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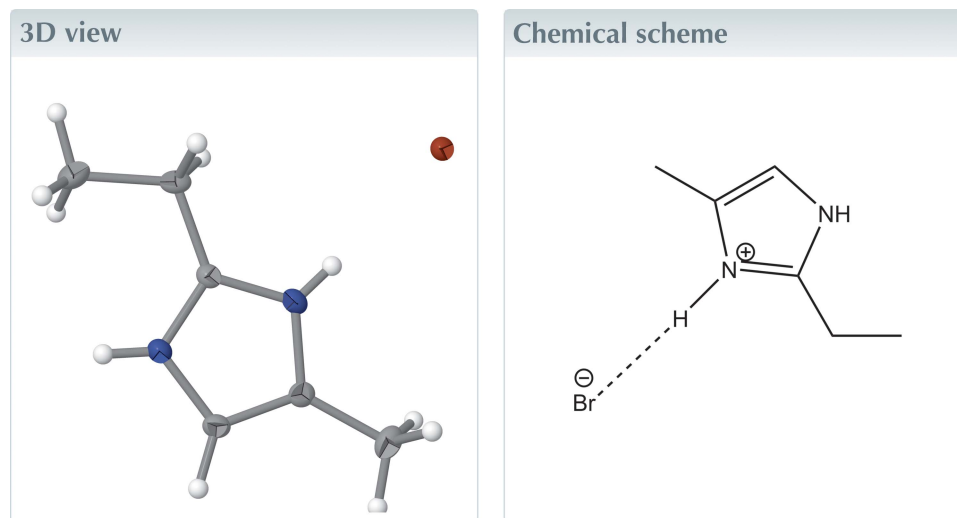
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Structural data: full structural data are available
from iucrdata.iucr.org

2-Ethyl-4-methyl-1*H*-imidazol-3-ium bromide

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In the title molecular salt, $C_6H_{11}N_2^+ \cdot Br^-$, the components are linked by $N-H \cdots Br \cdots H-N$ hydrogen bonds into $C(8)$ chains of alternating cations and anions propagating in the b -axis direction; these chains are cross-linked in the c -axis direction by weak $C-H \cdots Br$ hydrogen bonds.



Structure description

The unique structure of imidazole, containing two N atoms in a five-membered ring, permits it to accept a proton on one of its N atoms to form a cation and simultaneously deliver another proton from the other N atom to a suitable acceptor. In fact, this sort of shuttling action has been proposed as part of the catalytic mechanism of a number of enzymes (Mikulski & Silverman, 2010), and is consistent with the proton-conductivity properties of imidazole in the solid state where long hydrogen-bonded chains are present (Kawada *et al.*, 1970). These moieties and their derivatives have been implicated in proton-coupled electron-transfer processes (Huynh & Meyer, 2007; Onidas *et al.*, 2010). Consequently, there have been many theoretical (Scheiner & Yi, 1996; Kumar & Venkatnathan, 2015) and structural studies (Purdy *et al.*, 2007; Kim *et al.*, 2016) investigating these species. In this paper, we report a crystal structure containing the 2-ethyl-4-methyl-1*H*-imidazol-3-ium ($C_6H_{11}N_2^+$) cation. There have been four previous reports of structures containing this species (CSD refcode LEZSAL, Amanokura *et al.*, 2007; POJFOL, Beckett *et al.*, 2014; HOJJAT, Arici *et al.*, 2014; UMALAX, Kazimierzczuk *et al.*, 2016).

The title salt, **1**, crystallizes in the monoclinic space group $P2_1/c$ with one ion pair in the asymmetric unit (Fig. 1) and consists of $C_6H_{11}N_2^+$ cations and Br^- anions. The C8 methyl group is close to coplanar with the imidazole ring [$N1-C2-C7-C8 = -8.03(15)^\circ$]. Otherwise, the metrical parameters of the cation agree well with those observed in the other structures involving this species. In the extended structure, the component ions are

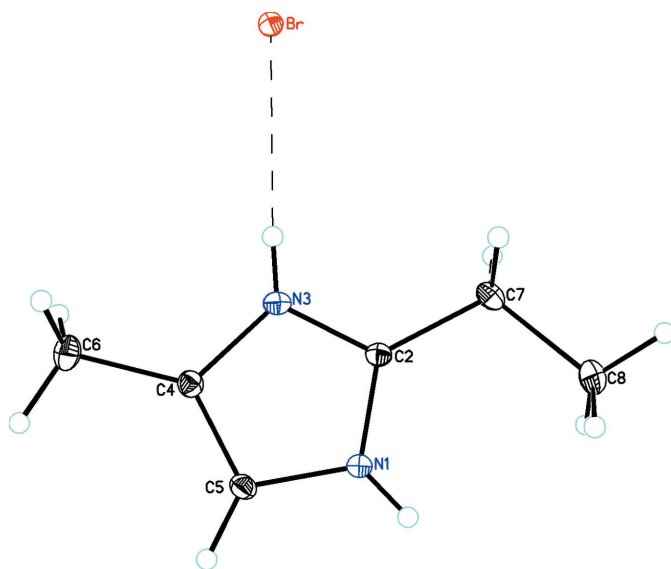


Figure 1
The molecular structure of **1** showing 30% displacement ellipsoids. The hydrogen bond is shown with a dashed line.

linked by N—H···Br···H—N hydrogen bonds (Table 1) into C(8) (Etter *et al.*, 1990) chains propagating in the *b*-axis direction. The chains are cross-linked in the *c*-axis direction by weak C—H···Br hydrogen bonds (Fig. 2).

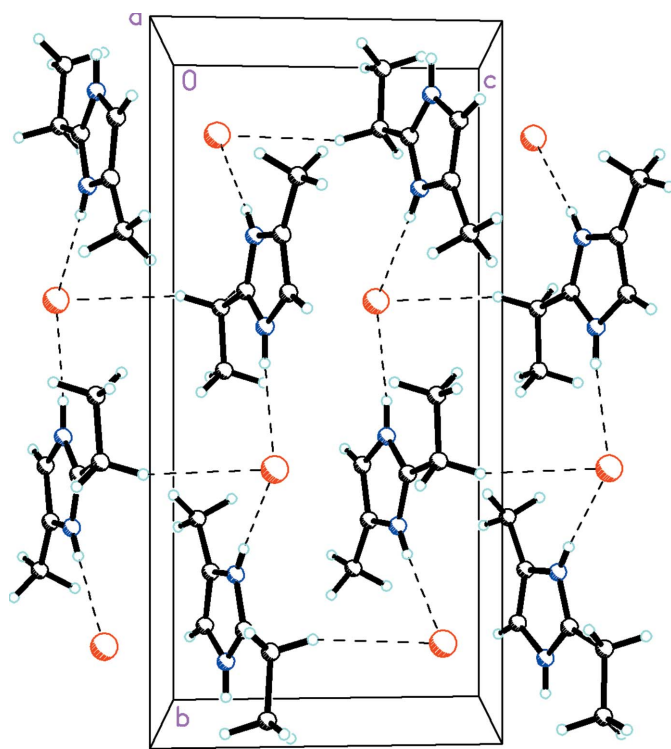


Figure 2
Packing diagram of **1** viewed down [100] showing how the cations and anions are linked into C(8) chains propagating in the *b*-axis direction.

Table 1
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>
N1—H1N···Br ⁱ	0.829 (17)	2.446 (17)	3.2490 (9)	163.3 (16)
N3—H3N···Br	0.780 (16)	2.485 (16)	3.2642 (8)	176.6 (16)
C5—H5A···Br ⁱⁱ	0.95	2.93	3.7842 (10)	151
C6—H6C···Br ⁱⁱⁱ	0.98	3.08	3.8349 (11)	135
C7—H7B···Br ^{iv}	0.99	2.93	3.8771 (11)	161

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

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₆ H ₁₁ N ₂ ⁺ ·Br [−]
<i>M_r</i>	191.08
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.8432 (6), 15.5962 (13), 7.5748 (7)
β (°)	94.360 (4)
<i>V</i> (Å ³)	806.10 (12)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ^{−1})	5.02
Crystal size (mm)	0.25 × 0.15 × 0.15
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.571, 0.747
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	24466, 3936, 3324
<i>R_{int}</i>	0.027
(<i>sin</i> θ / λ) _{max} (Å ^{−1})	0.836
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.019, 0.042, 1.03
No. of reflections	3936
No. of parameters	92
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ^{−3})	0.53, −0.36

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *SHELXTL* (Sheldrick 2008).

Synthesis and crystallization

The title compound resulted from an attempt to link two 2-ethyl-4-methylimidazole rings with a two-carbon chain by the reaction of 2-Et-4-Me-imidazole (6.20 g, 56.3 mmol) with BrCH₂CH₂Br (5.32 g, 28.3 mmol) in EtOH at 80°C overnight and several hours at 100°C. Ba(OH)₂·8H₂O (8.95 g, 28.3 mmol) was added with ethanol and water and heated to dissolve. On cooling, the mixture was rotovapped down and extracted between water and ether, and the ether layer was evaporated down to 3.1 g of an oil identified as primarily the starting imidazole by NMR. Recovery of about half of the starting imidazole must mean that the oligomer forms preferentially over the dimer. The barium ion was removed from the water layer by titration with H₂SO₄ followed by filtration. The solution was rotovapped down to an oil that precipitated a mass of salts on cooling. More crystals of **1**

crystallized from the oil over time, and were washed with *i*-PrOH to remove the oil for NMR. NMR of **1** in D₂O, DSS ref: ¹H, 1.26 (*t*, 3H), 2.88 (*q*, 2H) (Et), 2.20 (*s*, 3H) (Me), 4.70 (*s*, 1H) (C–H), 6.95 (*s*, 2H) (N–H); ¹³C, 11.8 (Me), 13.3, 21.8 (Et), 117.1 (C–H), 131.4 (4-C), 150.7 (2-C).

Refinement

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

Funding information

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full crystallographic data

IUCrData (2022). 7, x221172 [https://doi.org/10.1107/S2414314622011725]

2-Ethyl-4-methyl-1*H*-imidazol-3-ium bromide

Ray J. Butcher and Andrew P. Purdy

2-Ethyl-4-methyl-1*H*-imidazol-3-ium bromide*Crystal data*

$C_6H_{11}N_2^+Br^-$

$M_r = 191.08$

Monoclinic, $P2_1/c$

$a = 6.8432$ (6) Å

$b = 15.5962$ (13) Å

$c = 7.5748$ (7) Å

$\beta = 94.360$ (4)°

$V = 806.10$ (12) Å³

$Z = 4$

$F(000) = 384$

$D_x = 1.574$ Mg m⁻³

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

Cell parameters from 9911 reflections

$\theta = 3.0$ – 36.4 °

$\mu = 5.02$ mm⁻¹

$T = 100$ K

Prism, colorless

$0.25 \times 0.15 \times 0.15$ mm

Data collection

Bruker APEXII CCD

diffractometer

φ and ω scans

Absorption correction: multi-scan

(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.571$, $T_{\max} = 0.747$

24466 measured reflections

3936 independent reflections

3324 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 36.5$ °, $\theta_{\min} = 2.6$ °

$h = -11 \rightarrow 11$

$k = -26 \rightarrow 26$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.019$

$wR(F^2) = 0.042$

$S = 1.03$

3936 reflections

92 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0166P)^2 + 0.2838P]$

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

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

$\Delta\rho_{\max} = 0.53$ e Å⁻³

$\Delta\rho_{\min} = -0.36$ 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.

Refinement. All hydrogen atoms were located in difference Fourier maps and those attached to N were refined isotropically. Those attached to carbon atoms were refined in idealized geometry using a riding model with with atomic displacement parameters of $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ [for CH_3 , $1.5U_{\text{eq}}(\text{C})$] with C—H distances of 0.95 to 0.99 Å.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br	0.28697 (2)	0.12428 (2)	0.15497 (2)	0.01551 (3)
N1	0.63750 (12)	0.41897 (5)	0.31428 (11)	0.01531 (14)
H1N	0.631 (3)	0.4721 (11)	0.314 (2)	0.037 (5)*
C2	0.49850 (13)	0.36487 (6)	0.25237 (11)	0.01449 (16)
N3	0.56746 (12)	0.28564 (5)	0.28135 (11)	0.01568 (13)
H3N	0.503 (2)	0.2457 (9)	0.254 (2)	0.026 (4)*
C4	0.75365 (14)	0.28880 (6)	0.36671 (13)	0.01609 (15)
C5	0.79682 (13)	0.37312 (6)	0.38762 (13)	0.01694 (15)
H5A	0.914514	0.396452	0.442412	0.020*
C6	0.86990 (17)	0.21085 (7)	0.41511 (15)	0.02302 (19)
H6A	0.793013	0.172611	0.485620	0.035*
H6B	0.990828	0.227271	0.484469	0.035*
H6C	0.902634	0.181162	0.307207	0.035*
C7	0.30245 (14)	0.38674 (7)	0.16718 (13)	0.01933 (17)
H7A	0.201752	0.353879	0.225655	0.023*
H7B	0.296411	0.368801	0.041511	0.023*
C8	0.25416 (18)	0.48149 (8)	0.17584 (17)	0.0284 (2)
H8A	0.120458	0.491216	0.123853	0.043*
H8B	0.346648	0.514173	0.109621	0.043*
H8C	0.264154	0.500287	0.299648	0.043*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.01508 (4)	0.01385 (4)	0.01734 (4)	0.00039 (3)	−0.00055 (3)	−0.00153 (3)
N1	0.0149 (3)	0.0141 (3)	0.0167 (3)	−0.0012 (3)	−0.0004 (3)	−0.0013 (3)
C2	0.0152 (4)	0.0147 (4)	0.0135 (3)	−0.0015 (3)	0.0006 (3)	−0.0010 (3)
N3	0.0159 (3)	0.0150 (3)	0.0162 (3)	−0.0026 (3)	0.0014 (3)	−0.0022 (3)
C4	0.0150 (4)	0.0173 (4)	0.0160 (4)	0.0012 (3)	0.0015 (3)	−0.0011 (3)
C5	0.0131 (3)	0.0187 (4)	0.0188 (4)	−0.0006 (3)	−0.0001 (3)	−0.0023 (3)
C6	0.0240 (5)	0.0210 (4)	0.0244 (5)	0.0076 (4)	0.0038 (4)	0.0006 (4)
C7	0.0166 (4)	0.0238 (4)	0.0168 (4)	−0.0007 (3)	−0.0036 (3)	−0.0005 (3)
C8	0.0238 (5)	0.0265 (5)	0.0331 (6)	0.0058 (4)	−0.0089 (4)	0.0014 (4)

Geometric parameters (\AA , $^\circ$)

N1—C2	1.3299 (12)	C6—H6A	0.9800
N1—C5	1.3844 (13)	C6—H6B	0.9800
N1—H1N	0.829 (17)	C6—H6C	0.9800
C2—N3	1.3351 (12)	C7—C8	1.5167 (16)
C2—C7	1.4836 (13)	C7—H7A	0.9900
N3—C4	1.3851 (12)	C7—H7B	0.9900
N3—H3N	0.780 (16)	C8—H8A	0.9800
C4—C5	1.3545 (14)	C8—H8B	0.9800
C4—C6	1.4836 (14)	C8—H8C	0.9800

C5—H5A	0.9500		
C2—N1—C5	109.52 (8)	H6A—C6—H6B	109.5
C2—N1—H1N	126.7 (12)	C4—C6—H6C	109.5
C5—N1—H1N	123.7 (12)	H6A—C6—H6C	109.5
N1—C2—N3	107.15 (8)	H6B—C6—H6C	109.5
N1—C2—C7	127.33 (8)	C2—C7—C8	113.45 (8)
N3—C2—C7	125.52 (8)	C2—C7—H7A	108.9
C2—N3—C4	110.17 (8)	C8—C7—H7A	108.9
C2—N3—H3N	120.7 (12)	C2—C7—H7B	108.9
C4—N3—H3N	129.1 (12)	C8—C7—H7B	108.9
C5—C4—N3	105.90 (8)	H7A—C7—H7B	107.7
C5—C4—C6	131.20 (10)	C7—C8—H8A	109.5
N3—C4—C6	122.89 (9)	C7—C8—H8B	109.5
C4—C5—N1	107.24 (8)	H8A—C8—H8B	109.5
C4—C5—H5A	126.4	C7—C8—H8C	109.5
N1—C5—H5A	126.4	H8A—C8—H8C	109.5
C4—C6—H6A	109.5	H8B—C8—H8C	109.5
C4—C6—H6B	109.5		
C5—N1—C2—N3	-1.28 (10)	N3—C4—C5—N1	-0.29 (11)
C5—N1—C2—C7	178.55 (9)	C6—C4—C5—N1	178.35 (10)
N1—C2—N3—C4	1.11 (10)	C2—N1—C5—C4	0.98 (11)
C7—C2—N3—C4	-178.73 (9)	N1—C2—C7—C8	-8.03 (15)
C2—N3—C4—C5	-0.50 (11)	N3—C2—C7—C8	171.77 (10)
C2—N3—C4—C6	-179.27 (9)		

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>
N1—H1N...Br ⁱ	0.829 (17)	2.446 (17)	3.2490 (9)	163.3 (16)
N3—H3N...Br	0.780 (16)	2.485 (16)	3.2642 (8)	176.6 (16)
C5—H5A...Br ⁱⁱ	0.95	2.93	3.7842 (10)	151
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