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Crystal structures of *N*-[(4-phenylthiazol-2-yl)carbamothioyl]benzamide and *N*-{[4-(4-bromophenyl)thiazol-2-yl]carbamothioyl}benzamide from synchrotron X-ray diffraction

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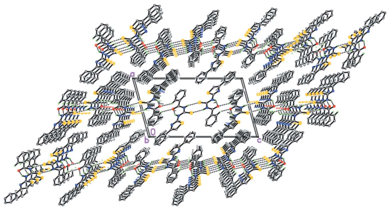
The title compounds, $C_{17}H_{13}N_3OS_2$, (I), and $C_{17}H_{12}BrN_3OS_2$, (II), are potential active pharmaceutical ingredients. Compound (I) comprises two almost planar fragments. The first is the central (carbamothioyl)amide (r.m.s. deviation = 0.038 Å), and the second consists of the thiazole and two phenyl rings (r.m.s. deviation = 0.053 Å). The dihedral angle between these planes is 15.17 (5)°. Unlike (I), compound (II) comprises three almost planar fragments. The first is the central *N*-(thiazol-2-ylcarbamothioyl)amide (r.m.s. deviation = 0.084 Å), and the two others comprise the bromophenyl and phenyl substituents, respectively. The dihedral angles between the central and two terminal planar fragments are 21.58 (7) and 17.90 (9)°, respectively. Both (I) and (II) feature an intramolecular N—H···O hydrogen bond, which closes an *S*(6) ring. In the crystal of (I), molecules form hydrogen-bonded layers parallel to (100) mediated by N—H···S and C—H···O hydrogen bonds. In the crystal of (II), molecules form a three-dimensional framework mediated by N—H···Br and C—H···O hydrogen bonds, as well as secondary S···Br [3.3507 (11) Å] and S···S [3.4343 (14) Å] interactions.



1. Chemical context

Thioureas are the subject of significant interest owing to their biological properties as fungicides, herbicides (Walpole *et al.*, 1998) and rodenticides (Sarkis & Faisal, 1985). It is also well-known that thiourea derivatives and their metal complexes exhibit analgesic (El-Serwy *et al.*, 2015), anti-inflammatory (Lin *et al.*, 2013), antimicrobial (Stefanska *et al.*, 2016) and anticancer (Rauf *et al.*, 2015) activities. Moreover, thiourea derivatives are valuable building blocks for the synthesis of amides, guanidines and a variety of heterocycles (*e.g.* Kidwai *et al.*, 2001; Du & Curran, 2003). Recently, thiourea derivatives were found to have use in organocatalysis (*e.g.* Connon, 2006; McCooey & Connon, 2005; Schreiner, 2003; Taylor & Jacobsen, 2006). For these reasons, a number of procedures have been reported for the synthesis of thioureas.

In this paper we report a synthetic approach for the preparation of the new thiourea derivatives (I) and (II) containing thiazole fragments, and their structural characterization by synchrotron single-crystal X-ray diffraction.

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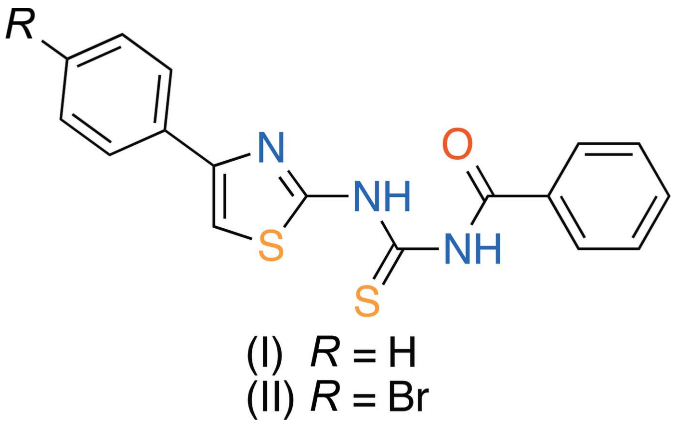

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.92	1.85	2.6145 (18)	139
N2—H2···S1^{i}	0.93	2.69	3.5845 (15)	162
C13—H13···O1^{ii}	0.95	2.44	3.299 (2)	150

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

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.88	1.93	2.644 (3)	138
N2—H2···Br1^{i}	0.88	2.97	3.692 (3)	141
C13—H13···O1^{ii}	0.95	2.53	3.340 (4)	144

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

2. Structural commentary

Compound (I), $C_{17}H_{13}N_3OS_2$, comprises two almost planar fragments. The first is the central (carbamothioyl)amide grouping (r.m.s. deviation = 0.038 Å), and the second consists of the thiazole and two phenyl rings (r.m.s. deviation = 0.053 Å) (Fig. 1). The dihedral angle between these planes is 15.17 (5)°.

Unlike (I), compound (II), $C_{17}H_{12}N_3OS_2Br$, comprises three almost planar fragments: the first is the central *N*-(thiazol-2-ylcarbamothioyl)amide (r.m.s. deviation = 0.084 Å), and the two others comprise the bromophenyl and phenyl substituents, respectively (Fig. 2). The dihedral angles between the central and two terminal fragments are 21.58 (7) and 17.90 (9)°, respectively.

The planarity of the fragments found in (I) and (II) is determined by the present of bond conjugation within each of them as well as the intramolecular N1—H1···O1 hydrogen bond (Tables 1 and 2, Figs. 1 and 2). The different molecular conformations observed for (I) and (II) may apparently be explained by the various systems of intermolecular interactions present in the crystals (see the *Supramolecular features* section below).

The bond-length and angle distribution within molecules (I) and (II) are almost identical and in good agreement with those observed in related compounds (Singh *et al.*, 2012, 2013). The values for the C—S—C angle in (I) [88.06 (8)°] and (II) [87.75 (14)°] are also very close to those in previously reported analogous structures [87.62 (7)–88.11 (8)°] (Yunus *et al.*, 2008; Saeed *et al.*, 2010).

3. Supramolecular features

Although the similarity of the molecular geometries and types of intramolecular hydrogen bonds might lead to similar packing motifs, this is not found in the case of (I) and (II). The intermolecular interactions, namely, N—H···X (X = S, Br) and C—H···O hydrogen bonding and the secondary S···S and S···Br interactions, combine in a different way, give rise to distinct packing motifs.

In (I), the crystal packing consists of hydrogen-bonded layers parallel to (100), in which the molecules are linked to each other by N2—H2···S1^{i} and C13—H13···O1^{ii} hydrogen bonds [Table 1, Fig. 3; symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$]. No secondary S···S intermolecular interactions were observed in (I).

The situation in the case of (II) is quite different. The molecules of (II) form a three-dimensional framework

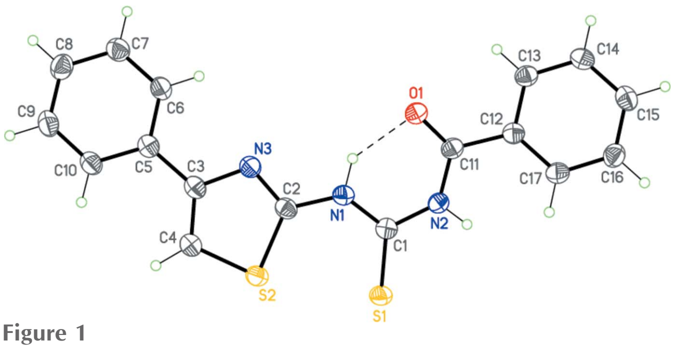

Figure 1
The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level. The dashed line indicates the intramolecular hydrogen bond. H atoms are presented as small spheres of arbitrary radius.

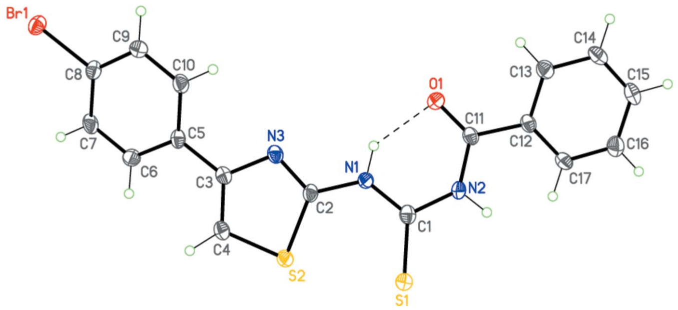

Figure 2
The molecular structure of (II). Displacement ellipsoids are shown at the 50% probability level. The dashed line indicates the intramolecular hydrogen bond. H atoms are presented as small spheres of arbitrary radius.

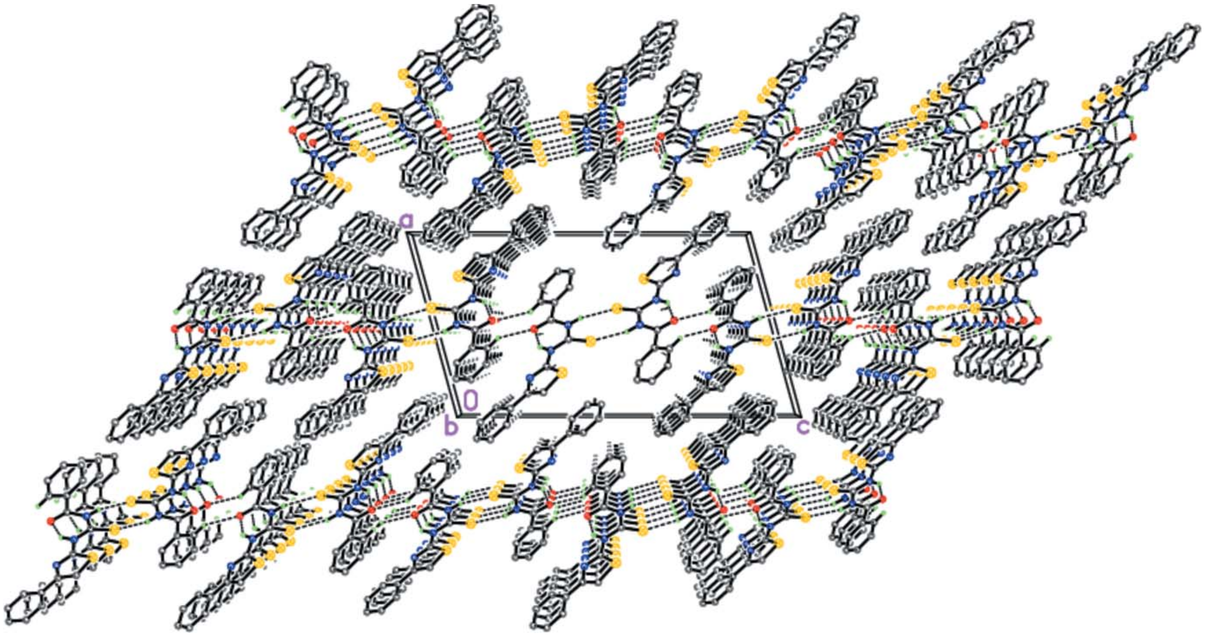

Figure 3
The crystal structure of (I) illustrating the hydrogen-bonded layers parallel to (100). Dashed lines indicate the intramolecular N—H⋯O and intermolecular N—H⋯S and C—H⋯O hydrogen bonds.

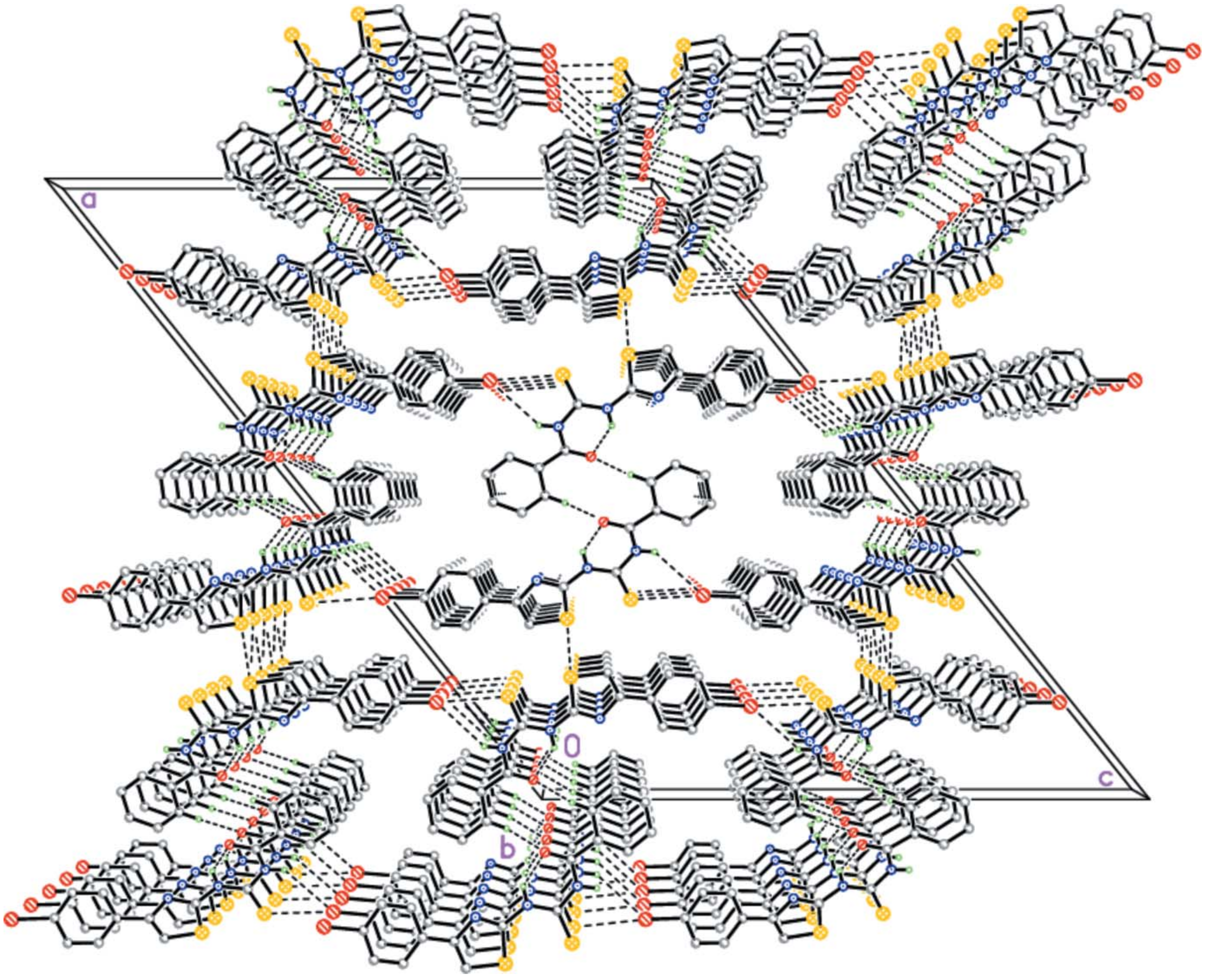

Figure 4
The crystal structure of (II). Dashed lines indicate the intramolecular N—H⋯O and intermolecular N—H⋯Br and C—H⋯O hydrogen bonds, as well as secondary intermolecular S⋯S and S⋯Br interactions.

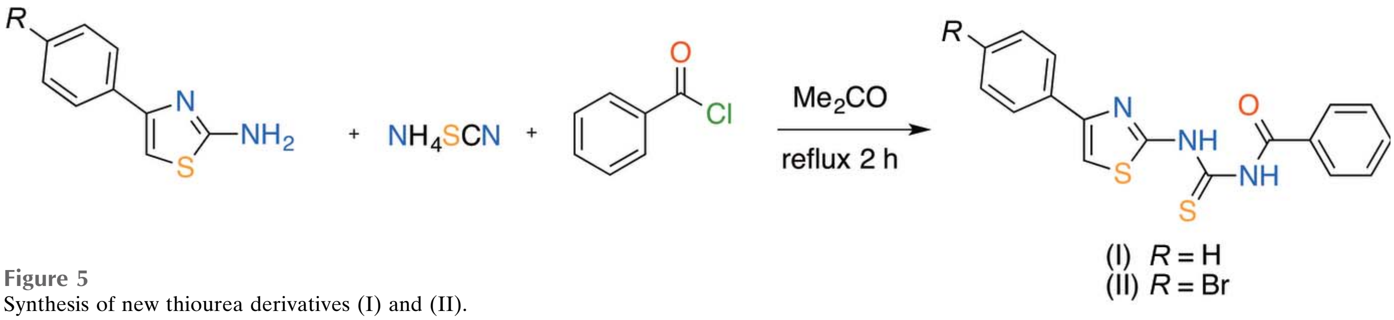

Figure 5
Synthesis of new thiourea derivatives (I) and (II).

mediated by the N2—H2⋯Br1^{i} and C13—H13⋯O1^{ii} hydrogen bonds (Table 2, Fig. 4) as well as the secondary S1⋯Br1^{iii} [3.3507 (11) Å] and S2⋯S2^{iv} [3.4343 (14) Å] interactions [symmetry codes: (i) $x, -y + 1, z - \frac{1}{2}$; (ii) $-x + 1, -y, -z + 1$; (iii) $x, -y + 1, -z + 1$; (iv) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; Fig. 4]. It should be pointed out that the secondary intermolecular S⋯Br and S⋯S interactions in (II) are significantly stronger than the intermolecular hydrogen bonds and, consequently, structure-forming.

4. Synthesis and crystallization

Benzoyl chloride (0.60 ml, 0.73 g, 5.19 mmol) was added over 5 min to a freshly prepared solution of NH_4SCN (0.39 g, 5.19 mmol) in acetone (40 ml), and the mixture was heated under reflux for 15 min. After heating, the appropriate 4-arylthiazol-2-amine (4.33 mmol) in acetone (10 ml) was added. The mixture was heated again under reflux for 2 h (Fig. 5). Then excess cracked ice was added with vigorous stirring. The resulting solid was collected and liberally washed with water. These compounds were isolated as pale-yellow crystalline solids in 41% and 45% yield for the 4-phenyl (I) and 4-(4-bromophenyl) (II) derivatives, respectively. Single crystals of the products were obtained by slow crystallization from *N*,*N*-dimethylformamide solution.

Spectroscopic and physical data for (I): m.p. 481–483 K. FTIR ν_{max} cm^{-1}: 3025, 1671, 1518, 1441, 1246, 1170, 668, 561. ^{1}H NMR (600 MHz, DMSO-d_6, 304 K): δ = 7.35 (*t*, 1H, *J* = 7.3), 7.45 (*t*, 2H, *J* = 7.6), 7.56 (*t*, 2H, *J* = 7.6), 7.69 (*t*, 1H, *J* = 7.4), 7.74 (*s*, 1H), 7.94 (*d*, 2H, *J* = 7.8), 8.03 (*d*, 2H, *J* = 7.8), 12.18 (*s*, 1H), 14.27 (*s*, 1H). Analysis calculated for $C_{17}H_{13}N_3OS_2$: C, 60.16; H, 3.86; N, 12.38. Found: C, 60.22; H, 3.93; N, 12.47.

Spectroscopic and physical data for (II): m.p. 484–486 K. FTIR ν_{max} cm^{-1}: 3395, 3055, 1674, 1515, 1488, 1244, 1165, 697.

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_{17}H_{13}N_3OS_2$	$C_{17}H_{12}BrN_3OS_2$
M_r	339.42	418.33
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $C2/c$
Temperature (K)	100	100
a, b, c (Å)	12.901 (3), 5.5160 (11), 23.143 (5)	37.210 (7), 4.0000 (8), 28.450 (6)
β (°)	105.32 (3)	128.69 (3)
V (Å^3)	1588.4 (6)	3305.2 (18)
Z	4	8
Radiation type	Synchrotron, λ = 0.96990 Å	Synchrotron, λ = 0.96990 Å
μ (mm^{-1})	0.81	1.56
Crystal size (mm)	0.15 × 0.10 × 0.05	0.07 × 0.05 × 0.03
Data collection		
Diffractometer	MAR CCD	MAR CCD
Absorption correction	Multi-scan (*SCALA*; Evans, 2006)	Multi-scan (*SCALA*; Evans, 2006)
T_{min}, T_{max}	0.870, 0.950	0.880, 0.930
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26393, 3395, 2899	13698, 3267, 2523
R_{int}	0.033	0.065
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.642	0.641
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.095, 1.03	0.040, 0.092, 1.02
No. of reflections	3395	3267
No. of parameters	209	217
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.32	0.62, −0.78

Computer programs: *Automar* (MarXperts, 2015), *iMOSFLM* (Battye *et al.*, 2011), *SHELXS97* and *SHELXTL* (Sheldrick, 2008) and *SHELXL2014* (Sheldrick, 2015).

^{1}H NMR (600 MHz, DMSO-d_6,304 K): $\delta = 7.57$ (t, 2H, $J = 7.7$), 7.64 (d, 2H, $J = 8.0$), 7.70 (t, 1H, $J = 7.5$), 7.83 (s, 1H), 7.90 (d, 2H, $J = 8.1$), 8.03 (d, 2H, $J = 7.7$), 1221 (s, 1H), 14.27 (s, 1H). Analysis calculated for $C_{17}H_{12}N_3OS_2Br$: C, 48.81; H, 2.89; N, 10.05. Found: C, 48.89; H, 2.95; N, 10.11.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. X-ray diffraction studies were carried out on the 'Belok' beamline (λ = 0.96990 Å) of the National Research Center 'Kurchatov Institute' (Moscow, Russian Federation) using a MAR CCD detector. For each compound, a total of 360 images were collected using an oscillation range of 1.0° (φ scan mode) and corrected for absorption using the *SCALA* program (Evans, 2006). The data were indexed, integrated and scaled using the utility *i*MOSFLM in the program *CCP4* (Battye *et al.*, 2011).

The hydrogen atoms of the amino groups were localized in the difference-Fourier map and included in the refinement with fixed positional (riding model) and isotropic displacement parameters [$U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm N})$]. The other hydrogen atoms were placed in calculated positions with C—H = 0.95 Å and refined using in a riding model with fixed isotropic displacement parameters [$U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$].

Acknowledgements

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supporting information

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Crystal structures of *N*-[(4-phenylthiazol-2-yl)carbamothioyl]benzamide and *N*-{[4-(4-bromophenyl)thiazol-2-yl]carbamothioyl}benzamide from synchrotron X-ray diffraction

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Computing details

For both compounds, data collection: *Automar* (MarXperts, 2015); cell refinement: *iMOSFLM* (Battye *et al.*, 2011); data reduction: *iMOSFLM* (Battye *et al.*, 2011); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

(I) *N*-[(4-Phenylthiazol-2-yl)carbamothioyl]benzamide

Crystal data

$C_{17}H_{13}N_3OS_2$
$M_r = 339.42$
Monoclinic, $P2_1/c$
$a = 12.901\ (3)$ Å
$b = 5.5160\ (11)$ Å
$c = 23.143\ (5)$ Å
$\beta = 105.32\ (3)°$
$V = 1588.4\ (6)$ Å^3
$Z = 4$

$F(000) = 704$
$D_x = 1.419$ Mg m^{-3}
Synchrotron radiation, $\lambda = 0.96990$ Å
Cell parameters from 600 reflections
$\theta = 2.4–34.0°$
$\mu = 0.81$ mm^{-1}
$T = 100$ K
Prism, colourless
0.15 × 0.10 × 0.05 mm

Data collection

MAR CCD diffractometer
φ scan
Absorption correction: multi-scan (SCALA; Evans, 2006)
$T_{min} = 0.870$, $T_{max} = 0.950$
26393 measured reflections

3395 independent reflections
2899 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 38.5°$, $\theta_{min} = 2.2°$
$h = -16\rightarrow16$
$k = -6\rightarrow7$
$l = -29\rightarrow28$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.095$
$S = 1.03$
3395 reflections
209 parameters

0 restraints
Primary atom site location: difference Fourier map
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2 + 0.566P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0035 (10)

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_{iso}*/U_{eq}
S1	0.41550 (3)	0.80075 (7)	0.45047 (2)	0.03118 (14)
S2	0.25885 (3)	1.09330 (7)	0.35070 (2)	0.02857 (14)
O1	0.47826 (9)	0.3167 (2)	0.30362 (5)	0.0333 (3)
N1	0.36884 (10)	0.6692 (2)	0.33491 (6)	0.0279 (3)
H1	0.3853	0.5686	0.3068	0.033*
N2	0.49953 (10)	0.4417 (2)	0.40077 (5)	0.0265 (3)
H2	0.5346	0.4048	0.4403	0.032*
N3	0.22879 (10)	0.8127 (2)	0.25771 (6)	0.0270 (3)
C1	0.42612 (12)	0.6327 (3)	0.39203 (7)	0.0262 (3)
C2	0.28765 (12)	0.8397 (3)	0.31264 (7)	0.0265 (3)
C3	0.15407 (12)	0.9994 (3)	0.24243 (7)	0.0266 (3)
C4	0.16011 (13)	1.1685 (3)	0.28659 (7)	0.0291 (3)
H4	0.1159	1.3086	0.2826	0.035*
C5	0.07557 (12)	0.9915 (3)	0.18273 (7)	0.0263 (3)
C6	0.07731 (13)	0.7958 (3)	0.14375 (7)	0.0292 (3)
H6	0.1300	0.6722	0.1555	0.035*
C7	0.00219 (13)	0.7826 (3)	0.08808 (8)	0.0342 (4)
H7	0.0038	0.6496	0.0623	0.041*
C8	−0.07530 (13)	0.9630 (3)	0.06996 (8)	0.0356 (4)
H8	−0.1264	0.9529	0.0320	0.043*
C9	−0.07725 (14)	1.1582 (3)	0.10782 (8)	0.0343 (4)
H9	−0.1298	1.2817	0.0956	0.041*
C10	−0.00247 (13)	1.1736 (3)	0.16369 (7)	0.0303 (4)
H10	−0.0043	1.3080	0.1891	0.036*
C11	0.52613 (12)	0.3002 (3)	0.35705 (7)	0.0268 (3)
C12	0.61647 (12)	0.1241 (3)	0.37854 (6)	0.0259 (3)
C13	0.62162 (12)	−0.0727 (3)	0.34049 (7)	0.0280 (3)
H13	0.5687	−0.0900	0.3034	0.034*
C14	0.70420 (13)	−0.2414 (3)	0.35736 (7)	0.0298 (3)
H14	0.7074	−0.3746	0.3319	0.036*
C15	0.78246 (13)	−0.2151 (3)	0.41177 (7)	0.0318 (4)
H15	0.8389	−0.3304	0.4232	0.038*
C16	0.77780 (13)	−0.0197 (3)	0.44932 (7)	0.0316 (4)
H16	0.8308	−0.0031	0.4864	0.038*

C17	0.69563 (12)	0.1514 (3)	0.43264 (7)	0.0282 (3)
H17	0.6934	0.2859	0.4579	0.034*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0401 (2)	0.0298 (2)	0.0231 (2)	0.00420 (17)	0.00737 (16)	−0.00296 (15)
S2	0.0325 (2)	0.0253 (2)	0.0282 (2)	0.00129 (15)	0.00863 (15)	−0.00300 (15)
O1	0.0376 (6)	0.0382 (7)	0.0228 (6)	0.0089 (5)	0.0059 (5)	−0.0010 (5)
N1	0.0319 (7)	0.0282 (7)	0.0236 (6)	0.0033 (6)	0.0075 (5)	−0.0021 (5)
N2	0.0288 (6)	0.0286 (7)	0.0214 (6)	0.0022 (5)	0.0056 (5)	0.0004 (5)
N3	0.0287 (6)	0.0259 (7)	0.0270 (7)	0.0016 (5)	0.0086 (5)	0.0007 (5)
C1	0.0271 (7)	0.0260 (8)	0.0264 (7)	−0.0013 (6)	0.0087 (6)	0.0004 (6)
C2	0.0300 (8)	0.0232 (8)	0.0282 (8)	0.0003 (6)	0.0110 (6)	0.0005 (6)
C3	0.0276 (7)	0.0231 (8)	0.0314 (8)	0.0003 (6)	0.0120 (6)	0.0024 (6)
C4	0.0301 (8)	0.0259 (8)	0.0318 (8)	0.0019 (6)	0.0089 (6)	0.0003 (6)
C5	0.0265 (7)	0.0239 (8)	0.0300 (8)	−0.0012 (6)	0.0103 (6)	0.0026 (6)
C6	0.0272 (7)	0.0254 (8)	0.0342 (8)	0.0016 (6)	0.0066 (6)	−0.0001 (6)
C7	0.0342 (9)	0.0286 (9)	0.0375 (9)	0.0005 (7)	0.0058 (7)	−0.0038 (7)
C8	0.0300 (8)	0.0388 (10)	0.0340 (8)	0.0002 (7)	0.0017 (7)	0.0012 (7)
C9	0.0330 (8)	0.0323 (9)	0.0377 (9)	0.0087 (7)	0.0098 (7)	0.0063 (7)
C10	0.0336 (8)	0.0270 (8)	0.0328 (8)	0.0053 (7)	0.0131 (7)	0.0019 (6)
C11	0.0282 (8)	0.0290 (8)	0.0234 (7)	−0.0012 (6)	0.0074 (6)	0.0001 (6)
C12	0.0274 (7)	0.0271 (8)	0.0243 (7)	−0.0009 (6)	0.0091 (6)	0.0011 (6)
C13	0.0291 (8)	0.0306 (8)	0.0252 (7)	−0.0022 (6)	0.0085 (6)	−0.0013 (6)
C14	0.0336 (8)	0.0287 (8)	0.0301 (8)	0.0000 (7)	0.0135 (6)	−0.0015 (6)
C15	0.0320 (8)	0.0309 (9)	0.0343 (9)	0.0065 (7)	0.0120 (7)	0.0050 (7)
C16	0.0290 (8)	0.0387 (10)	0.0259 (8)	0.0022 (7)	0.0053 (6)	0.0020 (7)
C17	0.0317 (8)	0.0287 (8)	0.0250 (8)	−0.0014 (7)	0.0089 (6)	−0.0011 (6)

Geometric parameters (Å, º)

S1—C1	1.6747 (16)	C7—C8	1.394 (2)
S2—C4	1.7313 (17)	C7—H7	0.9500
S2—C2	1.7447 (16)	C8—C9	1.393 (3)
O1—C11	1.2308 (19)	C8—H8	0.9500
N1—C1	1.348 (2)	C9—C10	1.397 (2)
N1—C2	1.401 (2)	C9—H9	0.9500
N1—H1	0.9210	C10—H10	0.9500
N2—C11	1.3909 (19)	C11—C12	1.498 (2)
N2—C1	1.395 (2)	C12—C17	1.399 (2)
N2—H2	0.9300	C12—C13	1.410 (2)
N3—C2	1.306 (2)	C13—C14	1.391 (2)
N3—C3	1.391 (2)	C13—H13	0.9500
C3—C4	1.371 (2)	C14—C15	1.398 (2)
C3—C5	1.482 (2)	C14—H14	0.9500
C4—H4	0.9500	C15—C16	1.396 (2)
C5—C10	1.408 (2)	C15—H15	0.9500

C5—C6	1.411 (2)	C16—C17	1.395 (2)
C6—C7	1.395 (2)	C16—H16	0.9500
C6—H6	0.9500	C17—H17	0.9500

C4—S2—C2	88.06 (8)	C9—C8—H8	120.2
C1—N1—C2	128.58 (13)	C7—C8—H8	120.2
C1—N1—H1	115.7	C8—C9—C10	120.43 (15)
C2—N1—H1	115.7	C8—C9—H9	119.8
C11—N2—C1	127.36 (13)	C10—C9—H9	119.8
C11—N2—H2	116.3	C9—C10—C5	120.55 (15)
C1—N2—H2	116.3	C9—C10—H10	119.7
C2—N3—C3	110.42 (13)	C5—C10—H10	119.7
N1—C1—N2	115.46 (13)	O1—C11—N2	122.31 (14)
N1—C1—S1	124.67 (12)	O1—C11—C12	121.44 (14)
N2—C1—S1	119.87 (11)	N2—C11—C12	116.25 (13)
N3—C2—N1	117.88 (14)	C17—C12—C13	119.85 (14)
N3—C2—S2	115.87 (12)	C17—C12—C11	123.20 (14)
N1—C2—S2	126.22 (12)	C13—C12—C11	116.92 (13)
C4—C3—N3	114.53 (14)	C14—C13—C12	119.92 (14)
C4—C3—C5	127.25 (14)	C14—C13—H13	120.0
N3—C3—C5	118.17 (14)	C12—C13—H13	120.0
C3—C4—S2	111.10 (12)	C13—C14—C15	120.06 (15)
C3—C4—H4	124.5	C13—C14—H14	120.0
S2—C4—H4	124.5	C15—C14—H14	120.0
C10—C5—C6	118.47 (15)	C16—C15—C14	120.09 (15)
C10—C5—C3	121.79 (14)	C16—C15—H15	120.0
C6—C5—C3	119.73 (14)	C14—C15—H15	120.0
C7—C6—C5	120.38 (15)	C15—C16—C17	120.29 (15)
C7—C6—H6	119.8	C15—C16—H16	119.9
C5—C6—H6	119.8	C17—C16—H16	119.9
C8—C7—C6	120.58 (16)	C16—C17—C12	119.77 (15)
C8—C7—H7	119.7	C16—C17—H17	120.1
C6—C7—H7	119.7	C12—C17—H17	120.1
C9—C8—C7	119.56 (16)		

C2—N1—C1—N2	177.74 (14)	C5—C6—C7—C8	0.3 (3)
C2—N1—C1—S1	−3.2 (2)	C6—C7—C8—C9	0.2 (3)
C11—N2—C1—N1	5.9 (2)	C7—C8—C9—C10	−0.2 (3)
C11—N2—C1—S1	−173.23 (12)	C8—C9—C10—C5	−0.4 (2)
C3—N3—C2—N1	−178.70 (13)	C6—C5—C10—C9	0.9 (2)
C3—N3—C2—S2	−0.34 (17)	C3—C5—C10—C9	−178.30 (14)
C1—N1—C2—N3	−166.94 (15)	C1—N2—C11—O1	−6.7 (2)
C1—N1—C2—S2	14.9 (2)	C1—N2—C11—C12	173.58 (14)
C4—S2—C2—N3	−0.53 (12)	O1—C11—C12—C17	157.43 (15)
C4—S2—C2—N1	177.67 (14)	N2—C11—C12—C17	−22.9 (2)
C2—N3—C3—C4	1.36 (19)	O1—C11—C12—C13	−20.5 (2)
C2—N3—C3—C5	−176.47 (13)	N2—C11—C12—C13	159.15 (13)
N3—C3—C4—S2	−1.76 (17)	C17—C12—C13—C14	1.2 (2)

C5—C3—C4—S2	175.84 (12)	C11—C12—C13—C14	179.22 (13)
C2—S2—C4—C3	1.25 (12)	C12—C13—C14—C15	−0.5 (2)
C4—C3—C5—C10	2.7 (2)	C13—C14—C15—C16	0.1 (2)
N3—C3—C5—C10	−179.82 (13)	C14—C15—C16—C17	−0.5 (2)
C4—C3—C5—C6	−176.52 (15)	C15—C16—C17—C12	1.2 (2)
N3—C3—C5—C6	1.0 (2)	C13—C12—C17—C16	−1.6 (2)
C10—C5—C6—C7	−0.9 (2)	C11—C12—C17—C16	−179.47 (14)
C3—C5—C6—C7	178.33 (14)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.92	1.85	2.6145 (18)	139
N2—H2···S1^{i}	0.93	2.69	3.5845 (15)	162
C13—H13···O1^{ii}	0.95	2.44	3.299 (2)	150

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+1, *y*−1/2, −*z*+1/2.

(II) *N*-{[4-(4-Bromophenyl)thiazol-2-yl]carbamothioyl}benzamide

Crystal data

$C_{17}H_{12}BrN_3OS_2$	$F(000) = 1680$
$M_r = 418.33$	$D_x = 1.681$ Mg m^{-3}
Monoclinic, *C*2/*c*	Synchrotron radiation, $\lambda = 0.96990$ Å
$a = 37.210$ (7) Å	Cell parameters from 500 reflections
$b = 4.0000$ (8) Å	$\theta = 4.0$–33.0°
$c = 28.450$ (6) Å	$\mu = 1.56$ mm^{-1}
$\beta = 128.69$ (3)°	$T = 100$ K
$V = 3305.2$ (18) Å^3	Prism, colourless
$Z = 8$	0.07 × 0.05 × 0.03 mm

Data collection

MAR CCD diffractometer	3267 independent reflections
φ scan	2523 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SCALA; Evans, 2006)	$R_{int} = 0.065$
$T_{min} = 0.880$, $T_{max} = 0.930$	$\theta_{max} = 38.4°$, $\theta_{min} = 4.0°$
13698 measured reflections	$h = -44 \rightarrow 44$
	$k = -4 \rightarrow 4$
	$l = -32 \rightarrow 32$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.040$	H-atom parameters constrained
$wR(F^2) = 0.092$	$w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.002$
3267 reflections	$\Delta\rho_{max} = 0.62$ e Å^{-3}
217 parameters	$\Delta\rho_{min} = -0.78$ e Å^{-3}
0 restraints	
Primary atom site location: difference Fourier map	

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}
Br1	0.66455 (2)	0.24056 (7)	0.96731 (2)	0.02282 (14)
S1	0.67189 (2)	0.95707 (16)	0.58750 (3)	0.02136 (19)
S2	0.70200 (2)	0.97423 (15)	0.71326 (3)	0.01827 (18)
O1	0.55011 (6)	0.3045 (5)	0.53088 (9)	0.0239 (5)
N1	0.62216 (7)	0.6652 (5)	0.61537 (10)	0.0176 (5)
H1	0.5969	0.5551	0.6017	0.021*
N2	0.59498 (7)	0.6073 (5)	0.51692 (9)	0.0194 (5)
H2	0.5969	0.6736	0.4890	0.023*
N3	0.64079 (7)	0.6390 (5)	0.71031 (9)	0.0178 (5)
C1	0.62849 (9)	0.7359 (6)	0.57480 (13)	0.0183 (7)
C2	0.65111 (9)	0.7460 (6)	0.67684 (13)	0.0173 (6)
C3	0.67476 (9)	0.7355 (6)	0.76996 (13)	0.0167 (6)
C4	0.70985 (8)	0.9180 (6)	0.77919 (12)	0.0197 (6)
H4	0.7353	1.0029	0.8172	0.024*
C5	0.67149 (8)	0.6265 (6)	0.81672 (11)	0.0175 (6)
C6	0.71033 (9)	0.6346 (7)	0.87798 (12)	0.0213 (6)
H6	0.7387	0.7176	0.8894	0.026*
C7	0.70779 (8)	0.5233 (6)	0.92191 (12)	0.0219 (7)
H7	0.7343	0.5286	0.9631	0.026*
C8	0.66619 (8)	0.4035 (6)	0.90546 (12)	0.0193 (6)
C9	0.62698 (9)	0.3949 (7)	0.84512 (12)	0.0223 (6)
H9	0.5986	0.3141	0.8340	0.027*
C10	0.63006 (9)	0.5062 (6)	0.80154 (12)	0.0216 (6)
H10	0.6034	0.5006	0.7604	0.026*
C11	0.55924 (8)	0.3889 (6)	0.49790 (12)	0.0187 (6)
C12	0.53267 (9)	0.2627 (6)	0.43455 (13)	0.0184 (7)
C13	0.48960 (8)	0.1152 (7)	0.40853 (12)	0.0216 (6)
H13	0.4785	0.1002	0.4308	0.026*
C14	0.46331 (9)	−0.0089 (6)	0.34991 (12)	0.0239 (7)
H14	0.4341	−0.1062	0.3321	0.029*
C15	0.47950 (9)	0.0089 (6)	0.31750 (13)	0.0253 (7)
H15	0.4613	−0.0754	0.2775	0.030*
C16	0.52255 (9)	0.1505 (7)	0.34332 (13)	0.0262 (7)
H16	0.5337	0.1612	0.3210	0.031*
C17	0.54912 (9)	0.2757 (6)	0.40176 (13)	0.0225 (7)
H17	0.5785	0.3702	0.4194	0.027*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0213 (2)	0.0297 (2)	0.0189 (2)	0.00396 (11)	0.01329 (17)	0.00383 (11)
S1	0.0214 (3)	0.0250 (3)	0.0184 (4)	−0.0048 (3)	0.0128 (3)	−0.0023 (3)
S2	0.0148 (3)	0.0215 (3)	0.0161 (4)	−0.0005 (2)	0.0085 (3)	−0.0005 (2)
O1	0.0196 (10)	0.0343 (11)	0.0182 (11)	−0.0039 (8)	0.0119 (9)	0.0011 (8)
N1	0.0130 (10)	0.0241 (11)	0.0136 (12)	−0.0010 (8)	0.0073 (10)	0.0011 (9)
N2	0.0181 (10)	0.0249 (12)	0.0119 (11)	−0.0010 (9)	0.0078 (9)	0.0018 (9)
N3	0.0145 (10)	0.0206 (11)	0.0136 (11)	0.0014 (9)	0.0066 (9)	0.0006 (9)
C1	0.0154 (13)	0.0199 (13)	0.0149 (15)	0.0050 (9)	0.0072 (12)	0.0032 (9)
C2	0.0154 (13)	0.0217 (14)	0.0132 (14)	0.0026 (9)	0.0082 (12)	0.0013 (9)
C3	0.0144 (13)	0.0169 (13)	0.0156 (15)	0.0024 (9)	0.0079 (12)	−0.0009 (9)
C4	0.0179 (12)	0.0214 (13)	0.0144 (14)	0.0000 (10)	0.0075 (11)	−0.0006 (10)
C5	0.0171 (12)	0.0196 (12)	0.0132 (13)	0.0035 (10)	0.0083 (11)	0.0004 (10)
C6	0.0141 (12)	0.0292 (14)	0.0185 (15)	0.0000 (11)	0.0091 (12)	0.0000 (11)
C7	0.0141 (12)	0.0308 (15)	0.0129 (14)	0.0024 (10)	0.0046 (11)	−0.0020 (10)
C8	0.0187 (12)	0.0231 (13)	0.0160 (14)	0.0038 (10)	0.0108 (11)	0.0004 (10)
C9	0.0186 (13)	0.0268 (14)	0.0211 (15)	−0.0028 (11)	0.0122 (12)	−0.0021 (11)
C10	0.0169 (12)	0.0291 (14)	0.0146 (14)	0.0000 (10)	0.0078 (11)	−0.0017 (10)
C11	0.0131 (12)	0.0221 (13)	0.0142 (14)	0.0019 (10)	0.0054 (11)	0.0031 (10)
C12	0.0135 (13)	0.0212 (14)	0.0144 (15)	0.0023 (9)	0.0057 (12)	0.0015 (9)
C13	0.0174 (13)	0.0244 (14)	0.0193 (15)	0.0022 (11)	0.0097 (12)	0.0018 (11)
C14	0.0148 (13)	0.0256 (14)	0.0218 (15)	−0.0017 (10)	0.0068 (12)	−0.0014 (11)
C15	0.0212 (13)	0.0269 (15)	0.0161 (14)	0.0000 (10)	0.0059 (12)	−0.0025 (11)
C16	0.0268 (15)	0.0312 (15)	0.0199 (15)	−0.0015 (12)	0.0142 (13)	−0.0025 (12)
C17	0.0153 (13)	0.0269 (15)	0.0186 (16)	−0.0029 (10)	0.0073 (13)	−0.0004 (10)

Geometric parameters (Å, º)

Br1—C8	1.913 (3)	C6—H6	0.9500
S1—C1	1.670 (3)	C7—C8	1.393 (4)
S2—C4	1.723 (3)	C7—H7	0.9500
S2—C2	1.743 (3)	C8—C9	1.395 (4)
O1—C11	1.228 (4)	C9—C10	1.388 (4)
N1—C1	1.345 (4)	C9—H9	0.9500
N1—C2	1.403 (4)	C10—H10	0.9500
N1—H1	0.8800	C11—C12	1.501 (4)
N2—C11	1.387 (3)	C12—C17	1.401 (5)
N2—C1	1.401 (3)	C12—C13	1.408 (4)
N2—H2	0.8800	C13—C14	1.394 (4)
N3—C2	1.302 (4)	C13—H13	0.9500
N3—C3	1.394 (3)	C14—C15	1.383 (4)
C3—C4	1.370 (4)	C14—H14	0.9500
C3—C5	1.476 (4)	C15—C16	1.398 (4)
C4—H4	0.9500	C15—H15	0.9500
C5—C10	1.401 (4)	C16—C17	1.392 (4)
C5—C6	1.407 (3)	C16—H16	0.9500

C6—C7	1.385 (4)	C17—H17	0.9500

C4—S2—C2	87.75 (14)	C7—C8—Br1	118.4 (2)
C1—N1—C2	127.7 (2)	C9—C8—Br1	120.9 (2)
C1—N1—H1	116.1	C10—C9—C8	119.0 (3)
C2—N1—H1	116.1	C10—C9—H9	120.5
C11—N2—C1	128.4 (3)	C8—C9—H9	120.5
C11—N2—H2	115.8	C9—C10—C5	121.6 (2)
C1—N2—H2	115.8	C9—C10—H10	119.2
C2—N3—C3	110.0 (2)	C5—C10—H10	119.2
N1—C1—N2	115.3 (2)	O1—C11—N2	122.0 (3)
N1—C1—S1	126.2 (2)	O1—C11—C12	122.4 (2)
N2—C1—S1	118.6 (2)	N2—C11—C12	115.6 (3)
N3—C2—N1	119.2 (2)	C17—C12—C13	119.6 (3)
N3—C2—S2	116.4 (2)	C17—C12—C11	123.6 (2)
N1—C2—S2	124.3 (2)	C13—C12—C11	116.8 (3)
C4—C3—N3	114.3 (3)	C14—C13—C12	119.7 (3)
C4—C3—C5	126.2 (2)	C14—C13—H13	120.2
N3—C3—C5	119.5 (2)	C12—C13—H13	120.2
C3—C4—S2	111.6 (2)	C15—C14—C13	120.4 (3)
C3—C4—H4	124.2	C15—C14—H14	119.8
S2—C4—H4	124.2	C13—C14—H14	119.8
C10—C5—C6	118.1 (3)	C14—C15—C16	120.3 (3)
C10—C5—C3	121.2 (2)	C14—C15—H15	119.9
C6—C5—C3	120.7 (2)	C16—C15—H15	119.9
C7—C6—C5	120.9 (3)	C17—C16—C15	119.9 (3)
C7—C6—H6	119.5	C17—C16—H16	120.1
C5—C6—H6	119.5	C15—C16—H16	120.1
C6—C7—C8	119.7 (2)	C16—C17—C12	120.2 (3)
C6—C7—H7	120.1	C16—C17—H17	119.9
C8—C7—H7	120.1	C12—C17—H17	119.9
C7—C8—C9	120.7 (3)		

C2—N1—C1—N2	176.6 (2)	C6—C7—C8—C9	−0.1 (4)
C2—N1—C1—S1	−3.2 (4)	C6—C7—C8—Br1	178.3 (2)
C11—N2—C1—N1	−7.5 (4)	C7—C8—C9—C10	0.3 (4)
C11—N2—C1—S1	172.2 (2)	Br1—C8—C9—C10	−178.0 (2)
C3—N3—C2—N1	177.7 (2)	C8—C9—C10—C5	0.0 (4)
C3—N3—C2—S2	−0.5 (3)	C6—C5—C10—C9	−0.5 (4)
C1—N1—C2—N3	−175.8 (2)	C3—C5—C10—C9	178.3 (2)
C1—N1—C2—S2	2.2 (4)	C1—N2—C11—O1	7.4 (4)
C4—S2—C2—N3	0.2 (2)	C1—N2—C11—C12	−172.4 (2)
C4—S2—C2—N1	−177.9 (2)	O1—C11—C12—C17	−161.6 (2)
C2—N3—C3—C4	0.6 (3)	N2—C11—C12—C17	18.2 (3)
C2—N3—C3—C5	−176.9 (2)	O1—C11—C12—C13	16.4 (4)
N3—C3—C4—S2	−0.5 (3)	N2—C11—C12—C13	−163.8 (2)
C5—C3—C4—S2	176.8 (2)	C17—C12—C13—C14	−1.6 (4)
C2—S2—C4—C3	0.17 (19)	C11—C12—C13—C14	−179.6 (2)

C4—C3—C5—C10	165.8 (2)	C12—C13—C14—C15	0.7 (4)
N3—C3—C5—C10	−17.0 (4)	C13—C14—C15—C16	0.3 (4)
C4—C3—C5—C6	−15.5 (4)	C14—C15—C16—C17	−0.4 (4)
N3—C3—C5—C6	161.7 (2)	C15—C16—C17—C12	−0.5 (4)
C10—C5—C6—C7	0.7 (4)	C13—C12—C17—C16	1.5 (4)
C3—C5—C6—C7	−178.1 (2)	C11—C12—C17—C16	179.4 (2)
C5—C6—C7—C8	−0.4 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.88	1.93	2.644 (3)	138
N2—H2···Br1^{i}	0.88	2.97	3.692 (3)	141
C13—H13···O1^{ii}	0.95	2.53	3.340 (4)	144

Symmetry codes: (i) *x*, −*y*+1, *z*−1/2; (ii) −*x*+1, −*y*, −*z*+1.