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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{\text{iso}}$*/$U_{\text{eq}}$ |
|---|---|---|---|---|
| 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 (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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, º)*

| | | | |
|---|---|---|---|
| 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 (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2···O1 | 0.88 | 1.85 | 2.590 (13) | 141 |
| N2*A*—H2*A*···O1*A* | 0.88 | 1.84 | 2.595 (14) | 142 |
| N1*A*—H1*A*···S1$^{i}$ | 0.88 | 3.07 | 3.825 (9) | 145 |
| N1—H1···S1*A*$^{ii}$ | 0.88 | 3.09 | 3.888 (10) | 151 |

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