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Monoclinic polymorph of 2-azaniumylmethyl-1*H*-benzimidazol-3-ium dichloride monohydrate

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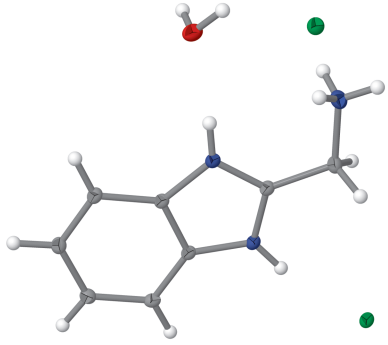
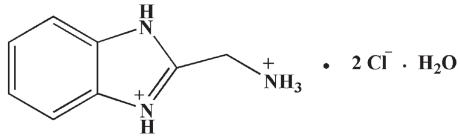
The title hydrated salt, $C_8H_{11}N_3^{2+}\cdot 2Cl^-\cdot H_2O$, is a monoclinic polymorph of the previously reported triclinic form. The compound crystallizes in space group $P2_1/c$ with $Z' = 1$. The crystal structure features N—H···O, N—H···Cl and O—H···Cl hydrogen bonds and aromatic π–π stacking interactions, forming a three-dimensional network.

3D view



Chemical scheme



Structure description

Benzimidazole-based systems have attracted attention as ligands for metal complexation owing to the desirable properties that are beneficial for biological applications such as anti-bacterial (Kankate *et al.*, 2019) and anti-hypertensive (Sharma *et al.*, 2013) effects. The materials applications of benzimidazole ligands include luminescent properties of their metal complexes, which can be applied in electroluminescent devices (Wu *et al.*, 2008). The larger conjugated π-system and the nitrogen electron donor of the secondary amine group of the benzimidazole moiety play an important role in determining the properties of the complexes. As part of our work in this area, we now describe the synthesis and structure of the title benzimidazolium salt, $C_8H_{11}N_3^{2+}\cdot 2Cl^-\cdot H_2O$.

A search of the Cambridge Structural Database (Version 6.00, update April 2025; Groom *et al.*, 2016) for the 2-ammoniumylmethyl-1*H* -benzimidazol-3-ium ($C_8H_{11}N_3^{2+}$) dication, generated three hits: a tetrachlorozinc(II) salt (CSD refcode COKXAC; Tapia-Benavides *et al.*, 2008), the solvent-free dichloride salt (NEPKOK; Malecki, 2011) and the triclinic polymorph of the title compound (NINWIT; Sen *et al.*, 2018).

The title compound crystallizes in a new monoclinic form in space group $P2_1/c$ compared with the previously reported triclinic form, in space group $P\overline{1}$ (Sen *et al.*, 2018). In the monoclinic polymorph, the asymmetric unit contains a benzimidazolium dication,

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1C···Cl1	0.84 (1)	2.32 (1)	3.0898 (8)	152 (1)
N1—H1D···Cl2^{i}	0.83 (1)	2.30 (1)	3.1262 (7)	177 (1)
N1—H1E···Cl2^{ii}	0.86 (1)	2.41 (1)	3.2430 (7)	163 (1)
N2—H2···Cl2	0.866 (16)	2.259 (16)	3.1099 (6)	167.2 (14)
N3—H3···O1	0.812 (15)	1.911 (16)	2.7197 (9)	173.6 (15)
O1—H1A···Cl2^{iii}	0.80 (1)	2.59 (1)	3.3752 (7)	169 (2)
O1—H1B···Cl1^{iv}	0.81 (1)	2.31 (1)	3.1209 (7)	173 (2)
C1—H1F···Cl1^{v}	0.988 (13)	2.793 (13)	3.7079 (8)	154.2 (10)
C5—H5···Cl1^{ii}	0.926 (13)	2.960 (13)	3.8515 (7)	162.1 (10)

Symmetry codes: (i) $-x+2, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $x-1, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $-x+1, -y, -z+1$; (v) $x+1, y, z$.

two chloride ions, and a water molecule with $Z' = 1$ (Fig. 1). In the more complex triclinic polymorph, the asymmetric unit contains three benzimidazolium dications, six chloride ions and three water molecules with $Z' = 3$ (Sen *et al.*, 2018). One notable feature is that in the solvent-free salt (Malecki, 2011), the pendant CH_2NH_3 moiety has a substantial torsion angle of *ca*. 59° relative to the plane of the fused rings, while in both monohydrate polymorphs, in all the unique molecules, that angle is < 10°, so that moiety is close to co-planar with the fused rings.

In the monoclinic polymorph described here, all the N—H groups form strong, charge-assisted, hydrogen bonds to either chloride anions or the water oxygen atom (Table 1). The water molecule forms O—H···Cl links to two chloride ions. The molecules pack in sheets in the *ab* plane and these sheets are then hydrogen bonded to their neighbours, generating a three-dimensional network (Fig. 2), similar to that of the triclinic polymorph. The cations also display aromatic π–π stacking in the *a*-axis direction with alternate molecules anti-parallel, with a shortest centroid–centroid separation of 3.4071 (4) Å.

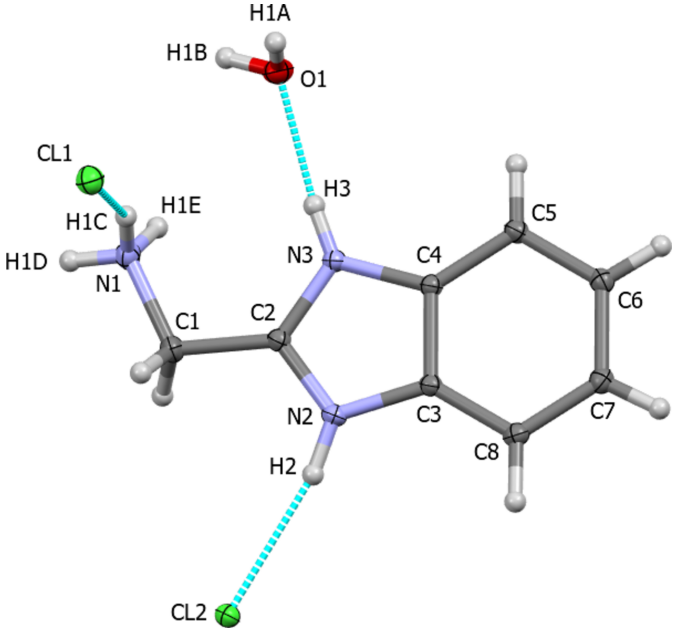


Figure 1
The asymmetric unit of the title compound with 50% probability ellipsoids showing hydrogen bonds as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_{11}N_3^{2+}\cdot 2Cl^-\cdot H_2O$
M_r	238.11
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	6.81630 (11), 12.09585 (19), 12.5226 (2)
β (°)	90.7201 (14)
V (Å^3)	1032.39 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.60
Crystal size (mm)	0.18 × 0.15 × 0.07
Data collection	
Diffractometer	Rigaku FRE+ diffractometer with HF Varimax confocal mirrors, a UG2 goniometer and HyPix 6000HE detector
Absorption correction	Analytical (CrystalisPro; Rigaku OD, 2024)
T_{min}, T_{max}	0.988, 0.994
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	49678, 5003, 4463
R_{int}	0.057
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.833
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.080, 1.06
No. of reflections	5003
No. of parameters	172
No. of restraints	5
H-atom treatment	Only H-atom coordinates refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.72, −0.22

Computer programs: *CrysAlis PRO* (Rigaku OD, 2024), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2019/3* (Sheldrick, 2015*b*) and *SHELXTL* (Sheldrick, 2008).

Synthesis and crystallization

The benzimidazolium cation was prepared following the reported procedure (Cescon & Day, 1962). About 1 mmol (5.46 g) of *o*-phenylenediamine and 1 mmol (5.68 g) of glycine were mixed and dissolved in 100 ml of hydrochloric acid (5 mol l^{-1}). The solution was refluxed for three days. The reaction mixture was cooled and placed in an ice bath over-

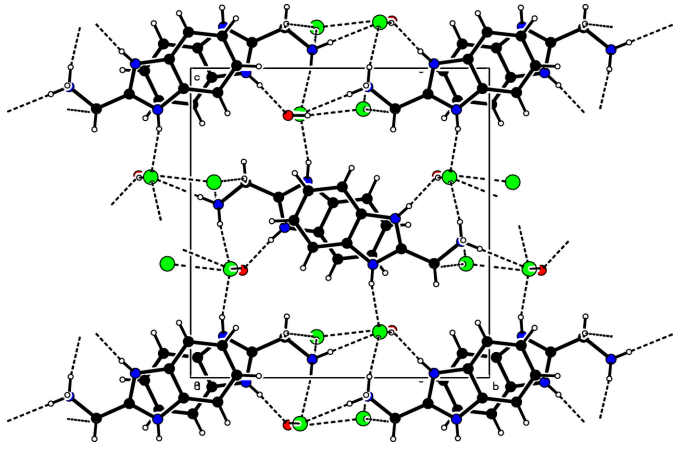


Figure 2
Crystal packing of the title compound viewed down [100].

night. The resulting purple crystals were isolated from the hydrochloric acid by filtration, and then recrystallized from ethanol solution, m.p. = 122 °C. From the same re-crystallization, some red crystals of the well known compound *o*-phenylenediamine dihydrochloride [CSD: PHNDMO; Stålhandske, 1974) were also identified. We have re-determined that structure to a slightly higher precision (Baskaran *et al.*, 2025)

Refinement

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

Acknowledgements

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full crystallographic data

IUCrData (2025). **10**, x250868 [https://doi.org/10.1107/S2414314625008685]

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2-Azaniumylmethyl-1*H*-benzimidazol-3-ium dichloride monohydrate

Crystal data

$C_8H_{11}N_3^{2+}\cdot 2Cl^-\cdot H_2O$
M_r = 238.11
Monoclinic, $P2_1/c$
a = 6.81630 (11) Å
b = 12.09585 (19) Å
c = 12.5226 (2) Å
β = 90.7201 (14)°
V = 1032.39 (3) Å^3
Z = 4
$F(000)$ = 496
D_x = 1.532 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 29865 reflections
θ = 2.3–38.0°
μ = 0.60 mm^{-1}
T = 100 K
Block, colourless
0.18 × 0.15 × 0.07 mm

Data collection

Rigaku FRE+ diffractometer with HF Varimax confocal mirrors, a UG2 goniometer and HyPix 6000HE detector
Radiation source: Rotating Anode
Detector resolution: 10 pixels mm^{-1}
profile data from ω–scans
Absorption correction: analytical (CrystalisPro; Rigaku OD, 2024)
T_{min} = 0.988, T_{max} = 0.994
49678 measured reflections
5003 independent reflections
4463 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
θ_{max} = 36.3°, θ_{min} = 2.3°
h = −11→11
k = −20→20
l = −20→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.080
S = 1.06
5003 reflections
172 parameters
5 restraints
Primary atom site location: iterative
Hydrogen site location: difference Fourier map
Only H-atom coordinates refined
$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 0.1488P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.72 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 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. The H atoms atoms were located in a difference Fourier map and their coordinates allowed to refine freely. U_{iso}(H) values were also freely refined except for those on N1 and C5–C8, which were contstrained and tied to those of the carrier atom with U_{iso}(H) = 1.5 U_{eq}(N) and 1.2 U_{eq}(C).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.78913 (11)	0.09281 (6)	0.55978 (6)	0.01490 (11)
H1C	0.6658 (17)	0.0874 (11)	0.5557 (11)	0.022*
H1D	0.824 (2)	0.0323 (10)	0.5836 (11)	0.022*
H1E	0.839 (2)	0.0984 (11)	0.4968 (9)	0.022*
C1	0.84801 (12)	0.18467 (7)	0.63089 (6)	0.01495 (13)
H1F	0.991 (2)	0.1798 (11)	0.6436 (10)	0.019 (3)*
H1G	0.777 (2)	0.1781 (11)	0.6978 (11)	0.023 (3)*
C2	0.80152 (10)	0.29464 (6)	0.58338 (6)	0.01152 (11)
N2	0.83825 (10)	0.38973 (5)	0.63375 (5)	0.01193 (11)
H2	0.896 (2)	0.3946 (13)	0.6957 (13)	0.030 (4)*
C3	0.79320 (10)	0.47665 (6)	0.56549 (6)	0.01090 (11)
C4	0.72336 (10)	0.42885 (6)	0.47064 (6)	0.01071 (11)
N3	0.73024 (9)	0.31486 (5)	0.48549 (5)	0.01132 (10)
H3	0.682 (2)	0.2691 (12)	0.4455 (12)	0.026 (3)*
C5	0.66377 (11)	0.49262 (6)	0.38340 (6)	0.01216 (12)
H5	0.6100 (18)	0.4613 (10)	0.3222 (10)	0.015*
C6	0.67891 (11)	0.60627 (6)	0.39581 (6)	0.01288 (12)
H6	0.6386 (19)	0.6514 (11)	0.3388 (10)	0.015*
C7	0.74867 (11)	0.65425 (6)	0.49147 (6)	0.01293 (12)
H7	0.7560 (19)	0.7282 (11)	0.4942 (10)	0.016*
C8	0.80654 (11)	0.59081 (6)	0.57854 (6)	0.01269 (12)
H8	0.8465 (19)	0.6234 (11)	0.6454 (10)	0.015*
O1	0.54805 (9)	0.17363 (5)	0.34741 (5)	0.01701 (11)
H1A	0.431 (2)	0.1721 (15)	0.3536 (14)	0.043 (4)*
H1B	0.577 (2)	0.1084 (12)	0.3475 (13)	0.038 (4)*
Cl1	0.35804 (3)	0.07804 (2)	0.63181 (2)	0.01669 (5)
Cl2	1.05821 (3)	0.36655 (2)	0.85168 (2)	0.01277 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0179 (3)	0.0114 (3)	0.0153 (3)	0.0012 (2)	0.0001 (2)	0.0004 (2)
C1	0.0182 (3)	0.0123 (3)	0.0142 (3)	−0.0003 (2)	−0.0031 (2)	0.0022 (2)
C2	0.0113 (3)	0.0122 (3)	0.0110 (3)	−0.0004 (2)	−0.0012 (2)	0.0006 (2)
N2	0.0129 (2)	0.0126 (3)	0.0102 (2)	−0.00059 (19)	−0.00245 (19)	0.00026 (19)
C3	0.0108 (3)	0.0118 (3)	0.0101 (3)	−0.0005 (2)	−0.00105 (19)	−0.0002 (2)
C4	0.0107 (3)	0.0110 (3)	0.0104 (3)	0.0001 (2)	−0.0005 (2)	−0.0004 (2)
N3	0.0121 (2)	0.0108 (2)	0.0109 (2)	−0.00018 (19)	−0.00197 (18)	−0.00061 (19)
C5	0.0126 (3)	0.0134 (3)	0.0104 (3)	0.0005 (2)	−0.0013 (2)	0.0000 (2)
C6	0.0131 (3)	0.0131 (3)	0.0124 (3)	0.0003 (2)	−0.0001 (2)	0.0015 (2)
C7	0.0128 (3)	0.0118 (3)	0.0142 (3)	−0.0007 (2)	0.0003 (2)	−0.0001 (2)

C8	0.0127 (3)	0.0127 (3)	0.0126 (3)	−0.0016 (2)	−0.0008 (2)	−0.0017 (2)
O1	0.0162 (3)	0.0157 (3)	0.0190 (3)	0.00068 (19)	−0.0038 (2)	−0.0036 (2)
Cl1	0.01671 (9)	0.01516 (9)	0.01815 (9)	0.00088 (6)	−0.00154 (6)	−0.00008 (6)
Cl2	0.01447 (8)	0.01281 (8)	0.01098 (7)	0.00039 (5)	−0.00244 (5)	−0.00001 (5)

Geometric parameters (Å, º)

N1—C1	1.4763 (10)	C4—N3	1.3920 (9)
N1—H1C	0.844 (12)	C4—C5	1.3938 (10)
N1—H1D	0.825 (11)	N3—H3	0.812 (15)
N1—H1E	0.864 (11)	C5—C6	1.3872 (11)
C1—C2	1.4896 (11)	C5—H5	0.926 (13)
C1—H1F	0.988 (13)	C6—C7	1.4085 (11)
C1—H1G	0.975 (14)	C6—H6	0.937 (13)
C2—N2	1.3340 (9)	C7—C8	1.3865 (10)
C2—N3	1.3355 (9)	C7—H7	0.897 (13)
N2—C3	1.3871 (9)	C8—H8	0.961 (13)
N2—H2	0.866 (16)	O1—H1A	0.802 (14)
C3—C8	1.3933 (10)	O1—H1B	0.813 (14)
C3—C4	1.3991 (10)		
C1—N1—H1C	111.0 (9)	C8—C3—C4	122.02 (7)
C1—N1—H1D	111.9 (10)	N3—C4—C5	131.45 (6)
H1C—N1—H1D	103.9 (13)	N3—C4—C3	106.58 (6)
C1—N1—H1E	112.7 (9)	C5—C4—C3	121.96 (6)
H1C—N1—H1E	110.5 (13)	C2—N3—C4	108.38 (6)
H1D—N1—H1E	106.5 (13)	C2—N3—H3	125.4 (11)
N1—C1—C2	112.11 (6)	C4—N3—H3	125.4 (11)
N1—C1—H1F	108.2 (8)	C6—C5—C4	116.11 (7)
C2—C1—H1F	108.8 (8)	C6—C5—H5	121.8 (8)
N1—C1—H1G	108.9 (8)	C4—C5—H5	122.0 (8)
C2—C1—H1G	108.1 (8)	C5—C6—C7	121.83 (7)
H1F—C1—H1G	110.7 (11)	C5—C6—H6	118.1 (8)
N2—C2—N3	109.88 (6)	C7—C6—H6	120.1 (8)
N2—C2—C1	122.91 (6)	C8—C7—C6	122.04 (7)
N3—C2—C1	127.10 (6)	C8—C7—H7	120.5 (8)
C2—N2—C3	108.87 (6)	C6—C7—H7	117.5 (8)
C2—N2—H2	124.2 (11)	C7—C8—C3	116.02 (6)
C3—N2—H2	126.5 (11)	C7—C8—H8	122.2 (8)
N2—C3—C8	131.71 (7)	C3—C8—H8	121.7 (8)
N2—C3—C4	106.27 (6)	H1A—O1—H1B	102.8 (17)
N1—C1—C2—N2	178.82 (7)	C1—C2—N3—C4	−175.26 (7)
N1—C1—C2—N3	−5.29 (11)	C5—C4—N3—C2	179.19 (8)
N3—C2—N2—C3	−1.28 (8)	C3—C4—N3—C2	−0.44 (8)
C1—C2—N2—C3	175.23 (7)	N3—C4—C5—C6	−179.18 (7)
C2—N2—C3—C8	−179.35 (8)	C3—C4—C5—C6	0.40 (11)
C2—N2—C3—C4	0.97 (8)	C4—C5—C6—C7	−0.60 (11)

N2—C3—C4—N3	−0.32 (8)	C5—C6—C7—C8	0.14 (12)
C8—C3—C4—N3	179.96 (7)	C6—C7—C8—C3	0.54 (11)
N2—C3—C4—C5	−179.99 (7)	N2—C3—C8—C7	179.61 (7)
C8—C3—C4—C5	0.28 (11)	C4—C3—C8—C7	−0.74 (11)
N2—C2—N3—C4	1.07 (8)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*C*···Cl1	0.84 (1)	2.32 (1)	3.0898 (8)	152 (1)
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O1—H1*A*···Cl2^{iii}	0.80 (1)	2.59 (1)	3.3752 (7)	169 (2)
O1—H1*B*···Cl1^{iv}	0.81 (1)	2.31 (1)	3.1209 (7)	173 (2)
C1—H1*F*···Cl1^{v}	0.988 (13)	2.793 (13)	3.7079 (8)	154.2 (10)
C5—H5···Cl1^{ii}	0.926 (13)	2.960 (13)	3.8515 (7)	162.1 (10)

Symmetry codes: (i) −*x*+2, *y*−1/2, −*z*+3/2; (ii) *x*, −*y*+1/2, *z*−1/2; (iii) *x*−1, −*y*+1/2, *z*−1/2; (iv) −*x*+1, −*y*, −*z*+1; (v) *x*+1, *y*, *z*.