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1-Ethyl-4-isopropyl-1,2,4-triazolium bromide

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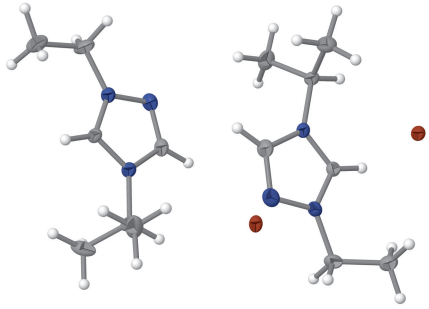
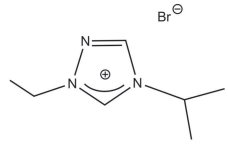
An ionic compound consisting of a triazolium cation and bromide anion, $C_7H_{14}N_3^+\cdot Br^-$, has been synthesized and structurally characterized using single-crystal X-ray diffraction and NMR. The compound crystallizes in the monoclinic space group $P2_1/m$ with the non-hydrogen atoms of one cation lying on general positions and the others lying on a mirror plane. One bromide ion also lies on the mirror. The extended structure exhibits only weak intermolecular interactions between heterocyclic C—H groups and Br^- ions.

3D view



Chemical scheme



Structure description

Asymmetric 1,2,4-triazolium cations are of interest due to their utility as cations in ionic liquids (ILs) and as precursors to N-heterocyclic carbenes (NHCs) (Dwivedi *et al.*, 2014; Nelson, 2015; Strassner *et al.*, 2013; Riederer *et al.*, 2011; Chianese *et al.*, 2004). The crystal structures of several triazolium salts have been reported (Peña Hueso *et al.*, 2022; Kumasaki *et al.*, 2021; Ponjan *et al.*, 2020; Guino-o *et al.*, 2015). We have synthesized many imidazolium and triazolium salts as precursors in the synthesis of NHC complexes of rhodium and iridium (Castaldi *et al.*, 2021; Gnanamgari *et al.*, 2007; Idrees *et al.*, 2017; Nichol *et al.*, 2011; Newman *et al.*, 2021; Rushlow *et al.*, 2022).

The molecular structure of the title compound is shown in Fig. 1. There are one and a half molecules in the asymmetric unit with the non-hydrogen atoms of the N1 cation (except C4) and Br1 lying on the (x, 3/4, z) mirror plane. All the atoms of the N4 cation and Br2 occupy general positions. The bond lengths in the triazolium rings indicate aromaticity with C—N bonds exhibiting distances in the range of 1.305 (2)–1.366 (2) Å and N—N bond distances near 1.365 Å; the N—C—N bond angles in the triazolium ring range from 106.93 (18) to 111.35 (18)°. The C1—N2—C5—C6 torsion angle of the ethyl side chain in the N1 cation is constrained to be 0° by symmetry and the corresponding C8—N5—C12—C13 torsion angle in the N4 cation is 24.4 (2)°.

The crystal packing of the title compound is displayed in Fig. 2. There are weak non-classical hydrogen-bonding interactions between the heterocyclic C—H groupings and

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···Br1^{i}	0.95	2.67	3.610 (2)	170
C2—H2···Br2^{i}	0.95	2.70	3.6344 (18)	166
C7—H7···Br2^{i}	0.95	2.69	3.6316 (15)	170
C8—H8···Br2^{i}	0.95	2.68	3.5635 (15)	156

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

bromide ions. These weak interactions are shown as dotted red lines in Fig. 2 and summarized in Table 1.

Synthesis and crystallization

1-Ethyl triazole was purchased from AmBeed. All other compounds used in the syntheses of the title compound were obtained from Sigma-Aldrich. All materials in the synthesis were used as received. The synthesis was performed under nitrogen using reagent grade solvents, which were used as received without further purification. NMR spectra were recorded at room temperature in $CDCl_3$ on a 400 MHz Varian spectrometer and referenced to the residual solvent peak (δ in p.p.m.).

1-Ethyl-1,2,4-triazole (2.01 g, 20.61 mmol) and isopropyl bromide (10.14 g, 82.4 mmol) were added to toluene (20 ml) and the mixture was refluxed for 48 h. Once cooled, the liquid was decanted, the white solid product that formed was washed with ether, filtered, and dried. The title compound crystallized as clear needles by slow diffusion of pentane into a CH_2Cl_2

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_7H_{14}N_3^+\cdot Br^-$
M_r	220.12
Crystal system, space group	Monoclinic, $P2_1/m$
Temperature (K)	100
a, b, c (Å)	8.1283 (2), 21.3822 (7), 8.6376 (2)
β (°)	101.713 (3)
V (Å^3)	1469.96 (7)
Z	6
Radiation type	Mo $K\alpha$
μ (mm^{-1})	4.14
Crystal size (mm)	0.38 × 0.25 × 0.04
Data collection	
Diffractometer	Rigaku XtaLAB Synergy-S
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD; 2022)
T_{min}, T_{max}	0.483, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	23168, 3747, 3142
R_{int}	0.036
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.022, 0.052, 1.04
No. of reflections	3747
No. of parameters	168
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.38, −0.29

Computer programs: *CrysAlis PRO* (Rigaku OD, 2022), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), and *publCIF* (Westrip, 2010).

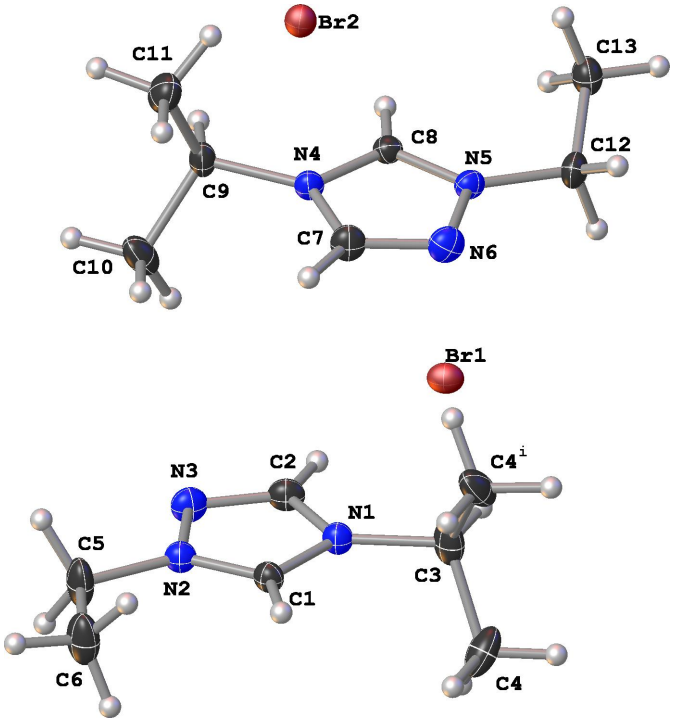


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. The N1 molecule (except C4) and Br1 lie on the (x, 3/4, z) mirror plane. Atom C4^{i} is generated by the symmetry operation $x, \frac{3}{2}-y, z$.

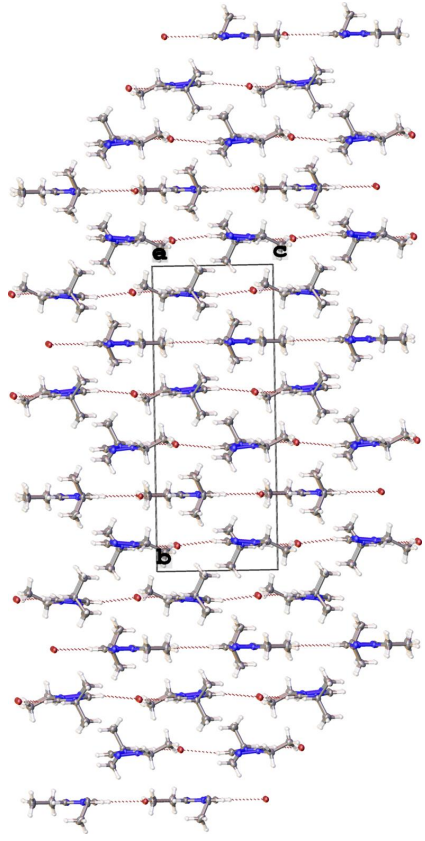


Figure 2
Crystal packing of the title compound shown along the a axis. Non-classical C—H···Br hydrogen-bonding interactions are shown as dotted red lines.

solution. Yield: 1.04 g (23%). ^{1}H NMR: $CDCl_3$, δ (p.p.m.) 11.99 (*s*, 1 H, N—C_5H—N), 8.85 (*s*, 1 H, N—C_3H—N), 5.13 (*m*, 1 H, $CH(CH_3)_2$), 4.63 (*q*, 2 H, N—CH_2), 1.74 (*d*, 6 H, $CH(CH_3)_2$), 1.65 (*t*, 3 H, CH_2CH_3). ^{13}C NMR: δ (p.p.m.) 142.27 (N—CH—N), 141.84 (N—CH—N), 53.15 [$CH(CH_3)_2$], 48.36 (N—CH_2), 23.14 [$CH(CH_3)_2$], 14.22 (N—CH_2CH_3).

Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

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Crystal data

$C_7H_{14}N_3^+\cdot Br^-$
M_r = 220.12
Monoclinic, $P2_1/m$
a = 8.1283 (2) Å
b = 21.3822 (7) Å
c = 8.6376 (2) Å
β = 101.713 (3)°
V = 1469.96 (7) Å^3
Z = 6
$F(000)$ = 672
D_x = 1.492 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9609 reflections
θ = 3.1–28.2°
μ = 4.14 mm^{-1}
T = 100 K
Plate, colourless
0.38 × 0.25 × 0.04 mm

Data collection

Rigaku XtaLAB Synergy-S diffractometer
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Mo) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD; 2022)
T_{min} = 0.483, T_{max} = 1.000
23168 measured reflections
3747 independent reflections
3142 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 28.3°, θ_{min} = 2.6°
h = −10→10
k = −27→28
l = −11→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.052
S = 1.04
3747 reflections
168 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0235P)^2 + 0.254P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Br1	0.65535 (3)	0.750000	0.86475 (2)	0.01997 (6)	
Br2	0.36575 (2)	0.58378 (2)	1.16793 (2)	0.01912 (5)	
N1	0.5536 (2)	0.750000	0.34816 (19)	0.0180 (4)	
N2	0.3012 (2)	0.750000	0.22004 (19)	0.0181 (4)	

N3	0.2904 (2)	0.750000	0.3756 (2)	0.0225 (4)	
C1	0.4576 (3)	0.750000	0.2031 (2)	0.0175 (4)	
H1	0.495511	0.750000	0.106069	0.021*	
C2	0.4471 (3)	0.750000	0.4505 (2)	0.0209 (4)	
H2	0.482097	0.750000	0.562368	0.025*	
C3	0.7407 (3)	0.750000	0.3888 (3)	0.0277 (5)	
H3	0.777584	0.750000	0.506529	0.033*	
C4	0.8056 (2)	0.80896 (8)	0.3239 (2)	0.0324 (4)	
H4A	0.772489	0.809040	0.208337	0.049*	
H4B	0.928441	0.810248	0.355041	0.049*	
H4C	0.757925	0.845690	0.366538	0.049*	
C5	0.1468 (3)	0.750000	0.0987 (3)	0.0315 (6)	
H5A	0.079611	0.787411	0.112921	0.038*	0.5
H5B	0.079611	0.712589	0.112921	0.038*	0.5
C6	0.1791 (3)	0.750000	−0.0638 (3)	0.0353 (6)	
H6A	0.225946	0.790528	−0.085598	0.053*	0.5
H6B	0.073605	0.742719	−0.139517	0.053*	0.5
H6C	0.259308	0.716754	−0.073790	0.053*	0.5
N4	0.45707 (16)	0.58697 (5)	0.70657 (14)	0.0163 (3)	
N5	0.71989 (15)	0.59178 (5)	0.80363 (14)	0.0170 (3)	
N6	0.70540 (17)	0.59818 (6)	0.64405 (15)	0.0234 (3)	
C7	0.5439 (2)	0.59462 (7)	0.58810 (18)	0.0223 (3)	
H7	0.493358	0.597046	0.478994	0.027*	
C8	0.57173 (19)	0.58536 (6)	0.84100 (17)	0.0167 (3)	
H8	0.550409	0.580476	0.944460	0.020*	
C9	0.27440 (18)	0.57739 (7)	0.69275 (18)	0.0198 (3)	
H9	0.249096	0.576878	0.801314	0.024*	
C10	0.1780 (2)	0.63095 (8)	0.6001 (2)	0.0296 (4)	
H10A	0.218468	0.670794	0.649669	0.044*	
H10B	0.057966	0.626396	0.599636	0.044*	
H10C	0.195525	0.630178	0.491108	0.044*	
C11	0.2264 (2)	0.51438 (8)	0.61529 (19)	0.0287 (4)	
H11A	0.240093	0.515644	0.505186	0.043*	
H11B	0.109054	0.505046	0.618208	0.043*	
H11C	0.299190	0.481809	0.672508	0.043*	
C12	0.88457 (19)	0.59542 (8)	0.9095 (2)	0.0242 (3)	
H12A	0.917169	0.639848	0.927513	0.029*	
H12B	0.969276	0.574799	0.859048	0.029*	
C13	0.8832 (2)	0.56445 (8)	1.06588 (18)	0.0246 (3)	
H13A	0.847326	0.520823	1.048013	0.037*	
H13B	0.804907	0.586585	1.119266	0.037*	
H13C	0.996325	0.565779	1.132088	0.037*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02633 (12)	0.01928 (12)	0.01483 (11)	0.000	0.00543 (8)	0.000
Br2	0.01946 (8)	0.02267 (9)	0.01542 (8)	−0.00045 (5)	0.00400 (6)	−0.00014 (5)

N1	0.0180 (9)	0.0217 (9)	0.0145 (8)	0.000	0.0036 (7)	0.000
N2	0.0193 (9)	0.0205 (9)	0.0149 (8)	0.000	0.0043 (7)	0.000
N3	0.0242 (10)	0.0261 (10)	0.0194 (9)	0.000	0.0094 (7)	0.000
C1	0.0181 (10)	0.0194 (11)	0.0142 (10)	0.000	0.0015 (8)	0.000
C2	0.0265 (11)	0.0219 (11)	0.0154 (10)	0.000	0.0066 (9)	0.000
C3	0.0196 (11)	0.0469 (15)	0.0148 (10)	0.000	−0.0009 (9)	0.000
C4	0.0238 (8)	0.0396 (10)	0.0359 (9)	−0.0128 (7)	0.0108 (7)	−0.0165 (8)
C5	0.0159 (11)	0.0541 (16)	0.0222 (12)	0.000	−0.0021 (9)	0.000
C6	0.0224 (12)	0.0617 (18)	0.0196 (11)	0.000	−0.0007 (9)	0.000
N4	0.0165 (6)	0.0197 (7)	0.0132 (6)	0.0001 (5)	0.0040 (5)	0.0014 (4)
N5	0.0169 (6)	0.0181 (7)	0.0171 (6)	−0.0005 (5)	0.0059 (5)	0.0009 (4)
N6	0.0244 (7)	0.0275 (7)	0.0204 (7)	−0.0008 (5)	0.0093 (5)	−0.0004 (5)
C7	0.0236 (8)	0.0278 (9)	0.0167 (7)	−0.0001 (6)	0.0068 (6)	−0.0005 (6)
C8	0.0170 (7)	0.0164 (7)	0.0170 (7)	0.0000 (5)	0.0041 (6)	0.0013 (5)
C9	0.0138 (7)	0.0284 (9)	0.0169 (7)	−0.0003 (6)	0.0023 (6)	0.0025 (6)
C10	0.0242 (8)	0.0386 (10)	0.0273 (8)	0.0118 (7)	0.0077 (7)	0.0102 (7)
C11	0.0231 (8)	0.0329 (9)	0.0280 (8)	−0.0061 (7)	0.0003 (7)	−0.0008 (7)
C12	0.0134 (7)	0.0286 (9)	0.0302 (9)	−0.0012 (6)	0.0035 (6)	0.0032 (7)
C13	0.0187 (8)	0.0305 (9)	0.0232 (8)	0.0006 (6)	0.0013 (6)	−0.0004 (6)

Geometric parameters (Å, º)

N1—C1	1.335 (2)	N4—C7	1.366 (2)
N1—C2	1.357 (3)	N4—C8	1.3337 (19)
N1—C3	1.490 (3)	N4—C9	1.4795 (19)
N2—N3	1.364 (2)	N5—N6	1.3662 (18)
N2—C1	1.308 (3)	N5—C8	1.316 (2)
N2—C5	1.463 (3)	N5—C12	1.4618 (19)
N3—C2	1.307 (3)	N6—C7	1.305 (2)
C3—C4	1.517 (2)	C9—C10	1.520 (2)
C3—C4^{i}	1.517 (2)	C9—C11	1.520 (2)
C5—C6	1.480 (3)	C12—C13	1.507 (2)
C1—N1—C2	106.43 (18)	C7—N4—C9	128.25 (12)
C1—N1—C3	126.56 (18)	C8—N4—C7	106.21 (13)
C2—N1—C3	127.01 (17)	C8—N4—C9	125.39 (13)
N3—N2—C5	119.20 (18)	N6—N5—C12	120.41 (13)
C1—N2—N3	111.63 (16)	C8—N5—N6	111.24 (12)
C1—N2—C5	129.18 (18)	C8—N5—C12	128.29 (13)
C2—N3—N2	103.67 (18)	C7—N6—N5	104.00 (13)
N2—C1—N1	106.93 (18)	N6—C7—N4	111.31 (13)
N3—C2—N1	111.35 (18)	N5—C8—N4	107.24 (13)
N1—C3—C4^{i}	109.14 (11)	N4—C9—C10	109.85 (12)
N1—C3—C4	109.14 (11)	N4—C9—C11	108.78 (12)
C4—C3—C4^{i}	112.4 (2)	C11—C9—C10	112.16 (13)
N2—C5—C6	112.79 (19)	N5—C12—C13	111.39 (13)
N2—N3—C2—N1	0.000 (1)	N5—N6—C7—N4	0.69 (16)

N3—N2—C1—N1	0.000 (1)	N6—N5—C8—N4	0.42 (15)
N3—N2—C5—C6	180.000 (1)	N6—N5—C12—C13	−158.90 (13)
C1—N1—C2—N3	0.000 (1)	C7—N4—C8—N5	0.01 (15)
C1—N1—C3—C4^{i}	−61.59 (13)	C7—N4—C9—C10	−56.70 (19)
C1—N1—C3—C4	61.59 (13)	C7—N4—C9—C11	66.41 (18)
C1—N2—N3—C2	0.000 (1)	C8—N4—C7—N6	−0.46 (16)
C1—N2—C5—C6	0.000 (1)	C8—N4—C9—C10	128.34 (14)
C2—N1—C1—N2	0.000 (1)	C8—N4—C9—C11	−108.55 (15)
C2—N1—C3—C4^{i}	118.41 (13)	C8—N5—N6—C7	−0.69 (16)
C2—N1—C3—C4	−118.41 (13)	C8—N5—C12—C13	24.4 (2)
C3—N1—C1—N2	180.000 (1)	C9—N4—C7—N6	−176.18 (13)
C3—N1—C2—N3	180.000 (1)	C9—N4—C8—N5	175.89 (12)
C5—N2—N3—C2	180.000 (1)	C12—N5—N6—C7	−177.94 (13)
C5—N2—C1—N1	180.000 (1)	C12—N5—C8—N4	177.41 (13)

Symmetry code: (i) x, $-y+3/2$, z.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···Br1^{ii}	0.95	2.67	3.610 (2)	170
C2—H2···Br2^{ii}	0.95	2.70	3.6344 (18)	166
C7—H7···Br2^{ii}	0.95	2.69	3.6316 (15)	170
C8—H8···Br2^{ii}	0.95	2.68	3.5635 (15)	156

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