

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

1-(2-Bromo-4-chlorophenyl)-3,3-dimethylthiourea

Gamal A. El-Hiti,^{a*} Keith Smith,^b Amany S. Hegazy,^b Mohammad Hayal Alotaibi^c and Benson M. Kariuki^{b*}^aCornea Research Chair, Department of Optometry, College of Applied Medical Sciences, King Saud University, PO Box 10219, Riyadh 11433, Saudi Arabia,^bSchool of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, Wales, and ^cPetrochemical Research Institute, King Abdulaziz City for Science and Technology, PO Box 6086, Riyadh 11442, Saudi Arabia

Correspondence e-mail: gelhiti@ksu.edu.sa, kariukib@cardiff.ac.uk

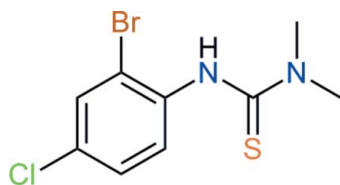
Received 9 May 2014; accepted 16 May 2014

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.028; wR factor = 0.077; data-to-parameter ratio = 17.3.

In the title compound, $\text{C}_9\text{H}_{10}\text{BrClN}_2\text{S}$, the dimethylthiourea group is twisted from the benzene ring plane by 54.38 (6)°. In the crystal, the amino groups are involved in the formation of $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds, which link the molecules into chains along $[010]$. Weak $\text{C}-\text{H}\cdots\text{Cl}$ interactions further link these chains into layers parallel to the ab plane.

Related literature

For related compounds, see: Maddani & Prabhu (2010); Yahyazadeh & Ghasemi (2013); Zhao *et al.* (2013). For convenient routes for modifying urea derivatives *via* organolithium intermediates, see: Smith *et al.* (1996, 1999, 2009, 2010, 2012, 2014). For the structures of related compounds, see: Zhao *et al.* (2008); Ramnathan *et al.* (1996).



Experimental

Crystal data

 $\text{C}_9\text{H}_{10}\text{BrClN}_2\text{S}$ $M_r = 293.61$ Monoclinic, $P2_1/n$ $a = 12.1369$ (3) Å $b = 7.9431$ (2) Å $c = 13.2230$ (4) Å $\beta = 115.386$ (3)° $V = 1151.67$ (6) Å³ $Z = 4$
Cu $K\alpha$ radiation
 $\mu = 8.40$ mm⁻¹ $T = 296$ K
 $0.28 \times 0.20 \times 0.09$ mm

Data collection

Agilent SuperNova (Dual, Cu at zero, Atlas) diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2014)
 $T_{\min} = 0.580$, $T_{\max} = 1.000$ 4291 measured reflections
2245 independent reflections
2078 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.015$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.077$
 $S = 1.04$
2245 reflections130 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.33$ e Å⁻³
 $\Delta\rho_{\min} = -0.39$ e Å⁻³

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{S1}^i$	0.86	2.67	3.349 (2)	137
$\text{C9}-\text{H9B}\cdots\text{Cl1}^{\text{ii}}$	0.96	2.81	3.696 (2)	153

Symmetry codes: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x - 1, y, z$.

Data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

The authors thank the College of Applied Medical Sciences Research Center and the Deanship of Scientific Research at King Saud University for funding this research.

Supporting information for this paper is available from the IUCr electronic archives (Reference: CV5457).

References

- Agilent (2014). *CrysAlis PRO*. Agilent Technologies, Yarnton, England.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Maddani, M. R. & Prabhu, K. R. (2010). *J. Org. Chem.* **75**, 2327–2332.
Ramnathan, A., Sivakumar, K., Janarthanan, N., Meerarani, D., Ramadas, K. & Fun, H.-K. (1996). *Acta Cryst.* **C52**, 411–414.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Smith, K., El-Hiti, G. A. & Alshammari, M. B. (2012). *Synthesis*, **44**, 2013–2022.
Smith, K., El-Hiti, G. A. & Alshammari, M. B. (2014). *Synthesis*, **46**, 394–402.
Smith, K., El-Hiti, G. A. & Hegazy, A. S. (2010). *Synthesis*, pp. 1371–1380.
Smith, K., El-Hiti, G. A., Hegazy, A. S., Fekri, A. & Kariuki, B. M. (2009). *Arkivoc* **xiv**, 266–300.
Smith, K., El-Hiti, G. A. & Shukla, A. P. (1999). *J. Chem. Soc. Perkin Trans. 1*, pp. 2305–2313.
Smith, K., Shukla, A. P. & Matthews, I. (1996). *Sulfur Lett.* **20**, 121–137.
Yahyazadeh, A. & Ghasemi, Z. (2013). *Eur. Chem. Bull.* **2**, 573–575.
Zhao, Q., Li, S., Huang, K., Wang, R. & Zhang, X. (2013). *Org. Lett.* **15**, 4014–4017.
Zhao, P. S., Qin, Y. Q., Zhang, J. & Jian, F. F. (2008). *Pol. J. Chem.* **82**, 2153–2165.

supporting information

Acta Cryst. (2014). E70, o704 [doi:10.1107/S1600536814011350]

1-(2-Bromo-4-chlorophenyl)-3,3-dimethylthiourea

Gamal A. El-Hiti, Keith Smith, Amany S. Hegazy, Mohammad Hayal Alotaibi and Benson M. Kariuki

S1. Structural commentary

Recently, various thiourea derivatives have been synthesised and showed broad interesting properties (Maddani & Prabhu, 2010; Yahyazadeh & Ghasemi, 2013; Zhao *et al.*, 2013). In a continuation of our research focused on new synthetic routes towards novel substituted urea derivatives (Smith *et al.*, 1996, 1999, 2009, 2010, 2012, 2014) we have synthesized 3-(2-bromo-4-chlorophenyl)-1,1-dimethylthiourea (I) in a high yield (Smith *et al.*, 1996). We have prepared the material again and crystallized it in high purity in order to obtain its crystal structure, which we present herein.

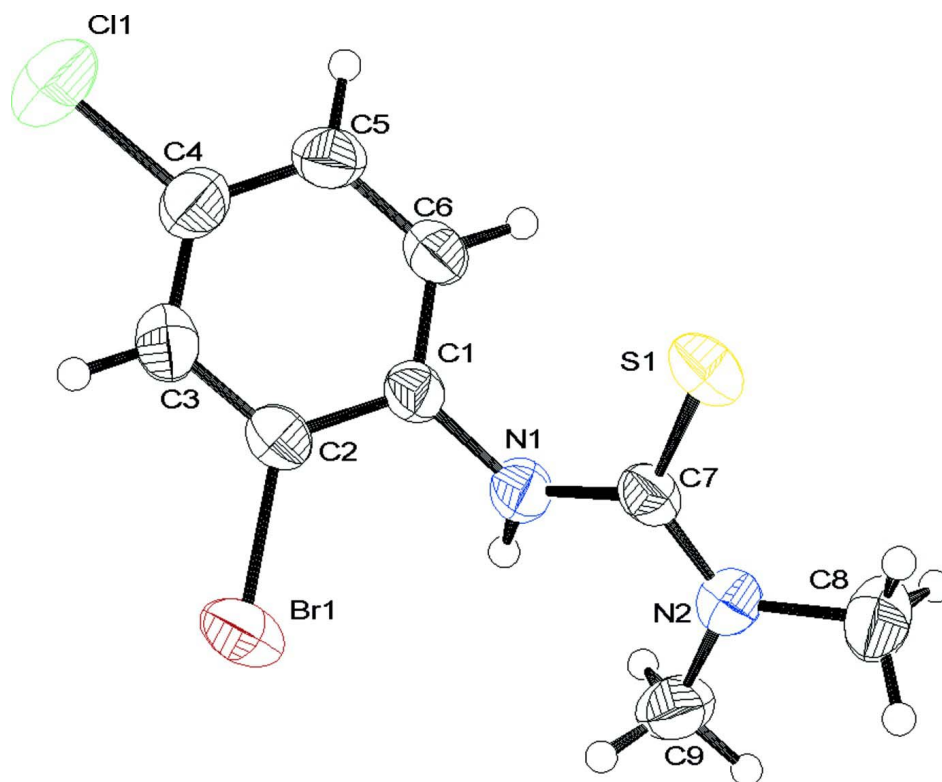
In (I) (Fig. 1), all bond lengths and angles are normal and correspond well to those observed in the related compounds (Zhao *et al.*, 2008; Ramnathan *et al.*, 1996). The non-hydrogen atoms in (I) fall into two planes with an interplanar angle of 54.38 (6)° between the bromo-chlorophenyl and dimethylthiourea groups. Each molecule is involved in N—H···S contacts (Table 1) with two neighbouring molecules, with one as an acceptor and the other as a donor, leading to the formation of zig-zag-chains in [010] (Fig 2). The bromo-chlorophenyl and dimethylthiourea groups of adjacent molecules are parallel in the stack forming chains of alternating S···Br···S groups with a separation of 4.07 Å and 4.11 Å between the atoms.

S2. Synthesis and crystallization

To a stirred solution of 2-bromo-4-chloro-1-isothiocyanatobenzene (12.43 g, 50.0 mmol) in anhydrous dioxane (120 ml) dimethylamine (7.10 g of 33% solution in ethanol, 52.0 mmol) was slowly added in a drop-wise manner over 5 min. The reaction mixture was stirred at room temperature for an extra 1 h. The solid obtained was collected by filtration and washed with dioxane (2 x 20 ml) and dried. Recrystallization from ethyl acetate gave 3-(2-bromo-4-chlorophenyl)-1,1-dimethylthiourea (13.80 g, 47.0 mmol; 94%) as yellow crystals, m.p. 193–194 °C [lit. 184–185 °C (ethyl acetate); Smith *et al.* (1996)]. ¹H NMR (500 MHz, CDCl₃, δ, p.p.m.) 7.97 (d, *J* = 8.8 Hz, 1 H, H-6), 7.59 (d, *J* = 2.3 Hz, 1 H, H-3), 7.32 (dd, *J* = 2.3, 8.8 Hz, 1 H, H-5), 7.17 (br, exch., 1 H, NH), 3.43 [s, 6 H, N(CH₃)₂]. ¹³C NMR (125 MHz, CDCl₃, δ, p.p.m.) 181.2 (s, C=S), 136.6 (s, C-1), 131.8 (d, C-3), 131.0 (s, C-4), 127.8 (d, C-6), 127.7 (d, C-5), 118.1 (s, C-2), 41.3 [q, N(CH₃)₂]. AP⁺—MS (*m/z*, %): 297 ([*MH*⁸¹Br³⁷Cl]⁺, 34), 295 ([*MH*⁸¹Br³⁵Cl and *MH*⁷⁹Br³⁷Cl]⁺, 100), 293 ([*MH*⁷⁹Br³⁵Cl]⁺, 80), 263 (12), 215 (22), 213 (50). HRMS (AP⁺): Calculated for C₉H₁₁⁷⁹Br³⁵ClN₂S [*MH*] 292.9515; found, 292.9515.

S3. Refinement

H atoms were positioned geometrically and refined using a riding model with *U*_{iso}(H) = 1.2 times *U*_{eq} for the atom they are bonded to except for the methyl groups where 1.5 times *U*_{eq} was used with free rotation about the C—C bond.

**Figure 1**

View of (I) showing atom labels and 50% probability displacement ellipsoids for non-H atoms.

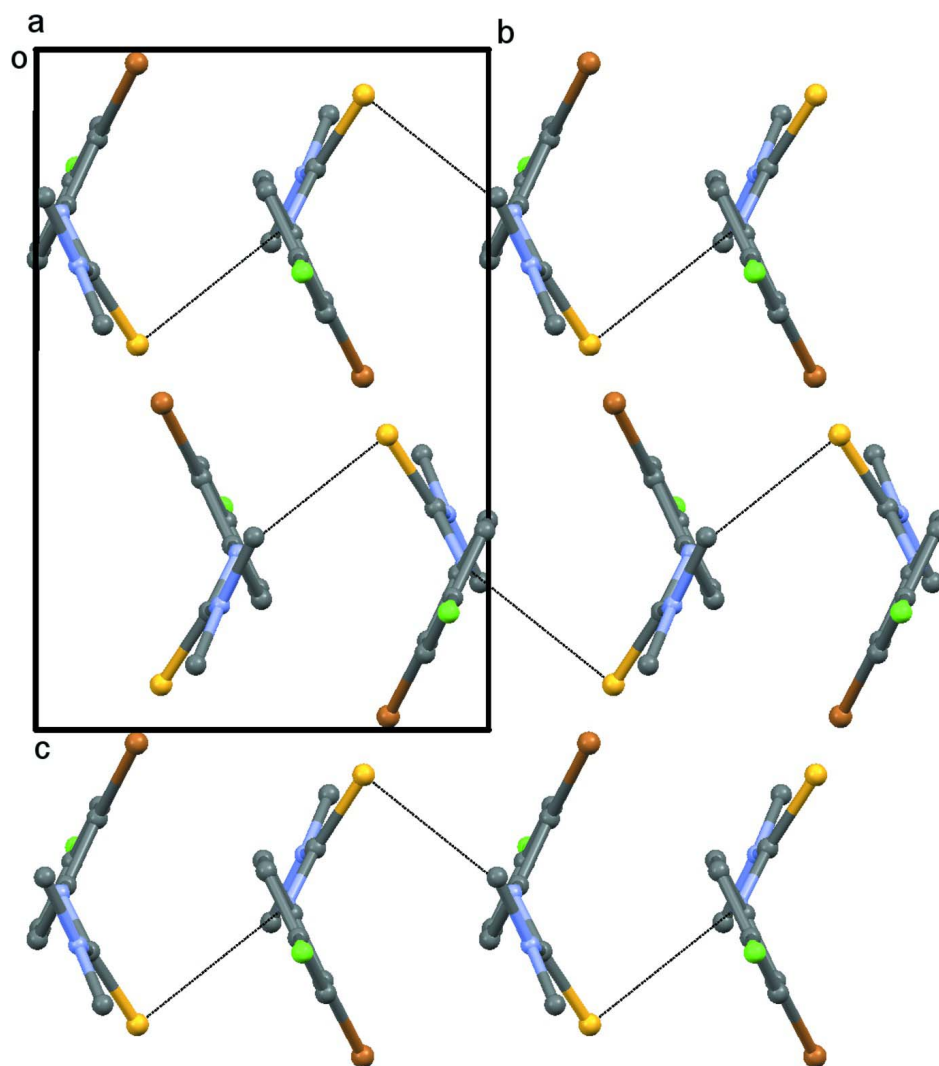


Figure 2

A portion of the crystal packing viewed along the *a* axis. N—H...S contacts are shown as dotted lines.

1-(2-Bromo-4-chlorophenyl)-3,3-dimethylthiourea

Crystal data

$C_9H_{10}BrClN_2S$

$M_r = 293.61$

Monoclinic, $P2_1/n$

$a = 12.1369 (3) \text{ \AA}$

$b = 7.9431 (2) \text{ \AA}$

$c = 13.2230 (4) \text{ \AA}$

$\beta = 115.386 (3)^\circ$

$V = 1151.67 (6) \text{ \AA}^3$

$Z = 4$

$F(000) = 584$

$D_x = 1.693 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$

Cell parameters from 2078 reflections

$\theta = 4.1\text{--}75.5^\circ$

$\mu = 8.40 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Plate, colourless

$0.28 \times 0.20 \times 0.09 \text{ mm}$

Data collection

Agilent SuperNova (Dual, Cu at zero, Atlas) diffractometer
 Radiation source: SuperNova (Cu) X-ray Source
 Mirror monochromator
 ω scans
 Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)
 $T_{\min} = 0.580$, $T_{\max} = 1.000$

4291 measured reflections
 2245 independent reflections
 2078 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.015$
 $\theta_{\max} = 73.5^\circ$, $\theta_{\min} = 4.1^\circ$
 $h = -13 \rightarrow 14$
 $k = -9 \rightarrow 6$
 $l = -16 \rightarrow 15$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.077$
 $S = 1.04$
 2245 reflections
 130 parameters
 0 restraints
 Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 0.4682P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.33 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.39 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXL2013 (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001x Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0048 (3)

Special details

Experimental. Absorption correction: CrysAlisPro (Agilent, 2014). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.85876 (18)	0.0661 (3)	0.22866 (16)	0.0377 (4)
C2	0.85637 (19)	0.1344 (3)	0.13058 (16)	0.0404 (4)
C3	0.9605 (2)	0.1405 (3)	0.11271 (19)	0.0495 (5)
H3	0.9581	0.1851	0.0468	0.059*
C4	1.0675 (2)	0.0794 (3)	0.1942 (2)	0.0523 (5)
C5	1.0726 (2)	0.0087 (3)	0.29241 (19)	0.0497 (5)
H5	1.1455	-0.0334	0.3465	0.060*
C6	0.96763 (19)	0.0022 (3)	0.30797 (17)	0.0440 (5)
H6	0.9699	-0.0460	0.3729	0.053*
C7	0.72784 (18)	0.1177 (3)	0.32603 (16)	0.0379 (4)
C8	0.5801 (3)	0.1471 (4)	0.4043 (2)	0.0638 (7)
H8A	0.5786	0.0517	0.4483	0.096*
H8B	0.5006	0.1978	0.3710	0.096*
H8C	0.6383	0.2278	0.4515	0.096*
C9	0.5176 (2)	0.0190 (4)	0.2169 (2)	0.0569 (6)
H9A	0.5032	0.0890	0.1533	0.085*
H9B	0.4443	0.0110	0.2274	0.085*

H9C	0.5416	-0.0913	0.2045	0.085*
Br1	0.70976 (2)	0.22178 (4)	0.01974 (2)	0.05768 (14)
Cl1	1.19895 (7)	0.08827 (15)	0.17270 (8)	0.0936 (3)
N1	0.74917 (15)	0.0536 (3)	0.24110 (14)	0.0442 (4)
H1	0.6901	-0.0001	0.1897	0.053*
N2	0.61441 (17)	0.0925 (3)	0.31655 (16)	0.0470 (4)
S1	0.83592 (5)	0.22395 (7)	0.43366 (4)	0.04637 (16)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0377 (9)	0.0420 (10)	0.0314 (9)	-0.0038 (8)	0.0129 (7)	-0.0039 (8)
C2	0.0436 (10)	0.0403 (10)	0.0335 (9)	-0.0009 (8)	0.0128 (8)	-0.0013 (8)
C3	0.0570 (13)	0.0531 (13)	0.0436 (11)	-0.0046 (10)	0.0264 (10)	0.0013 (10)
C4	0.0437 (11)	0.0644 (15)	0.0526 (12)	-0.0043 (10)	0.0242 (10)	-0.0078 (11)
C5	0.0395 (10)	0.0595 (14)	0.0420 (11)	0.0018 (9)	0.0098 (9)	-0.0050 (10)
C6	0.0451 (10)	0.0495 (12)	0.0327 (9)	0.0004 (9)	0.0123 (8)	0.0013 (8)
C7	0.0420 (10)	0.0375 (10)	0.0312 (9)	0.0047 (8)	0.0128 (8)	0.0048 (7)
C8	0.0684 (15)	0.0766 (18)	0.0611 (15)	0.0111 (14)	0.0416 (13)	0.0006 (13)
C9	0.0376 (10)	0.0679 (16)	0.0603 (14)	0.0018 (10)	0.0164 (10)	-0.0056 (12)
Br1	0.05856 (19)	0.0600 (2)	0.04035 (17)	0.01302 (11)	0.00771 (12)	0.00683 (10)
Cl1	0.0558 (4)	0.1432 (9)	0.0976 (6)	-0.0020 (4)	0.0480 (4)	-0.0011 (6)
N1	0.0376 (8)	0.0595 (11)	0.0339 (8)	-0.0088 (8)	0.0138 (7)	-0.0088 (8)
N2	0.0435 (9)	0.0547 (11)	0.0451 (9)	0.0054 (8)	0.0213 (8)	-0.0008 (8)
S1	0.0545 (3)	0.0447 (3)	0.0308 (3)	0.0000 (2)	0.0096 (2)	-0.00197 (19)

Geometric parameters (Å, °)

C1—C6	1.384 (3)	C7—N2	1.343 (3)
C1—C2	1.395 (3)	C7—N1	1.355 (3)
C1—N1	1.412 (3)	C7—S1	1.690 (2)
C2—C3	1.383 (3)	C8—N2	1.457 (3)
C2—Br1	1.887 (2)	C8—H8A	0.9600
C3—C4	1.372 (3)	C8—H8B	0.9600
C3—H3	0.9300	C8—H8C	0.9600
C4—C5	1.392 (3)	C9—N2	1.459 (3)
C4—Cl1	1.738 (2)	C9—H9A	0.9600
C5—C6	1.375 (3)	C9—H9B	0.9600
C5—H5	0.9300	C9—H9C	0.9600
C6—H6	0.9300	N1—H1	0.8600
C6—C1—C2	118.68 (18)	N1—C7—S1	122.03 (16)
C6—C1—N1	121.79 (18)	N2—C8—H8A	109.5
C2—C1—N1	119.39 (18)	N2—C8—H8B	109.5
C3—C2—C1	121.09 (19)	H8A—C8—H8B	109.5
C3—C2—Br1	118.76 (16)	N2—C8—H8C	109.5
C1—C2—Br1	120.14 (15)	H8A—C8—H8C	109.5
C4—C3—C2	118.7 (2)	H8B—C8—H8C	109.5

C4—C3—H3	120.7	N2—C9—H9A	109.5
C2—C3—H3	120.7	N2—C9—H9B	109.5
C3—C4—C5	121.6 (2)	H9A—C9—H9B	109.5
C3—C4—C11	118.89 (19)	N2—C9—H9C	109.5
C5—C4—C11	119.51 (19)	H9A—C9—H9C	109.5
C6—C5—C4	118.8 (2)	H9B—C9—H9C	109.5
C6—C5—H5	120.6	C7—N1—C1	126.45 (17)
C4—C5—H5	120.6	C7—N1—H1	116.8
C5—C6—C1	121.2 (2)	C1—N1—H1	116.8
C5—C6—H6	119.4	C7—N2—C8	120.9 (2)
C1—C6—H6	119.4	C7—N2—C9	122.72 (18)
N2—C7—N1	114.77 (18)	C8—N2—C9	116.3 (2)
N2—C7—S1	123.19 (16)		

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1...S1 ⁱ	0.86	2.67	3.3488 (19)	137
C9—H9B...C11 ⁱⁱ	0.96	2.81	3.696 (2)	153

Symmetry codes: (i) $-x+3/2, y-1/2, -z+1/2$; (ii) $x-1, y, z$.