



Crystal structure and Hirshfeld surface analysis of (*E*)-3-[(2,3-dichlorobenzylidene)amino]-5-phenylthiazolidin-2-iminium bromide

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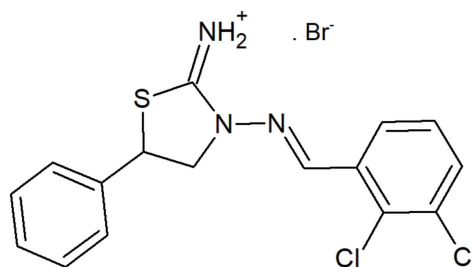
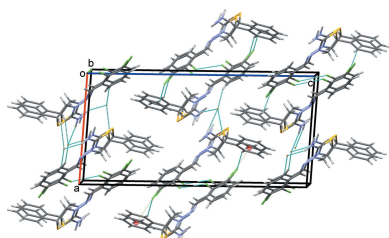
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In the cation of the title salt, C₁₆H₁₄Cl₂N₃S⁺·Br⁻, the central thiazolidine ring adopts an envelope conformation. The phenyl ring is disordered over two sites with a refined occupancy ratio of 0.541 (9):0.459 (9). In the crystal, C—H···Br and N—H···Br hydrogen bonds link the components into a three-dimensional network with the cations and anions stacked along the *b*-axis direction. Weak C—H···π interactions, which only involve the minor disorder component of the ring, also contribute to the molecular packing. In addition, there are also inversion-related Cl···Cl halogen bonds and C—Cl···π (ring) contacts. A Hirshfeld surface analysis was conducted to verify the contributions of the different intermolecular interactions.

1. Chemical context

Schiff bases of heterocyclic amines and their complexes have attracted attention over the past decades not only due to the relatively easy synthesis, but also in view of their potential biological, pharmacological and analytical applications (Akbari *et al.*, 2017; Gurbanov *et al.*, 2018*a,b*; Hazra *et al.*, 2018; Kvyatkovskaya *et al.*, 2017; Mahmoudi *et al.*, 2016, 2017*a,b*, 2018*a,b*; Mitoraj *et al.*, 2018; Shetnev *et al.*, 2017). Non-covalent interactions play an important role in the stabilization of coordination or supramolecular compounds derived from Schiff bases (Mahmudov *et al.*, 2016, 2017*a,b*; Zubkov *et al.*, 2018). Herein we report strong charge-assisted hydrogen bonds and halogen bonding in the structure of (*E*)-3-[(2,3-dichlorobenzylidene)amino]-5-phenylthiazolidin-2-iminium bromide.



2. Structural commentary

In the cation of the title salt (Fig. 1), the central thiazolidine ring (S1/N2/C1–C3) adopts an envelope conformation with puckering parameters $Q(2) = 0.205(4) \text{ \AA}$ and $\varphi(2) =$

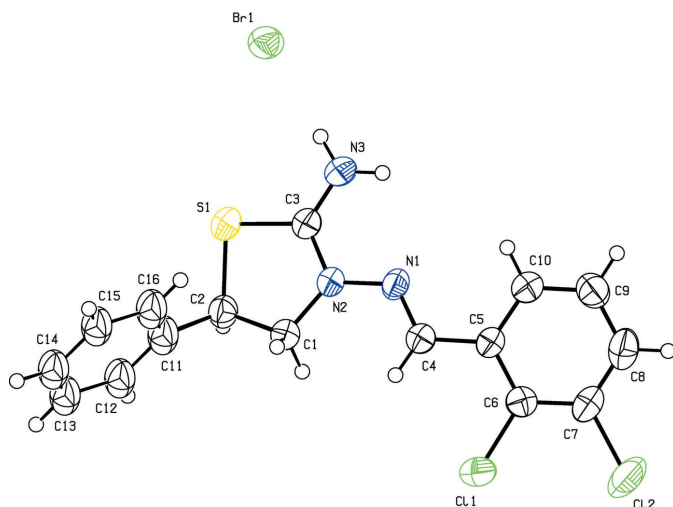


Figure 1
The molecular structure of the title salt. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radius. The minor disorder component is omitted for clarity.

222.1 (12)°. The dihedral angle between the mean plane of the central thiazolidine ring and the 2,3-dichlorobenzene ring (C5–C10) is 16.0 (2)° while this plane subtends angles of 79.1 (3) and 86.7 (4)° with the major and minor components (C11–C16 and C11/C12'–C16'), respectively, of the disordered phenyl ring. The dihedral angle between the two disorder components of the ring is 7.6 (4)° and these components are

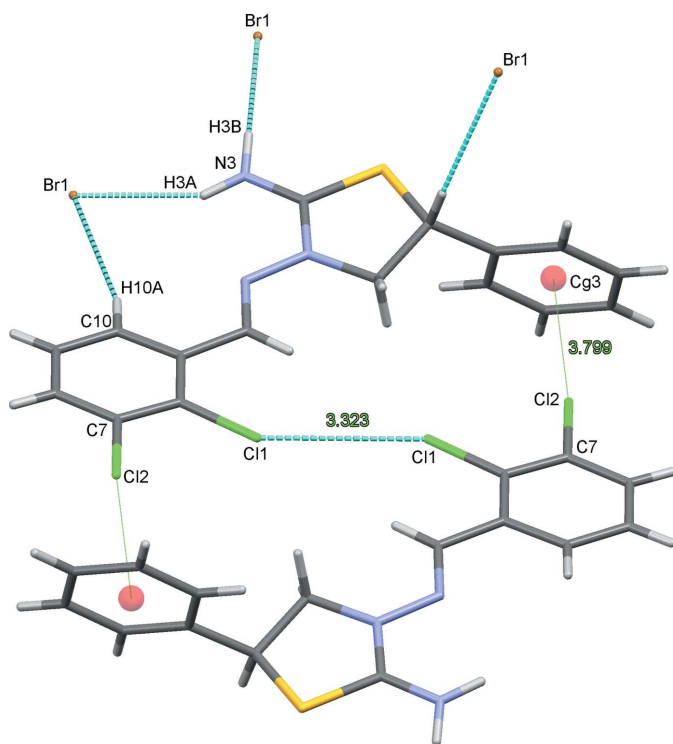


Figure 2
View of the full complement of contacts to an individual cation in the title salt. Only the major disorder component is shown. The symmetry-equivalent position for the cation with the label Cg3 is $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.

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

Cg3 and Cg4 are the centroids of the major and minor disorder components of the C11/C12–C16 and C11/C12'–C16' phenyl ring, respectively.

<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>
N3–H3A···Br1 ⁱ	0.90	2.51	3.303 (4)	147
N3–H3B···Br1	0.90	2.36	3.258 (4)	175
C13'–H13B···Cg3 ⁱⁱ	0.93	2.91	3.596 (12)	132
C13'–H13B···Cg4 ⁱⁱ	0.93	2.99	3.746 (12)	139
C2–H2A···Br1 ⁱⁱⁱ	0.98	2.87	3.778 (5)	154
C10–H10A···Br1 ⁱ	0.93	2.90	3.796 (5)	161
C7–Cl2···Cg3 ^{iv}	1.73 (1)	3.80 (1)	5.525 (6)	175 (1)
C7–Cl2···Cg4 ^{iv}	1.73 (1)	3.57 (1)	5.299 (6)	175 (1)

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

oriented to the 2,3-dichlorobenzene ring by 64.8 (3) and 72.4 (4)°, respectively. The N2–N1–C4–C5 bridge that links the thiazolidine and 2,3-dichlorobenzene rings has a torsion angle of 175.1 (4)°.

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, each cation forms C–H···Br and N–H···Br hydrogen bonds along with inversion-related Cl1···Cl1 halogen bonds and C7–Cl2···Cg3^{iv} and C7–Cl2···Cg4^{iv} contacts (Table 1; Fig. 2). Chains of cations form along the *a*-axis direction (Fig. 3). The crystal structure is further stabilized by C13'–H13B···Cg3ⁱⁱ and C13'–H13B···Cg4ⁱⁱ interactions involving the minor disorder component (Table 1). Overall, cations and anions are stacked along the *b*-axis direction (Fig. 4)

The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) of the title salt was generated by *CrystalExplorer3.1* (Wolff *et al.*, 2012), and comprised d_{norm} surface plots and two dimensional fingerprint plots (Spackman & McKinnon, 2002). A d_{norm} surface plot of the title salt is shown in Fig. 5. This plot

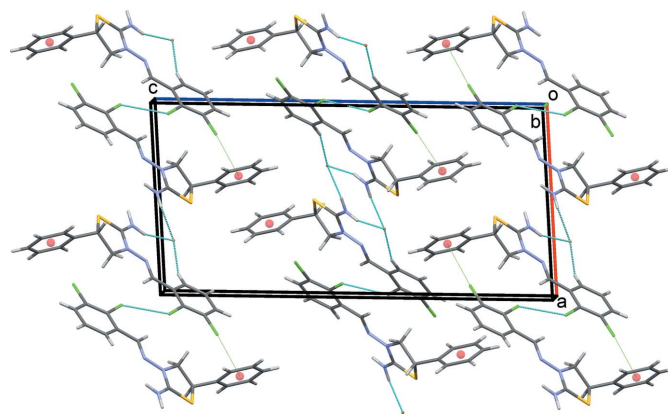


Figure 3
C–H···Br and N–H···Br hydrogen bonds and inversion-related Cl···Cl halogen bonds and C–Cl··· π contacts of the title salt viewed along the *b* axis. Only the major disorder component is shown.

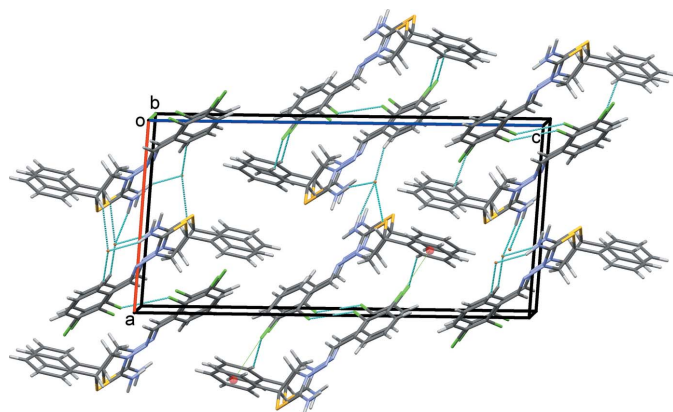


Figure 4
Overall packing of the title salt viewed along the *b* axis. Only the major disorder component is shown.

was generated to quantify and visualize the intermolecular interactions and to explain the observed crystal packing. The dark-red spots on the d_{norm} surface arise as a result of short interatomic contacts, while the other weaker intermolecular interactions appear as light-red spots.

The d_{norm} surface of the title salt shows a dark-red spot at the N–H hydrogen atom and on the bromide atom, which is the result of the strong N3–H3A···Br1¹ and N3–H3B···Br1 hydrogen bonds present in the structure (Fig. 5). Beside these two short intermolecular contacts, the C–H···Br interaction is shown as light-red spots on the d_{norm} surface. The short interatomic contacts in the title salt are given in Table 2.

A quantitative analysis of the intermolecular interactions can be made by studying the fingerprint plots that are shown with characteristic pseudo-symmetry wings in the d_e and d_i diagonal axes [d_e and d_i represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

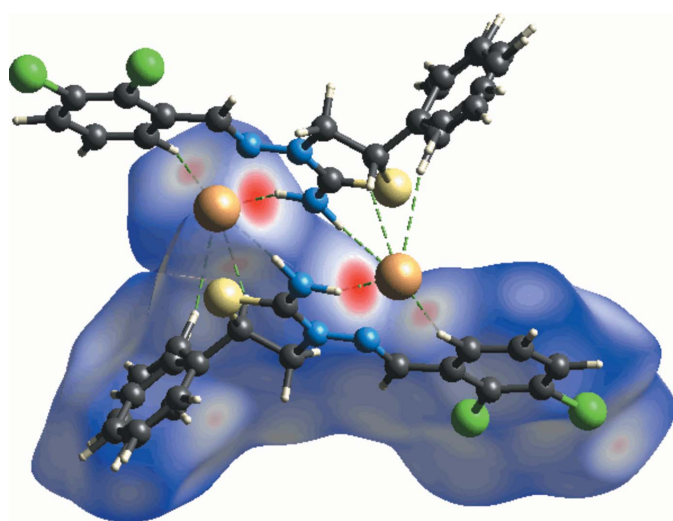


Figure 5
Hirshfeld surface of the title salt mapped with d_{norm} , showing the C–H···Br and N–H···Br hydrogen bonds.

Table 3
Percentage contributions of interatomic contacts to the Hirshfeld surface for the title salt.

Contact	Percentage contribution
H···H	25.4
Cl···H/H···Cl	19.1
C···H/H···C	18.2
Br···H/H···Br	16.2
S···H/H···S	5.9
Cl···C/C···Cl	4.4
N···H/H···N	2.7
C···C	1.9
Cl···N/N···Cl	1.4
C···N/N···C	1.3
Br···C/C···Br	1.0
Cl···Cl	0.8
S···N/N···S	0.7
S···C/C···S	0.4
Br···N/N···Br	0.3
Br···Cl/Cl···Br	0.3

These represent both the overall two-dimensional fingerprint plots and those that represent H···H, Cl···H/H···Cl, C···H/H···C and Br···H/H···Br contacts, respectively (Fig. 6*b–e*). The most significant intermolecular interactions are the H···H interaction (25.4%), which appear in the central region of the fingerprint plot with $d_e = d_i \approx 1.2$ Å (Fig. 6*b*). The reciprocal Cl···H/H···Cl interactions appear as two symmetrical broad wings with $d_e + d_i \approx 2.8$ Å and contribute 19.1% to the Hirshfeld surface (Fig. 6*c*). The reciprocal C···H/H···C and Br···H/H···Br interactions with 18.2% and 16.2% contributions are present as sharp symmetrical spikes at diagonal axes $d_e + d_i \approx 2.7$ and 2.4 Å, respectively (Fig. 6*d–e*). The percen-

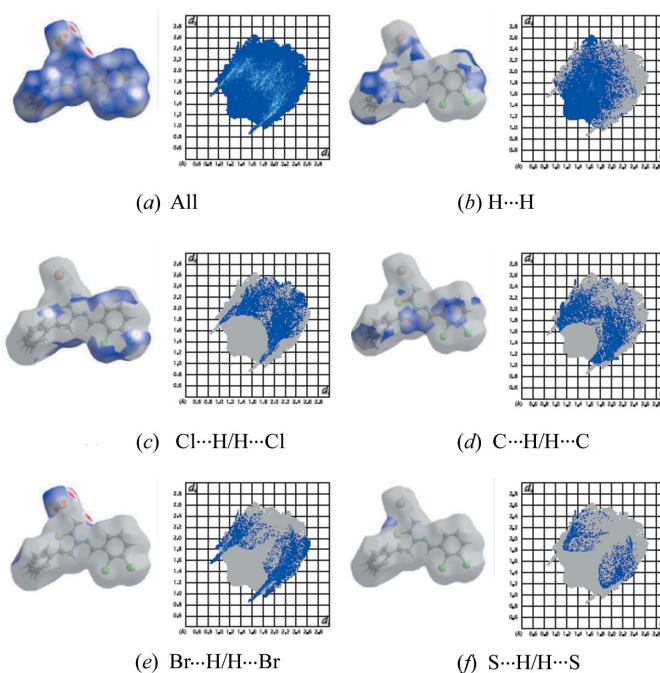


Figure 6
The two-dimensional fingerprint plots of the title salt, showing (a) all interactions, and delineated into (b) H···H, (c) Cl···H/H···Cl, (d) C···H/H···C, (e) Br···H/H···Br and (f) S···H/H···S interactions.

Table 2

Summary of short interatomic contacts (Å) in the title salt.

Atoms marked with an asterisk (*) are from the minor component (C11/C12–C16') of the disordered phenyl ring of the cation.

Contact	Distance	Symmetry operation
(C6)C11...C11(C6)	3.323 (2)	$2 - x, -y, 1 - z$
(C16')*H16B...H8A(C8)	2.56	$2 - x, 1 - y, 1 - z$
(C2)S1...*H14B(C14')	3.05	$1 - x, \frac{1}{2} + y, \frac{3}{2} - z$
(N3)H3B...Br1	2.36	x, y, z
(N3)H3A...Br1	2.51	$1 - x, 2 - y, 1 - z$
(S1)C3...C3(S1)	3.561 (6)	$1 - x, 1 - y, 1 - z$
(C1)H1B...Br1	3.06	$1 - x, 1 - y, 1 - z$
(C5)C10...*H14B(C14')	2.89	$x, \frac{1}{2} - y, -\frac{1}{2} + z$
(C14')*H14B...S1(C2)	3.05	$1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$
(C14')*H14B...C10(C5)	2.89	$x, \frac{1}{2} - y, \frac{1}{2} + z$
(C2)H2A...Br1	2.87	$x, -1 + y, z$

tage contributions of other intermolecular contacts are less than 6% in the Hirshfeld surface mapping (Table 3).

4. Database survey

A search of the Cambridge Structural Database (CSD Version 5.39, Nov 2017 plus three updates; Groom *et al.*, 2016) yielded six hits for 2-thiazolidiniminium compounds with four of them reporting essentially the same cation: [WILBIC (Marthi *et al.*, 1994), WILBOI (Marthi *et al.*, 1994), WILBOI01 (Marthi *et al.*, 1994), YITCEJ (Martem'yanova *et al.*, 1993a), YITCAF (Martem'yanova *et al.*, 1993b) and YOPLUK (Marthi *et al.*, 1995)]. In all cases, the 3-N atom carries a C substituent, not N as found in the title compound. The first three crystal structures were determined for racemic (WILBIC; Marthi *et al.*, 1994) and two optically active samples (WILBOI and WILBOI01; Marthi *et al.*, 1994) of 3-(2'-chloro-2'-phenylethyl)-2-thiazolidiniminium *p*-toluenesulfonate. In all three structures, the most disordered fragment of these molecules is the asymmetric C atom and the Cl atom attached to it. The disorder of the cation in the racemate corresponds to the presence of both enantiomers at each site in the ratio 0.821 (3):0.179 (3). The system of hydrogen bonds connecting two cations and two anions into 12-membered rings is identical in the racemic and in the optically active crystals. YITCEJ (Martem'yanova *et al.*, 1993a), is a product of the interaction of 2-amino-5-methylthiazoline with methyl iodide, with alkylation at the endocyclic nitrogen atom, while YITCAF (Martem'yanova *et al.*, 1993b) is a product of the reaction of 3-nitro-5-methoxy-, 3-nitro-5-chloro-, and 3-bromo-5-nitrosalicylaldehyde with the heterocyclic base to form the salt-like complexes.

5. Synthesis and crystallization

To a solution of 1 mmol of 3-amino-5-phenylthiazolidin-2-iminium bromide in 20 mL ethanol 1 mmol of 2,3-dichlorobenzaldehyde was added and the solution refluxed for 2 h. The reaction mixture was cooled down to precipitate the product as colourless single crystals. These were collected by filtration

Table 4

Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{14}Cl_2N_3S^+ \cdot Br^-$
M_r	431.17
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	11.2586 (8), 6.8886 (5), 23.0145 (16)
β (°)	93.678 (2)
V (Å ³)	1781.2 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	2.73
Crystal size (mm)	0.28 × 0.25 × 0.24
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2007)
T_{min}, T_{max}	0.483, 0.546
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20932, 3651, 2325
R_{int}	0.085
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.051, 0.123, 1.04
No. of reflections	3651
No. of parameters	182
No. of restraints	12
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.47, -0.61

Computer programs: APEX2 and SAINT (Bruker, 2007), SHELXS97 (Sheldrick, 2008), SHELXL2014 (Sheldrick, 2015), ORTEP-3 for Windows (Farrugia, 2012), Mercury (Macrae *et al.*, 2008) and PLATON (Spek, 2003).

and washed with cold acetone. The title compound was recrystallized from methanol by slow evaporation at room temperature over several days.

Yield 89%, m.p. 521 K. Analysis calculated for $C_{16}H_{14}BrCl_2N_3S$ ($M_r = 431.18$): C, 44.57; H, 3.27; N, 9.75. Found: C, 44.51; H, 3.23; N, 9.72%. ¹H NMR (300 MHz, DMSO-*d*₆): 4.62 (*k*, 1H, CH₂, ³*J*_{H-H} = 6.9); 4.96 (*t*, 1H, CH₂, ³*J*_{H-H} = 8.7); 5.59 (*t*, 1H, CH–Ar, ³*J*_{H-H} = 7.5); 7.38–8.50 (*m*, 7H, 7Ar–H); 8.35 (*s*, 1H, CH=); 10.56 (*s*, 1H, NH=). ¹³C NMR (75 MHz, DMSO-*d*₆): 46.62, 55.68, 127.28, 127.99, 128.48, 128.96, 129.11, 132.27, 132.41, 132.51, 133.04, 137.24, 145.89, 168.92. MS (ESI), *m/z*: 351.24 [$C_{16}H_{14}Cl_2N_3S$]⁺ and 79.88 Br⁻.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The H atoms were positioned geometrically [N–H = 0.90 Å and C–H = 0.93–0.97 Å] and were refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C,N)$. The phenyl ring in the cation is disordered over two positions with a site occupancy ratio of 0.541 (9):0.459 (9). Using DFIX, the bond distances in the two disorder components of the phenyl ring were set to 1.40 Å. Corresponding displacement parameters were also held to be the same using EADP.

Funding information

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supporting information

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Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *PLATON* (Spek, 2003).

(*E*)-3-[(2,3-Dichlorobenzylidene)amino]-5-phenylthiazolidin-2-iminium bromide

Crystal data

$C_{16}H_{14}Cl_2N_3S^+Br^-$
 $M_r = 431.17$
 Monoclinic, $P2_1/c$
 $a = 11.2586$ (8) Å
 $b = 6.8886$ (5) Å
 $c = 23.0145$ (16) Å
 $\beta = 93.678$ (2)°
 $V = 1781.2$ (2) Å³
 $Z = 4$

$F(000) = 864$
 $D_x = 1.608$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 5051 reflections
 $\theta = 2.5$ – 24.3 °
 $\mu = 2.73$ mm⁻¹
 $T = 296$ K
 Block, colourless
 $0.28 \times 0.25 \times 0.24$ mm

Data collection

Bruker APEXII CCD
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2007)
 $T_{\min} = 0.483$, $T_{\max} = 0.546$
 20932 measured reflections

3651 independent reflections
 2325 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.085$
 $\theta_{\max} = 26.4$ °, $\theta_{\min} = 2.5$ °
 $h = -14 \rightarrow 14$
 $k = -8 \rightarrow 8$
 $l = -28 \rightarrow 28$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.123$
 $S = 1.04$
 3651 reflections
 182 parameters
 12 restraints

Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map
 Hydrogen site location: mixed
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0342P)^2 + 3.7192P]$
 where $P = (F_o^2 + 2F_c^2)/3$

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

$$\Delta\rho_{\max} = 0.47 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.61 \text{ e } \text{\AA}^{-3}$$

Special details

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Br1	0.33815 (4)	0.95208 (8)	0.56902 (2)	0.05678 (19)	
Cl1	1.02426 (13)	0.1283 (2)	0.44079 (7)	0.0687 (4)	
Cl2	1.12966 (15)	0.2307 (2)	0.32291 (7)	0.0869 (5)	
S1	0.52713 (12)	0.4896 (2)	0.61266 (6)	0.0624 (4)	
N1	0.7591 (3)	0.5219 (5)	0.49730 (15)	0.0408 (9)	
N2	0.6952 (3)	0.4605 (6)	0.54294 (15)	0.0433 (9)	
N3	0.5794 (4)	0.7393 (6)	0.53057 (18)	0.0579 (12)	
H3A	0.624225	0.782615	0.502288	0.069*	
H3B	0.510005	0.793065	0.539518	0.069*	
C1	0.7176 (4)	0.2900 (7)	0.5795 (2)	0.0465 (11)	
H1A	0.787141	0.310790	0.605841	0.056*	
H1B	0.731818	0.177512	0.555530	0.056*	
C2	0.6072 (4)	0.2576 (7)	0.6139 (2)	0.0456 (11)	
H2A	0.556596	0.159930	0.593684	0.055*	
C3	0.6050 (4)	0.5758 (7)	0.5566 (2)	0.0436 (11)	
C4	0.8437 (4)	0.4154 (6)	0.48214 (18)	0.0380 (10)	
H4A	0.865728	0.304542	0.503231	0.046*	
C5	0.9060 (4)	0.4708 (6)	0.43080 (18)	0.0368 (10)	
C6	0.9857 (4)	0.3433 (6)	0.40648 (19)	0.0414 (10)	
C7	1.0339 (4)	0.3904 (8)	0.3543 (2)	0.0514 (13)	
C8	1.0074 (4)	0.5637 (9)	0.3272 (2)	0.0608 (14)	
H8A	1.039350	0.593679	0.292068	0.073*	
C9	0.9330 (5)	0.6929 (8)	0.3525 (2)	0.0586 (14)	
H9A	0.916921	0.812359	0.334891	0.070*	
C10	0.8825 (4)	0.6470 (7)	0.4033 (2)	0.0487 (12)	
H10A	0.831686	0.735272	0.419627	0.058*	
C11	0.6345 (4)	0.1918 (6)	0.67564 (14)	0.0609 (8)	
C12	0.6080 (6)	0.0096 (6)	0.6973 (3)	0.0609 (8)	0.541 (9)
H12A	0.571907	-0.083422	0.672760	0.073*	0.541 (9)
C13	0.6355 (8)	-0.0337 (10)	0.7556 (3)	0.0609 (8)	0.541 (9)
H13A	0.617773	-0.155583	0.770084	0.073*	0.541 (9)
C14	0.6895 (7)	0.1053 (15)	0.79226 (18)	0.0609 (8)	0.541 (9)
H14A	0.707872	0.076397	0.831271	0.073*	0.541 (9)
C15	0.7160 (6)	0.2875 (13)	0.7706 (2)	0.0609 (8)	0.541 (9)
H15A	0.752105	0.380540	0.795135	0.073*	0.541 (9)
C16	0.6885 (6)	0.3308 (7)	0.7123 (2)	0.0609 (8)	0.541 (9)

H16A	0.706240	0.452706	0.697811	0.073*	0.541 (9)
C12'	0.5874 (10)	0.0071 (10)	0.6850 (4)	0.0609 (8)	0.459 (9)
H12B	0.540937	-0.050445	0.654817	0.073*	0.459 (9)
C13'	0.6064 (10)	-0.0955 (17)	0.7373 (4)	0.0609 (8)	0.459 (9)
H13B	0.575083	-0.219058	0.741912	0.073*	0.459 (9)
C14'	0.6746 (10)	-0.0036 (19)	0.7822 (5)	0.0609 (8)	0.459 (9)
H14B	0.690965	-0.069494	0.817074	0.073*	0.459 (9)
C15'	0.7188 (10)	0.1846 (18)	0.7762 (4)	0.0609 (8)	0.459 (9)
H15B	0.758883	0.247056	0.807429	0.073*	0.459 (9)
C16'	0.7016 (9)	0.2771 (16)	0.7221 (3)	0.0609 (8)	0.459 (9)
H16B	0.735675	0.398420	0.716985	0.073*	0.459 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0494 (3)	0.0517 (3)	0.0702 (4)	0.0042 (3)	0.0114 (2)	0.0059 (3)
Cl1	0.0778 (9)	0.0476 (8)	0.0840 (10)	0.0186 (7)	0.0307 (8)	0.0078 (7)
Cl2	0.0899 (11)	0.0856 (11)	0.0910 (12)	0.0098 (9)	0.0511 (9)	-0.0178 (9)
S1	0.0564 (8)	0.0674 (9)	0.0669 (9)	0.0151 (7)	0.0308 (7)	0.0139 (7)
N1	0.041 (2)	0.044 (2)	0.039 (2)	-0.0015 (17)	0.0120 (16)	-0.0025 (17)
N2	0.045 (2)	0.046 (2)	0.041 (2)	0.0077 (18)	0.0128 (17)	0.0048 (18)
N3	0.052 (2)	0.057 (3)	0.067 (3)	0.019 (2)	0.025 (2)	0.011 (2)
C1	0.049 (3)	0.049 (3)	0.042 (3)	0.007 (2)	0.009 (2)	0.004 (2)
C2	0.043 (3)	0.051 (3)	0.044 (3)	-0.001 (2)	0.008 (2)	0.003 (2)
C3	0.042 (2)	0.045 (3)	0.044 (3)	0.002 (2)	0.009 (2)	0.001 (2)
C4	0.038 (2)	0.039 (3)	0.037 (2)	-0.0026 (19)	0.0010 (19)	-0.0036 (19)
C5	0.033 (2)	0.040 (2)	0.037 (2)	-0.0042 (19)	0.0035 (18)	-0.005 (2)
C6	0.039 (2)	0.039 (3)	0.046 (3)	-0.004 (2)	0.002 (2)	-0.002 (2)
C7	0.048 (3)	0.059 (3)	0.049 (3)	-0.004 (2)	0.015 (2)	-0.012 (3)
C8	0.051 (3)	0.084 (4)	0.048 (3)	-0.004 (3)	0.012 (2)	0.004 (3)
C9	0.055 (3)	0.061 (3)	0.060 (3)	0.005 (3)	0.007 (3)	0.015 (3)
C10	0.047 (3)	0.050 (3)	0.049 (3)	0.006 (2)	0.008 (2)	0.000 (2)
C11	0.0495 (16)	0.090 (2)	0.0436 (16)	0.0106 (16)	0.0043 (12)	0.0150 (15)
C12	0.0495 (16)	0.090 (2)	0.0436 (16)	0.0106 (16)	0.0043 (12)	0.0150 (15)
C13	0.0495 (16)	0.090 (2)	0.0436 (16)	0.0106 (16)	0.0043 (12)	0.0150 (15)
C14	0.0495 (16)	0.090 (2)	0.0436 (16)	0.0106 (16)	0.0043 (12)	0.0150 (15)
C15	0.0495 (16)	0.090 (2)	0.0436 (16)	0.0106 (16)	0.0043 (12)	0.0150 (15)
C16	0.0495 (16)	0.090 (2)	0.0436 (16)	0.0106 (16)	0.0043 (12)	0.0150 (15)
C12'	0.0495 (16)	0.090 (2)	0.0436 (16)	0.0106 (16)	0.0043 (12)	0.0150 (15)
C13'	0.0495 (16)	0.090 (2)	0.0436 (16)	0.0106 (16)	0.0043 (12)	0.0150 (15)
C14'	0.0495 (16)	0.090 (2)	0.0436 (16)	0.0106 (16)	0.0043 (12)	0.0150 (15)
C15'	0.0495 (16)	0.090 (2)	0.0436 (16)	0.0106 (16)	0.0043 (12)	0.0150 (15)
C16'	0.0495 (16)	0.090 (2)	0.0436 (16)	0.0106 (16)	0.0043 (12)	0.0150 (15)

Geometric parameters (Å, °)

Cl1—C6	1.720 (5)	C9—H9A	0.9300
Cl2—C7	1.730 (5)	C10—H10A	0.9300

S1—C3	1.712 (5)	C11—C12	1.3900
S1—C2	1.834 (5)	C11—C16	1.3900
N1—C4	1.269 (5)	C11—C16'	1.399 (2)
N1—N2	1.377 (5)	C11—C12'	1.400 (2)
N2—C3	1.342 (5)	C12—C13	1.3900
N2—C1	1.457 (6)	C12—H12A	0.9300
N3—C3	1.299 (6)	C13—C14	1.3900
N3—H3A	0.9000	C13—H13A	0.9300
N3—H3B	0.9001	C14—C15	1.3900
C1—C2	1.533 (6)	C14—H14A	0.9300
C1—H1A	0.9700	C15—C16	1.3900
C1—H1B	0.9700	C15—H15A	0.9300
C2—C11	1.503 (6)	C16—H16A	0.9300
C2—H2A	0.9800	C12'—C13'	1.400 (2)
C4—C5	1.463 (6)	C12'—H12B	0.9300
C4—H4A	0.9300	C13'—C14'	1.400 (2)
C5—C10	1.386 (6)	C13'—H13B	0.9300
C5—C6	1.398 (6)	C14'—C15'	1.399 (2)
C6—C7	1.388 (6)	C14'—H14B	0.9300
C7—C8	1.370 (7)	C15'—C16'	1.400 (2)
C8—C9	1.376 (7)	C15'—H15B	0.9300
C8—H8A	0.9300	C16'—H16B	0.9300
C9—C10	1.371 (7)		
C3—S1—C2	92.3 (2)	C8—C9—H9A	119.7
C4—N1—N2	118.1 (4)	C9—C10—C5	120.9 (5)
C3—N2—N1	115.9 (4)	C9—C10—H10A	119.5
C3—N2—C1	116.6 (4)	C5—C10—H10A	119.5
N1—N2—C1	127.4 (3)	C12—C11—C16	120.0
C3—N3—H3A	120.2	C16'—C11—C12'	117.1 (6)
C3—N3—H3B	114.9	C12—C11—C2	125.1 (4)
H3A—N3—H3B	124.4	C16—C11—C2	114.9 (4)
N2—C1—C2	107.4 (4)	C16'—C11—C2	131.6 (6)
N2—C1—H1A	110.2	C12'—C11—C2	111.2 (5)
C2—C1—H1A	110.2	C13—C12—C11	120.0
N2—C1—H1B	110.2	C13—C12—H12A	120.0
C2—C1—H1B	110.2	C11—C12—H12A	120.0
H1A—C1—H1B	108.5	C12—C13—C14	120.0
C11—C2—C1	114.2 (4)	C12—C13—H13A	120.0
C11—C2—S1	110.4 (3)	C14—C13—H13A	120.0
C1—C2—S1	106.2 (3)	C13—C14—C15	120.0
C11—C2—H2A	108.7	C13—C14—H14A	120.0
C1—C2—H2A	108.7	C15—C14—H14A	120.0
S1—C2—H2A	108.7	C16—C15—C14	120.0
N3—C3—N2	123.6 (4)	C16—C15—H15A	120.0
N3—C3—S1	122.6 (3)	C14—C15—H15A	120.0
N2—C3—S1	113.8 (3)	C15—C16—C11	120.0
N1—C4—C5	118.6 (4)	C15—C16—H16A	120.0

N1—C4—H4A	120.7	C11—C16—H16A	120.0
C5—C4—H4A	120.7	C11—C12'—C13'	123.5 (9)
C10—C5—C6	118.5 (4)	C11—C12'—H12B	118.3
C10—C5—C4	120.6 (4)	C13'—C12'—H12B	118.3
C6—C5—C4	120.8 (4)	C14'—C13'—C12'	117.0 (10)
C7—C6—C5	119.7 (4)	C14'—C13'—H13B	121.5
C7—C6—C11	119.8 (4)	C12'—C13'—H13B	121.5
C5—C6—C11	120.4 (3)	C15'—C14'—C13'	121.8 (10)
C8—C7—C6	120.7 (4)	C15'—C14'—H14B	119.1
C8—C7—C12	119.2 (4)	C13'—C14'—H14B	119.1
C6—C7—C12	120.1 (4)	C14'—C15'—C16'	118.7 (10)
C7—C8—C9	119.5 (5)	C14'—C15'—H15B	120.6
C7—C8—H8A	120.2	C16'—C15'—H15B	120.6
C9—C8—H8A	120.2	C11—C16'—C15'	121.7 (8)
C10—C9—C8	120.6 (5)	C11—C16'—H16B	119.2
C10—C9—H9A	119.7	C15'—C16'—H16B	119.2
C4—N1—N2—C3	-178.7 (4)	C8—C9—C10—C5	0.7 (8)
C4—N1—N2—C1	4.3 (6)	C6—C5—C10—C9	2.1 (7)
C3—N2—C1—C2	16.1 (6)	C4—C5—C10—C9	-174.5 (4)
N1—N2—C1—C2	-166.9 (4)	C1—C2—C11—C12	-112.2 (5)
N2—C1—C2—C11	-141.6 (4)	S1—C2—C11—C12	128.3 (4)
N2—C1—C2—S1	-19.8 (4)	C1—C2—C11—C16	69.0 (5)
C3—S1—C2—C11	140.2 (3)	S1—C2—C11—C16	-50.4 (4)
C3—S1—C2—C1	15.9 (4)	C1—C2—C11—C16'	58.9 (10)
N1—N2—C3—N3	-2.2 (7)	S1—C2—C11—C16'	-60.6 (9)
C1—N2—C3—N3	175.2 (5)	C1—C2—C11—C12'	-117.4 (7)
N1—N2—C3—S1	178.8 (3)	S1—C2—C11—C12'	123.1 (7)
C1—N2—C3—S1	-3.8 (5)	C16—C11—C12—C13	0.0
C2—S1—C3—N3	173.2 (4)	C2—C11—C12—C13	-178.7 (5)
C2—S1—C3—N2	-7.8 (4)	C11—C12—C13—C14	0.0
N2—N1—C4—C5	175.1 (4)	C12—C13—C14—C15	0.0
N1—C4—C5—C10	7.4 (6)	C13—C14—C15—C16	0.0
N1—C4—C5—C6	-169.2 (4)	C14—C15—C16—C11	0.0
C10—C5—C6—C7	-3.5 (6)	C12—C11—C16—C15	0.0
C4—C5—C6—C7	173.1 (4)	C2—C11—C16—C15	178.9 (4)
C10—C5—C6—C11	176.6 (3)	C16'—C11—C12'—C13'	-1.5 (15)
C4—C5—C6—C11	-6.8 (6)	C2—C11—C12'—C13'	175.4 (9)
C5—C6—C7—C8	2.2 (7)	C11—C12'—C13'—C14'	1.2 (16)
C11—C6—C7—C8	-177.9 (4)	C12'—C13'—C14'—C15'	2.0 (16)
C5—C6—C7—C12	-178.4 (3)	C13'—C14'—C15'—C16'	-4.9 (16)
C11—C6—C7—C12	1.6 (6)	C12'—C11—C16'—C15'	-1.5 (15)
C6—C7—C8—C9	0.6 (8)	C2—C11—C16'—C15'	-177.6 (7)
C12—C7—C8—C9	-178.8 (4)	C14'—C15'—C16'—C11	4.6 (16)
C7—C8—C9—C10	-2.1 (8)		

Hydrogen-bond geometry (Å, °)

Cg3 and Cg4 are the centroids of the major (C11-C16) and minor (C11/C12'-C16') disorder components, respectively, of the phenyl 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>
N3—H3 <i>A</i> \cdots Br1 ⁱ	0.90	2.51	3.303 (4)	147
N3—H3 <i>B</i> \cdots Br1	0.90	2.36	3.258 (4)	175
C13'—H13 <i>B</i> \cdots Cg3 ⁱⁱ	0.93	2.91	3.596 (12)	132
C13'—H13 <i>B</i> \cdots Cg4 ⁱⁱ	0.93	2.99	3.746 (12)	139
C2—H2 <i>A</i> \cdots Br1 ⁱⁱⁱ	0.98	2.87	3.778 (5)	154
C10—H10 <i>A</i> \cdots Br1 ⁱ	0.93	2.90	3.796 (5)	161
C7—C12 \cdots Cg3 ^{iv}	1.73 (1)	3.80 (1)	5.525 (6)	175 (1)
C7—C12 \cdots Cg4 ^{iv}	1.73 (1)	3.57 (1)	5.299 (6)	175 (1)

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