research communications

Crystal structure and Hirshfeld surface analysis of (E)-3-[(4-methylbenzylidene)amino]-5-phenylthiazolidin-2-iminium bromide N,N-dimethylformamide monosolvate

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In the cation of the title salt, $C_{17}H_{18}N_3S^+ \cdot Br^- \cdot C_3H_7NO$, the central thiazolidine ring adopts an envelope conformation with puckering parameters $Q(2) = 0.310 (3)$ Å and $\varphi(2) = 42.2 (6)°$. In the crystal, each cation is connected to two anions by N—H$\cdots$Br hydrogen bonds, forming an $R_4^2(8)$ motif parallel to the $(10\bar{1})$ plane. van der Waals interactions between the cations, anions and N,N-dimethylformamide molecules further stabilize the crystal structure in three dimensions. The most important contributions to the surface contacts are from H$\cdots$H (55.6%), C$\cdots$H/H$\cdots$C (17.9%) and Br$\cdots$H/H$\cdots$Br (7.0%) interactions, as concluded from a Hirshfeld analysis.

1. Chemical context

Sulfur and nitrogen-containing heterocyclic systems are of great interests in the fields of organic synthesis, drug design and material science (Abdelhamid et al., 2014; Pathania et al., 2019; Yin et al., 2020). In this context, thiazolidine derivatives play an important role in pharmaceutical and medicinal chemistry. Many commercially available drugs such as pioglitazone (an antidiabetic), penicillin, benzylpenicillin, ampicillin, oxacillin and amoxicillin (β-lactam antibiotics) contain a thiazolidine moiety. Studies in the field of thiazolidine chemistry have been well documented in the literature (D'hooghe & De Kimpe, 2006; Maharramov et al., 2011). Compounds incorporating thiazolidine and azomethine structural motifs have also found applications in coordination chemistry, catalysis, crystal design and material science (Asadov et al., 2016; Akbari Afkhami et al., 2017; Maharramov et al., 2018; Mahmudov et al., 2019, 2020).
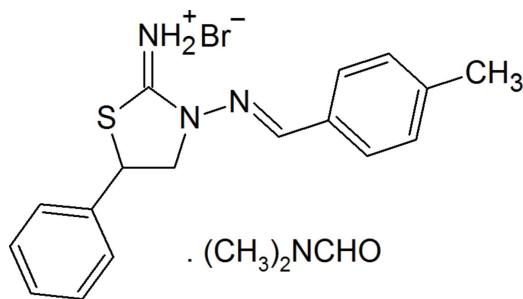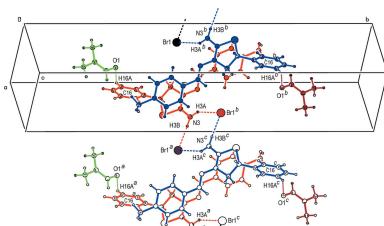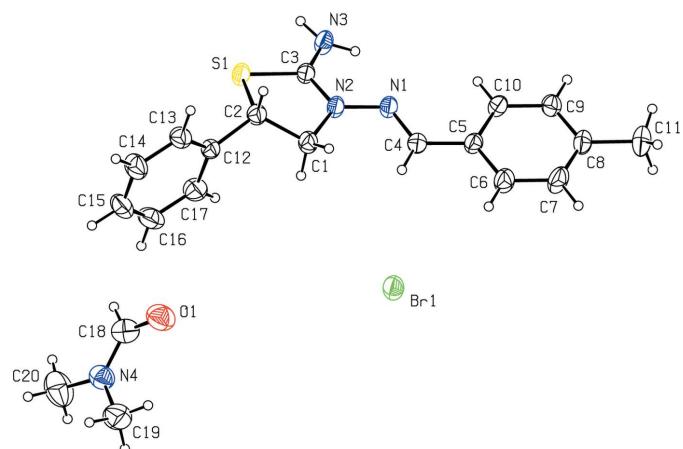
Figure 1
The molecular structure of the title salt, showing displacement ellipsoids drawn at the 30% probability level.

As part of our ongoing structural studies (Akkurt *et al.*, 2018*a*,*b*; Khalilov *et al.*, 2011, 2019), we report herein the crystal structure and Hirshfeld surface analysis of the title compound, (*E*)-3-[(4-methylbenzylidene)amino]-5-phenyl-thiazolidin-2-iminium bromide *N*,*N*-dimethylformamide monosolvate.

2. Structural commentary

As shown in Fig. 1, the central thiazolidine ring (S1/N2/C1–C3) of the cation adopts an envelope conformation with puckering parameters (Cremer & Pople, 1975) $Q(2) = 0.310 (3)$ Å and $\varphi(2) = 42.2 (6)°$ with atom C2 as the flap. The C=N double bond [N1=C4 = 1.272 (4) Å] is in a Z config-uration. The dihedral angle between the mean planes of the benzene (C5–C10) and phenyl (C12–C17) rings is 83.95 (18)° and they make dihedral angles of 16.60 (17) and 87.42 (17)°, respectively, with the mean plane of the thiazolidine ring. The N2—N1—C4—C5 bridge that links the thiazolidine and 4-methylbenzene rings has a torsion angle of −176.8 (3)°.
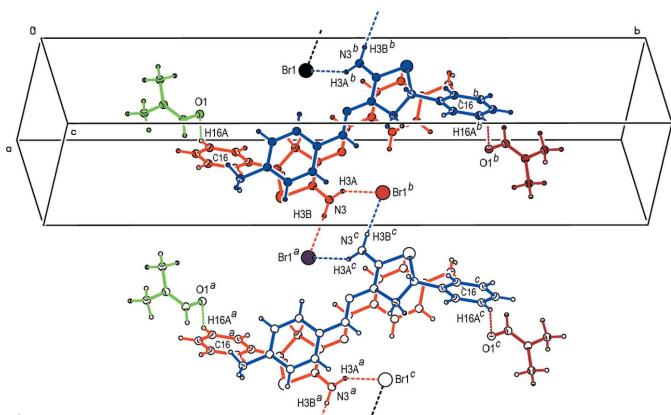
Figure 2
A view of hydrogen bonds between the cations, anions and *N*,*N*-dimethylformamide molecules of the title salt. The N—H···Br hydrogen bonds and C—H···O contacts are shown as dashed lines. Symmetry codes: (*a*) 1 + *x*, *y*, 1 + *z*; (*b*) 1 − *x*, 1 − *y*, 1 − *z*; (*c*) 2 − *x*, 1 − *y*, 2 − *z*.
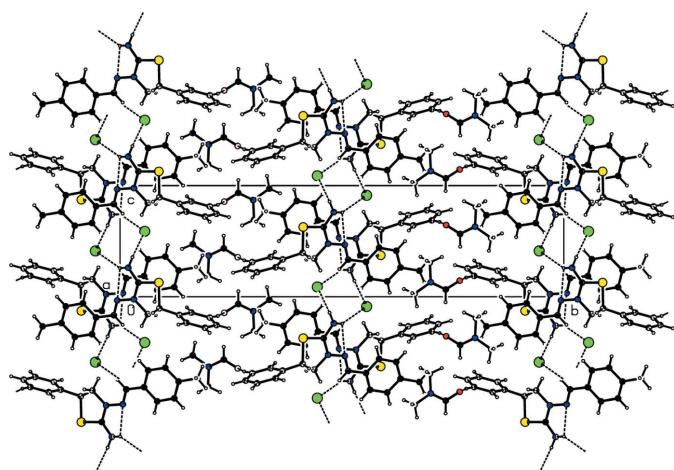
Figure 3
Crystal packing for the title salt viewed along the *a*-axis direction. Dashed lines indicate N—H···Br hydrogen bonds and C—H···O contacts.
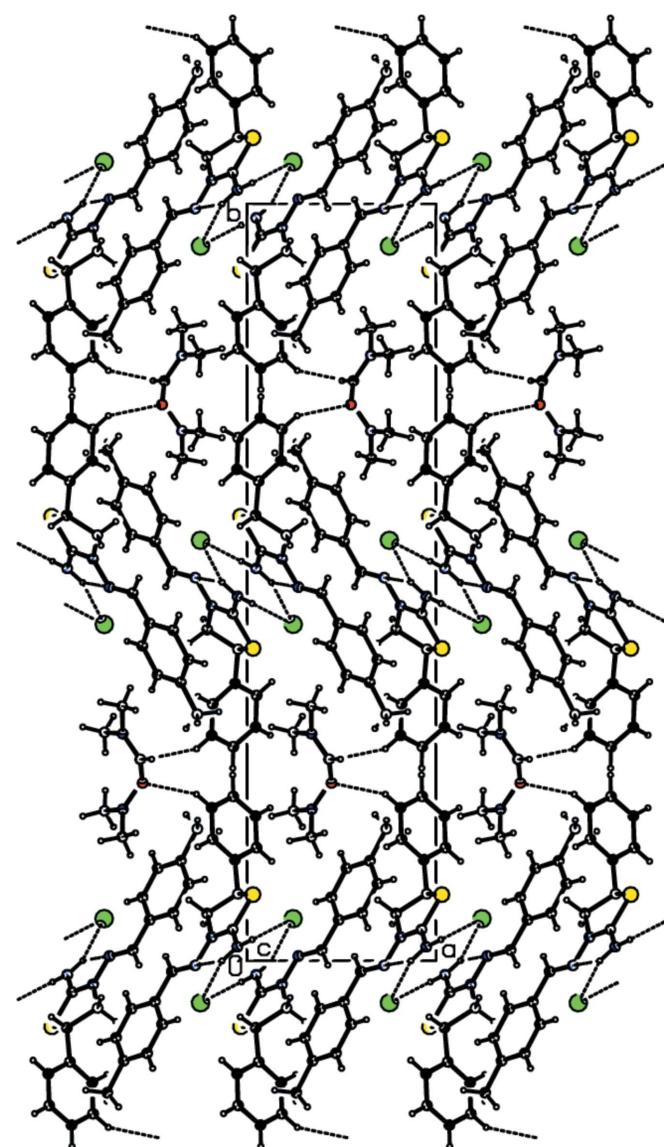
Figure 4
Crystal packing of the title salt viewed along the *c*-axis direction. Dashed lines indicate N—H···Br and C—H···O contacts.

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^i	0.90	2.57	3.368 (3)	148
N3—H3B$\cdots$Br1^{ii}	0.90	2.35	3.243 (2)	175
C16—H16A$\cdots$O1	0.93	2.54	3.391 (6)	153

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

3. Supramolecular features

In the crystal, each cation is connected to two anions by N—H$\cdots$Br hydrogen bonds forming an $R_4^2(8)$ motif parallel to the $(10\bar{1})$ plane, while *N,N*-dimethylformamide molecules are linked to the cations by C—H$\cdots$O contacts (Table 1; Figs. 2, 3 and 4). Furthermore, van der Waals interactions between the cations, anions and *N,N*-dimethylformamide molecules stabilize the crystal structure in three dimensions.

4. Hirshfeld surface analysis

Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) was used to investigate the hydrogen bonds and intermolecular interactions in the crystal structure. This was performed using *CrystalExplorer3.1* (Wolff *et al.*, 2012), and comprised d_{norm} surface plots and two-dimensional fingerprint plots (Spackman & McKinnon, 2002). The shorter and longer contacts are indicated as red and blue spots, respectively, on the Hirshfeld surfaces, and contacts with distances approximately equal to the sum of the van der Waals radii are represented as white spots. The contribution of interatomic

Table 2
Summary of short interatomic contacts (Å) in the title salt.

Contact	Distance	Symmetry operation
H3B$\cdots$Br1	2.35	$1+x, y, 1+z$
N1$\cdots$S1	3.533 (3)	$2-x, 1-y, 1-z$
H3A$\cdots$Br1	2.57	$1-x, 1-y, 1-z$
C9$\cdots$H19C	2.78	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$
H17A$\cdots$H9A	2.47	$1-x, 1-y, 1-z$
H6A$\cdots$H1A	2.50	$1-x, 1-y, -z$
H16A$\cdots$O1	2.54	x, y, z
H16A$\cdots$H18A	2.55	$x, \frac{1}{2}-y, -\frac{1}{2}+z$
H4A$\cdots$Br1	3.06	x, y, z
H13A$\cdots$Br1	3.08	$1+x, y, z$
H14A$\cdots$O1	2.84	$1+x, y, z$
O1$\cdots$H18A	2.76	$x, \frac{1}{2}-y, -\frac{1}{2}+z$
C20$\cdots$Br1	3.736 (5)	$x, \frac{1}{2}-y, \frac{1}{2}+z$

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

Contact	Percentage contribution
H$\cdots$H	55.6
C$\cdots$H/H$\cdots$C	17.9
Br$\cdots$H/H$\cdots$Br	7.0
S$\cdots$H/H$\cdots$S	4.6
N$\cdots$C/C$\cdots$N	3.8
O$\cdots$H/H$\cdots$O	3.2
N$\cdots$H/H$\cdots$N	2.9
S$\cdots$C/C$\cdots$S	2.4
C$\cdots$C	1.5
N$\cdots$S/S$\cdots$N	0.5
N$\cdots$N	0.4
Br$\cdots$C/C$\cdots$Br	0.2
Br$\cdots$S/S$\cdots$Br	0.2

contacts (Table 2) to the d_{norm} surface of the title compound is shown in Fig. 5. Fig. 6 indicates by the absence of red and blue triangles on the shape-index surface that π–π stacking interactions are not present in the crystal structure.

Fig. 7(*a*) shows the 2D fingerprint plot of the sum of the contacts contributing to the Hirshfeld surface represented in normal mode while those delineated into H$\cdots$H, C$\cdots$H/H$\cdots$C and Br$\cdots$H/H$\cdots$Br contacts are given in Fig. 7*b*–*d*,

Figure 5
A view of the three-dimensional Hirshfeld surface for the title salt, plotted over d_{norm} in the range −0.4961 to 1.2178 a.u. N—H$\cdots$Br hydrogen bonds and C—H$\cdots$O contacts are shown.
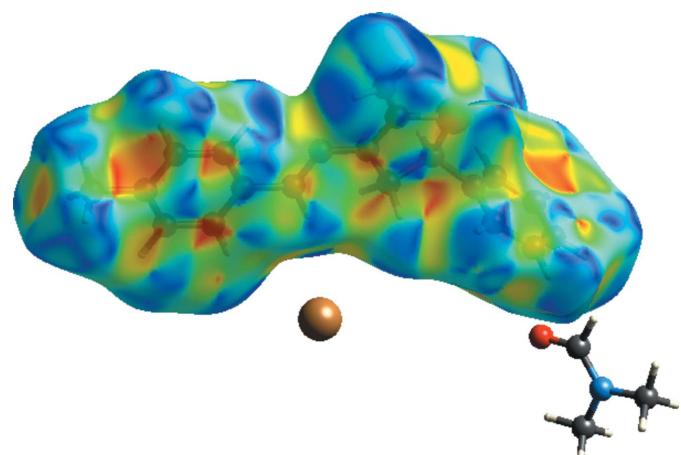
Figure 6
View of the three-dimensional Hirshfeld surface of the title salt plotted over shape-index.

(a) All...All 100 %

(b) H...H 55.6 %

(c) C...H / H...C 17.9 %
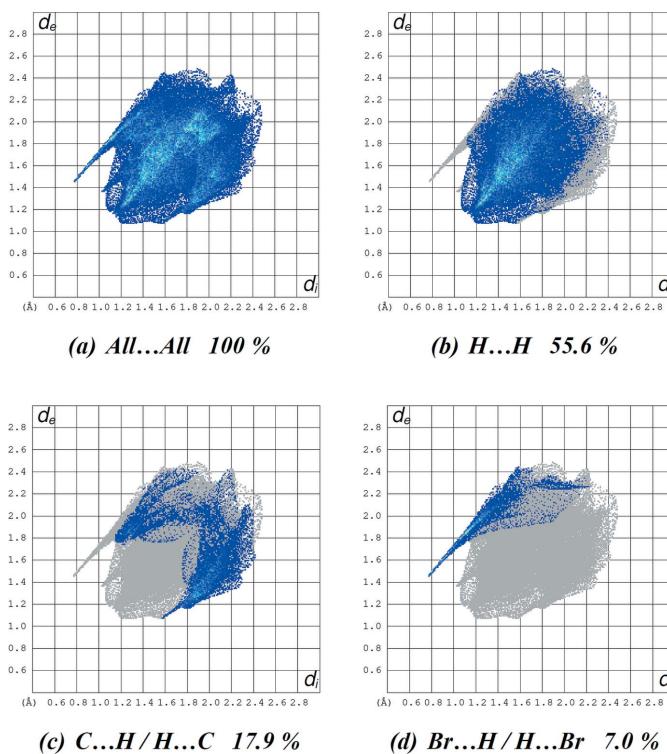


(d) Br...H / H...Br 7.0 %

Figure 7
A view of the two-dimensional fingerprint plots for the title salt, showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) C···H/H···C and (*d*) Br···H/H···Br interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

respectively. The most significant intermolecular interactions are the H···H interactions (55.6%) (Fig. 7*b*). The reciprocal C···H/H···C interactions appear as two symmetrical broad wings with $d_e + d_i \simeq 2.6$ Å and contribute 17.9% to the Hirshfeld surface (Fig. 7*c*). The reciprocal Br···H/H···Br interaction with a 7.0% contribution is seen as branch of sharp symmetrical spikes at diagonal axes $d_e + d_i \simeq 2.2$ Å (Fig. 7*d*). Furthermore, there are also O···H/H···O (3.2%), S···H/H···S (4.6%), N···C/C···N (3.8%), N···H/H···N (2.9%), S···C/C···S (2.4%), C···C (1.5%), Br···C/C···Br (0.2%), Br···S/S···Br (0.2%), N···N (0.4%) and N···S/S···N (0.5%) contacts (Table 3).

5. Database survey

A search of the Cambridge Structural Database CSD (Version 5.40, update of August 2019; Groom *et al.*, 2016) yielded eight 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.*, 1993*a*), YITCAF (Martem'yanova *et al.*, 1993*b*) 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) 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 endocylic 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.

The other closely related compounds are UDELUN (Akkurt *et al.*, 2018*a*) and ZIJQAN (Akkurt *et al.*, 2018*b*). In the crystal structure of UDELUN, the 3-N atom of the cation carries an N substituent, as found in the title compound. 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 and inversion-related Cl···Cl halogen bonds and C—Cl···π(ring) contacts also contribute to the molecular packing. In the crystal of ZIJQAN, 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. Furthermore, C—H···π interactions also help in the stabilization of the molecular packing.

Furthermore, in WILBIC, the thiazolidine ring adopts a twist conformation. In one of two molecules in the asymmetric unit of WILBOI, the thiazolidine ring is essentially planar, in the other it adopts a twist conformation. In the two molecules in the asymmetric unit of WILBOI01 and in YOPLUK, the thiazolidine rings exhibit a twist conformation. In YITCAF, the disordered thiazolidine ring has two components, which are planar. In YOPLUK, the thiazolidine ring is slightly puckered, with the nitrogen atom in an almost planar configuration. In the cations of UDELUN and ZIJQAN, the thiazolidine rings have an envelope conformation.

6. Synthesis and crystallization

To a solution of 3-amino-5-phenylthiazolidin-2-iminium bromide (1 mmol) in ethanol (20 ml) was added 4-methylbenzaldehyde (1 mmol). The mixture was refluxed for 2 h and then cooled. The reaction product precipitated from the reaction mixture as colorless crystals, was collected by filtration, washed with cold acetone (yield 54%; m.p. 501–502 K), and recrystallized from dimethylformamide to obtain single crystals.

^{1}H NMR (300 MHz, DMSO-d_6) : 2.33 (*s*, 3H, CH$_3$); 4.55 (*k*, 1H, CH$_2$, $^3J_{H-H}$ = 6.6); 4,88 (*t*, 1H, CH$_2$, $^3J_{H-H}$ = 8.1); 5.60 (*t*, 1H, CH—Ar, $^3J_{H-H}$ = 7.5); 7.28–7.98 (*m*, 9H, 9Ar—H); 8.41 (*s*, 1H, CH=); 10.33 (*s*, 2H, N$^+$H=). ^{13}C NMR (75 MHz,

Table 4
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{18}N_3S^+ \cdot Br^- \cdot C_3H_7NO$
M_r	449.41
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	8.4326 (6), 31.778 (2), 8.4680 (6)
β (°)	110.052 (2)
V (Å^3)	2131.6 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.04
Crystal size (mm)	$0.18 \times 0.14 \times 0.10$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2003)
T_{min}, T_{max}	0.702, 0.807
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	29638, 4039, 2873
R_{int}	0.076
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.609
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.087, 1.03
No. of reflections	4039
No. of parameters	248
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.38, −0.61

Computer programs: *APEX2* and *SAINT* (Bruker, 2003), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

DMSO-d_6): 21.27; 45.36; 55.90; 127.79; 128.69; 128.86; 129.09; 129.46; 130.21; 137.50; 141.68; 151.04; 167.50. MS (ESI), m/z: 296.40 [$C_{17}H_{18}N_3S$]$^+$ and 79.88 Br$^-$.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. All H atoms were placed geometrically (N—H = 0.90 Å and C—H = 0.93–0.98 Å) and refined as riding atoms with U_{iso}(H) = 1.2 or $1.5U_{eq}$(C, N).

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supporting information

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Computing details

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT* (Bruker, 2003); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

(*E*)-3-[(4-Methylbenzylidene)amino]-5-phenylthiazolidin-2-iminium bromide *N,N*-dimethylformamide monosolvate

Crystal data

$C_{17}H_{18}N_3S^+ \cdot Br^- \cdot C_3H_7NO$	$F(000) = 928$
$M_r = 449.41$	$D_x = 1.400$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.4326$ (6) Å	Cell parameters from 7783 reflections
$b = 31.778$ (2) Å	$\theta = 2.6$–$25.5°$
$c = 8.4680$ (6) Å	$\mu = 2.04$ mm^{-1}
$\beta = 110.052$ (2)°	$T = 296$ K
$V = 2131.6$ (3) Å^3	Plate, colourless
$Z = 4$	$0.18 \times 0.14 \times 0.10$ mm

Data collection

Bruker APEXII CCD diffractometer	4039 independent reflections
φ and ω scans	2873 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2003)	$R_{int} = 0.076$
	$\theta_{max} = 25.7°$, $\theta_{min} = 2.6°$
$T_{min} = 0.702$, $T_{max} = 0.807$	$h = -10 \rightarrow 10$
29638 measured reflections	$k = -38 \rightarrow 38$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	248 parameters
Least-squares matrix: full	0 restraints
$R[F^2 > 2\sigma(F^2)] = 0.038$	Hydrogen site location: mixed
$wR(F^2) = 0.087$	H-atom parameters constrained
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0236P)^2 + 1.7903P]$
4039 reflections	where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}

Extinction correction: *SHELXL2018/3*
(Sheldrick, 2015b),
$Fc^* = kFc[1 + 0.001 xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0081 (7)

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^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Br1	0.24500 (5)	0.44440 (2)	0.08820 (4)	0.06338 (16)
N1	0.7272 (3)	0.50622 (7)	0.4672 (3)	0.0454 (6)
N2	0.8146 (3)	0.46878 (7)	0.4775 (3)	0.0462 (6)
N3	0.9508 (3)	0.48154 (8)	0.7609 (3)	0.0542 (7)
H3A	0.869458	0.500223	0.757513	0.065*
H3B	1.029166	0.472122	0.855943	0.065*
N4	0.3431 (4)	0.20008 (10)	0.3700 (4)	0.0690 (8)
O1	0.4488 (4)	0.26513 (10)	0.3557 (4)	0.0891 (8)
S1	1.03303 (10)	0.41267 (2)	0.62732 (10)	0.0505 (2)
C1	0.7900 (4)	0.43751 (10)	0.3435 (4)	0.0535 (8)
H1A	0.771425	0.451273	0.236395	0.064*
H1B	0.693711	0.419711	0.333814	0.064*
C2	0.9532 (4)	0.41145 (9)	0.3953 (4)	0.0478 (7)
H2A	1.034938	0.425774	0.354929	0.057*
C3	0.9255 (4)	0.45875 (9)	0.6271 (4)	0.0429 (7)
C4	0.6040 (4)	0.51408 (9)	0.3334 (4)	0.0487 (7)
H4A	0.571043	0.494228	0.247559	0.058*
C5	0.5142 (4)	0.55408 (9)	0.3137 (4)	0.0459 (7)
C6	0.3893 (4)	0.56328 (11)	0.1627 (4)	0.0628 (9)
H6A	0.359656	0.543477	0.076567	0.075*
C7	0.3078 (5)	0.60187 (12)	0.1387 (5)	0.0695 (10)
H7A	0.223309	0.607480	0.036564	0.083*
C8	0.3491 (4)	0.63205 (10)	0.2626 (4)	0.0532 (8)
C9	0.4726 (4)	0.62221 (10)	0.4137 (4)	0.0521 (8)
H9A	0.502433	0.642090	0.499513	0.063*
C10	0.5529 (4)	0.58380 (10)	0.4409 (4)	0.0485 (7)
H10A	0.633347	0.577780	0.545053	0.058*
C11	0.2619 (5)	0.67440 (11)	0.2337 (5)	0.0770 (11)
H11A	0.261055	0.685750	0.128290	0.116*
H11B	0.321407	0.693239	0.322952	0.116*
H11C	0.147992	0.671094	0.231326	0.116*
C12	0.9372 (4)	0.36634 (9)	0.3360 (4)	0.0454 (7)
C13	1.0517 (4)	0.35074 (10)	0.2659 (4)	0.0565 (8)
H13A	1.132036	0.368508	0.248893	0.068*
C14	1.0464 (5)	0.30867 (11)	0.2212 (5)	0.0709 (10)

H14A	1.123460	0.298109	0.174733	0.085*
C15	0.9283 (5)	0.28289 (11)	0.2456 (5)	0.0734 (11)
H15A	0.925525	0.254635	0.216122	0.088*
C16	0.8144 (5)	0.29779 (12)	0.3122 (5)	0.0732 (11)
H16A	0.733331	0.279913	0.326952	0.088*
C17	0.8191 (4)	0.33936 (11)	0.3578 (5)	0.0629 (9)
H17A	0.741175	0.349390	0.404218	0.076*
C18	0.4359 (5)	0.23379 (14)	0.4343 (5)	0.0757 (11)
H18A	0.496399	0.233544	0.549077	0.091*
C19	0.2468 (6)	0.19812 (15)	0.1924 (6)	0.0934 (13)
H19A	0.250819	0.224946	0.141811	0.140*
H19B	0.131711	0.191116	0.176912	0.140*
H19C	0.293996	0.176990	0.140581	0.140*
C20	0.3410 (7)	0.16367 (15)	0.4722 (7)	0.1129 (17)
H20A	0.410879	0.168951	0.586481	0.169*
H20B	0.383236	0.139639	0.430398	0.169*
H20C	0.227360	0.158275	0.467287	0.169*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0746 (3)	0.0552 (2)	0.0497 (2)	0.01350 (18)	0.00753 (16)	−0.00653 (16)
N1	0.0476 (14)	0.0418 (14)	0.0449 (14)	0.0098 (11)	0.0133 (12)	0.0017 (11)
N2	0.0505 (14)	0.0416 (14)	0.0405 (13)	0.0138 (12)	0.0077 (11)	−0.0006 (11)
N3	0.0609 (17)	0.0538 (16)	0.0409 (14)	0.0202 (13)	0.0086 (12)	0.0019 (12)
N4	0.069 (2)	0.065 (2)	0.078 (2)	−0.0069 (16)	0.0321 (17)	−0.0073 (17)
O1	0.086 (2)	0.079 (2)	0.104 (2)	−0.0168 (16)	0.0357 (17)	−0.0018 (18)
S1	0.0531 (5)	0.0452 (4)	0.0473 (4)	0.0140 (4)	0.0095 (3)	0.0008 (4)
C1	0.0604 (19)	0.0461 (19)	0.0471 (18)	0.0104 (15)	0.0094 (15)	−0.0076 (14)
C2	0.0498 (18)	0.0444 (17)	0.0476 (17)	0.0037 (14)	0.0147 (14)	−0.0016 (14)
C3	0.0442 (16)	0.0406 (16)	0.0413 (17)	0.0064 (13)	0.0113 (13)	0.0000 (13)
C4	0.0479 (18)	0.0434 (17)	0.0497 (18)	0.0040 (14)	0.0102 (15)	−0.0016 (14)
C5	0.0430 (16)	0.0447 (17)	0.0470 (17)	0.0054 (14)	0.0115 (13)	0.0078 (14)
C6	0.072 (2)	0.056 (2)	0.0482 (19)	0.0137 (18)	0.0048 (16)	0.0026 (16)
C7	0.070 (2)	0.072 (2)	0.054 (2)	0.023 (2)	0.0047 (17)	0.0182 (19)
C8	0.0527 (19)	0.0461 (18)	0.064 (2)	0.0116 (15)	0.0239 (16)	0.0149 (16)
C9	0.0494 (18)	0.0470 (19)	0.062 (2)	0.0054 (15)	0.0219 (16)	−0.0039 (15)
C10	0.0431 (17)	0.0530 (19)	0.0463 (17)	0.0099 (15)	0.0112 (13)	0.0016 (15)
C11	0.084 (3)	0.058 (2)	0.091 (3)	0.028 (2)	0.032 (2)	0.022 (2)
C12	0.0468 (17)	0.0408 (16)	0.0432 (17)	0.0035 (14)	0.0086 (13)	−0.0027 (13)
C13	0.0511 (19)	0.050 (2)	0.071 (2)	−0.0044 (16)	0.0246 (17)	−0.0015 (17)
C14	0.072 (2)	0.054 (2)	0.096 (3)	0.0031 (19)	0.042 (2)	−0.016 (2)
C15	0.082 (3)	0.044 (2)	0.094 (3)	−0.0072 (19)	0.030 (2)	−0.0156 (19)
C16	0.068 (2)	0.060 (2)	0.090 (3)	−0.021 (2)	0.025 (2)	−0.010 (2)
C17	0.053 (2)	0.065 (2)	0.077 (2)	−0.0029 (18)	0.0293 (18)	−0.0042 (19)
C18	0.068 (2)	0.086 (3)	0.073 (3)	−0.008 (2)	0.023 (2)	−0.007 (2)
C19	0.089 (3)	0.090 (3)	0.092 (3)	−0.002 (3)	0.018 (2)	−0.026 (3)
C20	0.142 (5)	0.082 (3)	0.139 (5)	−0.005 (3)	0.079 (4)	0.021 (3)

Geometric parameters (Å, º)

N1—C4	1.272 (4)	C8—C9	1.380 (4)
N1—N2	1.386 (3)	C8—C11	1.513 (4)
N2—C3	1.330 (4)	C9—C10	1.376 (4)
N2—C1	1.468 (4)	C9—H9A	0.9300
N3—C3	1.299 (4)	C10—H10A	0.9300
N3—H3A	0.9000	C11—H11A	0.9600
N3—H3B	0.9000	C11—H11B	0.9600
N4—C18	1.328 (5)	C11—H11C	0.9600
N4—C19	1.445 (5)	C12—C17	1.374 (4)
N4—C20	1.448 (5)	C12—C13	1.387 (4)
O1—C18	1.223 (5)	C13—C14	1.386 (5)
S1—C3	1.722 (3)	C13—H13A	0.9300
S1—C2	1.846 (3)	C14—C15	1.359 (5)
C1—C2	1.535 (4)	C14—H14A	0.9300
C1—H1A	0.9700	C15—C16	1.355 (5)
C1—H1B	0.9700	C15—H15A	0.9300
C2—C12	1.510 (4)	C16—C17	1.373 (5)
C2—H2A	0.9800	C16—H16A	0.9300
C4—C5	1.459 (4)	C17—H17A	0.9300
C4—H4A	0.9300	C18—H18A	0.9300
C5—C6	1.381 (4)	C19—H19A	0.9600
C5—C10	1.385 (4)	C19—H19B	0.9600
C6—C7	1.386 (5)	C19—H19C	0.9600
C6—H6A	0.9300	C20—H20A	0.9600
C7—C8	1.375 (5)	C20—H20B	0.9600
C7—H7A	0.9300	C20—H20C	0.9600
C4—N1—N2	118.6 (2)	C8—C9—H9A	119.1
C3—N2—N1	116.8 (2)	C9—C10—C5	120.3 (3)
C3—N2—C1	116.1 (2)	C9—C10—H10A	119.9
N1—N2—C1	127.0 (2)	C5—C10—H10A	119.9
C3—N3—H3A	116.4	C8—C11—H11A	109.5
C3—N3—H3B	116.4	C8—C11—H11B	109.5
H3A—N3—H3B	124.4	H11A—C11—H11B	109.5
C18—N4—C19	120.2 (4)	C8—C11—H11C	109.5
C18—N4—C20	121.7 (4)	H11A—C11—H11C	109.5
C19—N4—C20	118.0 (4)	H11B—C11—H11C	109.5
C3—S1—C2	90.96 (13)	C17—C12—C13	118.5 (3)
N2—C1—C2	105.6 (2)	C17—C12—C2	122.3 (3)
N2—C1—H1A	110.6	C13—C12—C2	119.1 (3)
C2—C1—H1A	110.6	C14—C13—C12	120.0 (3)
N2—C1—H1B	110.6	C14—C13—H13A	120.0
C2—C1—H1B	110.6	C12—C13—H13A	120.0
H1A—C1—H1B	108.7	C15—C14—C13	119.8 (3)
C12—C2—C1	116.6 (3)	C15—C14—H14A	120.1
C12—C2—S1	109.4 (2)	C13—C14—H14A	120.1

C1—C2—S1	104.9 (2)	C16—C15—C14	120.9 (3)
C12—C2—H2A	108.6	C16—C15—H15A	119.6
C1—C2—H2A	108.6	C14—C15—H15A	119.6
S1—C2—H2A	108.6	C15—C16—C17	119.8 (3)
N3—C3—N2	123.2 (3)	C15—C16—H16A	120.1
N3—C3—S1	123.0 (2)	C17—C16—H16A	120.1
N2—C3—S1	113.8 (2)	C16—C17—C12	121.0 (3)
N1—C4—C5	120.4 (3)	C16—C17—H17A	119.5
N1—C4—H4A	119.8	C12—C17—H17A	119.5
C5—C4—H4A	119.8	O1—C18—N4	125.7 (4)
C6—C5—C10	118.5 (3)	O1—C18—H18A	117.2
C6—C5—C4	119.4 (3)	N4—C18—H18A	117.2
C10—C5—C4	122.0 (3)	N4—C19—H19A	109.5
C5—C6—C7	120.4 (3)	N4—C19—H19B	109.5
C5—C6—H6A	119.8	H19A—C19—H19B	109.5
C7—C6—H6A	119.8	N4—C19—H19C	109.5
C8—C7—C6	121.5 (3)	H19A—C19—H19C	109.5
C8—C7—H7A	119.3	H19B—C19—H19C	109.5
C6—C7—H7A	119.3	N4—C20—H20A	109.5
C7—C8—C9	117.6 (3)	N4—C20—H20B	109.5
C7—C8—C11	121.0 (3)	H20A—C20—H20B	109.5
C9—C8—C11	121.5 (3)	N4—C20—H20C	109.5
C10—C9—C8	121.8 (3)	H20A—C20—H20C	109.5
C10—C9—H9A	119.1	H20B—C20—H20C	109.5
C4—N1—N2—C3	−170.3 (3)	C6—C7—C8—C11	178.7 (4)
C4—N1—N2—C1	5.3 (4)	C7—C8—C9—C10	0.2 (5)
C3—N2—C1—C2	−24.2 (4)	C11—C8—C9—C10	−179.8 (3)
N1—N2—C1—C2	160.2 (3)	C8—C9—C10—C5	1.8 (5)
N2—C1—C2—C12	150.8 (3)	C6—C5—C10—C9	−2.6 (5)
N2—C1—C2—S1	29.7 (3)	C4—C5—C10—C9	175.9 (3)
C3—S1—C2—C12	−149.7 (2)	C1—C2—C12—C17	−50.1 (4)
C3—S1—C2—C1	−23.9 (2)	S1—C2—C12—C17	68.6 (3)
N1—N2—C3—N3	1.9 (4)	C1—C2—C12—C13	133.7 (3)
C1—N2—C3—N3	−174.2 (3)	S1—C2—C12—C13	−107.5 (3)
N1—N2—C3—S1	−178.1 (2)	C17—C12—C13—C14	−0.7 (5)
C1—N2—C3—S1	5.8 (4)	C2—C12—C13—C14	175.6 (3)
C2—S1—C3—N3	−168.3 (3)	C12—C13—C14—C15	0.3 (6)
C2—S1—C3—N2	11.6 (2)	C13—C14—C15—C16	0.4 (6)
N2—N1—C4—C5	−176.8 (3)	C14—C15—C16—C17	−0.8 (6)
N1—C4—C5—C6	175.2 (3)	C15—C16—C17—C12	0.4 (6)
N1—C4—C5—C10	−3.3 (5)	C13—C12—C17—C16	0.3 (5)
C10—C5—C6—C7	1.5 (5)	C2—C12—C17—C16	−175.9 (3)
C4—C5—C6—C7	−177.0 (3)	C19—N4—C18—O1	0.5 (6)
C5—C6—C7—C8	0.5 (6)	C20—N4—C18—O1	177.5 (4)
C6—C7—C8—C9	−1.4 (5)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···Br1[i]	0.90	2.57	3.368 (3)	148
N3—H3*B*···Br1[ii]	0.90	2.35	3.243 (2)	175
C16—H16*A*···O1	0.93	2.54	3.391 (6)	153

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*+1, *y*, *z*+1.