



Crystal structure and Hirshfeld surface analysis of (*E*)-3-[(4-fluorobenzylidene)amino]-5-phenylthiazolidin-2-iminium bromide

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In the cation of the title salt, C₁₆H₁₅FN₃S⁺·Br⁻, the phenyl ring is disordered over two sets of sites with a refined occupancy ratio of 0.503 (4):0.497 (4). The mean plane of the thiazolidine ring makes dihedral angles of 13.51 (14), 48.6 (3) and 76.5 (3)° with the fluorophenyl ring and the major- and minor-disorder components of the phenyl ring, respectively. The central thiazolidine ring adopts an envelope conformation. In the crystal, centrosymmetrically related cations and anions are linked into dimeric units *via* N—H···Br hydrogen bonds, which are further connected by weak C—H···Br hydrogen bonds into chains parallel to [110]. Hirshfeld surface analysis and two-dimensional fingerprint plots indicate that the most important contributions to the crystal packing are from H···H (44.3%), Br···H/H···Br (16.8%), C···H/H···C (13.9%), F···H/H···F (10.3%) and S···H/H···S (3.8%) interactions.

1. Chemical context

Noncovalent interactions, both intermolecular and intramolecular, occur in virtually every substance and play an important role in the synthesis, catalysis, design of materials and biological processes (Akbari *et al.*, 2017; Gurbanov *et al.*, 2018; Kopylovich *et al.*, 2011; Maharramov *et al.*, 2010; Mahmoudi *et al.*, 2018*a,b,c*; Mahmudov *et al.*, 2011, 2013, 2014*a,b*, 2015, 2017*a,b*, 2019; Shixaliyev *et al.*, 2013, 2018). On the other hand, Schiff bases and related hydrazone ligands and their complexes have attracted attention over the past decades due to their potential biological, pharmacological and analytical applications (Kopylovich *et al.*, 2011; Mahmoudi *et al.*, 2018*a,b,c*; Mahmudov *et al.*, 2013). Heterocyclic amines are also widely used in the synthesis of Schiff bases, which provide different kinds of noncovalent interactions. As a further study in this field, we report herein the crystal structure and Hirshfeld surface analysis of the title compound.

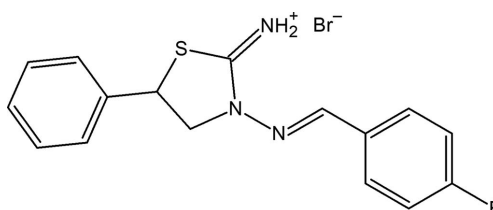
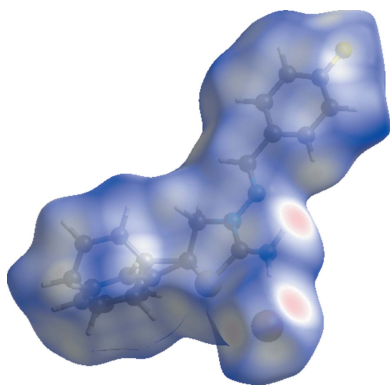


Table 1
Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------|-------|-------------|-------------|---------------|
| $N3-H3A\cdots Br1$ | 0.90 | 2.36 | 3.2557 (18) | 172 |
| $N3-H3B\cdots Br1^i$ | 0.90 | 2.55 | 3.3552 (18) | 150 |
| $C4-H4A\cdots Br1^{ii}$ | 0.93 | 2.99 | 3.726 (2) | 137 |

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

2. Structural commentary

The thiazolidine ring (S1/N2/C1–C3) in the cation of the title salt (Fig. 1) adopts an envelope conformation, with puckering parameters of $Q(2) = 0.321(3)$ Å and $\varphi(2) = 43.3(5)^\circ$. The mean plane of the thiazolidine ring makes dihedral angles of $13.51(14)$, $48.6(3)$ and $76.5(3)^\circ$ with the fluorophenyl ring (C5–C10) and the major- and minor-disorder components (C11–C16 and C11'–C16') of the phenyl ring, respectively. The N2–N1–C4–C5 bridge that links the thiazolidine and 4-fluorophenyl rings has a torsion angle of $-177.36(19)^\circ$.

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, centrosymmetrically related cations and anions are linked *via* pairs of N–H \cdots Br hydrogen bonds (Table 1) into dimeric units forming rings of $R_4^2(8)$ graph-set motif (Fig. 2). The dimers are further connected by weak C–H \cdots Br interactions to form chains running parallel to [110].

Hirshfeld surface analysis was used to investigate the presence of hydrogen bonds and intermolecular interactions in the crystal structure. 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 2D fingerprint plots (Spackman &

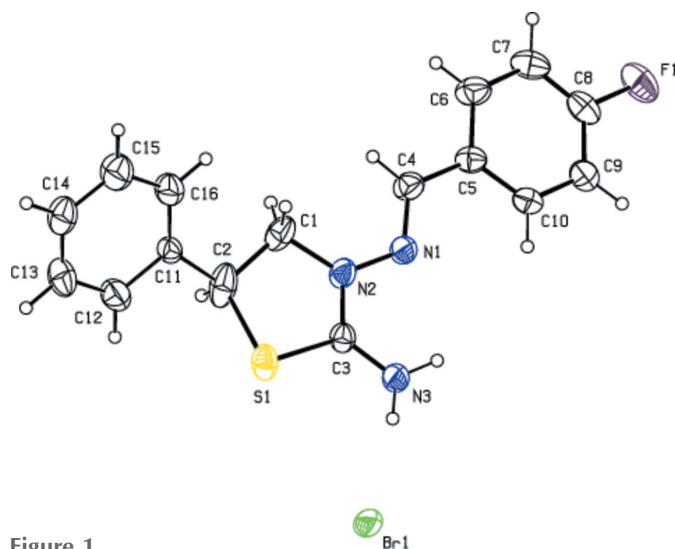


Figure 1
The molecular structure of the title salt. Displacement ellipsoids are drawn at the 30% probability level. H atoms are shown as spheres of arbitrary radius. The minor-disorder component has been omitted for clarity

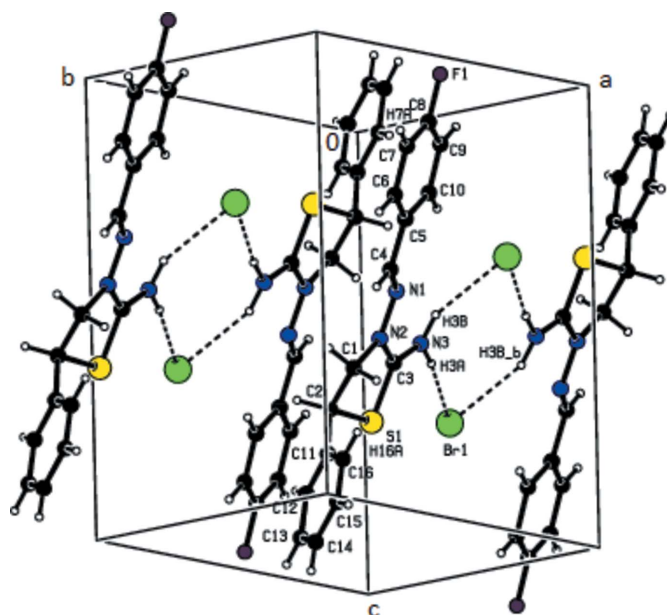


Figure 2
A view of the intermolecular N–H \cdots Br hydrogen bonds of the title salt in the unit cell. The minor-disorder component has been omitted for clarity

McKinnon, 2002). The plots of the Hirshfeld surface mapped over d_{norm} using a standard surface resolution with a fixed colour scale of -1.4747 (red) to 1.2166 a.u. (blue) is shown in Fig. 3. This plot was generated to quantify and visualize the intermolecular interactions and to explain the observed crystal packing.

The shape index of the Hirshfeld surface is a tool to visualize π – π stacking interactions by the presence of adjacent red and blue triangles; if there are no adjacent red and/or blue

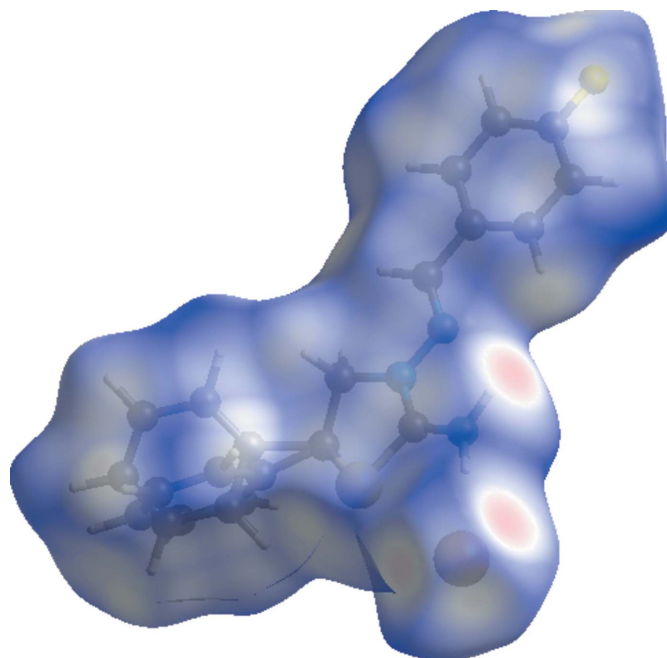


Figure 3
Hirshfeld surface of the title salt mapped with d_{norm} .

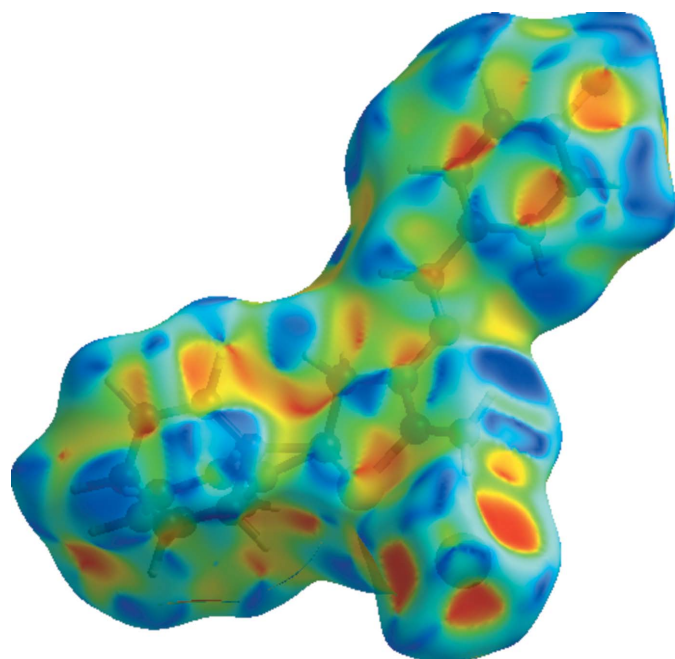


Figure 4
Hirshfeld surface of the title salt mapped with shape index.

Table 2
Percentage contributions of interatomic contacts to the Hirshfeld surface for the title salt.

| Contact | Percentage contribution |
|---------------|-------------------------|
| H...H | 44.3 |
| Br...H/H...Br | 16.8 |
| C...H/H...C | 13.9 |
| F...H/H...F | 10.3 |
| S...H/H...S | 3.8 |
| N...C/C...N | 3.6 |
| S...C/C...S | 2.7 |
| N...H/H...N | 1.8 |
| C...C | 1.5 |
| N...N | 0.7 |
| Br...C/C...Br | 0.3 |
| S...N/N...S | 0.3 |
| F...C/C...F | 0.2 |

triangles, then there are no π - π interactions. Fig. 4 clearly suggest that there are no π - π interactions present in the title salt.

Fig. 5(a) shows the 2D fingerprint of the sum of the contacts contributing to the Hirshfeld surface represented in normal mode. These represent both the overall 2D fingerprint plots

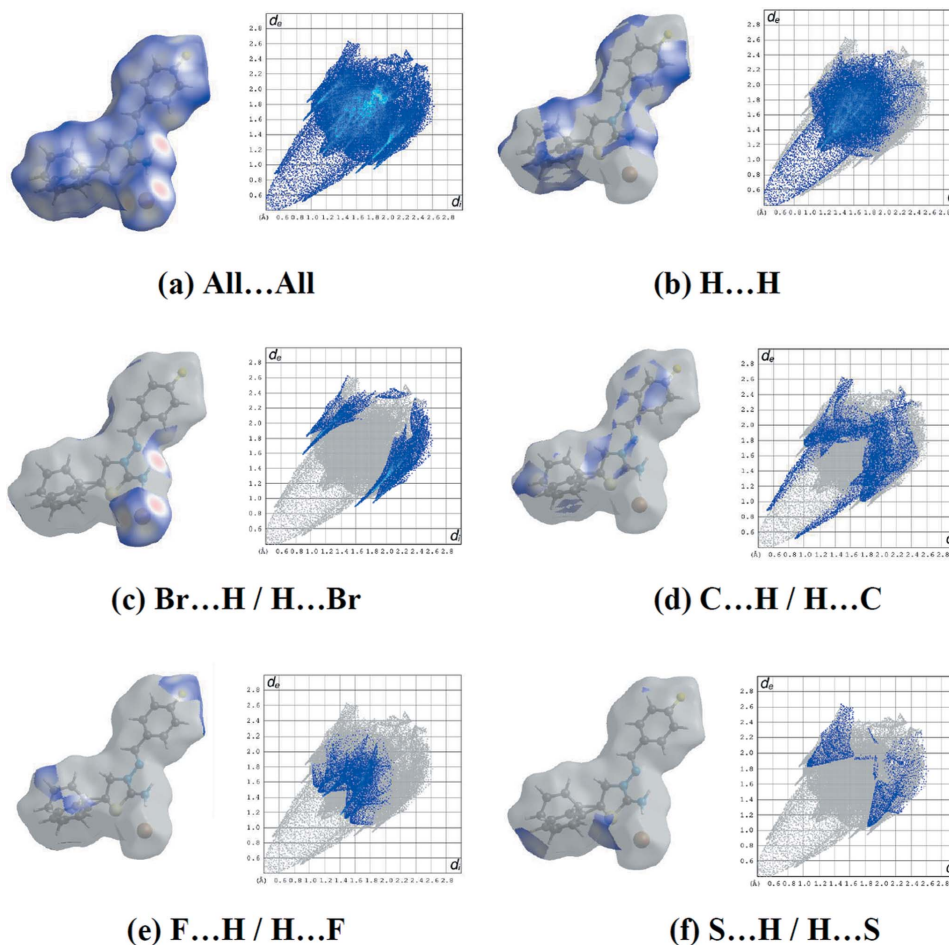


Figure 5
The 2D fingerprint plots of the title salt, showing (a) all interactions, and delineated into (b) H...H, (c) Br...H/H...Br, (d) C...H/H...C, (e) F...H/H...F and (f) S...H/H...S interactions [d_e and d_i represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

and those that represent H···H (44.3%), Br···H/H···Br (16.8%), C···H/H···C (13.9%), F···H/H···F (10.3%) and S···H/H···S (3.8%) contacts, respectively (Figs. 5*b–f*). The most significant intermolecular interactions are the H···H interactions (44.3%) (Fig. 6*b*). All the contributions to the Hirshfeld surface are given in Table 2.

3.1. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.40, update of November 2018; Groom *et al.*, 2016) for 2-thiazolidiniminium compounds gave seven hits, *viz.* UDELUN (Akkurt *et al.*, 2018), WILBIC (Marthi *et al.*, 1994), WILBOI (Marthi *et al.*, 1994), WILBOI01 (Marthi *et al.*, 1994), YITCEJ (Martem'yanova *et al.*, 1993*a*), YITCAF (Martem'yanova *et al.*, 1993*b*) and YOPLUK (Marthi *et al.*, 1995).

In the crystal of UDELUN (Akkurt *et al.*, 2018), 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.

In the remaining structures, the 3-N atom carries a C-substituent instead of an N-substituent, 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.*, 1993*a*) is a product of the interaction of 2-amino-5-methylthiazoline with methyl iodide, with alkylation at the endocyclic N atom, while YITCAF (Martem'yanova *et al.*, 1993*b*) 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.

4. Synthesis and crystallization

To a solution of 3-amino-5-phenylthiazolidin-2-iminium bromide (1 mmol) in ethanol (20 ml) was added 4-fluorobenzaldehyde (1 mmol). The mixture was refluxed for 2 h and then cooled. The reaction product precipitated from the reaction mixture as colourless single crystals, was collected by filtration and washed with cold acetone (yield 64%; m.p. 544–545 K). Analysis calculated (%) for C₁₆H₁₅BrFN₃S: C 50.53, H 3.98, N 11.05; found: C 50.47, H 3.93, N 11.00. ¹H NMR (300 MHz, DMSO-*d*₆): 4.56 (*k*, 1H, CH₂, ³*J*_{H-H} = 6.6 Hz), 4.87 (*t*, 1H, CH₂,

Table 3
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | C ₁₆ H ₁₅ FN ₃ S ⁺ ·Br [−] |
| <i>M</i> _r | 380.28 |
| Crystal system, space group | Triclinic, <i>P</i> $\bar{1}$ |
| Temperature (K) | 296 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 8.0599 (3), 8.6086 (4), 12.7608 (5) |
| α , β , γ (°) | 96.548 (2), 92.518 (2), 111.065 (2) |
| <i>V</i> (Å ³) | 817.39 (6) |
| <i>Z</i> | 2 |
| Radiation type | Mo <i>K</i> α |
| μ (mm ^{−1}) | 2.65 |
| Crystal size (mm) | 0.16 × 0.12 × 0.09 |
| Data collection | |
| Diffractometer | Bruker APEXII CCD |
| Absorption correction | Multi-scan (<i>SADABS</i> ; Bruker, 2003) |
| <i>T</i> _{min} , <i>T</i> _{max} | 0.664, 0.782 |
| No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections | 12009, 3321, 2672 |
| <i>R</i> _{int} | 0.025 |
| (<i>sin</i> θ / λ) _{max} (Å ^{−1}) | 0.627 |
| Refinement | |
| <i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i> | 0.029, 0.077, 1.04 |
| No. of reflections | 3321 |
| No. of parameters | 254 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ^{−3}) | 0.37, −0.48 |

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

³*J*_{H-H} = 7.8 Hz), 5.60 (*t*, 1H, CH-Ar, 3*J*_{H-H} = 7.8 Hz), 7.32–8.16 (*m*, 9H, 9Ar-H), 8.45 (*s*, 1H, CH=), 10.37 (*s*, 2H, NH₂). ¹³C NMR (75 MHz, DMSO-*d*₆): 45.39, 55.97, 116.05, 127.81, 128.91, 129.13, 129.60, 131.05, 131.17, 137.55, 150.00, 167.89. MS (ESI), *m/z*: 300.36 [C₁₆H₁₅FN₃S]⁺ and 79.88 Br[−].

5. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were positioned geometrically and refined using a riding model, with N—H = 0.90 Å and C—H = 0.93–0.98 Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(C,N). The phenyl ring in the cation is disordered over two sets of sites with an occupancy ratio of 0.503 (4):0.497 (4). Seven outliers (001; $\bar{3}05$; $\bar{1}43$; 010; $\bar{2}75$; $\bar{2}$, $\bar{1}$,12; and $\bar{7}53$) were omitted in the final cycles of refinement.

Acknowledgements

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supporting information

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Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (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); software used to prepare material for publication: *PLATON* (Spek, 2003).

(*E*)-3-[(4-Fluorobenzylidene)amino]-5-phenylthiazolidin-2-iminium bromide

Crystal data

$C_{16}H_{15}FN_3S^+ \cdot Br^-$
 $M_r = 380.28$
 Triclinic, $P\bar{1}$
 $a = 8.0599$ (3) Å
 $b = 8.6086$ (4) Å
 $c = 12.7608$ (5) Å
 $\alpha = 96.548$ (2)°
 $\beta = 92.518$ (2)°
 $\gamma = 111.065$ (2)°
 $V = 817.39$ (6) Å³

$Z = 2$
 $F(000) = 384$
 $D_x = 1.545$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 5655 reflections
 $\theta = 2.6$ – 26.3 °
 $\mu = 2.65$ mm⁻¹
 $T = 296$ K
 Plate, colorless
 $0.16 \times 0.12 \times 0.09$ mm

Data collection

Bruker APEXII CCD
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2003)
 $T_{\min} = 0.664$, $T_{\max} = 0.782$
 12009 measured reflections

3321 independent reflections
 2672 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\max} = 26.5$ °, $\theta_{\min} = 2.7$ °
 $h = -10 \rightarrow 7$
 $k = -10 \rightarrow 10$
 $l = -14 \rightarrow 15$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.077$
 $S = 1.03$
 3321 reflections
 254 parameters
 0 restraints

Hydrogen site location: mixed
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 0.2228P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.37$ e Å⁻³
 $\Delta\rho_{\min} = -0.48$ e Å⁻³

Special details

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

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

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|-------------|--------------|--------------|----------------------------------|-----------|
| Br1 | 0.28837 (4) | -0.06846 (3) | 0.65093 (2) | 0.07274 (12) | |
| S1 | 0.50535 (9) | 0.40641 (8) | 0.72511 (4) | 0.06317 (17) | |
| F1 | 1.1652 (2) | 0.6889 (3) | 0.07197 (13) | 0.0994 (6) | |
| N1 | 0.7677 (2) | 0.5288 (2) | 0.48291 (13) | 0.0510 (4) | |
| C1 | 0.7491 (4) | 0.6768 (3) | 0.66453 (19) | 0.0676 (7) | |
| H1A | 0.765957 | 0.780305 | 0.635640 | 0.081* | |
| H1B | 0.859205 | 0.688530 | 0.704392 | 0.081* | |
| N2 | 0.6981 (3) | 0.5342 (2) | 0.57951 (13) | 0.0540 (4) | |
| C2 | 0.5974 (5) | 0.6381 (4) | 0.73431 (19) | 0.0803 (9) | |
| H2A | 0.506784 | 0.680819 | 0.710523 | 0.096* | |
| N3 | 0.5389 (3) | 0.2468 (2) | 0.54077 (14) | 0.0564 (5) | |
| H3A | 0.472588 | 0.153018 | 0.566419 | 0.068* | |
| H3B | 0.598218 | 0.240158 | 0.483319 | 0.068* | |
| C3 | 0.5851 (3) | 0.3881 (3) | 0.60334 (16) | 0.0489 (5) | |
| C4 | 0.8962 (3) | 0.6588 (3) | 0.46468 (18) | 0.0583 (6) | |
| H4A | 0.943400 | 0.751707 | 0.516854 | 0.070* | |
| C5 | 0.9692 (3) | 0.6619 (3) | 0.36204 (18) | 0.0532 (5) | |
| C6 | 1.0980 (3) | 0.8092 (3) | 0.3405 (2) | 0.0691 (7) | |
| H6A | 1.139096 | 0.902914 | 0.392330 | 0.083* | |
| C7 | 1.1660 (4) | 0.8188 (4) | 0.2431 (2) | 0.0767 (8) | |
| H7A | 1.254083 | 0.916970 | 0.229104 | 0.092* | |
| C8 | 1.1011 (3) | 0.6810 (4) | 0.1683 (2) | 0.0665 (7) | |
| C9 | 0.9756 (3) | 0.5314 (3) | 0.1862 (2) | 0.0659 (6) | |
| H9A | 0.935350 | 0.438646 | 0.133610 | 0.079* | |
| C10 | 0.9115 (3) | 0.5229 (3) | 0.28380 (19) | 0.0592 (6) | |
| H10A | 0.827792 | 0.422230 | 0.298028 | 0.071* | |
| C11 | 0.6893 (9) | 0.7289 (7) | 0.8505 (5) | 0.0447 (13) | 0.503 (4) |
| C12 | 0.5575 (7) | 0.6983 (7) | 0.9197 (5) | 0.0691 (15) | 0.503 (4) |
| H12A | 0.439229 | 0.635805 | 0.894732 | 0.083* | 0.503 (4) |
| C13 | 0.6019 (12) | 0.7611 (13) | 1.0269 (6) | 0.074 (2) | 0.503 (4) |
| H13A | 0.513251 | 0.739287 | 1.073481 | 0.089* | 0.503 (4) |
| C14 | 0.7747 (12) | 0.8546 (10) | 1.0639 (5) | 0.0740 (16) | 0.503 (4) |
| H14A | 0.804349 | 0.898834 | 1.135130 | 0.089* | 0.503 (4) |
| C15 | 0.9041 (8) | 0.8822 (8) | 0.9946 (4) | 0.0811 (17) | 0.503 (4) |
| H15A | 1.022734 | 0.943608 | 1.019215 | 0.097* | 0.503 (4) |
| C16 | 0.8600 (7) | 0.8201 (7) | 0.8893 (4) | 0.0660 (14) | 0.503 (4) |
| H16A | 0.949586 | 0.841027 | 0.843322 | 0.079* | 0.503 (4) |
| C11' | 0.5982 (9) | 0.7008 (8) | 0.8494 (5) | 0.0489 (14) | 0.497 (4) |
| C12' | 0.5168 (7) | 0.8137 (6) | 0.8805 (4) | 0.0631 (13) | 0.497 (4) |

| | | | | | |
|------|-------------|-------------|------------|-------------|-----------|
| H12B | 0.447047 | 0.841350 | 0.831371 | 0.076* | 0.497 (4) |
| C13' | 0.5408 (8) | 0.8852 (7) | 0.9865 (5) | 0.0759 (18) | 0.497 (4) |
| H13B | 0.488252 | 0.962201 | 1.007970 | 0.091* | 0.497 (4) |
| C14' | 0.6390 (15) | 0.8437 (12) | 1.0570 (7) | 0.079 (3) | 0.497 (4) |
| H14B | 0.655646 | 0.893516 | 1.127240 | 0.094* | 0.497 (4) |
| C15' | 0.7133 (14) | 0.7321 (12) | 1.0286 (5) | 0.0843 (19) | 0.497 (4) |
| H15B | 0.779040 | 0.702274 | 1.078940 | 0.101* | 0.497 (4) |
| C16' | 0.6923 (8) | 0.6598 (8) | 0.9226 (5) | 0.0793 (17) | 0.497 (4) |
| H16B | 0.744737 | 0.582013 | 0.902974 | 0.095* | 0.497 (4) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|------|-------------|--------------|--------------|---------------|--------------|---------------|
| Br1 | 0.0842 (2) | 0.05494 (16) | 0.05450 (16) | −0.00131 (12) | 0.02403 (12) | −0.00748 (11) |
| S1 | 0.0911 (4) | 0.0681 (4) | 0.0419 (3) | 0.0401 (3) | 0.0203 (3) | 0.0126 (3) |
| F1 | 0.1003 (12) | 0.1287 (15) | 0.0746 (10) | 0.0375 (11) | 0.0439 (9) | 0.0375 (10) |
| N1 | 0.0588 (10) | 0.0484 (10) | 0.0428 (9) | 0.0154 (9) | 0.0093 (8) | 0.0067 (8) |
| C1 | 0.1015 (19) | 0.0518 (13) | 0.0448 (12) | 0.0257 (13) | −0.0005 (12) | −0.0010 (10) |
| N2 | 0.0706 (12) | 0.0494 (10) | 0.0385 (9) | 0.0183 (9) | 0.0088 (8) | 0.0032 (8) |
| C2 | 0.145 (3) | 0.0759 (18) | 0.0422 (13) | 0.0652 (19) | 0.0157 (15) | 0.0117 (12) |
| N3 | 0.0696 (11) | 0.0478 (10) | 0.0492 (10) | 0.0162 (9) | 0.0199 (9) | 0.0087 (8) |
| C3 | 0.0593 (12) | 0.0513 (12) | 0.0400 (10) | 0.0240 (10) | 0.0079 (9) | 0.0079 (9) |
| C4 | 0.0643 (14) | 0.0516 (13) | 0.0492 (12) | 0.0108 (11) | 0.0016 (10) | 0.0044 (10) |
| C5 | 0.0504 (12) | 0.0514 (12) | 0.0535 (12) | 0.0119 (10) | 0.0028 (10) | 0.0139 (10) |
| C6 | 0.0733 (16) | 0.0558 (14) | 0.0663 (15) | 0.0074 (12) | 0.0053 (13) | 0.0159 (12) |
| C7 | 0.0708 (16) | 0.0692 (17) | 0.0845 (19) | 0.0101 (13) | 0.0177 (14) | 0.0362 (16) |
| C8 | 0.0585 (14) | 0.0891 (19) | 0.0617 (15) | 0.0311 (14) | 0.0196 (12) | 0.0303 (14) |
| C9 | 0.0575 (14) | 0.0732 (16) | 0.0636 (15) | 0.0204 (12) | 0.0141 (11) | 0.0049 (12) |
| C10 | 0.0515 (12) | 0.0560 (13) | 0.0627 (14) | 0.0092 (10) | 0.0148 (11) | 0.0103 (11) |
| C11 | 0.052 (3) | 0.043 (3) | 0.043 (3) | 0.018 (3) | 0.015 (3) | 0.012 (2) |
| C12 | 0.060 (3) | 0.084 (4) | 0.059 (4) | 0.021 (3) | 0.014 (3) | 0.005 (3) |
| C13 | 0.084 (6) | 0.101 (6) | 0.045 (4) | 0.042 (5) | 0.018 (4) | 0.009 (4) |
| C14 | 0.100 (5) | 0.083 (5) | 0.042 (3) | 0.038 (4) | 0.006 (3) | 0.001 (3) |
| C15 | 0.085 (4) | 0.096 (4) | 0.055 (3) | 0.029 (3) | 0.003 (3) | 0.001 (3) |
| C16 | 0.066 (3) | 0.077 (3) | 0.049 (3) | 0.020 (3) | 0.011 (2) | 0.003 (2) |
| C11' | 0.051 (4) | 0.053 (3) | 0.036 (3) | 0.009 (3) | 0.016 (3) | 0.007 (2) |
| C12' | 0.066 (3) | 0.058 (3) | 0.065 (3) | 0.019 (2) | 0.009 (2) | 0.020 (2) |
| C13' | 0.092 (4) | 0.057 (3) | 0.083 (4) | 0.031 (3) | 0.041 (3) | 0.006 (3) |
| C14' | 0.095 (7) | 0.073 (5) | 0.042 (4) | 0.002 (5) | 0.013 (4) | −0.004 (3) |
| C15' | 0.087 (5) | 0.111 (7) | 0.055 (4) | 0.037 (5) | −0.011 (3) | 0.012 (4) |
| C16' | 0.084 (4) | 0.096 (4) | 0.072 (4) | 0.053 (4) | 0.008 (3) | 0.002 (3) |

Geometric parameters (Å, °)

| | | | |
|-------|-----------|----------|-----------|
| S1—C3 | 1.720 (2) | C9—C10 | 1.369 (3) |
| S1—C2 | 1.848 (3) | C9—H9A | 0.9300 |
| F1—C8 | 1.353 (3) | C10—H10A | 0.9300 |
| N1—C4 | 1.276 (3) | C11—C16 | 1.353 (8) |

| | | | |
|------------|-------------|----------------|------------|
| N1—N2 | 1.380 (2) | C11—C12 | 1.383 (7) |
| C1—N2 | 1.465 (3) | C12—C13 | 1.393 (10) |
| C1—C2 | 1.506 (4) | C12—H12A | 0.9300 |
| C1—H1A | 0.9700 | C13—C14 | 1.364 (14) |
| C1—H1B | 0.9700 | C13—H13A | 0.9300 |
| N2—C3 | 1.339 (3) | C14—C15 | 1.370 (9) |
| C2—C11' | 1.505 (6) | C14—H14A | 0.9300 |
| C2—C11 | 1.607 (7) | C15—C16 | 1.370 (7) |
| C2—H2A | 0.9800 | C15—H15A | 0.9300 |
| N3—C3 | 1.297 (3) | C16—H16A | 0.9300 |
| N3—H3A | 0.9001 | C11'—C16' | 1.333 (9) |
| N3—H3B | 0.9000 | C11'—C12' | 1.389 (8) |
| C4—C5 | 1.458 (3) | C12'—C13' | 1.394 (8) |
| C4—H4A | 0.9300 | C12'—H12B | 0.9300 |
| C5—C6 | 1.386 (3) | C13'—C14' | 1.334 (12) |
| C5—C10 | 1.390 (3) | C13'—H13B | 0.9300 |
| C6—C7 | 1.379 (4) | C14'—C15' | 1.329 (15) |
| C6—H6A | 0.9300 | C14'—H14B | 0.9300 |
| C7—C8 | 1.358 (4) | C15'—C16' | 1.399 (9) |
| C7—H7A | 0.9300 | C15'—H15B | 0.9300 |
| C8—C9 | 1.373 (4) | C16'—H16B | 0.9300 |
| | | | |
| C3—S1—C2 | 90.65 (11) | C10—C9—H9A | 121.0 |
| C4—N1—N2 | 117.98 (19) | C8—C9—H9A | 121.0 |
| N2—C1—C2 | 105.8 (2) | C9—C10—C5 | 121.2 (2) |
| N2—C1—H1A | 110.6 | C9—C10—H10A | 119.4 |
| C2—C1—H1A | 110.6 | C5—C10—H10A | 119.4 |
| N2—C1—H1B | 110.6 | C16—C11—C12 | 118.7 (5) |
| C2—C1—H1B | 110.6 | C16—C11—C2 | 133.2 (5) |
| H1A—C1—H1B | 108.7 | C12—C11—C2 | 108.2 (5) |
| C3—N2—N1 | 116.37 (17) | C11—C12—C13 | 120.0 (6) |
| C3—N2—C1 | 115.67 (18) | C11—C12—H12A | 120.0 |
| N1—N2—C1 | 127.52 (19) | C13—C12—H12A | 120.0 |
| C11'—C2—C1 | 129.4 (4) | C14—C13—C12 | 120.3 (7) |
| C1—C2—C11 | 104.7 (3) | C14—C13—H13A | 119.8 |
| C11'—C2—S1 | 104.9 (3) | C12—C13—H13A | 119.8 |
| C1—C2—S1 | 105.04 (17) | C13—C14—C15 | 119.0 (6) |
| C11—C2—S1 | 112.7 (2) | C13—C14—H14A | 120.5 |
| C1—C2—H2A | 111.4 | C15—C14—H14A | 120.5 |
| C11—C2—H2A | 111.4 | C16—C15—C14 | 120.5 (6) |
| S1—C2—H2A | 111.4 | C16—C15—H15A | 119.7 |
| C3—N3—H3A | 117.3 | C14—C15—H15A | 119.7 |
| C3—N3—H3B | 119.6 | C11—C16—C15 | 121.5 (5) |
| H3A—N3—H3B | 120.5 | C11—C16—H16A | 119.2 |
| N3—C3—N2 | 123.59 (19) | C15—C16—H16A | 119.2 |
| N3—C3—S1 | 123.18 (17) | C16'—C11'—C12' | 118.8 (6) |
| N2—C3—S1 | 113.23 (16) | C16'—C11'—C2 | 119.7 (5) |
| N1—C4—C5 | 120.0 (2) | C12'—C11'—C2 | 121.2 (5) |

| | | | |
|---------------|--------------|---------------------|------------|
| N1—C4—H4A | 120.0 | C11'—C12'—C13' | 119.1 (5) |
| C5—C4—H4A | 120.0 | C11'—C12'—H12B | 120.4 |
| C6—C5—C10 | 118.6 (2) | C13'—C12'—H12B | 120.4 |
| C6—C5—C4 | 119.1 (2) | C14'—C13'—C12' | 120.3 (6) |
| C10—C5—C4 | 122.3 (2) | C14'—C13'—H13B | 119.9 |
| C7—C6—C5 | 120.8 (3) | C12'—C13'—H13B | 119.9 |
| C7—C6—H6A | 119.6 | C15'—C14'—C13' | 121.0 (8) |
| C5—C6—H6A | 119.6 | C15'—C14'—H14B | 119.5 |
| C8—C7—C6 | 118.3 (2) | C13'—C14'—H14B | 119.5 |
| C8—C7—H7A | 120.9 | C14'—C15'—C16' | 119.7 (8) |
| C6—C7—H7A | 120.9 | C14'—C15'—H15B | 120.1 |
| F1—C8—C7 | 119.0 (2) | C16'—C15'—H15B | 120.1 |
| F1—C8—C9 | 117.9 (3) | C11'—C16'—C15' | 121.0 (6) |
| C7—C8—C9 | 123.1 (2) | C11'—C16'—H16B | 119.5 |
| C10—C9—C8 | 118.0 (3) | C15'—C16'—H16B | 119.5 |
| | | | |
| C4—N1—N2—C3 | -169.1 (2) | C6—C5—C10—C9 | -2.0 (4) |
| C4—N1—N2—C1 | 3.0 (3) | C4—C5—C10—C9 | 176.7 (2) |
| C2—C1—N2—C3 | -26.1 (3) | C1—C2—C11—C16 | -1.1 (7) |
| C2—C1—N2—N1 | 161.8 (2) | S1—C2—C11—C16 | 112.5 (6) |
| N2—C1—C2—C11' | 155.8 (4) | C1—C2—C11—C12 | -179.8 (4) |
| N2—C1—C2—C11 | 150.2 (3) | S1—C2—C11—C12 | -66.2 (5) |
| N2—C1—C2—S1 | 31.4 (2) | C16—C11—C12—C13 | 0.1 (10) |
| C3—S1—C2—C11' | -163.6 (3) | C2—C11—C12—C13 | 178.9 (6) |
| C3—S1—C2—C1 | -24.92 (19) | C11—C12—C13—C14 | 0.8 (14) |
| C3—S1—C2—C11 | -138.3 (3) | C12—C13—C14—C15 | -1.5 (15) |
| N1—N2—C3—N3 | -0.7 (3) | C13—C14—C15—C16 | 1.4 (12) |
| C1—N2—C3—N3 | -173.7 (2) | C12—C11—C16—C15 | -0.2 (9) |
| N1—N2—C3—S1 | 179.87 (14) | C2—C11—C16—C15 | -178.7 (5) |
| C1—N2—C3—S1 | 6.8 (3) | C14—C15—C16—C11 | -0.6 (10) |
| C2—S1—C3—N3 | -168.1 (2) | C1—C2—C11'—C16' | -64.5 (7) |
| C2—S1—C3—N2 | 11.35 (19) | S1—C2—C11'—C16' | 59.9 (7) |
| N2—N1—C4—C5 | -177.36 (19) | C1—C2—C11'—C12' | 109.3 (6) |
| N1—C4—C5—C6 | 174.4 (2) | S1—C2—C11'—C12' | -126.3 (5) |
| N1—C4—C5—C10 | -4.2 (4) | C16'—C11'—C12'—C13' | 2.2 (9) |
| C10—C5—C6—C7 | 0.8 (4) | C2—C11'—C12'—C13' | -171.6 (5) |
| C4—C5—C6—C7 | -177.9 (2) | C11'—C12'—C13'—C14' | -0.9 (9) |
| C5—C6—C7—C8 | 1.2 (4) | C12'—C13'—C14'—C15' | -1.0 (13) |
| C6—C7—C8—F1 | 179.3 (2) | C13'—C14'—C15'—C16' | 1.5 (16) |
| C6—C7—C8—C9 | -2.3 (4) | C12'—C11'—C16'—C15' | -1.7 (11) |
| F1—C8—C9—C10 | 179.6 (2) | C2—C11'—C16'—C15' | 172.2 (6) |
| C7—C8—C9—C10 | 1.1 (4) | C14'—C15'—C16'—C11' | -0.2 (14) |
| C8—C9—C10—C5 | 1.0 (4) | | |

Hydrogen-bond geometry (Å, °)

| <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 | 0.90 | 2.36 | 3.2557 (18) | 172 |

| | | | | |
|----------------------------|------|------|-------------|-----|
| N3—H3B···Br1 ⁱ | 0.90 | 2.55 | 3.3552 (18) | 150 |
| C4—H4A···Br1 ⁱⁱ | 0.93 | 2.99 | 3.726 (2) | 137 |

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