

Received 4 January 2018

Accepted 19 January 2018

Edited by J. Simpson, University of Otago, New Zealand

**Keywords:** crystal structure; carbonylhydrazide; methylation; weak hydrogen bonds.**CCDC references:** 1818231; 1818230; 1818229; 1818228**Supporting information:** this article has supporting information at journals.iucr.org/e

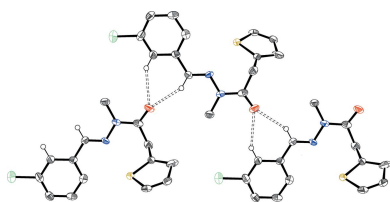
# Different packing motifs of isomeric (*E*)-*N'*-(halophenylmethylidene)-*N*-methyl-2-(thiophen-2-yl)acetohydrazides controlled by C—H···O interactions

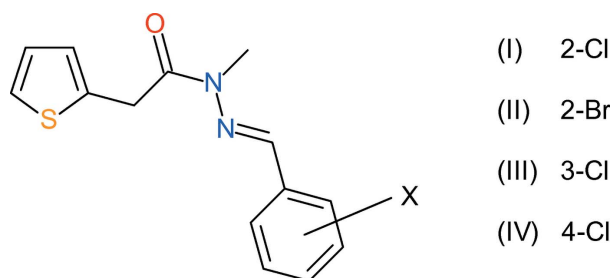
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The crystal structures of three isomeric (*E*)-*N'*-(chlorophenylmethylidene)-*N*-methyl-2-(thiophen-2-yl)acetohydrazides (C<sub>14</sub>H<sub>13</sub>ClN<sub>2</sub>OS) are described, with the Cl atom in *ortho* (I), *meta* (III) and *para* (IV) positions in the benzene ring. The *ortho*-bromo derivative (II) (C<sub>14</sub>H<sub>13</sub>BrN<sub>2</sub>OS), which is isostructural with its chloro congener (I), is also reported. Molecules (I)–(III) have similar conformations, which approximate to L-shapes, as indicated by their N—C—C—C<sub>t</sub> (t = thiophene) torsion angles of −90.1 (3), −91.44 (18) and −90.7 (9)°, respectively. The conformation of (IV) is different, with an equivalent torsion angle of −170.75 (11)° corresponding to a more extended shape for the molecule. The thiophene ring in each structure features 'flip' rotational disorder. The packing for (I) and (II) features inversion dimers, linked by pairs of C—H···O interactions, which generate R<sub>2</sub><sup>2</sup>(14) loops. In the crystal of (III), [010] C(8) chains arise, with adjacent molecules linked by pairs of C—H···O hydrogen bonds. The packing for (IV) features unusually short C—H···O interactions arising from an H atom attached to the benzene ring (H···O = 2.18 Å), which lead to C(9) [301] chains. Hirshfeld fingerprint percentage contact contributions are similar for the four title compounds.

## 1. Chemical context

We have reported the syntheses and anti-TB activities of acetamido derivatives, 2-(*R,R'*NCOCH<sub>2</sub>)-thiophene, *R* = alkyl (Nora de Souza *et al.*, 2008), and more recently thienyl acetohydrazide derivatives, 2-(ArCH=N—NHCOCH<sub>2</sub>)-thiophene (Cardoso *et al.*, 2014). We are now studying the related family of methylated 2-[ArCH=N—N(CH<sub>3</sub>)COCH<sub>2</sub>]-thiophene compounds, with different substituents attached to the benzene ring. The biological activities of these compounds will be reported elsewhere: here, we present the crystal structures of three isomeric chloro derivatives (and one bromo derivative) in this family bearing a halogen atom at different sites on the benzene ring, *viz.* (*E*)-*N'*-(2-chlorophenylmethylidene)-*N*-methyl-2-(thiophen-2-yl)acetohydrazide (I), (*E*)-*N'*-(2-bromophenylmethylidene)-*N*-methyl-2-(thiophen-2-yl)acetohydrazide (II), (*E*)-*N'*-(3-chlorophenylmethylidene)-*N*-methyl-2-(thiophen-2-yl)acetohydrazide (III) and (*E*)-*N'*-(4-chlorophenylmethylidene)-*N*-methyl-2-(thiophen-2-yl)acetohydrazide (IV). These complement our recent structural study (Cardoso *et al.*, 2016a) of isomeric *ortho*-, *meta*- and *para*-nitro derivatives in the same family.

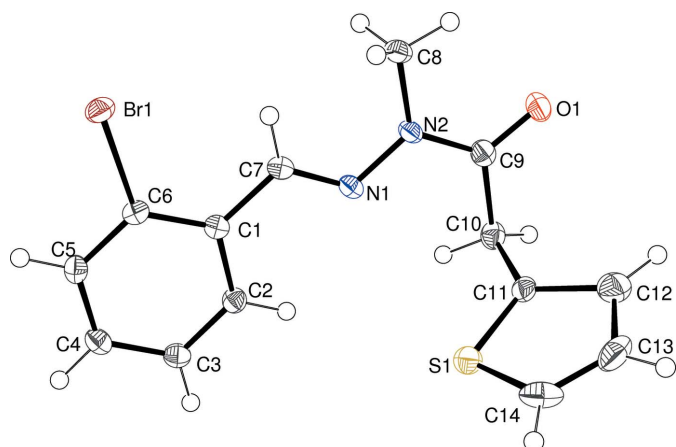




## 2. Structural commentary

The molecular structure of (I) is shown in Fig. 1, which indicates that the expected methylation has occurred at atom N2. The thiophene ring (S1/C11–C14) shows ‘flip’ disorder (compare, for example, Sonar *et al.*, 2005; Wagner *et al.*, 2006) over two conformations rotated by  $\sim 180^\circ$  about the C10–C11 bond in a 0.658 (4):0.342 (4) ratio: the major orientation has the S atom pointing towards the C1–C6 benzene ring at the other end of the molecule. The dihedral angle between the thiophene and benzene rings is  $77.92(8)^\circ$ . The central CH=N–N(CH<sub>3</sub>)–C(=O) fragment (C7/C8/C9/N1/N2/O1) in (I) is almost planar (r.m.s. deviation = 0.013 Å) and subtends dihedral angles of  $0.89(12)^\circ$  and  $78.80(9)^\circ$  with the benzene and thiophene rings, respectively. Thus, the major twist in the molecule occurs about the C9–C10 bond [N2–C9–C10–C11 =  $-90.1(3)^\circ$ ], giving the molecule an approximate overall L-shape. The N1–N2 bond length of 1.372 (3) Å is significantly shortened compared to the reference value of  $\sim 1.41$  Å for an isolated N–N single bond and the C9–N2 amide bond of 1.377 (3) Å is clearly lengthened: these data can be interpreted in terms of significant delocalization of electrons over the methyldene–acetohydrazide group.

Compound (II) (Fig. 2) is isostructural with (I); comparable geometrical data are as follows: C1–C6 benzene ring = ‘A’, thiophene ring = ‘B’ [disorder occupancies =

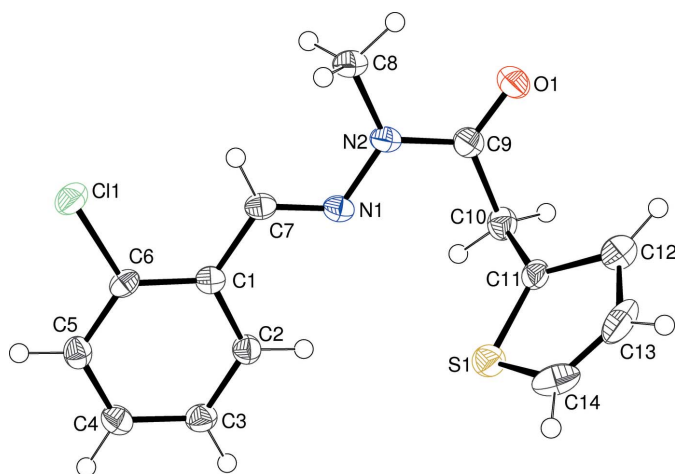


**Figure 2**

The molecular structure of (II), showing 50% probability displacement ellipsoids. Only the major orientation of the thiophene ring is shown.

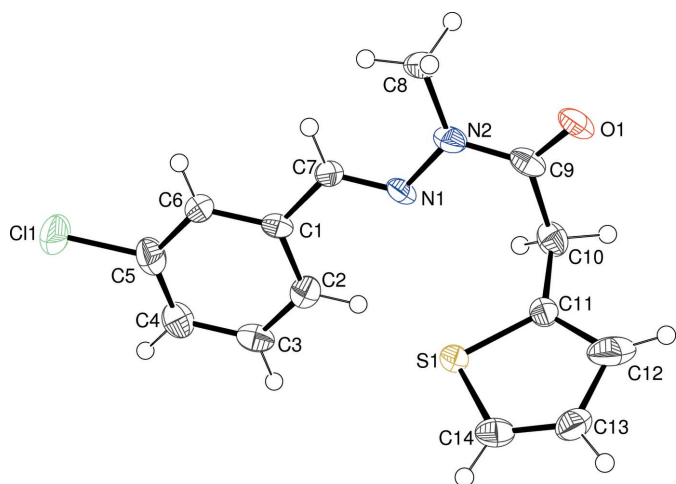
0.677 (3):0.323 (3)], linking chain (r.m.s. deviation = 0.009 Å) = ‘C’; dihedral angles A/B, A/C and B/C =  $75.89(5)^\circ$ ,  $1.53(8)^\circ$  and  $77.37(6)^\circ$ , respectively; N2–C9–C10–C11 =  $-91.44(18)^\circ$ , N1–N2 = 1.3720 (19) Å and C9–N2 = 1.375 (2) Å. These data are very similar to the corresponding values for (I); the only significant (and expected) difference is the C6–Br1 bond length of 1.9064 (16) Å in (II) compared to the C6–Cl1 distance of 1.748 (3) Å in (I).

The molecular structure of (III) can be seen in Fig. 3: again the methylation of N2 has occurred as expected. The dihedral angle between the thiophene ring [rotationally disordered over two orientations in a 0.81 (1):0.19 (1) ratio] and the C1–C6 benzene ring is  $66.0(2)^\circ$ . The approximately planar central C7/C8/C9/N1/N2/O1 group in (II) (r.m.s. deviation = 0.043 Å) subtends dihedral angles of  $5.9(5)^\circ$  with the benzene ring and  $62.9(3)^\circ$  with the thiophene ring. As in (I) and (II), the major twist occurs about the C9–C10 bond [N2–C9–C10–C11 =  $-90.7(9)^\circ$ ], giving the molecule an approximate overall L-shape. The N1–N2 and C9–N2 bond lengths in (III) are



**Figure 1**

The molecular structure of (I), showing 50% probability displacement ellipsoids. Only the major orientation of the thiophene ring is shown.



**Figure 3**

The molecular structure of (III), showing 50% probability displacement ellipsoids. Only the major orientation of the thiophene ring is shown.

**Table 1**

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

Cg1 is the centroid of the thiophene ring, Cg2 is the centroid of the benzene ring.

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C13–H13···O1 <sup>i</sup>	0.95	2.54	3.410 (4)	153
C3–H3···Cg1 <sup>ii</sup>	0.95	2.83	3.612 (3)	140
C8–H8A···Cg2 <sup>iii</sup>	0.98	2.71	3.544 (3)	144

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

**Table 2**

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

Cg1 is the centroid of the thiophene ring, Cg2 is the centroid of the benzene ring.

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C13–H13···O1 <sup>i</sup>	0.95	2.53	3.424 (2)	156
C3–H3···Cg1 <sup>ii</sup>	0.95	2.82	3.6021 (18)	141
C8–H8A···Cg2 <sup>iii</sup>	0.98	2.67	3.495 (2)	142

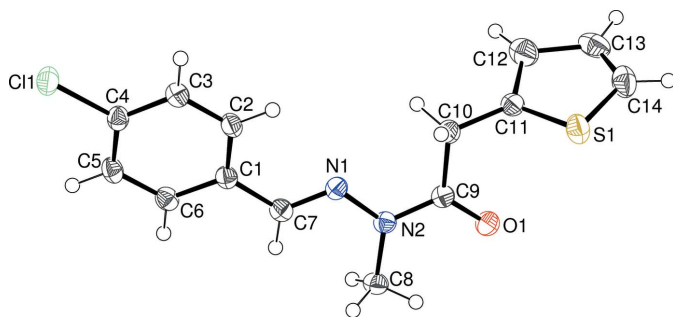
 Symmetry codes: (i)  $-x + 1, -y, -z$ ; (ii)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (iii)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ .

1.379 (9) and 1.363 (11) Å, respectively, which again can be ascribed to electronic effects.

As with the other compounds, (IV) is methylated at N2 (Fig. 4) and has a disordered thiophene ring [major/minor disorder components = 0.671 (2):0.329 (2)]. The dihedral angles between the benzene ring 'A', thiophene ring 'B' and CH=N–N(CH<sub>3</sub>)–C(=O)–CH<sub>2</sub> fragment 'C' (r.m.s. deviation = 0.031 Å), are *A/B* = 81.82 (4), *A/C* = 14.79 (4) and *B/C* = 69.70 (5)°. These are roughly consistent with the equivalent data for (I)–(III), but the conformation of (IV) is definitely different, as indicated by the N2–C9–C10–C11 torsion angle of  $-170.75$  (11)°: this reflects the fact that the thiophene ring points away from the rest of the molecule. Bond-length data [N1–N2 = 1.3778 (14) Å and C9–N2 = 1.3693 (16) Å] within the methyldene–acetohydrazide group for (IV) are consistent with the equivalent data for (I), (II) and (III).

### 3. Supramolecular features

The packing motifs in (I) and (II) feature inversion dimers linked by pairs of C–H···O interactions (Fig. 5; Tables 1 and


**Figure 4**

The molecular structure of (IV), showing 50% probability displacement ellipsoids. Only the major orientation of the thiophene ring is shown.

**Table 3**

Hydrogen-bond geometry (Å, °) for (III).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C6–H6···O1 <sup>i</sup>	0.95	2.62	3.474 (9)	150
C7–H7···O1 <sup>i</sup>	0.95	2.52	3.381 (9)	152
C12–H12···Cl1 <sup>ii</sup>	0.95	2.83	3.415 (7)	121

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

**Table 4**

Hydrogen-bond geometry (Å, °) for (IV).

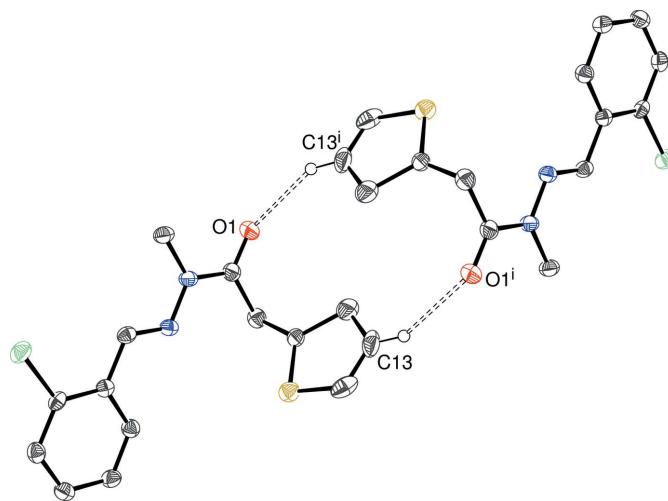
Cg1 is the centroid of the benzene ring.

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C5–H5···O1 <sup>i</sup>	0.95	2.18	3.1250 (15)	172
C3–H3···Cl1 <sup>ii</sup>	0.95	2.95	3.8044 (14)	151
C12–H12···Cl1 <sup>iii</sup>	0.95	2.98	3.7960 (10)	145
C8–H8C···Cg1 <sup>iv</sup>	0.98	2.73	3.5592 (14)	142

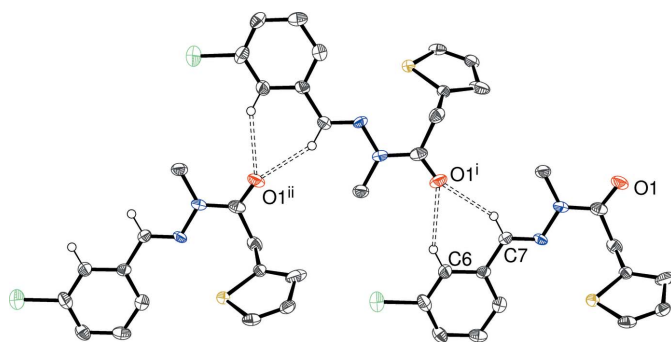
 Symmetry codes: (i)  $x - \frac{3}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (ii)  $-x, -y, -z$ ; (iii)  $x + 1, y, z + 1$ ; (iv)  $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ .

2), with the C–H grouping part of the thiophene ring: this generates an  $R_2^2(14)$  loop. Weak C–H··· $\pi$  interactions consolidate the structures, but there are no aromatic  $\pi$ – $\pi$  stacking interactions [minimum centroid–centroid separation = 4.86 Å for (I) and 4.85 Å for (II)].

The packing in (III) features two C–H···O interactions (Table 3) arising from benzene and adjacent methine C–H groups, which link the molecules into [010] chains (Fig. 6), with adjacent molecules in the chain related by the  $2_1$  screw axis in the *b* direction. The C6 interaction is long, but deemed to be just significant, as it is consolidating the C7 bond. Individually, each C–H···O bond generates a  $C(8)$  chain; collectively  $R_2^1(6)$  loops arise. A very weak C–H···Cl bond is also observed. There are no C–H··· $\pi$  contacts in (III) and we consider that the shortest ring–centroid separation of


**Figure 5**

An inversion dimer in the crystal of (I) linked by a pair of C–H···O interactions. [Symmetry code: (i)  $-x, -y, 1 - z$ .] All H atoms except H13 have been omitted for clarity.

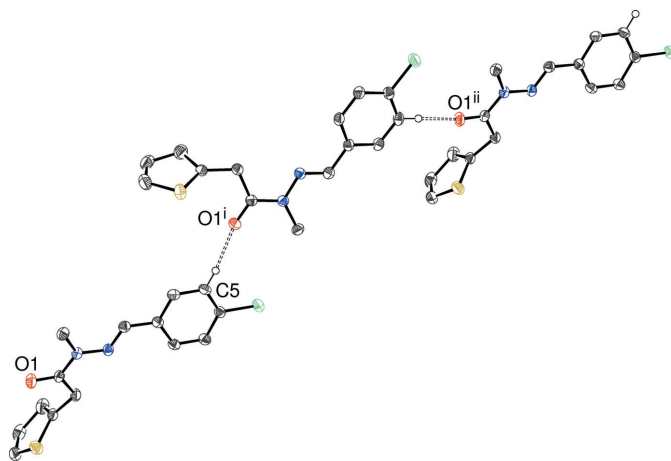


**Figure 6**  
Fragment of an [010] hydrogen-bonded chain in the crystal of (III). [Symmetry codes: (i)  $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (ii)  $x, y - 1, z$ .] All H atoms except H6 and H7 have been omitted for clarity.

4.219 (5) Å is far too long to be regarded as a bonding interaction.

In the crystal of (IV), an unusually short C–H...O interaction (Table 4) with H...O = 2.18 Å leads to C(9) chains (Fig. 7) propagating in the [301] direction. The acceptor O atom deviates from the plane of C11/C4/C5/H5 by 0.239 (6) Å. One reason for the short contact could be the presence of the adjacent electron-withdrawing Cl substituent, which will tend to ‘activate’ the H atom (Steiner, 1996). Two extremely weak C–H...Cl interactions and a C–H... $\pi$  contact occur, but there is no  $\pi$ – $\pi$  stacking (minimum centroid–centroid separation = 4.42 Å) in the crystal of (IV).

Hirshfeld surface fingerprint plots for (I)–(IV) (supplementary Figs. 1–4) were calculated with *CrystalExplorer17* (Turner *et al.*, 2017) and percentage contact-surface contributions (McKinnon *et al.*, 2007) are listed in Table 5. As might be expected, the percentage contact data for the isomeric (I) and (II) are very similar but it is interesting that the data for (III) and (IV) barely differ from those of the first two compounds, despite their different crystal structures: in every case H...H contacts dominate the packing. This is quite



**Figure 7**  
Fragment of a [301] hydrogen-bonded chain in the crystal of (IV). [Symmetry codes: (i)  $x - \frac{3}{2}, \frac{1}{2} - y, z - \frac{1}{2}$ ; (ii)  $x - 3, y, z - 1$ .] All H atoms except H5 have been omitted for clarity.

**Table 5**  
Hirshfeld contact interactions (%).

Contact type	(I)	(II)	(III)	(IV)
H...H	43.6	43.0	38.5	41.5
C...H/H...C	21.3	20.8	18.1	23.5
Hal...H/H...Hal	12.5	13.0	15.2	16.0
O...H/H...O	9.4	9.6	9.7	7.1
C...C	2.5	2.4	4.7	1.6
N...H/H...N	1.4	1.3	3.9	3.3
S...H/H...S	1.9	1.8	2.9	2.0

different to the recently reported (*E*)-*N'*-(3-cyanorophenylmethylidene)-*N*-methyl-2-(thiophen-2-yl)acetohydrazide (V) and (*E*)-*N'*-(4-methoxyphenylmethylidene)-*N*-methyl-2-(thiophen-2-yl)acetohydrazide (VI) (Cardoso *et al.*, 2017), where the percentage contributions of the different intermolecular contacts to the fingerprint plots differ by up to 20%.

#### 4. Database survey

A survey of the Cambridge Structural Database (Groom *et al.*, 2016) updated to June 2017 for the common central –CH=N–N(CH<sub>3</sub>)–C(=O)–CH<sub>2</sub>– fragment of the title compounds revealed seven matches, *viz.* ALAHEC (Cardoso *et al.*, 2016b); FOTMUX (Ramírez *et al.*, 2009a); KULREP (Ramírez *et al.*, 2009b); OFEBIL (Cao *et al.*, 2007), and EYUBAD, EYUBEH and EYUBIL; this latter trio of recodes correspond to the three isomeric nitro compounds (Cardoso *et al.*, 2016a) noted in the *Chemical Context* section above. To this list will soon be added the structures of (V) and (VI) noted above.

#### 5. Synthesis and crystallization

The appropriate thienyl acetohydrazide derivative (Cardoso *et al.*, 2014) (0.20 g, 1.0 equiv.) was suspended in acetone (5 ml) and potassium carbonate (4.0 equiv.) was added. The reaction mixture was stirred at room temperature for 30 min. and methyl iodide (4.0 equiv.) was added. The reaction mixture was maintained at 313 K, until thin-layer chromatography indicated the reaction was complete. The mixture was then rotary evaporated to leave a residue, which was dissolved in water (20 ml) and extracted with ethyl acetate (3 × 10 ml). The organic fractions were combined, dried with anhydrous MgSO<sub>4</sub>, filtered and the solvent evaporated at reduced pressure. The crystals used for the intensity data collections were recrystallized from methanol solution.

(*E*)-*N'*-(2-Chlorophenylmethylidene)-*N*-methyl-2-(thiophen-2-yl)acetohydrazide (I); yield: 66%; yellow solid; m.p. 91–92 °C. <sup>1</sup>H NMR (400 MHz; DMSO):  $\delta$  8.10–8.08 (2H; *m*; H-11' and N=CH), 7.57–7.54 (1H; *m*; H-8'), 7.47–7.44 (2H; *m*; H-9' and H-10'), 7.36 (1H; *dd*;  $J_{\text{HH}} = 4.1$  and 1.0 Hz; H-5), 6.98–6.97 (1H; *m*; H-4), 6.96–6.94 (1H; *m*; H-3), 4.39 (2H; *s*; CH<sub>2</sub>), 3.36 (3H; *s*; N-CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz; DMSO):  $\delta$  171.0 (C=O), 136.9 (N=CH), 135.8 (C-2), 133.2 (C-6'), 131.6 (C-7'), 131.1 (C-9'), 129.9 (C-8'), 127.6 (C-11'), 127.2 (C-10'), 126.7 (C-3),

**Table 6**  
Experimental details.

	(I)	(II)	(III)	(IV)
Crystal data				
Chemical formula	C <sub>14</sub> H <sub>13</sub> ClN <sub>2</sub> OS	C <sub>14</sub> H <sub>13</sub> BrN <sub>2</sub> OS	C <sub>14</sub> H <sub>13</sub> ClN <sub>2</sub> OS	C <sub>14</sub> H <sub>13</sub> ClN <sub>2</sub> OS
<i>M<sub>r</sub></i>	292.77	337.23	292.77	292.77
Crystal system, space group	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i>	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i>	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>
Temperature (K)	100	100	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.1918 (7), 20.3575 (14), 7.2721 (5)	9.4479 (7), 20.2175 (14), 7.2552 (5)	4.2194 (2), 13.0131 (9), 25.0758 (18)	6.7454 (5), 20.2993 (14), 10.1592 (7)
β (°)	96.360 (2)	96.9343 (13)	93.752 (4)	97.510 (2)
<i>V</i> (Å <sup>3</sup> )	1352.40 (17)	1375.70 (17)	1373.90 (15)	1379.14 (17)
<i>Z</i>	4	4	4	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm <sup>-1</sup> )	0.43	3.13	0.42	0.42
Crystal size (mm)	0.53 × 0.24 × 0.18	0.26 × 0.06 × 0.05	0.22 × 0.01 × 0.01	0.30 × 0.17 × 0.10
Data collection				
Diffractometer	Rigaku Mercury CCD	Rigaku Mercury CCD	Rigaku Mercury CCD	Rigaku Mercury CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2004)	Multi-scan ( <i>SADABS</i> ; Bruker, 2004)	Multi-scan ( <i>SADABS</i> ; Bruker, 2004)	Multi-scan ( <i>SADABS</i> ; Bruker, 2004)
<i>T</i> <sub>min</sub> – <i>T</i> <sub>max</sub>	0.710, 1.000	0.756, 1.000	0.615, 1.000	0.843, 1.000
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	18992, 2988, 2553	14778, 3163, 2897	12868, 3121, 1766	14763, 3165, 2929
<i>R</i> <sub>int</sub>	0.032	0.040	0.127	0.033
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.649	0.650	0.648	0.650
Refinement				
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.052, 0.117, 1.22	0.025, 0.064, 1.06	0.116, 0.297, 1.16	0.033, 0.091, 1.05
No. of reflections	2988	3163	3121	3165
No. of parameters	175	174	184	174
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.37, -0.41	0.48, -0.43	1.00, -0.45	0.53, -0.40

Computer programs: *CrystalClear* (Rigaku, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3* (Farrugia, 1997) and *publCIF* (Westrip, 2010).

126.5 (C-4), 125.2 (C-5), 34.2 (N-CH<sub>3</sub>), 28.0 (CH<sub>2</sub>). MS/ESI: [*M* + Na]: 315. IR ν<sub>max</sub> (cm<sup>-1</sup>; KBr pellet): 1680 (C=O); 3689 (N-CH<sub>3</sub>).

(*E*)-*N'*-(2-Bromophenylmethylidene)-*N*-methyl-2-(thiophen-2-yl)acetohydrazide (II); yield: 70%; yellow solid; m.p. 87–88 °C. <sup>1</sup>H NMR (400 MHz; DMSO): δ 8.07 (1H; *dd*; *J*<sub>HH</sub> = 7.6 and 1.6 Hz; H-11'), 8.03 (1H; *s*; N=CH), 7.72 (1H; *dd*; *J*<sub>HH</sub> = 8.0 and 0.8 Hz; H-8'), 7.49 (1H; *t*; *J*<sub>HH</sub> = 7.6 Hz; H-10'), 7.39–7.35 (2H; *m*; H-9' and H-5), 6.98–6.94 (2H; *m*; H-3 and H-4), 4.39 (2H; *s*; CH<sub>2</sub>), 3.36 (3H; *s*; N-CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz; DMSO): δ 171.0 (C=O), 138.1 (N=CH), 136.9 (C-2), 133.2 (C-6'), 133.0 (C-8'), 131.4 (C-9'), 128.1 (C-3), 127.6 (C-10' and C-11'), 126.7 (C-4), 125.2 (C-5), 123.5 (C-7'), 34.2 (N-CH<sub>3</sub>), 28.0 (CH<sub>2</sub>). MS/ESI: [*M* + Na]: 359. IR ν<sub>max</sub> (cm<sup>-1</sup>; KBr pellet): 1680 (C=O); 3676 (N-CH<sub>3</sub>).

(*E*)-*N'*-(3-Chlorophenylmethylidene)-*N*-methyl-2-(thiophen-2-yl)acetohydrazide (III); yield: 64%; yellow solid; m.p. 120–121 °C. <sup>1</sup>H NMR (500 MHz, DMSO): δ 7.97 (1H; *s*; CH=N), 7.80 (2H; *d*; *J*<sub>HH</sub> = 9.0 Hz; C<sub>6</sub>H<sub>6</sub>), 7.50 (2H; *d*; *J*<sub>HH</sub> = 8.5 Hz; C<sub>6</sub>H<sub>6</sub>), 7.30 (1H; *dd*; *J*<sub>HH</sub> = 5.5 and 1.5 Hz; H-5), 6.97 (1H; *d*; *J*<sub>HH</sub> = 2.5 Hz; H-3), 6.94–6.93 (1H; *m*; H-4), 4.37 (2H; *s*; CH<sub>2</sub>), 3.34 (3H; *s*; CH<sub>3</sub>). <sup>13</sup>C NMR (500 MHz, DMSO): δ 170.3 (C-2'), 138.8 (CH=N), 136.7 (C-2), 133.7 (phenyl), 133.3 (phenyl), 128.3 (phenyl), 128.2 (C<sub>6</sub>H<sub>6</sub>), 126.0 (C-4), 125.9 (C-3), 124.3 (C-5), 33.8 (CH<sub>3</sub>), 27.6 (CH<sub>2</sub>). IR ν<sub>max</sub> (cm<sup>-1</sup>; KBr pellet): 1681 (C=O); 3715 (N-CH<sub>3</sub>).

(*E*)-*N'*-(4-Chlorophenylmethylidene)-*N*-methyl-2-(thiophen-2-yl)acetohydrazide (IV); yield: 55%; yellow solid; m.p. 121–122 °C. <sup>1</sup>H NMR (400 MHz; DMSO): δ 8.00 (1H; *s*; N=CH), 7.84 (2H; *d*; *J*<sub>HH</sub> = 8.4 Hz; H-7' and H-11'), 7.54 (2H; *d*; *J*<sub>HH</sub> = 8.4 Hz; H-8' and H-10'), 7.35 (1H; *dd*; *J*<sub>HH</sub> = 4.8 and 0.8 Hz; H-5), 6.98–6.93 (2H; *m*; H-3 and H-4), 4.36 (2H; *s*; CH<sub>2</sub>), 3.32 (3H; *s*; N-CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz; DMSO): δ 170.7 (C=O), 139.4 (N=CH), 137.0 (C-2), 134.1 (C-9'), 133.6 (C-6'), 128.8 (C-7' and C-11'), 128.7 (C-8' and C-10'), 126.6 (C-3), 126.5 (C-4), 125.1 (C-5), 34.2 (N-CH<sub>3</sub>), 28.0 (CH<sub>2</sub>). MS/ESI: [*M* + Na]: 315. IR ν<sub>max</sub> (cm<sup>-1</sup>; KBr pellet): 1680 (C=O); 3689 (N-CH<sub>3</sub>).

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 6. H atoms were placed geometrically (C–H = 0.95–1.00 Å) and refined as riding atoms. The constraint *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(carrier) or 1.5*U*<sub>eq</sub>(methyl) was applied in all cases. The *N*-methyl group was allowed to rotate, but not to tip, to best fit the electron density (AFIX 137 instruction in *SHELXL*; Sheldrick, 2015); in every case, this group rotated from its initial calculated orientation to minimize steric interaction with H7; the final optimized geometry leads to a short (H···O ~ 2.35 Å) intramolecular C8–H···O1 contact but we do not regard this as a bond. The thiophene rings show ~180° 'flip' rotational disorder about the C10–



C11 bond for all compounds. The crystal of (III) used for data collection was small and data quality was poor. In the refinement, difference maps indicated significant unmodelled electron density in the vicinity of C4. This was modelled in terms of a minor impurity/disorder component with the Cl atom bonded to C4 rather than C3. Even after the disorder modelling, the residuals are high, but we deem the refinement to be acceptable in terms of its chemical information content.

### Acknowledgements

We thank the EPSRC National Crystallography Service (University of Southampton) for the X-ray data collections.

### References

- Bruker (2004). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cao, X.-Y., Harrowfield, J., Nitschke, J., Ramírez, J., Stadler, A.-M., Kyritsakas-Gruber, N., Madalan, A., Rissanen, K., Russo, L., Vaughan, G. & Lehn, J.-M. (2007). *Eur. J. Inorg. Chem.* pp. 2944–2965.
- Cardoso, L. N. F., Bispo, M. L. F., Kaiser, C. R., Wardell, J. L., Wardell, S. M. S. V., Lourenço, M. C. S. S., Bezerra, F. A. F., Soares, R. P. P., Rocha, M. N. & de Souza, M. V. N. (2014). *Arch. Pharm. Chem. Life Sci.* **347**, 432–448.
- Cardoso, L. N. F., Nogueira, T. C. M., Kaiser, C. R., Wardell, J. L., de Souza, M. V. N. & Harrison, W. T. A. (2017). *Acta Cryst.* **E73**, 1636–1641.
- Cardoso, L. N. F., Nogueira, T. C. M., Kaiser, C. R., Wardell, J. L., de Souza, M. V. N., Lancaster, S. T. & Harrison, W. T. A. (2016a). *Acta Cryst.* **E72**, 1677–1682.
- Cardoso, L. N. F., Nogueira, T. C. M., Kaiser, C. R., Wardell, J. L., Wardell, S. M. S. V. & de Souza, M. V. N. (2016b). *Z. Kristallogr.* **231**, 167–187.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814.
- Nora de Souza, M., Ferreira, M. L., Mendonca Nogueira, T., Borges Goncalves, R., Peralta, M. A., Silva Lourenco, M. & Vicente, F. R. (2008). *Lett. Drug. Des. Discov.* **5**, 221–224.
- Ramírez, J., Brelot, L., Osinska, I. & Stadler, A.-M. (2009b). *J. Mol. Struct.* **931**, 20–24.
- Ramírez, J., Stadler, A.-M., Rogez, G., Drillon, M. & Lehn, J.-M. (2009a). *Inorg. Chem.* **48**, 2456–2463.
- Rigaku (2012). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Sonar, V. N., Parkin, S. & Crooks, P. A. (2005). *Acta Cryst.* **E61**, o933–o935.
- Steiner, T. (1996). *Crystallogr. Rev.* **6**, 1–51.
- Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. University of Western Australia; <http://hirshfeldsurface.net>.
- Wagner, P., Officer, D. L. & Kubicki, M. (2006). *Acta Cryst.* **E62**, o5931–o5932.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

## supporting information

*Acta Cryst.* (2018). E74, 313-318 [https://doi.org/10.1107/S2056989018001251]

## Different packing motifs of isomeric (*E*)-*N'*-(halophenylmethylidene)-*N*-methyl-2-(thiophen-2-yl)acetohydrazides controlled by C—H $\cdots$ O interactions

Laura N. F. Cardoso, Thais C. M. Nogueira, James L. Wardell, Marcus V. N. de Souza and William T. A. Harrison

### Computing details

For all structures, data collection: *CrystalClear* (Rigaku, 2012); cell refinement: *CrystalClear* (Rigaku, 2012); data reduction: *CrystalClear* (Rigaku, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### (*E*)-*N'*-(2-Chlorophenylmethylidene)-*N*-methyl-2-(thiophen-2-yl)acetohydrazide (I)

#### Crystal data

C<sub>14</sub>H<sub>13</sub>ClN<sub>2</sub>OS

*M<sub>r</sub>* = 292.77

Monoclinic, *P*2<sub>1</sub>/*c*

*a* = 9.1918 (7) Å

*b* = 20.3575 (14) Å

*c* = 7.2721 (5) Å

$\beta$  = 96.360 (2)°

*V* = 1352.40 (17) Å<sup>3</sup>

*Z* = 4

*F*(000) = 608

*D<sub>x</sub>* = 1.438 Mg m<sup>-3</sup>

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

Cell parameters from 18890 reflections

$\theta$  = 2.0–27.5°

$\mu$  = 0.43 mm<sup>-1</sup>

*T* = 100 K

Block, colourless

0.53 × 0.24 × 0.18 mm

#### Data collection

Rigaku Mercury CCD  
diffractometer

$\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2004)

*T<sub>min</sub>* = 0.710, *T<sub>max</sub>* = 1.000

18992 measured reflections

2988 independent reflections

2553 reflections with *I* > 2 $\sigma$ (*I*)

*R<sub>int</sub>* = 0.032

$\theta_{\max}$  = 27.5°,  $\theta_{\min}$  = 2.2°

*h* = -11→11

*k* = -26→26

*l* = -9→9

#### Refinement

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

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.052

*wR*(*F*<sup>2</sup>) = 0.117

*S* = 1.22

2988 reflections

175 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

*w* = 1/[ $\sigma^2(F_o^2) + (0.0254P)^2 + 1.9705P$ ]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

( $\Delta/\sigma$ )<sub>max</sub> < 0.001

$\Delta\rho_{\max}$  = 0.37 e Å<sup>-3</sup>

$$\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL-2014/7  
(Sheldrick 2015),  
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$   
Extinction coefficient: 0.0035 (9)

### Special details

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

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.4009 (3)	0.30066 (11)	0.2999 (3)	0.0205 (5)	
C2	0.2682 (3)	0.32749 (12)	0.2216 (4)	0.0238 (5)	
H2	0.1913	0.2989	0.1741	0.029*	
C3	0.2462 (3)	0.39464 (12)	0.2116 (4)	0.0261 (5)	
H3	0.1551	0.4117	0.1578	0.031*	
C4	0.3576 (3)	0.43717 (12)	0.2804 (4)	0.0264 (6)	
H4	0.3421	0.4833	0.2749	0.032*	
C5	0.4909 (3)	0.41239 (12)	0.3568 (3)	0.0249 (5)	
H5	0.5680	0.4413	0.4017	0.030*	
C6	0.5107 (3)	0.34485 (12)	0.3669 (3)	0.0216 (5)	
C7	0.4218 (3)	0.22913 (11)	0.3101 (3)	0.0219 (5)	
H7	0.5122	0.2109	0.3624	0.026*	
C8	0.4721 (3)	0.09617 (12)	0.3393 (4)	0.0264 (5)	
H8A	0.4937	0.1124	0.4663	0.040*	
H8B	0.5519	0.1084	0.2671	0.040*	
H8C	0.4625	0.0482	0.3408	0.040*	
C9	0.2211 (3)	0.08562 (12)	0.1850 (4)	0.0250 (5)	
C10	0.0768 (3)	0.11842 (12)	0.1155 (4)	0.0273 (6)	
H10A	0.0953	0.1628	0.0676	0.033*	
H10B	0.0252	0.0923	0.0136	0.033*	
C11	-0.0155 (3)	0.12331 (12)	0.2724 (4)	0.0242 (5)	
C12	-0.08888 (16)	0.06244 (7)	0.3623 (2)	0.0380 (5)	0.658 (4)
H12	-0.0897	0.0174	0.3275	0.046*	0.658 (4)
S1A	-0.08888 (16)	0.06244 (7)	0.3623 (2)	0.0380 (5)	0.342 (4)
C13	-0.1560 (3)	0.09474 (17)	0.5151 (5)	0.0457 (9)	
H13	-0.2067	0.0702	0.5989	0.055*	
C14	-0.1418 (3)	0.16036 (16)	0.5300 (4)	0.0382 (7)	
H14	-0.1818	0.1853	0.6227	0.046*	
N1	0.3152 (2)	0.19186 (9)	0.2469 (3)	0.0214 (4)	
N2	0.3356 (2)	0.12514 (9)	0.2554 (3)	0.0230 (4)	
O1	0.2336 (2)	0.02600 (9)	0.1856 (3)	0.0337 (5)	
Cl1	0.67905 (7)	0.31638 (3)	0.47232 (10)	0.03056 (18)	
S1	-0.04886 (10)	0.19336 (4)	0.37322 (13)	0.0294 (3)	0.658 (4)
C12A	-0.04886 (10)	0.19336 (4)	0.37322 (13)	0.0294 (3)	0.342 (4)
H12A	-0.0232	0.2375	0.3490	0.035*	0.342 (4)



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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0228 (13)	0.0230 (11)	0.0163 (11)	0.0015 (9)	0.0041 (9)	0.0001 (8)
C2	0.0236 (13)	0.0232 (12)	0.0245 (13)	-0.0008 (9)	0.0014 (10)	-0.0001 (9)
C3	0.0240 (13)	0.0255 (12)	0.0285 (14)	0.0041 (9)	0.0020 (11)	0.0030 (10)
C4	0.0313 (14)	0.0212 (11)	0.0271 (14)	0.0010 (10)	0.0049 (11)	0.0015 (9)
C5	0.0263 (14)	0.0259 (12)	0.0231 (13)	-0.0046 (9)	0.0059 (11)	-0.0019 (9)
C6	0.0177 (12)	0.0288 (12)	0.0187 (12)	0.0019 (9)	0.0039 (10)	0.0005 (9)
C7	0.0227 (13)	0.0240 (12)	0.0196 (12)	0.0042 (9)	0.0045 (10)	0.0007 (9)
C8	0.0264 (14)	0.0255 (12)	0.0276 (14)	0.0070 (10)	0.0046 (11)	0.0036 (10)
C9	0.0274 (14)	0.0244 (12)	0.0244 (13)	0.0000 (9)	0.0080 (11)	0.0007 (9)
C10	0.0264 (14)	0.0279 (12)	0.0268 (14)	-0.0028 (10)	-0.0006 (11)	0.0007 (10)
C11	0.0180 (12)	0.0245 (12)	0.0290 (14)	-0.0007 (9)	-0.0023 (10)	0.0032 (9)
C12	0.0284 (8)	0.0372 (8)	0.0476 (10)	0.0021 (6)	0.0006 (7)	-0.0009 (6)
S1A	0.0284 (8)	0.0372 (8)	0.0476 (10)	0.0021 (6)	0.0006 (7)	-0.0009 (6)
C13	0.0185 (15)	0.058 (2)	0.060 (2)	-0.0021 (12)	0.0017 (14)	0.0294 (16)
C14	0.0324 (16)	0.0531 (18)	0.0287 (16)	0.0180 (13)	0.0023 (13)	0.0023 (12)
N1	0.0252 (11)	0.0203 (9)	0.0193 (10)	0.0035 (8)	0.0053 (8)	0.0014 (7)
N2	0.0249 (11)	0.0198 (10)	0.0249 (11)	0.0045 (8)	0.0049 (9)	0.0016 (8)
O1	0.0355 (12)	0.0219 (9)	0.0453 (12)	-0.0006 (7)	0.0115 (9)	0.0001 (8)
Cl1	0.0200 (3)	0.0360 (3)	0.0346 (4)	0.0024 (2)	-0.0017 (3)	-0.0010 (3)
S1	0.0278 (5)	0.0300 (5)	0.0302 (5)	0.0010 (3)	0.0021 (4)	-0.0037 (3)
C12A	0.0278 (5)	0.0300 (5)	0.0302 (5)	0.0010 (3)	0.0021 (4)	-0.0037 (3)

*Geometric parameters (Å, °)*

C1—C6	1.399 (3)	C9—N2	1.378 (3)
C1—C2	1.399 (3)	C9—C10	1.520 (4)
C1—C7	1.469 (3)	C10—C11	1.499 (4)
C2—C3	1.383 (3)	C10—H10A	0.9900
C2—H2	0.9500	C10—H10B	0.9900
C3—C4	1.391 (4)	C11—S1A	1.586 (3)
C3—H3	0.9500	C11—C12	1.586 (3)
C4—C5	1.383 (4)	C11—C12A	1.648 (3)
C4—H4	0.9500	C11—S1	1.648 (3)
C5—C6	1.388 (3)	C12—C13	1.483 (4)
C5—H5	0.9500	C12—H12	0.9500
C6—C11	1.748 (3)	S1A—C13	1.483 (4)
C7—N1	1.283 (3)	C13—C14	1.345 (5)
C7—H7	0.9500	C13—H13	0.9500
C8—N2	1.457 (3)	C14—C12A	1.642 (3)
C8—H8A	0.9800	C14—S1	1.642 (3)
C8—H8B	0.9800	C14—H14	0.9500
C8—H8C	0.9800	N1—N2	1.372 (3)
C9—O1	1.219 (3)	C12A—H12A	0.9500
C6—C1—C2	117.0 (2)	C11—C10—H10A	109.9

C6—C1—C7	122.3 (2)	C9—C10—H10A	109.9
C2—C1—C7	120.7 (2)	C11—C10—H10B	109.9
C3—C2—C1	121.6 (2)	C9—C10—H10B	109.9
C3—C2—H2	119.2	H10A—C10—H10B	108.3
C1—C2—H2	119.2	C10—C11—S1A	124.4 (2)
C2—C3—C4	119.9 (2)	C10—C11—C12	124.4 (2)
C2—C3—H3	120.0	C10—C11—C12A	123.04 (19)
C4—C3—H3	120.0	S1A—C11—C12A	112.59 (17)
C5—C4—C3	120.1 (2)	C10—C11—S1	123.04 (19)
C5—C4—H4	119.9	C12—C11—S1	112.59 (17)
C3—C4—H4	119.9	C13—C12—C11	101.16 (18)
C4—C5—C6	119.2 (2)	C13—C12—H12	129.4
C4—C5—H5	120.4	C11—C12—H12	129.4
C6—C5—H5	120.4	C13—S1A—C11	101.16 (18)
C5—C6—C1	122.2 (2)	C14—C13—C12	117.1 (3)
C5—C6—C11	117.13 (19)	C14—C13—S1A	117.1 (3)
C1—C6—C11	120.61 (18)	C14—C13—H13	121.4
N1—C7—C1	118.5 (2)	C12—C13—H13	121.4
N1—C7—H7	120.7	C13—C14—C12A	113.8 (2)
C1—C7—H7	120.7	C13—C14—S1	113.8 (2)
N2—C8—H8A	109.5	C13—C14—H14	123.1
N2—C8—H8B	109.5	S1—C14—H14	123.1
H8A—C8—H8B	109.5	C7—N1—N2	118.3 (2)
N2—C8—H8C	109.5	N1—N2—C9	117.8 (2)
H8A—C8—H8C	109.5	N1—N2—C8	121.8 (2)
H8B—C8—H8C	109.5	C9—N2—C8	120.4 (2)
O1—C9—N2	120.8 (2)	C14—S1—C11	95.27 (15)
O1—C9—C10	121.1 (2)	C14—C12A—C11	95.27 (15)
N2—C9—C10	118.0 (2)	C14—C12A—H12A	132.4
C11—C10—C9	108.8 (2)	C11—C12A—H12A	132.4
C6—C1—C2—C3	-0.3 (4)	S1—C11—C12—C13	-2.6 (2)
C7—C1—C2—C3	179.6 (2)	C10—C11—S1A—C13	176.2 (2)
C1—C2—C3—C4	0.0 (4)	C12A—C11—S1A—C13	-2.6 (2)
C2—C3—C4—C5	0.8 (4)	C11—C12—C13—C14	2.0 (3)
C3—C4—C5—C6	-1.2 (4)	C11—S1A—C13—C14	2.0 (3)
C4—C5—C6—C1	1.0 (4)	S1A—C13—C14—C12A	-0.6 (3)
C4—C5—C6—C11	-177.7 (2)	C12—C13—C14—S1	-0.6 (3)
C2—C1—C6—C5	-0.2 (4)	C1—C7—N1—N2	179.5 (2)
C7—C1—C6—C5	179.9 (2)	C7—N1—N2—C9	-179.2 (2)
C2—C1—C6—C11	178.47 (18)	C7—N1—N2—C8	2.1 (3)
C7—C1—C6—C11	-1.5 (3)	O1—C9—N2—N1	178.6 (2)
C6—C1—C7—N1	179.4 (2)	C10—C9—N2—N1	-4.2 (3)
C2—C1—C7—N1	-0.5 (4)	O1—C9—N2—C8	-2.7 (4)
O1—C9—C10—C11	87.0 (3)	C10—C9—N2—C8	174.4 (2)
N2—C9—C10—C11	-90.1 (3)	C13—C14—S1—C11	-1.0 (3)
C9—C10—C11—S1A	-70.0 (3)	C10—C11—S1—C14	-176.6 (2)
C9—C10—C11—C12	-70.0 (3)	C12—C11—S1—C14	2.24 (19)

C9—C10—C11—C12A	108.7 (2)	C13—C14—C12A—C11	-1.0 (3)
C9—C10—C11—S1	108.7 (2)	C10—C11—C12A—C14	-176.6 (2)
C10—C11—C12—C13	176.2 (2)	S1A—C11—C12A—C14	2.24 (19)

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

Cg1 is the centroid of the thiophene ring, Cg2 is the centroid of the benzene ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C13—H13 $\cdots$ O1 <sup>i</sup>	0.95	2.54	3.410 (4)	153
C3—H3 $\cdots$ Cg1 <sup>ii</sup>	0.95	2.83	3.612 (3)	140
C8—H8A $\cdots$ Cg2 <sup>iii</sup>	0.98	2.71	3.544 (3)	144

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

## (II)

*Crystal data*

$C_{14}H_{13}BrN_2OS$

$M_r = 337.23$

Monoclinic,  $P2_1/c$

$a = 9.4479$  (7)  $\text{\AA}$

$b = 20.2175$  (14)  $\text{\AA}$

$c = 7.2552$  (5)  $\text{\AA}$

$\beta = 96.9343$  (13) $^\circ$

$V = 1375.70$  (17)  $\text{\AA}^3$

$Z = 4$

$F(000) = 680$

$D_x = 1.628$   $\text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$   $\text{\AA}$

Cell parameters from 14004 reflections

$\theta = 2.4\text{--}27.5^\circ$

$\mu = 3.13$   $\text{mm}^{-1}$

$T = 100$  K

Rod, light brown

$0.26 \times 0.06 \times 0.05$  mm

*Data collection*

Rigaku Mercury CCD  
diffractometer

$\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2004)

$T_{\min} = 0.756$ ,  $T_{\max} = 1.000$

14778 measured reflections

3163 independent reflections

2897 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 2.4^\circ$

$h = -12 \rightarrow 11$

$k = -26 \rightarrow 26$

$l = -8 \rightarrow 9$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.064$

$S = 1.06$

3163 reflections

174 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.029P)^2 + 0.8865P]$

where  $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.48$   $\text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.43$   $\text{e \AA}^{-3}$

*Special details*

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.09809 (17)	0.30257 (8)	0.1963 (2)	0.0165 (3)	
C2	0.22907 (18)	0.32858 (8)	0.2763 (2)	0.0187 (3)	
H2	0.3031	0.2991	0.3235	0.022*	
C3	0.25292 (18)	0.39601 (9)	0.2878 (2)	0.0206 (3)	
H3	0.3425	0.4124	0.3426	0.025*	
C4	0.14614 (19)	0.43993 (8)	0.2194 (2)	0.0207 (3)	
H4	0.1633	0.4862	0.2257	0.025*	
C5	0.01471 (18)	0.41630 (8)	0.1420 (2)	0.0193 (3)	
H5	-0.0594	0.4461	0.0973	0.023*	
C6	-0.00727 (17)	0.34818 (9)	0.1306 (2)	0.0173 (3)	
C7	0.07642 (17)	0.23064 (8)	0.1846 (2)	0.0171 (3)	
H7	-0.0121	0.2128	0.1309	0.020*	
C8	0.02550 (18)	0.09658 (9)	0.1503 (3)	0.0208 (3)	
H8A	0.0048	0.1134	0.0232	0.031*	
H8B	-0.0523	0.1087	0.2217	0.031*	
H8C	0.0345	0.0483	0.1475	0.031*	
C9	0.26952 (19)	0.08518 (9)	0.3080 (2)	0.0203 (3)	
C10	0.41014 (18)	0.11767 (9)	0.3834 (3)	0.0218 (4)	
H10A	0.3923	0.1624	0.4309	0.026*	
H10B	0.4585	0.0911	0.4870	0.026*	
C11	0.50282 (17)	0.12232 (8)	0.2296 (3)	0.0199 (3)	
C12	0.57818 (11)	0.06159 (5)	0.14775 (16)	0.0320 (3)	0.677 (3)
H12	0.5796	0.0166	0.1856	0.038*	0.677 (3)
S1A	0.57818 (11)	0.06159 (5)	0.14775 (16)	0.0320 (3)	0.323 (3)
C13	0.6464 (2)	0.09279 (12)	-0.0038 (3)	0.0368 (5)	
H13	0.6988	0.0675	-0.0828	0.044*	
C14	0.6306 (2)	0.15886 (11)	-0.0243 (3)	0.0316 (4)	
H14	0.6708	0.1834	-0.1168	0.038*	
N1	0.17897 (15)	0.19243 (7)	0.2481 (2)	0.0171 (3)	
N2	0.15849 (15)	0.12529 (7)	0.2374 (2)	0.0177 (3)	
O1	0.25756 (14)	0.02499 (6)	0.3042 (2)	0.0272 (3)	
S1	0.53516 (6)	0.19288 (3)	0.12608 (9)	0.02306 (19)	0.677 (3)
C12A	0.53516 (6)	0.19288 (3)	0.12608 (9)	0.02306 (19)	0.323 (3)
H12A	0.5082	0.2373	0.1464	0.028*	0.323 (3)
Br1	-0.18904 (2)	0.31960 (2)	0.01542 (3)	0.02297 (7)	

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0183 (8)	0.0179 (8)	0.0135 (8)	-0.0010 (6)	0.0025 (6)	-0.0001 (6)
C2	0.0183 (8)	0.0192 (8)	0.0179 (8)	0.0008 (6)	-0.0001 (6)	0.0008 (6)
C3	0.0201 (8)	0.0207 (8)	0.0206 (9)	-0.0030 (6)	0.0012 (7)	-0.0018 (6)
C4	0.0256 (8)	0.0163 (8)	0.0207 (9)	-0.0019 (6)	0.0050 (7)	-0.0011 (6)
C5	0.0213 (8)	0.0189 (8)	0.0181 (9)	0.0042 (6)	0.0043 (6)	0.0018 (6)
C6	0.0164 (7)	0.0215 (8)	0.0140 (8)	-0.0010 (6)	0.0019 (6)	0.0004 (6)

C7	0.0185 (7)	0.0183 (8)	0.0145 (8)	-0.0031 (6)	0.0021 (6)	-0.0008 (6)
C8	0.0203 (8)	0.0184 (8)	0.0239 (9)	-0.0048 (6)	0.0038 (7)	-0.0028 (7)
C9	0.0236 (8)	0.0192 (8)	0.0191 (9)	0.0005 (7)	0.0074 (7)	-0.0006 (6)
C10	0.0219 (8)	0.0211 (8)	0.0219 (9)	0.0030 (7)	0.0002 (7)	-0.0001 (7)
C11	0.0150 (7)	0.0200 (8)	0.0236 (9)	0.0010 (6)	-0.0020 (6)	-0.0026 (7)
C12	0.0259 (5)	0.0317 (6)	0.0370 (6)	-0.0031 (4)	-0.0013 (4)	0.0004 (4)
S1A	0.0259 (5)	0.0317 (6)	0.0370 (6)	-0.0031 (4)	-0.0013 (4)	0.0004 (4)
C13	0.0170 (8)	0.0462 (13)	0.0465 (14)	0.0014 (8)	0.0012 (8)	-0.0239 (10)
C14	0.0305 (10)	0.0408 (12)	0.0240 (10)	-0.0174 (9)	0.0047 (8)	-0.0038 (8)
N1	0.0208 (7)	0.0141 (7)	0.0168 (7)	-0.0024 (5)	0.0043 (6)	-0.0013 (5)
N2	0.0196 (7)	0.0132 (6)	0.0205 (7)	-0.0027 (5)	0.0036 (6)	-0.0017 (5)
O1	0.0291 (7)	0.0167 (6)	0.0371 (8)	0.0010 (5)	0.0099 (6)	0.0005 (5)
S1	0.0217 (3)	0.0234 (3)	0.0237 (3)	-0.0004 (2)	0.0013 (2)	0.0023 (2)
C12A	0.0217 (3)	0.0234 (3)	0.0237 (3)	-0.0004 (2)	0.0013 (2)	0.0023 (2)
Br1	0.01578 (10)	0.02638 (11)	0.02587 (12)	-0.00184 (6)	-0.00109 (7)	0.00178 (7)

*Geometric parameters (Å, °)*

C1—C6	1.398 (2)	C9—N2	1.375 (2)
C1—C2	1.404 (2)	C9—C10	1.523 (2)
C1—C7	1.470 (2)	C10—C11	1.502 (2)
C2—C3	1.383 (2)	C10—H10A	0.9900
C2—H2	0.9500	C10—H10B	0.9900
C3—C4	1.390 (2)	C11—S1A	1.571 (2)
C3—H3	0.9500	C11—C12	1.571 (2)
C4—C5	1.385 (2)	C11—C12A	1.6576 (19)
C4—H4	0.9500	C11—S1	1.6576 (19)
C5—C6	1.394 (2)	C12—C13	1.481 (3)
C5—H5	0.9500	C12—H12	0.9500
C6—Br1	1.9064 (16)	S1A—C13	1.481 (3)
C7—N1	1.281 (2)	C13—C14	1.350 (3)
C7—H7	0.9500	C13—H13	0.9500
C8—N2	1.457 (2)	C14—C12A	1.648 (2)
C8—H8A	0.9800	C14—S1	1.648 (2)
C8—H8B	0.9800	C14—H14	0.9500
C8—H8C	0.9800	N1—N2	1.3720 (19)
C9—O1	1.222 (2)	C12A—H12A	0.9500
C6—C1—C2	116.73 (15)	C11—C10—H10A	109.9
C6—C1—C7	122.98 (15)	C9—C10—H10A	109.9
C2—C1—C7	120.28 (15)	C11—C10—H10B	109.9
C3—C2—C1	121.56 (16)	C9—C10—H10B	109.9
C3—C2—H2	119.2	H10A—C10—H10B	108.3
C1—C2—H2	119.2	C10—C11—S1A	124.27 (14)
C2—C3—C4	120.15 (16)	C10—C11—C12	124.27 (14)
C2—C3—H3	119.9	C10—C11—C12A	123.11 (13)
C4—C3—H3	119.9	S1A—C11—C12A	112.62 (12)
C5—C4—C3	120.09 (16)	C10—C11—S1	123.11 (13)



C5—C4—H4	120.0	C12—C11—S1	112.62 (12)
C3—C4—H4	120.0	C13—C12—C11	101.85 (12)
C4—C5—C6	119.01 (15)	C13—C12—H12	129.1
C4—C5—H5	120.5	C11—C12—H12	129.1
C6—C5—H5	120.5	C13—S1A—C11	101.85 (12)
C5—C6—C1	122.46 (15)	C14—C13—C12	116.81 (17)
C5—C6—Br1	116.44 (12)	C14—C13—S1A	116.81 (17)
C1—C6—Br1	121.09 (13)	C14—C13—H13	121.6
N1—C7—C1	118.82 (15)	C12—C13—H13	121.6
N1—C7—H7	120.6	C13—C14—C12A	113.69 (17)
C1—C7—H7	120.6	C13—C14—S1	113.69 (17)
N2—C8—H8A	109.5	C13—C14—H14	123.2
N2—C8—H8B	109.5	S1—C14—H14	123.2
H8A—C8—H8B	109.5	C7—N1—N2	118.76 (14)
N2—C8—H8C	109.5	N1—N2—C9	117.80 (14)
H8A—C8—H8C	109.5	N1—N2—C8	121.80 (14)
H8B—C8—H8C	109.5	C9—N2—C8	120.38 (14)
O1—C9—N2	120.96 (16)	C14—S1—C11	94.95 (10)
O1—C9—C10	120.78 (16)	C14—C12A—C11	94.95 (10)
N2—C9—C10	118.20 (15)	C14—C12A—H12A	132.5
C11—C10—C9	108.77 (14)	C11—C12A—H12A	132.5
C6—C1—C2—C3	-0.5 (3)	S1—C11—C12—C13	-2.72 (14)
C7—C1—C2—C3	179.45 (16)	C10—C11—S1A—C13	176.72 (15)
C1—C2—C3—C4	0.0 (3)	C12A—C11—S1A—C13	-2.72 (14)
C2—C3—C4—C5	1.0 (3)	C11—C12—C13—C14	1.9 (2)
C3—C4—C5—C6	-1.3 (3)	C11—S1A—C13—C14	1.9 (2)
C4—C5—C6—C1	0.7 (3)	S1A—C13—C14—C12A	-0.4 (2)
C4—C5—C6—Br1	-178.15 (13)	C12—C13—C14—S1	-0.4 (2)
C2—C1—C6—C5	0.2 (2)	C1—C7—N1—N2	179.85 (14)
C7—C1—C6—C5	-179.79 (16)	C7—N1—N2—C9	-179.36 (15)
C2—C1—C6—Br1	179.02 (12)	C7—N1—N2—C8	2.2 (2)
C7—C1—C6—Br1	-1.0 (2)	O1—C9—N2—N1	179.36 (16)
C6—C1—C7—N1	179.85 (16)	C10—C9—N2—N1	-3.3 (2)
C2—C1—C7—N1	-0.1 (2)	O1—C9—N2—C8	-2.2 (2)
O1—C9—C10—C11	85.9 (2)	C10—C9—N2—C8	175.12 (15)
N2—C9—C10—C11	-91.44 (18)	C13—C14—S1—C11	-1.24 (17)
C9—C10—C11—S1A	-72.27 (19)	C10—C11—S1—C14	-177.05 (15)
C9—C10—C11—C12	-72.27 (19)	C12—C11—S1—C14	2.39 (13)
C9—C10—C11—C12A	107.11 (16)	C13—C14—C12A—C11	-1.24 (17)
C9—C10—C11—S1	107.11 (16)	C10—C11—C12A—C14	-177.05 (15)
C10—C11—C12—C13	176.72 (15)	S1A—C11—C12A—C14	2.39 (13)

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

Cg1 is the centroid of the thiophene ring, Cg2 is the centroid of the benzene ring.

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C13—H13 $\cdots$ O1 <sup>i</sup>	0.95	2.53	3.424 (2)	156

C3—H3...Cg1 <sup>ii</sup>	0.95	2.82	3.6021 (18)	141
C8—H8A...Cg2 <sup>iii</sup>	0.98	2.67	3.495 (2)	142

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

## (III)

*Crystal data*C<sub>14</sub>H<sub>13</sub>ClN<sub>2</sub>O<sub>5</sub> $M_r = 292.77$ Monoclinic,  $P2_1/n$  $a = 4.2194$  (2) Å $b = 13.0131$  (9) Å $c = 25.0758$  (18) Å $\beta = 93.752$  (4)° $V = 1373.90$  (15) Å<sup>3</sup> $Z = 4$  $F(000) = 608$  $D_x = 1.415$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71075$  Å

Cell parameters from 9584 reflections

 $\theta = 2.9$ – $27.5$ ° $\mu = 0.42$  mm<sup>-1</sup> $T = 100$  K

Needle, colourless

0.22 × 0.01 × 0.01 mm

*Data collection*Rigaku Mercury CCD  
diffractometer $\omega$  scansAbsorption correction: multi-scan  
(SADABS; Bruker, 2004) $T_{\min} = 0.615$ ,  $T_{\max} = 1.000$ 

12868 measured reflections

3121 independent reflections

1766 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.127$  $\theta_{\max} = 27.4$ °,  $\theta_{\min} = 2.9$ ° $h = -5 \rightarrow 5$  $k = -16 \rightarrow 16$  $l = -32 \rightarrow 32$ *Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.116$  $wR(F^2) = 0.297$  $S = 1.16$ 

3121 reflections

184 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Hydrogen site location: mixed

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0832P)^2 + 8.0037P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.006$  $\Delta\rho_{\max} = 1.00$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -0.45$  e Å<sup>-3</sup>*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<sup>2</sup>)*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.2176 (17)	0.2480 (6)	0.1409 (2)	0.0278 (15)	
C2	0.0167 (16)	0.2955 (6)	0.1012 (3)	0.0281 (15)	
H2	-0.0133	0.3679	0.1017	0.034*	
C3	-0.1373 (17)	0.2366 (6)	0.0613 (3)	0.0339 (18)	
H3	-0.2716	0.2690	0.0344	0.041*	
C4	-0.0966 (18)	0.1304 (6)	0.0603 (3)	0.0352 (17)	

H4	-0.2041	0.0901	0.0332	0.042*	0.854 (7)
C5	0.098 (2)	0.0838 (6)	0.0994 (3)	0.0383 (18)	
H5	0.1284	0.0115	0.0987	0.046*	0.146 (7)
C6	0.2538 (18)	0.1414 (6)	0.1398 (3)	0.0322 (17)	
H6	0.3852	0.1082	0.1668	0.039*	
C7	0.3910 (16)	0.3074 (5)	0.1837 (3)	0.0258 (15)	
H7	0.5213	0.2733	0.2105	0.031*	
C8	0.7209 (18)	0.4074 (6)	0.2680 (3)	0.0335 (17)	
H8A	0.5903	0.3557	0.2847	0.050*	
H8B	0.7949	0.4582	0.2949	0.050*	
H8C	0.9042	0.3739	0.2534	0.050*	
C9	0.5187 (17)	0.5634 (6)	0.2228 (3)	0.0307 (17)	
C10	0.3000 (17)	0.6118 (6)	0.1778 (3)	0.0324 (17)	
H10A	0.1189	0.5651	0.1691	0.039*	
H10B	0.2137	0.6774	0.1907	0.039*	
C11	0.4715 (15)	0.6322 (5)	0.1277 (2)	0.0245 (14)	
C12	0.5901 (13)	0.7328 (5)	0.11266 (19)	0.048 (2)	0.795 (9)
H12	0.5807	0.7956	0.1319	0.058*	0.795 (9)
S1A	0.5901 (13)	0.7328 (5)	0.11266 (19)	0.048 (2)	0.205 (9)
C13	0.7313 (18)	0.7147 (6)	0.0596 (3)	0.0353 (17)	
H13	0.8266	0.7681	0.0404	0.042*	
C14	0.7127 (17)	0.6182 (6)	0.0416 (3)	0.0342 (17)	
H14	0.7921	0.5975	0.0087	0.041*	
N1	0.3638 (13)	0.4055 (4)	0.1843 (2)	0.0250 (13)	
N2	0.5314 (14)	0.4588 (5)	0.2249 (2)	0.0302 (13)	
O1	0.6759 (12)	0.6183 (4)	0.25450 (18)	0.0362 (13)	
Cl1	0.1534 (7)	-0.04694 (19)	0.09763 (10)	0.0537 (9)	0.854 (7)
Cl2	-0.296 (5)	0.0407 (14)	0.0203 (7)	0.067 (7)	0.146 (7)
S1	0.5363 (5)	0.53654 (16)	0.08241 (8)	0.0261 (7)	0.795 (9)
C12A	0.5363 (5)	0.53654 (16)	0.08241 (8)	0.0261 (7)	0.205 (9)
H12A	0.4903	0.4651	0.0810	0.031*	0.205 (9)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.035 (4)	0.031 (4)	0.018 (3)	0.001 (3)	0.007 (3)	0.000 (3)
C2	0.026 (4)	0.026 (4)	0.033 (4)	0.000 (3)	0.008 (3)	0.001 (3)
C3	0.025 (4)	0.053 (5)	0.024 (3)	-0.002 (3)	0.001 (3)	0.000 (3)
C4	0.032 (4)	0.035 (4)	0.038 (4)	-0.006 (3)	-0.001 (3)	-0.010 (4)
C5	0.046 (5)	0.030 (4)	0.039 (4)	-0.002 (4)	0.001 (3)	-0.007 (3)
C6	0.042 (4)	0.028 (4)	0.027 (3)	0.000 (3)	0.003 (3)	0.001 (3)
C7	0.027 (4)	0.029 (4)	0.022 (3)	0.003 (3)	0.002 (3)	0.001 (3)
C8	0.041 (4)	0.035 (4)	0.024 (3)	-0.008 (3)	-0.003 (3)	0.004 (3)
C9	0.029 (4)	0.045 (5)	0.019 (3)	-0.004 (3)	0.007 (3)	-0.005 (3)
C10	0.030 (4)	0.035 (4)	0.032 (4)	0.004 (3)	0.002 (3)	-0.008 (3)
C11	0.024 (3)	0.025 (4)	0.024 (3)	0.005 (3)	-0.004 (3)	-0.001 (3)
C12	0.051 (4)	0.063 (4)	0.029 (3)	-0.004 (3)	-0.008 (2)	0.013 (2)
S1A	0.051 (4)	0.063 (4)	0.029 (3)	-0.004 (3)	-0.008 (2)	0.013 (2)

C13	0.041 (4)	0.035 (4)	0.029 (4)	-0.003 (4)	-0.007 (3)	0.008 (3)
C14	0.032 (4)	0.045 (5)	0.024 (3)	-0.001 (3)	-0.007 (3)	0.004 (3)
N1	0.030 (3)	0.028 (3)	0.017 (2)	-0.001 (2)	0.001 (2)	-0.005 (2)
N2	0.035 (3)	0.034 (3)	0.020 (3)	-0.001 (3)	-0.003 (2)	-0.004 (3)
O1	0.047 (3)	0.042 (3)	0.020 (2)	-0.005 (3)	0.003 (2)	-0.008 (2)
Cl1	0.085 (2)	0.0220 (12)	0.0519 (15)	-0.0009 (12)	-0.0112 (13)	-0.0015 (11)
Cl2	0.086 (13)	0.059 (11)	0.059 (10)	-0.023 (9)	0.028 (9)	-0.035 (9)
S1	0.0310 (12)	0.0240 (11)	0.0228 (10)	0.0019 (9)	-0.0021 (7)	-0.0015 (8)
C12A	0.0310 (12)	0.0240 (11)	0.0228 (10)	0.0019 (9)	-0.0021 (7)	-0.0015 (8)

*Geometric parameters (Å, °)*

C1—C6	1.395 (10)	C9—C10	1.545 (10)
C1—C2	1.408 (10)	C10—C11	1.514 (9)
C1—C7	1.478 (10)	C10—H10A	0.9900
C2—C3	1.388 (10)	C10—H10B	0.9900
C2—H2	0.9500	C11—S1A	1.461 (9)
C3—C4	1.394 (11)	C11—C12	1.461 (9)
C3—H3	0.9500	C11—C12A	1.718 (7)
C4—C5	1.377 (11)	C11—S1	1.718 (7)
C4—C12	1.724 (17)	C12—C13	1.511 (9)
C4—H4	0.9500	C12—H12	0.9500
C5—C6	1.392 (10)	S1A—C13	1.511 (9)
C5—C11	1.718 (8)	C13—C14	1.334 (11)
C5—H5	0.9500	C13—H13	0.9500
C6—H6	0.9500	C14—C12A	1.682 (8)
C7—N1	1.281 (9)	C14—S1	1.682 (8)
C7—H7	0.9500	C14—H14	0.9500
C8—N2	1.464 (9)	N1—N2	1.387 (8)
C8—H8A	0.9800	Cl1—H5	0.7679
C8—H8B	0.9800	Cl2—Cl2 <sup>i</sup>	2.21 (3)
C8—H8C	0.9800	Cl2—H4	0.8086
C9—O1	1.229 (8)	C12A—H12A	0.9500
C9—N2	1.364 (10)		
C6—C1—C2	119.0 (7)	C11—C10—C9	112.5 (6)
C6—C1—C7	119.0 (7)	C11—C10—H10A	109.1
C2—C1—C7	122.0 (7)	C9—C10—H10A	109.1
C3—C2—C1	119.9 (7)	C11—C10—H10B	109.1
C3—C2—H2	120.0	C9—C10—H10B	109.1
C1—C2—H2	120.0	H10A—C10—H10B	107.8
C2—C3—C4	120.5 (7)	S1A—C11—C10	124.1 (6)
C2—C3—H3	119.7	C12—C11—C10	124.1 (6)
C4—C3—H3	119.7	S1A—C11—C12A	114.0 (5)
C5—C4—C3	119.5 (7)	C10—C11—C12A	121.8 (5)
C5—C4—C12	111.2 (9)	C12—C11—S1	114.0 (5)
C3—C4—C12	128.8 (10)	C10—C11—S1	121.8 (5)
C5—C4—H4	120.0	C11—C12—C13	104.4 (6)

C3—C4—H4	120.4	C11—C12—H12	127.8
C12—C4—H4	10.5	C13—C12—H12	127.8
C4—C5—C6	120.8 (7)	C11—S1A—C13	104.4 (6)
C4—C5—C11	119.6 (6)	C14—C13—C12	115.3 (7)
C6—C5—C11	119.6 (6)	C14—C13—S1A	115.3 (7)
C4—C5—H5	120.0	C14—C13—H13	122.4
C6—C5—H5	119.2	C12—C13—H13	122.4
C11—C5—H5	0.5	C13—C14—C12A	114.1 (6)
C5—C6—C1	120.2 (7)	C13—C14—S1	114.1 (6)
C5—C6—H6	119.9	C13—C14—H14	123.0
C1—C6—H6	119.9	S1—C14—H14	123.0
N1—C7—C1	119.3 (6)	C7—N1—N2	117.7 (6)
N1—C7—H7	120.3	C9—N2—N1	117.0 (6)
C1—C7—H7	120.3	C9—N2—C8	120.2 (6)
N2—C8—H8A	109.5	N1—N2—C8	122.7 (6)
N2—C8—H8B	109.5	C5—C11—H5	0.6
H8A—C8—H8B	109.5	C4—C12—C12 <sup>i</sup>	158.2 (15)
N2—C8—H8C	109.5	C4—C12—H4	12.4
H8A—C8—H8C	109.5	C12 <sup>i</sup> —C12—H4	154.9
H8B—C8—H8C	109.5	C14—S1—C11	92.3 (4)
O1—C9—N2	122.5 (7)	C14—C12A—C11	92.3 (4)
O1—C9—C10	120.5 (7)	C14—C12A—H12A	133.9
N2—C9—C10	117.1 (6)	C11—C12A—H12A	133.9
C6—C1—C2—C3	-1.1 (10)	S1—C11—C12—C13	0.5 (6)
C7—C1—C2—C3	179.0 (6)	C10—C11—S1A—C13	-178.3 (6)
C1—C2—C3—C4	0.4 (10)	C12A—C11—S1A—C13	0.5 (6)
C2—C3—C4—C5	0.1 (11)	C11—C12—C13—C14	-0.1 (8)
C2—C3—C4—C12	171.4 (9)	C11—S1A—C13—C14	-0.1 (8)
C3—C4—C5—C6	0.1 (12)	S1A—C13—C14—C12A	-0.3 (8)
C12—C4—C5—C6	-172.7 (8)	C12—C13—C14—S1	-0.3 (8)
C3—C4—C5—C11	-179.0 (6)	C1—C7—N1—N2	-179.6 (6)
C12—C4—C5—C11	8.3 (10)	O1—C9—N2—N1	-174.7 (6)
C4—C5—C6—C1	-0.8 (11)	C10—C9—N2—N1	4.3 (9)
C11—C5—C6—C1	178.3 (6)	O1—C9—N2—C8	4.1 (10)
C2—C1—C6—C5	1.3 (10)	C10—C9—N2—C8	-176.9 (6)
C7—C1—C6—C5	-178.8 (7)	C7—N1—N2—C9	175.3 (6)
C6—C1—C7—N1	178.6 (6)	C7—N1—N2—C8	-3.5 (9)
C2—C1—C7—N1	-1.5 (10)	C5—C4—C12—C12 <sup>i</sup>	123 (4)
O1—C9—C10—C11	88.1 (8)	C3—C4—C12—C12 <sup>i</sup>	-49 (5)
N2—C9—C10—C11	-90.9 (8)	C13—C14—S1—C11	0.6 (6)
C9—C10—C11—S1A	-100.6 (8)	C12—C11—S1—C14	-0.6 (5)
C9—C10—C11—C12	-100.6 (8)	C10—C11—S1—C14	178.3 (6)
C9—C10—C11—C12A	80.6 (7)	C13—C14—C12A—C11	0.6 (6)
C9—C10—C11—S1	80.6 (7)	S1A—C11—C12A—C14	-0.6 (5)
C10—C11—C12—C13	-178.3 (6)	C10—C11—C12A—C14	178.3 (6)

Symmetry code: (i)  $-x-1, -y, -z$ .



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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6—H6 $\cdots$ O1 <sup>ii</sup>	0.95	2.62	3.474 (9)	150
C7—H7 $\cdots$ O1 <sup>ii</sup>	0.95	2.52	3.381 (9)	152
C12—H12 $\cdots$ C11 <sup>iii</sup>	0.95	2.83	3.415 (7)	121

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

(IV)

Crystal data

$C_{14}H_{13}ClN_2OS$

$M_r = 292.77$

Monoclinic,  $P2_1/n$

$a = 6.7454$  (5)  $\text{\AA}$

$b = 20.2993$  (14)  $\text{\AA}$

$c = 10.1592$  (7)  $\text{\AA}$

$\beta = 97.510$  (2) $^\circ$

$V = 1379.14$  (17)  $\text{\AA}^3$

$Z = 4$

$F(000) = 608$

$D_x = 1.410$  Mg  $\text{m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$   $\text{\AA}$

Cell parameters from 14502 reflections

$\theta = 2.3\text{--}27.5^\circ$

$\mu = 0.42$   $\text{mm}^{-1}$

$T = 100$  K

Block, colourless

$0.30 \times 0.17 \times 0.10$  mm

Data collection

Rigaku Mercury CCD  
diffractometer

$\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2004)

$T_{\min} = 0.843$ ,  $T_{\max} = 1.000$

14763 measured reflections

3165 independent reflections

2929 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 2.9^\circ$

$h = -7 \rightarrow 8$

$k = -25 \rightarrow 26$

$l = -12 \rightarrow 13$

Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.091$

$S = 1.05$

3165 reflections

174 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.4663P]$

where  $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.53$  e  $\text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.40$  e  $\text{\AA}^{-3}$

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. ( $<1$ )
C1	0.30559 (18)	0.18484 (6)	0.17665 (11)	0.0232 (2)	
C2	0.29278 (19)	0.11619 (6)	0.16729 (12)	0.0258 (3)	

H2	0.4040	0.0899	0.2020	0.031*	
C3	0.1195 (2)	0.08611 (6)	0.10784 (13)	0.0277 (3)	
H3	0.1109	0.0395	0.1019	0.033*	
C4	-0.04180 (18)	0.12533 (6)	0.05692 (12)	0.0251 (2)	
C5	-0.03348 (19)	0.19335 (7)	0.06381 (12)	0.0266 (3)	
H5	-0.1446	0.2194	0.0281	0.032*	
C6	0.14082 (19)	0.22248 (6)	0.12410 (12)	0.0260 (3)	
H6	0.1484	0.2691	0.1298	0.031*	
C7	0.48613 (18)	0.21894 (6)	0.23753 (11)	0.0245 (2)	
H7	0.4946	0.2655	0.2313	0.029*	
C8	0.8228 (2)	0.29167 (6)	0.32415 (13)	0.0273 (3)	
H8A	0.7962	0.2998	0.2284	0.041*	
H8B	0.9595	0.3055	0.3571	0.041*	
H8C	0.7279	0.3168	0.3695	0.041*	
C9	0.94915 (18)	0.18717 (6)	0.42531 (11)	0.0236 (2)	
C10	0.91435 (19)	0.11392 (6)	0.44594 (13)	0.0266 (3)	
H10A	0.7816	0.1076	0.4756	0.032*	
H10B	0.9145	0.0905	0.3605	0.032*	
C11	1.0726 (2)	0.08513 (6)	0.54718 (13)	0.0259 (3)	
C12	1.03317 (13)	0.06569 (4)	0.68966 (8)	0.0410 (3)	0.671 (2)
H12	0.9132	0.0677	0.7291	0.049*	0.671 (2)
S1A	1.03317 (13)	0.06569 (4)	0.68966 (8)	0.0410 (3)	0.329 (2)
C13	1.2424 (3)	0.04236 (7)	0.74842 (14)	0.0396 (3)	
H13	1.2706	0.0278	0.8378	0.048*	
C14	1.3836 (2)	0.04368 (7)	0.66669 (16)	0.0395 (3)	
H14	1.5174	0.0298	0.6934	0.047*	
N1	0.63255 (15)	0.18647 (5)	0.29910 (10)	0.0232 (2)	
N2	0.80022 (16)	0.22142 (5)	0.35017 (10)	0.0236 (2)	
O1	1.10231 (14)	0.21470 (5)	0.47402 (9)	0.0312 (2)	
Cl1	-0.26110 (5)	0.08829 (2)	-0.01956 (3)	0.03259 (11)	
S1	1.30619 (7)	0.07115 (3)	0.51710 (5)	0.03532 (17)	0.671 (2)
C12A	1.30619 (7)	0.07115 (3)	0.51710 (5)	0.03532 (17)	0.329 (2)
H12A	1.3712	0.0770	0.4405	0.042*	0.329 (2)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0233 (6)	0.0282 (6)	0.0185 (5)	0.0020 (5)	0.0043 (4)	0.0013 (4)
C2	0.0234 (6)	0.0285 (6)	0.0252 (6)	0.0048 (5)	0.0019 (4)	0.0040 (5)
C3	0.0269 (6)	0.0266 (6)	0.0293 (6)	0.0026 (5)	0.0024 (5)	0.0024 (5)
C4	0.0214 (6)	0.0320 (6)	0.0220 (5)	0.0012 (5)	0.0031 (4)	0.0006 (5)
C5	0.0235 (6)	0.0321 (6)	0.0242 (6)	0.0077 (5)	0.0034 (5)	0.0020 (5)
C6	0.0273 (6)	0.0259 (6)	0.0253 (6)	0.0047 (5)	0.0054 (5)	0.0012 (4)
C7	0.0268 (6)	0.0260 (6)	0.0212 (5)	0.0016 (5)	0.0052 (4)	0.0000 (4)
C8	0.0329 (7)	0.0230 (6)	0.0257 (6)	-0.0020 (5)	0.0027 (5)	0.0011 (4)
C9	0.0260 (6)	0.0250 (6)	0.0196 (5)	-0.0025 (5)	0.0025 (4)	-0.0024 (4)
C10	0.0261 (6)	0.0239 (6)	0.0283 (6)	-0.0027 (5)	-0.0026 (5)	-0.0009 (5)
C11	0.0279 (6)	0.0225 (6)	0.0261 (6)	-0.0031 (5)	-0.0008 (5)	-0.0014 (4)

C12	0.0490 (5)	0.0350 (4)	0.0364 (4)	-0.0036 (3)	-0.0046 (3)	0.0007 (3)
S1A	0.0490 (5)	0.0350 (4)	0.0364 (4)	-0.0036 (3)	-0.0046 (3)	0.0007 (3)
C13	0.0586 (10)	0.0293 (7)	0.0281 (6)	-0.0053 (6)	-0.0050 (6)	0.0039 (5)
C14	0.0347 (7)	0.0341 (7)	0.0459 (8)	0.0038 (6)	-0.0088 (6)	-0.0062 (6)
N1	0.0231 (5)	0.0272 (5)	0.0191 (5)	-0.0023 (4)	0.0026 (4)	-0.0017 (4)
N2	0.0256 (5)	0.0227 (5)	0.0221 (5)	-0.0025 (4)	0.0019 (4)	-0.0009 (4)
O1	0.0304 (5)	0.0282 (5)	0.0325 (5)	-0.0069 (4)	-0.0050 (4)	-0.0004 (4)
C11	0.02389 (17)	0.03644 (19)	0.03586 (19)	0.00052 (12)	-0.00205 (12)	-0.00053 (12)
S1	0.0304 (3)	0.0429 (3)	0.0313 (3)	0.00544 (19)	-0.00098 (18)	0.00246 (18)
C12A	0.0304 (3)	0.0429 (3)	0.0313 (3)	0.00544 (19)	-0.00098 (18)	0.00246 (18)

*Geometric parameters (Å, °)*

C1—C6	1.3961 (17)	C9—N2	1.3693 (16)
C1—C2	1.3987 (18)	C9—C10	1.5241 (17)
C1—C7	1.4656 (17)	C10—C11	1.5007 (17)
C2—C3	1.3851 (18)	C10—H10A	0.9900
C2—H2	0.9500	C10—H10B	0.9900
C3—C4	1.3922 (18)	C11—S1A	1.5564 (15)
C3—H3	0.9500	C11—C12	1.5564 (15)
C4—C5	1.3834 (19)	C11—C12A	1.6679 (14)
C4—C11	1.7484 (13)	C11—S1	1.6679 (14)
C5—C6	1.3852 (18)	C12—C13	1.5337 (19)
C5—H5	0.9500	C12—H12	0.9500
C6—H6	0.9500	S1A—C13	1.5337 (19)
C7—N1	1.2805 (16)	C13—C14	1.343 (2)
C7—H7	0.9500	C13—H13	0.9500
C8—N2	1.4619 (16)	C14—C12A	1.6388 (16)
C8—H8A	0.9800	C14—S1	1.6388 (16)
C8—H8B	0.9800	C14—H14	0.9500
C8—H8C	0.9800	N1—N2	1.3778 (14)
C9—O1	1.2210 (15)	C12A—H12A	0.9500
C6—C1—C2	118.70 (11)	C11—C10—H10A	109.3
C6—C1—C7	118.62 (11)	C9—C10—H10A	109.3
C2—C1—C7	122.67 (11)	C11—C10—H10B	109.3
C3—C2—C1	120.66 (11)	C9—C10—H10B	109.3
C3—C2—H2	119.7	H10A—C10—H10B	108.0
C1—C2—H2	119.7	C10—C11—S1A	122.91 (11)
C2—C3—C4	118.94 (12)	C10—C11—C12	122.91 (11)
C2—C3—H3	120.5	C10—C11—C12A	123.03 (10)
C4—C3—H3	120.5	S1A—C11—C12A	114.06 (9)
C5—C4—C3	121.82 (12)	C10—C11—S1	123.03 (10)
C5—C4—C11	118.56 (10)	C12—C11—S1	114.06 (9)
C3—C4—C11	119.61 (10)	C13—C12—C11	100.36 (9)
C4—C5—C6	118.35 (11)	C13—C12—H12	129.8
C4—C5—H5	120.8	C11—C12—H12	129.8
C6—C5—H5	120.8	C13—S1A—C11	100.36 (9)

C5—C6—C1	121.52 (12)	C14—C13—C12	116.37 (12)
C5—C6—H6	119.2	C14—C13—S1A	116.37 (12)
C1—C6—H6	119.2	C14—C13—H13	121.8
N1—C7—C1	120.55 (11)	C12—C13—H13	121.8
N1—C7—H7	119.7	C13—C14—C12A	114.47 (12)
C1—C7—H7	119.7	C13—C14—S1	114.47 (12)
N2—C8—H8A	109.5	C13—C14—H14	122.8
N2—C8—H8B	109.5	S1—C14—H14	122.8
H8A—C8—H8B	109.5	C7—N1—N2	117.49 (11)
N2—C8—H8C	109.5	C9—N2—N1	117.06 (10)
H8A—C8—H8C	109.5	C9—N2—C8	120.64 (10)
H8B—C8—H8C	109.5	N1—N2—C8	122.29 (10)
O1—C9—N2	120.92 (11)	C14—S1—C11	94.72 (8)
O1—C9—C10	121.88 (11)	C14—C12A—C11	94.72 (8)
N2—C9—C10	117.20 (10)	C14—C12A—H12A	132.6
C11—C10—C9	111.45 (10)	C11—C12A—H12A	132.6
C6—C1—C2—C3	-0.44 (18)	C10—C11—S1A—C13	-178.00 (11)
C7—C1—C2—C3	-179.43 (11)	C12A—C11—S1A—C13	1.98 (11)
C1—C2—C3—C4	0.27 (19)	C11—C12—C13—C14	-1.60 (14)
C2—C3—C4—C5	0.17 (19)	C11—S1A—C13—C14	-1.60 (14)
C2—C3—C4—C11	179.53 (9)	S1A—C13—C14—C12A	0.63 (17)
C3—C4—C5—C6	-0.41 (19)	C12—C13—C14—S1	0.63 (17)
C11—C4—C5—C6	-179.78 (9)	C1—C7—N1—N2	177.91 (10)
C4—C5—C6—C1	0.23 (18)	O1—C9—N2—N1	-179.97 (11)
C2—C1—C6—C5	0.18 (18)	C10—C9—N2—N1	-0.43 (15)
C7—C1—C6—C5	179.22 (11)	O1—C9—N2—C8	1.27 (18)
C6—C1—C7—N1	172.64 (11)	C10—C9—N2—C8	-179.20 (11)
C2—C1—C7—N1	-8.36 (17)	C7—N1—N2—C9	174.66 (10)
O1—C9—C10—C11	8.78 (17)	C7—N1—N2—C8	-6.59 (16)
N2—C9—C10—C11	-170.75 (11)	C13—C14—S1—C11	0.60 (13)
C9—C10—C11—S1A	106.71 (12)	C10—C11—S1—C14	178.36 (11)
C9—C10—C11—C12	106.71 (12)	C12—C11—S1—C14	-1.62 (10)
C9—C10—C11—C12A	-73.26 (14)	C13—C14—C12A—C11	0.60 (13)
C9—C10—C11—S1	-73.26 (14)	C10—C11—C12A—C14	178.36 (11)
C10—C11—C12—C13	-178.00 (11)	S1A—C11—C12A—C14	-1.62 (10)
S1—C11—C12—C13	1.98 (11)		

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

Cg1 is the centroid of the benzene ring.

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C5—H5 $\cdots$ O1 <sup>i</sup>	0.95	2.18	3.1250 (15)	172
C3—H3 $\cdots$ C11 <sup>ii</sup>	0.95	2.95	3.8044 (14)	151
C12—H12 $\cdots$ C11 <sup>iii</sup>	0.95	2.98	3.7960 (10)	145
C8—H8C $\cdots$ Cg1 <sup>iv</sup>	0.98	2.73	3.5592 (14)	142

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