



Crystal structure and Hirshfeld surface analysis of (*E*)-5-phenyl-3-[(pyridin-4-ylmethylidene)amino]thiazolidin-2-iminium bromide monohydrate

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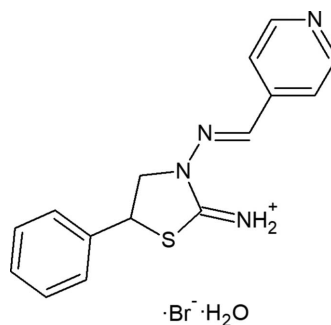
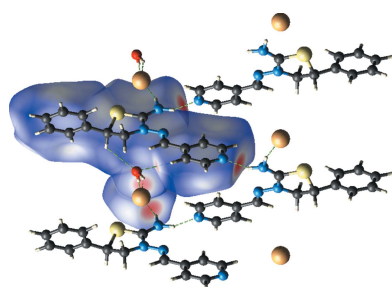
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In the cation of the title salt, $C_{15}H_{15}N_4S^+ \cdot Br^- \cdot H_2O$, the central thiazolidine ring adopts an envelope conformation with puckering parameters $Q(2) = 0.279$ (4) Å and $\varphi(2) = 222.5$ (9)°. The mean plane of the thiazolidine ring makes dihedral angles of 12.4 (2) and 66.8 (3)° with the pyridine and phenyl rings, respectively. The pyridine ring in the title molecule is essentially planar (r.m.s deviation = 0.005 Å). In the crystal, the cations, anions and water molecules are linked into a three-dimensional network, which forms cross layers parallel to the (120) and ($\bar{1}20$) planes *via* O—H···Br, N—H···Br and N—H···N hydrogen bonds. C—H··· π interactions also help in the stabilization of the molecular packing. Hirshfeld surface analysis and 2D (two-dimensional) fingerprint plots indicate that the most important contributions to the crystal packing are from H···H (35.5%), C···H/H···C (23.9%), Br···H/H···Br (16.4%), N···H/H···N (10.6%) and S···H/H···S (7.9%) interactions.

1. Chemical context

Schiff bases and related hydrazone compounds play an important role in coordination and medicinal chemistry due to their high coordination ability (Mahmoudi *et al.*, 2017*a,b,c*; Mitoraj *et al.*, 2018; Shixaliyev *et al.*, 2013*a*), application of those metal complexes in catalysis (Jlassi *et al.*, 2014; Gurbanov *et al.*, 2018; Mahmudov *et al.*, 2014; Shixaliyev *et al.*, 2013*b*, 2014), biological properties (Abedi *et al.*, 2014), *etc.* Inter- and intramolecular weak interactions may also effect their properties (Mahmudov *et al.*, 2016, 2017*a,b*). Herein we found strong O—H···Br[−] and N⁺—H···Br[−] types of charge-assisted hydrogen bonds in (*E*)-5-phenyl-3-[(pyridin-4-ylmethylidene)amino]thiazolidin-2-iminium bromide monohydrate.



2. Structural commentary

The thiazolidine ring (atoms S1/C1–C4) in the cation of the title salt (Fig. 1) adopts an envelope conformation with the

Table 1

Hydrogen-bond geometry (Å, °).

Cg2 and Cg3 are the centroids of the N4/C5–C9 pyridine and C10–C15 phenyl ring, respectively.

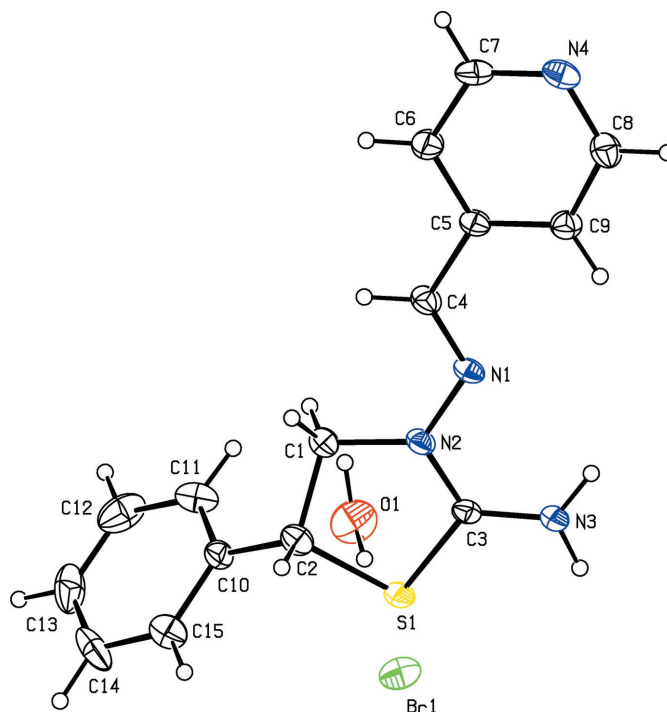
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1C···Br1	0.95	2.39	3.333 (4)	169
O1–H1D···Br1 ⁱ	0.95	2.56	3.427 (5)	152
N3–H3A···Br1 ⁱⁱ	0.90	2.45	3.333 (4)	167
N3–H3B···N4 ⁱⁱⁱ	0.90	1.99	2.840 (6)	158
C9–H9A···Cg2 ⁱⁱⁱ	0.93	2.96	3.650 (5)	132
C12–H12A···Cg3 ^{iv}	0.93	2.82	3.565 (8)	137
C15–H15A···Cg3 ^v	0.93	2.80	3.548 (6)	135

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

puckering parameters (Cremer & Pople, 1975) $Q(2) = 0.279$ (4) Å and $\varphi(2) = 222.5$ (9)°. The mean plane of the thiazolidine ring makes dihedral angles of 12.4 (2) and 66.8 (3)° with the pyridine (N4/C5–C9) and phenyl (C10–C15) rings, respectively. The pyridine ring of the title molecule is essentially planar (r.m.s deviation = 0.005 Å). The N2–N1–C4–C5 bridge that links the thiazolidine and 2,3-dichlorobenzene rings has a torsion angle of 178.3 (4)°.

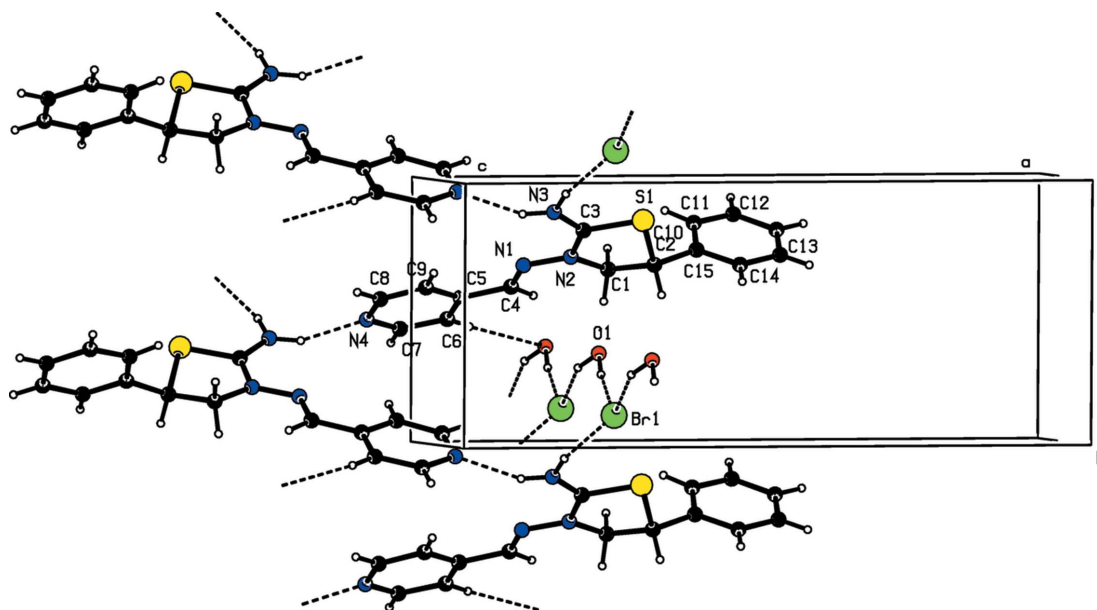
3. Supramolecular features and Hirshfeld surface analysis

As shown in Figs. 2 and 3, in the crystal, the cations, anions and water molecules are linked into a three-dimensional network, which forms cross layers parallel to the (120) and ($\bar{1}20$) planes via O–H···Br, N–H···Br and N–H···N hydrogen bonds (Table 1). Furthermore, C–H··· π interactions also help in the stabilization of the molecular packing (Table 1).


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.

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 (two-dimensional) fingerprint plots (Spackman & McKinnon, 2002). The plots of the Hirshfeld


Figure 2

A view of the intermolecular hydrogen bonds of the title compound along the a axis.

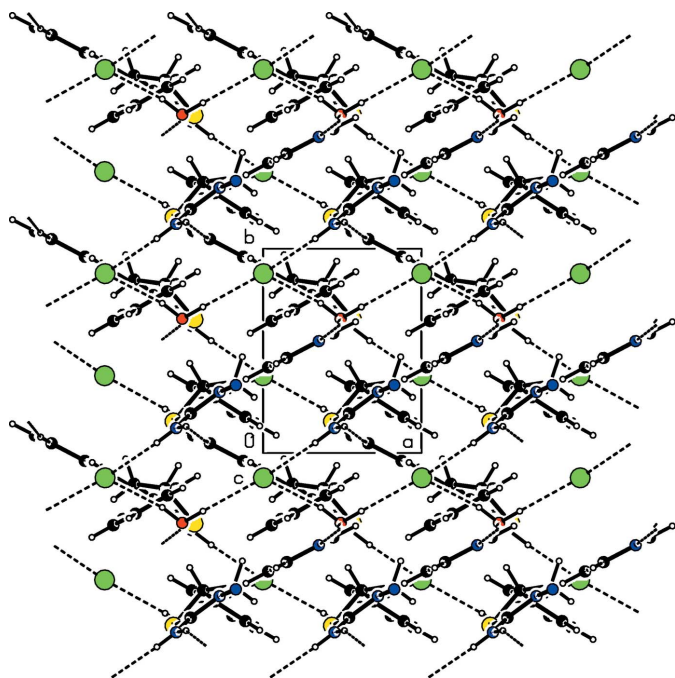


Figure 3
A view of the packing and intermolecular hydrogen bonding of the title compound along the *c* axis.

surface mapped over d_{norm} using a standard surface resolution with a fixed colour scale of -0.5782 (red) to 1.2417 a.u. (blue) is shown in Fig. 4. This plot 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.

Fig. 5(a) shows the 2D fingerprint plot of the sum of the contacts contributing to the Hirshfeld surface represented in normal mode. These represent both the overall two-dimensional fingerprint plots and those that represent $\text{H}\cdots\text{H}$,

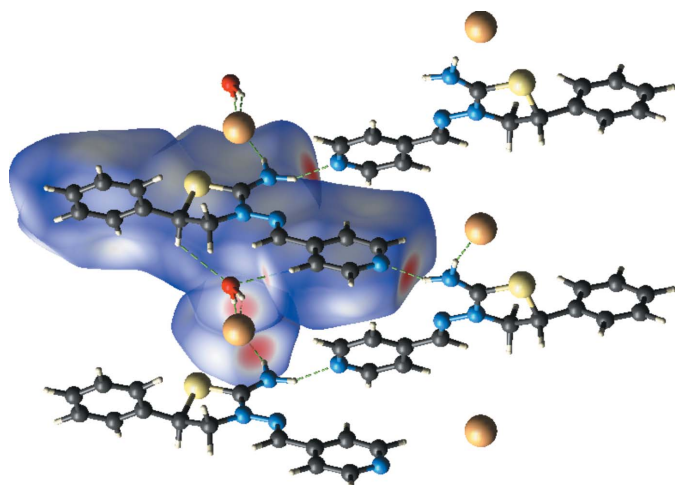


Figure 4
Hirshfeld surface of the title compound mapped over d_{norm} .

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

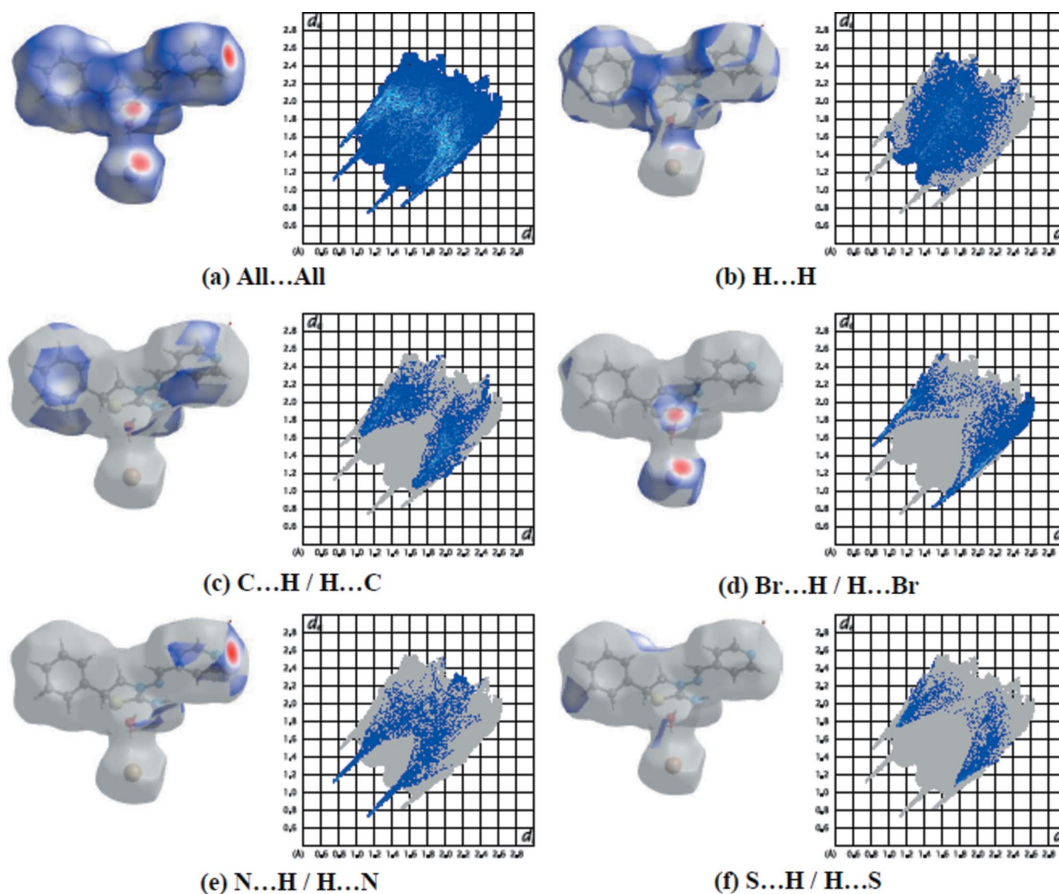
Contact	Percentage contribution
$\text{H}\cdots\text{H}$	35.5
$\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$	23.9
$\text{Br}\cdots\text{H}/\text{H}\cdots\text{Br}$	16.4
$\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$	10.6
$\text{S}\cdots\text{H}/\text{H}\cdots\text{S}$	7.9
$\text{Br}\cdots\text{C}/\text{C}\cdots\text{Br}$	1.1
$\text{Br}\cdots\text{N}/\text{N}\cdots\text{Br}$	1.0
$\text{Br}\cdots\text{S}/\text{S}\cdots\text{Br}$	0.6
$\text{C}\cdots\text{N}/\text{N}\cdots\text{C}$	0.3
$\text{N}\cdots\text{N}/\text{N}\cdots\text{N}$	0.1

$\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$, $\text{Br}\cdots\text{H}/\text{H}\cdots\text{Br}$, $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$ and $\text{S}\cdots\text{H}/\text{H}\cdots\text{S}$ contacts, respectively (Figs. 5b–f). The most significant intermolecular interactions are the $\text{H}\cdots\text{H}$ interactions (35.5%) (Fig. 5b). The reciprocal $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ interactions appear as two symmetrical broad wings with $d_e + d_i \approx 2.7$ Å and contribute 23.9% to the Hirshfeld surface (Fig. 5c). The reciprocal $\text{Br}\cdots\text{H}/\text{H}\cdots\text{Br}$, $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$ and $\text{S}\cdots\text{H}/\text{H}\cdots\text{S}$ interactions with 16.4, 10.6 and 7.9% contributions are present as sharp symmetrical spikes at diagonal axes $d_e + d_i \approx 2.3$, 2.9 and 2.8 Å, respectively (Figs. 5d–f). Furthermore, there are $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ (2.8%), $\text{Br}\cdots\text{C}/\text{C}\cdots\text{Br}$ (1.1%), $\text{Br}\cdots\text{N}/\text{N}\cdots\text{Br}$ (1.0%), $\text{Br}\cdots\text{S}/\text{S}\cdots\text{Br}$ (0.6%), $\text{N}\cdots\text{C}/\text{C}\cdots\text{N}$ (0.3%) and $\text{N}\cdots\text{N}$ (0.1%) contacts (Table 2).

4. Database survey

In a recent article of ours, which on the crystal structure of (*E*)-3-[(2,3-dichlorobenzylidene)amino]-5-phenylthiazolidin-2-iminium bromide (Akkurt *et al.*, 2018), the 3-N atom of the cation carries an N substituent, as found in the title compound. In the crystal, $\text{C}-\text{H}\cdots\text{Br}$ and $\text{N}-\text{H}\cdots\text{Br}$ hydrogen bonds link the components into a three-dimensional network with the cations and anions stacked along the *b*-axis direction. Weak $\text{C}-\text{H}\cdots\pi$ interactions and inversion-related $\text{Cl}\cdots\text{Cl}$ halogen bonds and $\text{C}-\text{Cl}\cdots\pi(\text{ring})$ contacts also contribute to the molecular packing.

In addition, a search of the Cambridge Structural Database (CSD Version 5.39, November 2017 + 3 updates; Groom *et al.*, 2016) yielded six hits for 2-thiazolidiniminium compounds, with four of them reporting essentially the same cation [CSD refcodes 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


Figure 5

The two-dimensional fingerprint plots of the title compound, showing (a) all interactions, and delineated into (b) H...H, (c) C...H/H...C, (d) Br...H/H...Br, (e) N...H/H...N 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].

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 N 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 the solution of 1 mmol of 3-amino-5-phenylthiazolidin-2-iminium bromide in 20 ml ethanol was added 1 mmol of isonicotinaldehyde and the solution was refluxed for 2 h. The reaction mixture was then cooled. Reaction products were precipitated from the reaction mixture as colourless single crystals, collected by filtration and washed with cold acetone.

Yield: 57%; m.p.: 496 K. Analysis calculated for $C_{15}H_{15}BrN_4S$: C 49.59, H 4.16, N 15.42%; found: C 49.52, H 4.11, N 15.35%. 1H NMR (300 MHz, DMSO- d_6): δ 4.57 (*q*, 1H,

CH_2 , $^3J_{H-H} = 6.6$ Hz), 4.89 (*t*, 1H, CH_2 , $^3J_{H-H} = 8.1$ Hz), 5.62 (*t*, 1H, CH-Ar, $^3J_{H-H} = 7.5$ Hz), 7.37–7.57 (*m*, 5H, 5 Ar-H), 8.015–7.998 (*d*, 2H, $2CH_{arom}$, $^3J_{H-H} = 5.1$ Hz), 8.46 (*s*, 1H, CH=), 8.728–8.711 (*d*, 2H, $2CH_{arom}$, $^3J_{H-H} = 5.1$ Hz), 10.52 (*s*, 2H, $NH_2=$). ^{13}C NMR (75MHz, DMSO- d_6): δ 45.54, 56.00, 122.17, 127.86, 128.98, 129.16, 137.43, 140.16, 148.88, 150.31, 168.98. MS (ESI), m/z : 283.36 [$C_{15}H_{15}N_4S$] $^+$ and 79.88 Br^- .

6. 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 O–H = 0.95 Å, N–H = 0.90 Å and C–H = 0.93–0.98 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$ or $1.5U_{eq}(O)$ for the H atoms of the water molecule.

Acknowledgements

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Table 3

Experimental details.

Crystal data	
Chemical formula	C ₁₅ H ₁₅ N ₄ S ⁺ ·Br ⁻ ·H ₂ O
<i>M_r</i>	381.30
Crystal system, space group	Monoclinic, <i>P2</i> ₁
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.8515 (8), 7.5304 (10), 18.859 (3)
β (°)	93.979 (5)
<i>V</i> (Å ³)	829.0 (2)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	2.61
Crystal size (mm)	0.19 × 0.15 × 0.14
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2007)
<i>T</i> _{min} , <i>T</i> _{max}	0.623, 0.698
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	12061, 3373, 3107
<i>R</i> _{int}	0.076
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.626
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.037, 0.087, 1.08
No. of reflections	3373
No. of parameters	199
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.49, -0.47
Absolute structure	Flack <i>x</i> determined using 1291 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.004 (8)

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2009).

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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); software used to prepare material for publication: *PLATON* (Spek, 2009).

(*E*)-5-Phenyl-3-[(pyridin-4-ylmethylidene)amino]thiazolidin-2-iminium bromide monohydrate

Crystal data

$C_{15}H_{15}N_4S^+ \cdot Br^- \cdot H_2O$

$M_r = 381.30$

Monoclinic, $P2_1$

$a = 5.8515$ (8) Å

$b = 7.5304$ (10) Å

$c = 18.859$ (3) Å

$\beta = 93.979$ (5)°

$V = 829.0$ (2) Å³

$Z = 2$

$F(000) = 388$

$D_x = 1.527$ Mg m⁻³

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

Cell parameters from 6867 reflections

$\theta = 2.9$ – 26.4 °

$\mu = 2.61$ mm⁻¹

$T = 296$ K

Block, colorless

$0.19 \times 0.15 \times 0.14$ mm

Data collection

Bruker APEXII CCD
diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2007)

$T_{\min} = 0.623$, $T_{\max} = 0.698$

12061 measured reflections

3373 independent reflections

3107 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.076$

$\theta_{\max} = 26.4$ °, $\theta_{\min} = 2.9$ °

$h = -7 \rightarrow 7$

$k = -9 \rightarrow 9$

$l = -21 \rightarrow 23$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.087$

$S = 1.08$

3373 reflections

199 parameters

1 restraint

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0256P)^2 + 0.6286P]$

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

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

$$\Delta\rho_{\max} = 0.49 \text{ e } \text{\AA}^{-3}$$

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

Absolute structure: Flack x determined using
1291 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: 0.004 (8)

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.00107 (9)	0.87805 (8)	0.76086 (3)	0.05140 (19)
O1	0.4881 (7)	0.6571 (7)	0.7445 (3)	0.0670 (13)
H1D	0.619040	0.714648	0.766487	0.100*
H1C	0.362040	0.733228	0.751357	0.100*
S1	0.4339 (2)	0.15399 (19)	0.67953 (6)	0.0382 (3)
N1	0.8263 (6)	0.3319 (5)	0.8366 (2)	0.0295 (9)
N2	0.7239 (7)	0.2983 (5)	0.7699 (2)	0.0303 (8)
N3	0.4501 (6)	0.1215 (6)	0.8202 (2)	0.0355 (9)
H3A	0.328282	0.049581	0.812009	0.043*
H3B	0.512382	0.129791	0.865099	0.043*
N4	1.3503 (8)	0.5477 (6)	1.0413 (2)	0.0411 (10)
C1	0.8150 (8)	0.3485 (7)	0.7026 (2)	0.0355 (11)
H1A	0.942871	0.272508	0.692765	0.043*
H1B	0.867805	0.470588	0.704580	0.043*
C2	0.6215 (9)	0.3270 (6)	0.6453 (3)	0.0367 (11)
H2A	0.535751	0.438691	0.640770	0.044*
C3	0.5413 (7)	0.1933 (6)	0.7656 (2)	0.0280 (9)
C4	1.0129 (8)	0.4175 (6)	0.8403 (3)	0.0342 (11)
H4A	1.078821	0.452819	0.799119	0.041*
C5	1.1255 (8)	0.4610 (6)	0.9111 (2)	0.0303 (9)
C6	1.3363 (9)	0.5471 (7)	0.9143 (3)	0.0399 (12)
H6A	1.405181	0.577708	0.872999	0.048*
C7	1.4407 (9)	0.5859 (8)	0.9808 (3)	0.0415 (12)
H7A	1.582539	0.642081	0.982961	0.050*
C8	1.1475 (10)	0.4651 (8)	1.0373 (3)	0.0421 (12)
H8A	1.081980	0.437142	1.079457	0.051*
C9	1.0312 (8)	0.4194 (6)	0.9743 (3)	0.0349 (11)
H9A	0.890877	0.361247	0.974094	0.042*
C10	0.6939 (9)	0.2728 (7)	0.5720 (3)	0.0354 (11)
C11	0.8870 (10)	0.1764 (8)	0.5602 (3)	0.0501 (14)
H11A	0.977907	0.131751	0.598504	0.060*
C12	0.9462 (10)	0.1458 (11)	0.4924 (5)	0.064 (2)
H12A	1.081948	0.086515	0.485002	0.077*
C13	0.8064 (13)	0.2022 (10)	0.4350 (3)	0.0626 (19)
H13A	0.846758	0.180147	0.389002	0.075*

C14	0.6057 (15)	0.2916 (9)	0.4462 (3)	0.0610 (19)
H14A	0.508677	0.327949	0.407801	0.073*
C15	0.5505 (11)	0.3266 (7)	0.5146 (3)	0.0450 (13)
H15A	0.415794	0.386965	0.522268	0.054*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0357 (2)	0.0535 (3)	0.0647 (4)	0.0010 (3)	0.0019 (2)	-0.0076 (4)
O1	0.059 (3)	0.059 (3)	0.084 (4)	0.016 (3)	0.013 (2)	-0.008 (3)
S1	0.0326 (5)	0.0560 (8)	0.0249 (5)	-0.0080 (6)	-0.0050 (4)	-0.0042 (5)
N1	0.0331 (19)	0.029 (2)	0.0250 (18)	-0.0004 (14)	-0.0079 (14)	-0.0049 (13)
N2	0.0325 (19)	0.0329 (19)	0.0245 (19)	-0.0024 (16)	-0.0055 (15)	-0.0013 (15)
N3	0.0296 (18)	0.051 (3)	0.0252 (19)	-0.0036 (19)	-0.0033 (15)	0.0017 (18)
N4	0.043 (2)	0.043 (3)	0.036 (2)	0.003 (2)	-0.0098 (18)	-0.0099 (19)
C1	0.037 (2)	0.042 (3)	0.028 (2)	-0.002 (2)	-0.0003 (17)	-0.001 (2)
C2	0.040 (2)	0.034 (3)	0.035 (3)	0.0068 (19)	-0.002 (2)	-0.0006 (18)
C3	0.0238 (19)	0.031 (2)	0.028 (2)	0.0050 (18)	-0.0030 (16)	-0.0005 (18)
C4	0.038 (2)	0.037 (3)	0.027 (2)	-0.0021 (19)	-0.0028 (18)	-0.0039 (18)
C5	0.032 (2)	0.030 (2)	0.029 (2)	-0.0017 (18)	-0.0043 (18)	-0.0047 (18)
C6	0.039 (3)	0.046 (3)	0.034 (3)	-0.009 (2)	0.000 (2)	-0.006 (2)
C7	0.031 (2)	0.047 (3)	0.045 (3)	-0.003 (2)	-0.009 (2)	-0.011 (2)
C8	0.050 (3)	0.047 (3)	0.030 (3)	0.000 (2)	0.004 (2)	-0.004 (2)
C9	0.033 (2)	0.037 (3)	0.035 (2)	-0.0021 (18)	-0.0004 (18)	-0.0032 (18)
C10	0.038 (2)	0.040 (3)	0.027 (2)	-0.007 (2)	-0.0022 (19)	0.0002 (19)
C11	0.044 (3)	0.048 (3)	0.056 (3)	0.005 (3)	-0.014 (3)	-0.007 (3)
C12	0.045 (3)	0.067 (4)	0.084 (5)	-0.005 (4)	0.018 (3)	-0.031 (4)
C13	0.093 (5)	0.061 (4)	0.036 (3)	-0.017 (4)	0.026 (3)	-0.010 (3)
C14	0.103 (6)	0.045 (3)	0.032 (3)	-0.007 (4)	-0.019 (3)	0.012 (2)
C15	0.051 (3)	0.037 (3)	0.046 (3)	0.006 (2)	-0.005 (2)	-0.003 (2)

Geometric parameters (Å, °)

O1—H1D	0.9500	C5—C9	1.384 (7)
O1—H1C	0.9500	C5—C6	1.391 (7)
S1—C3	1.725 (4)	C6—C7	1.389 (7)
S1—C2	1.848 (5)	C6—H6A	0.9300
N1—C4	1.266 (6)	C7—H7A	0.9300
N1—N2	1.380 (5)	C8—C9	1.372 (7)
N2—C3	1.327 (6)	C8—H8A	0.9300
N2—C1	1.459 (6)	C9—H9A	0.9300
N3—C3	1.310 (6)	C10—C11	1.374 (8)
N3—H3A	0.9000	C10—C15	1.384 (7)
N3—H3B	0.9000	C11—C12	1.367 (10)
N4—C7	1.322 (8)	C11—H11A	0.9300
N4—C8	1.337 (8)	C12—C13	1.378 (11)
C1—C2	1.519 (6)	C12—H12A	0.9300
C1—H1A	0.9700	C13—C14	1.383 (11)

C1—H1B	0.9700	C13—H13A	0.9300
C2—C10	1.529 (7)	C14—C15	1.376 (9)
C2—H2A	0.9800	C14—H14A	0.9300
C4—C5	1.484 (6)	C15—H15A	0.9300
C4—H4A	0.9300		
H1D—O1—H1C	106.0	C7—C6—C5	118.0 (5)
C3—S1—C2	91.2 (2)	C7—C6—H6A	121.0
C4—N1—N2	117.6 (4)	C5—C6—H6A	121.0
C3—N2—N1	117.5 (4)	N4—C7—C6	123.8 (5)
C3—N2—C1	116.3 (4)	N4—C7—H7A	118.1
N1—N2—C1	125.7 (4)	C6—C7—H7A	118.1
C3—N3—H3A	118.3	N4—C8—C9	123.4 (5)
C3—N3—H3B	123.4	N4—C8—H8A	118.3
H3A—N3—H3B	117.9	C9—C8—H8A	118.3
C7—N4—C8	117.3 (4)	C8—C9—C5	119.0 (5)
N2—C1—C2	106.9 (4)	C8—C9—H9A	120.5
N2—C1—H1A	110.3	C5—C9—H9A	120.5
C2—C1—H1A	110.3	C11—C10—C15	119.2 (5)
N2—C1—H1B	110.3	C11—C10—C2	124.8 (5)
C2—C1—H1B	110.3	C15—C10—C2	116.0 (5)
H1A—C1—H1B	108.6	C12—C11—C10	120.4 (6)
C1—C2—C10	115.6 (4)	C12—C11—H11A	119.8
C1—C2—S1	104.9 (3)	C10—C11—H11A	119.8
C10—C2—S1	109.6 (3)	C11—C12—C13	120.5 (6)
C1—C2—H2A	108.8	C11—C12—H12A	119.8
C10—C2—H2A	108.8	C13—C12—H12A	119.8
S1—C2—H2A	108.8	C12—C13—C14	119.6 (6)
N3—C3—N2	124.7 (4)	C12—C13—H13A	120.2
N3—C3—S1	121.8 (4)	C14—C13—H13A	120.2
N2—C3—S1	113.5 (3)	C15—C14—C13	119.6 (6)
N1—C4—C5	119.3 (4)	C15—C14—H14A	120.2
N1—C4—H4A	120.3	C13—C14—H14A	120.2
C5—C4—H4A	120.3	C14—C15—C10	120.5 (6)
C9—C5—C6	118.3 (4)	C14—C15—H15A	119.7
C9—C5—C4	123.1 (4)	C10—C15—H15A	119.7
C6—C5—C4	118.6 (4)		
C4—N1—N2—C3	173.3 (4)	C8—N4—C7—C6	0.8 (8)
C4—N1—N2—C1	1.8 (7)	C5—C6—C7—N4	-0.8 (9)
C3—N2—C1—C2	22.4 (6)	C7—N4—C8—C9	-0.1 (8)
N1—N2—C1—C2	-166.1 (4)	N4—C8—C9—C5	-0.4 (8)
N2—C1—C2—C10	-148.0 (4)	C6—C5—C9—C8	0.3 (7)
N2—C1—C2—S1	-27.1 (5)	C4—C5—C9—C8	-179.9 (5)
C3—S1—C2—C1	21.6 (3)	C1—C2—C10—C11	27.7 (7)
C3—S1—C2—C10	146.3 (4)	S1—C2—C10—C11	-90.6 (6)
N1—N2—C3—N3	0.9 (7)	C1—C2—C10—C15	-152.3 (5)
C1—N2—C3—N3	173.2 (5)	S1—C2—C10—C15	89.3 (5)

N1—N2—C3—S1	-177.7 (3)	C15—C10—C11—C12	5.0 (9)
C1—N2—C3—S1	-5.5 (5)	C2—C10—C11—C12	-175.1 (6)
C2—S1—C3—N3	171.0 (4)	C10—C11—C12—C13	-3.8 (11)
C2—S1—C3—N2	-10.3 (4)	C11—C12—C13—C14	0.6 (11)
N2—N1—C4—C5	178.3 (4)	C12—C13—C14—C15	1.4 (10)
N1—C4—C5—C9	-3.0 (7)	C13—C14—C15—C10	-0.1 (9)
N1—C4—C5—C6	176.7 (5)	C11—C10—C15—C14	-3.1 (9)
C9—C5—C6—C7	0.2 (8)	C2—C10—C15—C14	177.0 (5)
C4—C5—C6—C7	-179.6 (5)		

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

Cg2 and Cg3 are the centroids of the N4/C5–C9 pyridine and the C10–C15 phenyl ring, respectively.

<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>
O1—H1C \cdots Br1	0.95	2.39	3.333 (4)	169
O1—H1D \cdots Br1 ⁱ	0.95	2.56	3.427 (5)	152
N3—H3A \cdots Br1 ⁱⁱ	0.90	2.45	3.333 (4)	167
N3—H3B \cdots N4 ⁱⁱⁱ	0.90	1.99	2.840 (6)	158
C9—H9A \cdots Cg2 ⁱⁱⁱ	0.93	2.96	3.650 (5)	132
C12—H12A \cdots Cg3 ^{iv}	0.93	2.82	3.565 (8)	137
C15—H15A \cdots Cg3 ^v	0.93	2.80	3.548 (6)	135

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