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3-(2-Hydroxyethyl)-1-(4-nitrophenyl)-1*H*-imidazol-3-ium bromide

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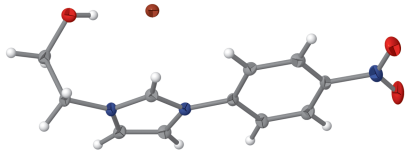
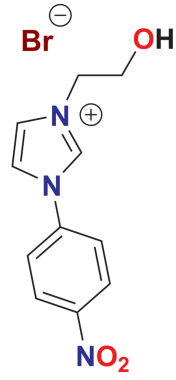
The molecular structure of the title salt, $C_{11}H_{12}N_3O_3^+\cdot Br^-$, reveals near co-planarity between the the imidazole and 4-nitrobenzene moieties with a dihedral angle of 8.99 (14)° between their planes. A prominent feature in the molecular packing is the bromide anion acting as a double acceptor for O—H···Br and C—H···Br hydrogen-bonds, leading to a linear chain propagating along [$\bar{1}$10]. The crystal studied was refined as an inversion twin, with the minor component = 0.081 (8).

3D view



Chemical scheme



Structure description

The title crystal is an imidazolium bromide salt based on a 1-(4-nitrophenyl)-1*H*-imidazol-3-yl moiety (Ibrahim & Bala, 2016; Illam *et al.*, 2021), which is functionalized at the 1,3-diazole wingtip with a 2-hydroxyethyl group. Unlike analogues with a fused 1*H*-benzo[*d*] backbone (Kumar *et al.*, 2015), derivatives of the title salt with the 1*H*-imidazol-3-yl moiety do not show any potential as chemodosimeters. The incorporation of oxygen-containing functionalities in the design of these imidazolium salts is motivated by the desire to increase the solubility of the ligand/precursor in common solvents (Garrison & Young, 2005), and, upon coordination, to enhance the electron density around the metal, thereby stabilizing the metal center during a catalytic cycle (Simpson *et al.*, 2015). We recently explored the potential of such NO_2-functionalized imidazolylidene–Co^{II}/Ni^{II} complexes as viable green catalysts for aryl C—N coupling reactions of aryl amines with aryl bromides (Ibrahim & Bala, 2016). In a continuation of this work designed to develop new derivatives with superior catalytic abilities, the title compound was synthesized and analyzed by X-ray crystallography.

The asymmetric unit of the title salt comprises an imidazolyl cation and a bromide anion (Fig. 1). The conformation of the cationic species is such that the dihedral angle

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···Br1	0.84	2.42	3.2509 (19)	171
C3—H3···Br1^{i}	0.95	2.71	3.572 (2)	151

Symmetry code: (i) $x+\frac{1}{2}, y-\frac{1}{2}, z$.

between the imidazole and 4-nitrobenzene planes is 8.99 (14)° while the orientation of the ethanolyl side is almost orthogonal with respect to the imidazole plane [C7—N3—C10—C11 torsion angle = 95.1 (4)°]. A prominent feature of the molecular packing relates to the bromide anion acting as a double acceptorm with the hydroxyl-H1 atom and the H3 atom of a neighboring 4-nitrophenyl moiety to form a linear supramolecular chain propagatingalong [$\bar{1}$10] (Table 1; Fig. 2).

Synthesis and crystallization

The title compound was synthesized with a slight modification of the reported protocol (Ibrahim & Bala, 2016). A mixture of *N*-*p*-nitrophenyl imidazole (0.5 g, 0.003 mol) and 2-bromoethanol (0.56 g, 0.005 mol; 0.35 ml, ρ = 1.76 g cm^{-3}, 95%) was refluxed overnight in acetonitrile under an inert dinitrogen atmosphere. Removal of the solvent followed by washing with ethyl acetate afforded a yellow precipitate, which yielded the title salt as an air-stable yellow solid after drying *in vacuo*. Slow diffusion of diethyl ether into a methanolic solution of the isolated title salt afforded suitable single crystals for the X-ray diffraction analysis. Yield: 0.70 g, 0.002 mol, 85.7%. m.p. 475–477 K. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.03 (*s*, 1H, NCHN), 8.52 (*d*, *J* = 9.0 Hz, 2H, CH$_{(phenyl)}$), 8.47 (*d*, *J* = 1.6 Hz, 1H, CH$_{(imidazolyl)}$), 8.11 (*d*, *J* = 9.1 Hz, 2H, CH$_{(benzyl)}$), 8.06 (*s*, 1H, CH$_{(imidazolyl)}$), 4.33 (*t*, *J* = 10.0 Hz, 2H, CH$_{2(ethanoyl)}$), 3.84 (*t*, *J* = 10.0 Hz, 2H, CH$_2$(hydroxyethy), 3.35 (*s*, *b*, 1H, OH(hydroxyethyl)). ^{13}C NMR (100 MHz, DMSO-d_6): δ 147.5 (NCN), 139.2, 136.4, 125.6, 124.1, 122.9, 120.9, 59.1 (CH$_2$), 52.4 (CH$_2$). FTIR (ν(O—H) 3243, ν(aryl C—H) 3090, ν(alkyl C—H) 2958, ν(C═N) 1552, ν(NO$_2$) 1522 & 1341, ν(C—O) 1222, ν(phenyl) 854 cm^{-1}. LRMS-ES^{+}: *m*/*z* (%) 234.0550 (100) [(*M* − Br)]$^{+}$.

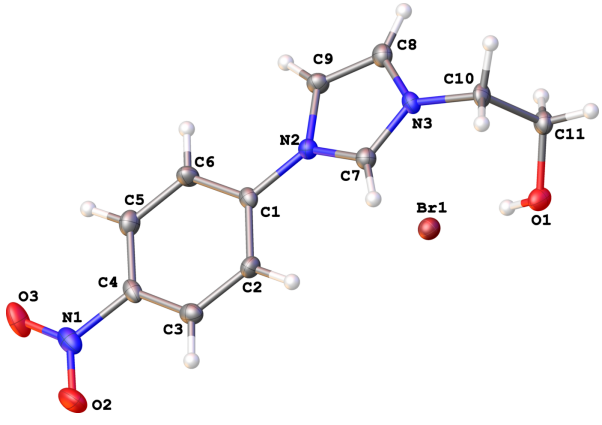


Figure 1
The asymmetric unit of the title compound showing the atom-labeling scheme and displacement ellipsoids at the 50% probability level.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_{12}N_3O_3^{+}\cdot Br^{-}$
M_r	314.15
Crystal system, space group	Monoclinic, *Cc*
Temperature (K)	100
a, *b*, *c* (Å)	6.4352 (4), 12.2697 (11), 15.5936 (10)
β (°)	90.290 (3)
V (Å^3)	1231.22 (16)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	3.34
Crystal size (mm)	0.38 × 0.21 × 0.14
Data collection	
Diffractometer	Bruker SMART APEXII area detector
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.661, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9019, 3051, 2930
R_{int}	0.019
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.673
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.017, 0.037, 1.03
No. of reflections	3051
No. of parameters	165
No. of restraints	2
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.36, −0.23
Absolute structure	Refined as an inversion twin
Absolute structure parameter	0.081 (8)

Computer programs: *COSMO* and *SAINT* (Bruker, 2010), *SHELXT2013* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

Table 2 provides a summary of the crystal data, data collection and structure refinement details. The structure was refined as an inversion twin, with the minor component = 0.081 (8).

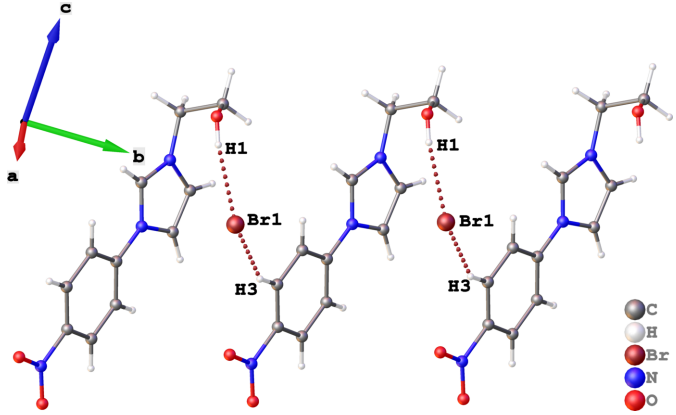


Figure 2
Representation of intermolecular O1—H1···Br1 and C3—H3···Br1 hydrogen bonds (brown dotted bonds) within the crystal of the title compound.

Acknowledgements

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full crystallographic data

IUCrData (2024). **9**, x241138 [https://doi.org/10.1107/S2414314624011386]

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(I)

Crystal data

$C_{11}H_{12}N_3O^{3+}\cdot Br^-$
M_r = 314.15
Monoclinic, *Cc*
a = 6.4352 (4) Å
b = 12.2697 (11) Å
c = 15.5936 (10) Å
β = 90.290 (3)°
V = 1231.22 (16) Å^3
Z = 4
F(000) = 632
D_x = 1.695 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 6616 reflections
θ = 3.3–28.5°
μ = 3.34 mm^{-1}
T = 100 K
Slab, light yellow
0.38 × 0.21 × 0.14 mm

Data collection

Bruker SMART APEXII area detector diffractometer
Detector resolution: 7.9 pixels mm^{-1}
ω and *φ* scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.661, T_{max} = 0.746
9019 measured reflections
3051 independent reflections
2930 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 28.6°, θ_{min} = 2.6°
h = −8→8
k = −16→16
l = −20→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.017
$wR(F^2)$ = 0.037
S = 1.03
3051 reflections
165 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0076P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Absolute structure: Refined as an inversion twin
Absolute structure parameter: 0.081 (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.

Refinement. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.52235 (5)	0.56771 (2)	0.24805 (3)	0.01782 (6)
C2	0.6133 (4)	0.2573 (2)	0.12029 (17)	0.0170 (5)
H2	0.588284	0.236441	0.177996	0.020*
O2	1.1242 (3)	0.15187 (18)	−0.01212 (14)	0.0336 (6)
O1	0.2180 (3)	0.45365 (14)	0.38751 (12)	0.0204 (4)
H1	0.298129	0.475858	0.348926	0.031*
C11	0.0084 (5)	0.4666 (3)	0.3601 (2)	0.0178 (7)
H11A	−0.007513	0.538803	0.332540	0.021*
H11B	−0.083443	0.464705	0.410782	0.021*
C10	−0.0603 (5)	0.3781 (2)	0.29685 (18)	0.0165 (6)
H10A	−0.035231	0.305423	0.322381	0.020*
H10B	−0.211178	0.385282	0.285381	0.020*
N3	0.0538 (4)	0.38742 (19)	0.21627 (15)	0.0140 (5)
C7	0.2242 (4)	0.33242 (19)	0.19668 (16)	0.0160 (5)
H7	0.287958	0.278530	0.231755	0.019*
N2	0.2926 (3)	0.36462 (15)	0.11964 (13)	0.0141 (4)
C1	0.4742 (4)	0.32634 (19)	0.07739 (15)	0.0145 (5)
C3	0.7879 (4)	0.2196 (2)	0.07779 (17)	0.0185 (5)
H3	0.883162	0.171970	0.105583	0.022*
C4	0.8207 (3)	0.2526 (2)	−0.00536 (18)	0.0164 (5)
N1	1.0073 (4)	0.21336 (18)	−0.05093 (16)	0.0229 (5)
O3	1.0345 (4)	0.24477 (17)	−0.12456 (14)	0.0306 (5)
C8	0.0106 (6)	0.4587 (3)	0.1501 (2)	0.0178 (7)
H8	−0.102340	0.508493	0.147718	0.021*
C6	0.5101 (4)	0.3571 (2)	−0.00708 (17)	0.0182 (6)
H6	0.414163	0.403271	−0.035965	0.022*
C5	0.6850 (4)	0.3206 (2)	−0.04886 (17)	0.0193 (5)
H5	0.711834	0.341669	−0.106364	0.023*
C9	0.1575 (4)	0.44526 (18)	0.08943 (17)	0.0168 (5)
H9	0.166987	0.483219	0.036499	0.020*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01789 (10)	0.01860 (10)	0.01696 (10)	−0.00135 (15)	−0.00015 (7)	0.00074 (15)
C2	0.0190 (14)	0.0193 (12)	0.0127 (12)	0.0002 (11)	−0.0003 (11)	0.0011 (9)
O2	0.0239 (12)	0.0384 (13)	0.0386 (14)	0.0131 (10)	0.0002 (10)	−0.0074 (10)
O1	0.0181 (9)	0.0268 (9)	0.0163 (9)	−0.0040 (7)	0.0012 (7)	0.0031 (7)
C11	0.0188 (16)	0.0178 (14)	0.0169 (15)	−0.0021 (12)	0.0021 (12)	−0.0041 (12)
C10	0.0163 (14)	0.0203 (14)	0.0130 (13)	−0.0032 (11)	0.0056 (11)	−0.0004 (11)
N3	0.0143 (12)	0.0110 (10)	0.0167 (11)	−0.0017 (9)	0.0034 (9)	−0.0022 (8)
C7	0.0169 (13)	0.0154 (11)	0.0157 (12)	−0.0011 (9)	0.0011 (9)	0.0000 (9)
N2	0.0153 (10)	0.0128 (9)	0.0144 (10)	−0.0004 (8)	0.0006 (8)	−0.0001 (7)
C1	0.0143 (12)	0.0127 (11)	0.0165 (13)	−0.0017 (9)	0.0018 (10)	−0.0033 (9)
C3	0.0176 (13)	0.0158 (12)	0.0219 (13)	0.0014 (10)	−0.0021 (10)	−0.0017 (10)

C4	0.0134 (15)	0.0148 (10)	0.0211 (12)	−0.0034 (12)	0.0045 (12)	−0.0060 (9)
N1	0.0181 (12)	0.0186 (11)	0.0320 (14)	−0.0028 (9)	0.0050 (10)	−0.0081 (10)
O3	0.0319 (13)	0.0271 (11)	0.0329 (12)	0.0010 (9)	0.0190 (10)	0.0008 (9)
C8	0.0196 (16)	0.0170 (14)	0.0170 (15)	−0.0008 (12)	0.0011 (12)	−0.0026 (11)
C6	0.0178 (14)	0.0189 (13)	0.0180 (14)	0.0042 (11)	0.0007 (11)	0.0037 (10)
C5	0.0226 (14)	0.0194 (12)	0.0159 (12)	−0.0037 (10)	0.0034 (10)	0.0009 (10)
C9	0.0182 (12)	0.0143 (11)	0.0179 (13)	0.0018 (9)	−0.0006 (10)	0.0022 (9)

Geometric parameters (Å, º)

C2—H2	0.9500	C7—N2	1.341 (3)
C2—C1	1.400 (3)	N2—C1	1.424 (3)
C2—C3	1.387 (4)	N2—C9	1.398 (3)
O2—N1	1.224 (3)	C1—C6	1.391 (3)
O1—H1	0.8400	C3—H3	0.9500
O1—C11	1.421 (4)	C3—C4	1.376 (4)
C11—H11A	0.9900	C4—N1	1.479 (3)
C11—H11B	0.9900	C4—C5	1.383 (4)
C11—C10	1.530 (4)	N1—O3	1.225 (3)
C10—H10A	0.9900	C8—H8	0.9500
C10—H10B	0.9900	C8—C9	1.351 (5)
C10—N3	1.463 (3)	C6—H6	0.9500
N3—C7	1.325 (3)	C6—C5	1.378 (4)
N3—C8	1.379 (4)	C5—H5	0.9500
C7—H7	0.9500	C9—H9	0.9500
C1—C2—H2	120.3	C2—C1—N2	120.2 (2)
C3—C2—H2	120.3	C6—C1—C2	120.5 (2)
C3—C2—C1	119.4 (2)	C6—C1—N2	119.3 (2)
C11—O1—H1	109.5	C2—C3—H3	120.6
O1—C11—H11A	109.1	C4—C3—C2	118.7 (2)
O1—C11—H11B	109.1	C4—C3—H3	120.6
O1—C11—C10	112.7 (3)	C3—C4—N1	119.1 (2)
H11A—C11—H11B	107.8	C3—C4—C5	122.7 (2)
C10—C11—H11A	109.1	C5—C4—N1	118.2 (2)
C10—C11—H11B	109.1	O2—N1—C4	117.5 (2)
C11—C10—H10A	109.5	O2—N1—O3	124.6 (3)
C11—C10—H10B	109.5	O3—N1—C4	117.9 (2)
H10A—C10—H10B	108.1	N3—C8—H8	126.0
N3—C10—C11	110.7 (2)	C9—C8—N3	107.9 (3)
N3—C10—H10A	109.5	C9—C8—H8	126.0
N3—C10—H10B	109.5	C1—C6—H6	120.0
C7—N3—C10	125.3 (2)	C5—C6—C1	120.0 (2)
C7—N3—C8	108.3 (3)	C5—C6—H6	120.0
C8—N3—C10	126.3 (3)	C4—C5—H5	120.7
N3—C7—H7	125.3	C6—C5—C4	118.6 (2)
N3—C7—N2	109.4 (2)	C6—C5—H5	120.7
N2—C7—H7	125.3	N2—C9—H9	126.7

C7—N2—C1	126.3 (2)	C8—C9—N2	106.7 (2)
C7—N2—C9	107.7 (2)	C8—C9—H9	126.7
C9—N2—C1	126.0 (2)		
C2—C1—C6—C5	−0.8 (4)	N2—C1—C6—C5	−179.9 (2)
C2—C3—C4—N1	179.6 (2)	C1—C2—C3—C4	0.8 (4)
C2—C3—C4—C5	−1.0 (4)	C1—N2—C9—C8	−178.1 (2)
O1—C11—C10—N3	−66.2 (3)	C1—C6—C5—C4	0.6 (4)
C11—C10—N3—C7	95.1 (4)	C3—C2—C1—N2	179.2 (2)
C11—C10—N3—C8	−80.8 (3)	C3—C2—C1—C6	0.0 (4)
C10—N3—C7—N2	−177.1 (2)	C3—C4—N1—O2	0.6 (3)
C10—N3—C8—C9	177.1 (2)	C3—C4—N1—O3	−179.2 (2)
N3—C7—N2—C1	178.5 (2)	C3—C4—C5—C6	0.2 (4)
N3—C7—N2—C9	0.4 (3)	N1—C4—C5—C6	179.7 (2)
N3—C8—C9—N2	−0.3 (3)	C8—N3—C7—N2	−0.6 (3)
C7—N3—C8—C9	0.6 (3)	C5—C4—N1—O2	−178.9 (2)
C7—N2—C1—C2	−7.5 (3)	C5—C4—N1—O3	1.4 (4)
C7—N2—C1—C6	171.7 (2)	C9—N2—C1—C2	170.3 (2)
C7—N2—C9—C8	−0.1 (3)	C9—N2—C1—C6	−10.6 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···Br1	0.84	2.42	3.2509 (19)	171
C3—H3···Br1^{i}	0.95	2.71	3.572 (2)	151

Symmetry code: (i) *x*+1/2, *y*−1/2, *z*.