4-[(Benzylamino)carbonyl]-1-methylpyridinium halogenide salts: X-ray diffraction study and Hirshfeld surface analysis

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Two salts of 4-[(benzylamino)carbonyl]-1-methylpyridinium (Am) with chloride (C14H15N2O+Cl−) and bromide (C14H15N2O+Br−) anions were studied and compared with the iodide salt. AmCl crystallizes in the centrosymmetric space group P21/n while AmBr and AmI form crystals in the Sohncke space group P212121. Crystals of AmBr are isostructural to those of AmI. The cation and anion are bound by an N–H···Hal hydrogen bond. Hirshfeld surface analysis was used to compare different types of intermolecular interactions in the three structures under study.

1. Chemical context

Organic salts are of great importance for the pharmaceutical industry (Stahl & Wermuth, 2002). Many drugs are produced in the form of salts because of their higher solubility as compared to neutral compounds. The pharmacokinetic properties may be modified by the choice of counter-ion (Guerrieri et al., 2010; He et al., 2018). Therefore, the study of the ability of an active pharmaceutical ingredient to form salts with different ions is an actual problem.

4-[(Benzylamino)carbonyl]-1-methylpyridinium iodide is known as a multimodal antiviral drug (Buhtiarova et al., 2003; Frolov et al., 2004; Boltz et al., 2018; Cocking et al., 2018). This salt crystallized in the P212121 orthorhombic space group and was studied by single-crystal X-ray diffraction, powder diffraction, IR spectroscopy and DSC (Drebushchak et al., 2017). Screening varying different solvents and crystallization conditions did not reveal the formation of any other polymorphs.

In the present work we studied salts of the 4-[(benzylamino)carbonyl]-1-methylpyridinium cation with chloride and bromide anions and compared their molecular and crystal structures with that of the iodide salt.
2. Structural commentary

Usually organic salts are obtained following hydrogen transfer within an acid–base pair. The equilibrium between the neutral acid–base pair and their cation–anion pair depends on external conditions such as temperature, concentration, nature of solvent, etc (Stahl & Nakano, 2002). As a result, organic cations formed upon protonation are not stable and can be deprotonated. The quaternization of the pyridine nitrogen atom also results in cation formation (Wei et al., 2018). However, such a cation is much more stable than its protonated analogue and can form salts with different anions.

The organic cation is formed due to the quaternization of the pyridine moiety in the two salts under study (Fig. 1). The positive charge is located at the pyridine nitrogen atom. The carbamide group and the pyridine ring are slightly non-coplanar in the chloride salt and coplanar in the bromide salt [the C5—C4—C7—O1 torsion angle is $-13.3 (4)^\circ$ in AmCl and $-1.4 (16)^\circ$ in AmBr]. The intramolecular contacts H2···C3 = 2.57 Å, H2···H3 = 2.05 Å in AmCl and H2···C3 = 2.65 Å, H2···H3 = 2.16 Å in AmBr are shorter than the sums of the corresponding van der Waals radii (H···C = 2.87 Å and H···H = 2.34 Å; Zefirov, 1997) and point to a steric repulsion between the carbamide and pyridine fragments in the cations of AmCl and AmBr. The phenyl fragment of the benzyl substituent is positioned orthogonally to the carbamide unit and rotated around the N2—C8 bond [the C7—N2—C8—C9 torsion angle is $-88.1 (4)^\circ$ in AmCl and $93.5 (12)^\circ$ in AmBr while the N2—C8—C9—C10 torsion angle is $-24.3 (4)^\circ$ in AmCl and 103.8 (12)$^\circ$ in AmBr].

The AmCl salt crystallizes in the centrosymmetric $P2_1/n$ space group while the AmBr salt crystallizes in the Sohncke space group $P2_12_12_1$, similar to the AmI salt (Drebushchak et al., 2017). The cation does not contain an asymmetric atom.

3. Supramolecular features

Analysis of the intermolecular interactions revealed that an N—H···Hal intermolecular hydrogen bond is present in both of the salts under study (Tables 1 and 2). This hydrogen bond

![Figure 1](image1.png)

Figure 1
Molecular structures of the title 4-[(benzylamino)carbonyl]-1-methylpyridinium halogenide salts. Displacement ellipsoids are shown with 50% probability level.

![Figure 2](image2.png)

Figure 2
Crystal structure of 4-[(benzylamino)carbonyl]-1-methylpyridinium chloride. X—H···Cl hydrogen bonds are shown as dashed cyan lines.

![Figure 3](image3.png)

Figure 3
Crystal structure of 4-[(benzylamino)carbonyl]-1-methylpyridinium bromide. X—H···Br hydrogen bonds are shown as dashed cyan lines.
is strongest in the AmCl salt as a result of the higher negativity of chloride anions as compared to bromide and iodide counter-ions. In addition, a set of C—H /Cl/Cl intermolecular hydrogen bonds is found in AmCl (Fig. 2) while only two C—H /Hal/ hydrogen bonds are present in the crystal structure of AmBr (Figs. 3 and 4; Tables 1 and 2). Generally, the presence of pyridine and benzene rings in a molecule can lead to the formation of π–π stacking interactions in the crystalline phase. However, no such stacking interactions were found in the AmCl and AmBr crystals.

4. Hirshfeld surface analysis

The formation of intermolecular interactions in the two salts under study and the AmI salt can be compared using Hirshfeld surface analysis and two-dimensional fingerprint plots [Turner et al., 2017]. The Hirshfeld surfaces were obtained for the cations using a standard high surface resolution, mapped over \( d_{\text{norm}} \). The red spots on the \( d_{\text{norm}} \) surfaces correspond to contacts that are shorter than the van der Waals radii sum of the closest atoms (Fig. 4). Such red spots are observed on all the hydrogen atoms participating in the above-mentioned intermolecular hydrogen bonds (Tables 1 and 2). It should be noted that the brightness of the spot on the hydrogen atom decreases with an increase in the radius of the halogen atom, indicating a weakening of the hydrogen bond.

The hydrogen bonds and short contacts of the cations found in the structures of AmCl, AmBr and AmI are shown in the two-dimensional fingerprint plots presented in Fig. 5a–c. It should be noted that the fingerprint plots constructed for the

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Table 1

| \( D—H \cdot \cdot \cdot A \) | \( D—H \) | \( H \cdot \cdot \cdot A \) | \( A \cdot \cdot \cdot A \) | \( D—H \cdot \cdot \cdot A \) |
|--------------------------|--------|-----------------|-----------------|-------------------|
| N2—H2 —Cl1               | 0.92 (3) | 2.26 (3)       | 3.163 (3)               | 165 (2)          |
| C1—H1C —Cl1i             | 0.96    | 2.89            | 3.513 (3)               | 124              |
| C1—H1A —Cl1a             | 0.96    | 2.72            | 3.633 (3)               | 160              |
| C2—H2A —Cl1a             | 0.93    | 2.59            | 3.474 (3)               | 160              |
| C3—H3 —Cl1               | 0.93    | 2.63            | 3.531 (3)               | 165              |

Symmetry codes: (i) \(-x + 2, -y + 1, -z + 1\); (ii) \(-x + 2, -y + 2, -z + 1\).

Table 2

| \( D—H \cdot \cdot \cdot A \) | \( D—H \) | \( H \cdot \cdot \cdot A \) | \( A \cdot \cdot \cdot A \) | \( D—H \cdot \cdot \cdot A \) |
|--------------------------|--------|-----------------|-----------------|-------------------|
| N2—H2 —Br1               | 0.86    | 2.68            | 3.468 (9)                  | 154              |
| C1—H1A —Br1i             | 0.96    | 3.04            | 3.913 (13)               | 152              |
| C1—H1C —Br1a             | 0.96    | 3.01            | 3.901 (13)               | 154              |

Symmetry codes: (i) \(x - \frac{1}{4} - y + \frac{1}{4} - z\); (ii) \(x - 1, y, z\).

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Figure 4

Hirshfeld surfaces of the cation in the (a) AmCl, (b) AmBr and (c) AmI salts mapped over \( d_{\text{norm}} \).

Figure 5

Two-dimensional fingerprint plots for the cation in the three salts under study: (a) AmCl, (b) AmBr and (c) AmI.

Figure 6

Contributions of the different types of interactions to the total Hirshfeld surface of the cation in three halogenide salts.
cations in structures AmBr and AmI are very similar (Fig. 5b and 5c). The main contribution to the total Hirshfeld surface (49.4% in AmCl, 50.8% in AmBr, 51.0% in AmI) is provided by H ⋅ ⋅ ⋅ H short contacts (Fig. 6). The contribution of C ⋅ ⋅ ⋅ H-H ⋅ ⋅ ⋅ C contacts is much smaller but also significant (23.9% in AmCl, 19.9% in AmBr, 20.2% in AmI). The similar contributions of Hal ⋅ ⋅ ⋅ H/H ⋅ ⋅ ⋅ Hal contacts (10.2% in AmCl, 10.5% in AmBr, 9.9% in AmI) and O ⋅ ⋅ ⋅ H/H ⋅ ⋅ ⋅ O contacts (9.4% in AmCl, 7.6% in AmBr, 7.9% in AmI) are slightly surprising because of the absence of $X-H-H$ intermolecular interactions in the structures under study. The presence of two aromatic rings in the cation could result in the formation of stacking interactions in the crystal, but the contribution of the C ⋅ ⋅ ⋅ C contacts is the smallest (2.9% in AmCl, 6.7% in AmBr, 6.4% in AmI). The small contribution of the C ⋅ ⋅ ⋅ C contacts agrees with the results of the traditional analysis of intermolecular interactions in a crystal using the shortest distances between atoms belonging to neighbouring molecules (see Supramolecular features section). It should be noted that the contribution of the C ⋅ ⋅ ⋅ C contacts is more than twice as high in the crystals of AmBr and AmI compared to AmCl. This can be explained by a mutual orientation of the pyridine and benzene rings belonging to neighbouring molecules in the AmBr and AmI crystals. However, there are no effective $\pi-\pi$ interaction between these rings because the distances and angles between the planar $\pi$ systems are too large.

5. Database survey

A search of the Cambridge Structural Database (Version 5.42, update of November 2020; Groom et al., 2016) revealed the structure of the Am salt (refcode BEBFIA; Drebushchak et al., 2017). A comparison with the AmBr and AmI crystal structures showed that they are isostructural.

6. Synthesis and crystallization

The synthesis of salts of 4-[(benzylamino)carbonyl]-1-methylpyridinium halide was carried out according to the reaction scheme below.

**Synthesis and crystallization of AmCl**

520 mL of acetonitrile was cooled to 273–277 K in a glass flask. Chloromethane (87.8 g, 1.739 mol) was dissolved at this temperature. Benzylamide isonicotinic acid (245.78 g, 1.16 mol) and 600 mL of cooled acetonitrile and acetonitrile solution saturated with chloromethane were loaded into an autoclave. The autoclave was closed and heated to 373 K. The mixture was incubated for 3 h at this temperature. After that, the mixture was allowed to cool to room temperature. The reaction mixture was transferred into a glass flask and cooled to 273–275 K. The reaction mixture was filtered and the precipitate was rinsed on the filter with 200 mL of cooled acetonitrile. The product was dried at 313 K for 12 h. Yield 226 g of crude 4-[(benzylamino)carbonyl]-1-methylpyridinium chloride (75%); white crystals.

226 g of crude 4-[(benzylamino)carbonyl]-1-methylpyridinium chloride were dissolved in 265 mL of 90% ethanol and 660 mL of 2-propanol, and 4.25 g activated charcoal were added. The reaction mixture was heated to boiling point, stirred at boiling for 30 min and filtered. The obtained solution was let to spontaneously cool to a temperature of 303 K, then to a temperature of 278–283 K in a cooling water bath, and stirred for 2 h at this temperature. The reaction mixture was filtrated and the precipitate rinsed on the filter with 110 mL of cold 2-propanol. The product was dried at 313 K for 12 h. Yield 180.8 g of 4-[(benzylamino)carbonyl]-1-methylpyridinium chloride (80%); white crystals; m.p. 474–477 K.

**Synthesis and crystallization of AmBr.**

4-[(Benzylamino)carbonyl]-1-methylpyridinium iodide (57.7 g, 0.163 mol), silver bromide (33.77 g, 0.180 mol) and 700 mL of water were loaded into a glass flask. The mixture was stirred for 72 h. The sediment was filtered off. The solvent was evaporated under reduced pressure. 300 mL of acetonitrile were added to the precipitate and the mixture was refluxed for 2 h. The reaction mixture was allowed to spontaneously cool to a temperature of 303 K. The reaction mixture was filtered and the precipitate was rinsed on the filter with 50 mL of cold acetonitrile. The product was dried at 313 K for 12 h. Yield 14 g of 4-[(benzylamino)carbonyl]-1-methylpyridinium bromide (28%); white crystals; m.p. 465–468 K.

The crystals of AmCl and AmBr were grown as very small colourless and yellow parallelepipeds, respectively, in contrast to the well-grown yellow block-shaped crystals of AmI.
7. Spectroscopic characterization

Both salts under consideration were fully characterized by IR, $^1$H NMR and $^{13}$C NMR spectroscopy. IR spectra of solid samples were acquired on a Thermo Fisher Scientific Nicolet iS50 FTIR spectrometer. $^1$H NMR spectra of samples were measured in DMSO-$d_6$ on a 600 MHz Varian spectrometer. $^{13}$C NMR spectra of samples were taken in DMSO-$d_6$ on a 150 MHz Varian spectrometer.

The characteristic vibration frequencies of the main functional groups according to the data of FTIR spectroscopy are shown in Table 3. The full spectroscopic data are presented below and in Figs. 7 and 8. As can be seen from Table 3, the main difference in IR spectra concerns the valence vibrations of the N—H group and vibrations of C—H bonds in the pyridine ring.

AmCl:

IR spectrum (cm$^{-1}$) (Fig. 7): 592.40, 631.16, 659.97, 667.17, 702.46, 727.71, 857.87, 890.80, 989.03, 1156.13, 1229.22, 1260.13, 1284.00, 1305.82, 1312.72, 1342.62, 1416.08, 1453.14, 1497.17, 1516.77, 1572.84, 1656.90, 2981.77, 2994.48, 3009.82, 3049.81, 3166.99.

$^1$H NMR (600 MHz, DMSO-$d_6$, p.p.m.):

- $\delta$ = 4.40 (s, 3H, CH$_3$), 4.48–4.49 (d, 2H, CH$_2$), 7.21–7.36 (m, 5H, Ar), 8.59 (d, 2H, Py), 9.21 (d, 2H, Py), 10.47 (s, H, NH).

Figure 7
IR spectrum of the AmCl salt.

AmBr:

IR spectrum (cm$^{-1}$) (Fig. 8): 592.40, 631.16, 659.97, 667.17, 702.46, 727.71, 857.87, 890.80, 989.03, 1156.13, 1229.22, 1260.13, 1284.00, 1305.82, 1312.72, 1342.62, 1416.08, 1453.14, 1497.17, 1516.77, 1572.84, 1656.90, 2981.77, 2994.48, 3009.82, 3049.81, 3166.99.

$^1$H NMR (600 MHz, DMSO-$d_6$, p.p.m.):

- $\delta$ = 4.40 (s, 3H, CH$_3$), 4.48–4.49 (d, 2H, CH$_2$), 7.21–7.36 (m, 5H, Ar), 8.59 (d, 2H, Py), 9.21 (d, 2H, Py), 10.47 (s, H, NH).

Figure 8
IR spectrum of the AmBr salt.
$^{13}$C NMR (150 MHz, DMSO-$d_6$, p.p.m.): $\delta = 43.42$ (CH$_2$), 48.37 (CH$_3$), 125.98, 146.94, 147.91 (Py), 127.44, 128.00, 128.75, 139.03 (Ar), 162.12 (C=O).

AnBr:

IR spectrum (cm$^{-1}$) (Fig. 8): 594.84, 616.74, 620.98, 644.78, 702.12, 759.15, 779.19, 864.09, 962.63, 1079.02, 1149.96, 1188.49, 1219.68, 1244.69, 1287.03, 1305.58, 1330.58, 1416.56, 1451.22, 1493.51, 1504.69, 1544.19, 1571.63, 1643.77, 1658.70, 3001.16, 3041.63, 3198.25.

$^1$H NMR (400 MHz, DMSO-$d_6$, p.p.m.): $\delta = 4.41$ (s, 3H, CH$_3$), 4.51 (d, 2H, CH$_2$), 7.23–7.36 (m, 5H, Ar), 8.48 (d, 2H, Py), 9.21 (d, 2H, Py), 9.92 (s, H, NH).

$^{13}$C NMR (100 MHz, DMSO-$d_6$, p.p.m.): $\delta = 43.52$ (CH$_2$), 48.50 (CH$_3$), 125.87, 146.99, 147.97 (Py), 127.56, 128.00, 128.84, 138.83 (Ar), 162.31 (C=O).

8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. All of the hydrogen atoms were located in difference-Fourier maps. They were included in calculated positions and treated as riding with C–H = 0.96 Å, $U_{iso}(H) = 1.5U_{eq}$ for methyl groups and with C$_{ar}$–H = 0.93 Å, C$_{sp^2}$–H = 0.97 Å, $U_{iso}(H) = 1.2U_{eq}$ for all other hydrogen atoms.

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4-[(Benzylamino)carbonyl]-1-methylpyridinium halogenide salts: X-ray diffraction study and Hirshfeld surface analysis

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Computing details
For both structures, data collection: CrysAlis PRO (Rigaku OD, 2018); cell refinement: CrysAlis PRO (Rigaku OD, 2018); data reduction: CrysAlis PRO (Rigaku OD, 2018); program(s) used to solve structure: SHELXT2014/5 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2016/6 (Sheldrick, 2015b); molecular graphics: Mercury (Macrae et al., 2020); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

4-[(Benzylamino)carbonyl]-1-methylpyridinium chloride (AmCl)

Crystal data
C14H15N2O+·Cl−
Mr = 262.73
Monoclinic, P21/n
a = 8.5222 (7) Å
b = 5.6875 (3) Å
c = 27.1720 (14) Å
β = 91.243 (6)°
V = 1316.71 (15) Å3
Z = 4

F(000) = 552
Dc = 1.325 Mg m−3
Mo Ka radiation, λ = 0.71073 Å
Cell parameters from 766 reflections
θ = 3.2–20.4°
µ = 0.28 mm−1
T = 293 K
Block, colorless
0.30 × 0.20 × 0.10 mm

Data collection
Xcalibur, Sapphire3
diffractometer
Radiation source: Enhance (Mo) X-ray Source
Detector resolution: 16.1827 pixels mm−1
ω scans
Absorption correction: multi-scan
(CrysAlisPro, Rigaku OD 2018)
Tmin = 0.624, Tmax = 1.000
5343 measured reflections
2302 independent reflections
1529 reflections with I > 2σ(I)
Rint = 0.048
θmax = 25.0°, θmin = 3.0°
h = −10→9
k = −6→6
l = −31→26

Refinement
Least-squares matrix: full
R[F2 > 2σ(F2)] = 0.051
wR(F2) = 0.119
S = 1.05
2302 reflections
168 parameters
0 restraints

Hydrogen site location: mixed
H atoms treated by a mixture of independent
and constrained refinement
w = 1/[σ2(Fo2) + (0.034P)2] where P = (Fo2 + 2Fc2)/3
(Δ/σ)max < 0.001
Δρmax = 0.18 e Å−3
Δρmin = −0.16 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.

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

|     | x      | y      | z      | Uiso* / Ueq |
|-----|--------|--------|--------|-------------|
| Cl1 | 1.00363 (10) | 0.87872 (14) | 0.60412 (3) | 0.0644 (3)  |
| O1  | 0.5912 (3)  | 0.1775 (4)  | 0.57992 (7) | 0.0685 (7)  |
| N1  | 0.7393 (3)  | 0.5404 (4)  | 0.42221 (8) | 0.0507 (6)  |
| N2  | 0.7762 (3)  | 0.4394 (5)  | 0.60568 (9) | 0.0568 (7)  |
| H2  | 0.844 (4)   | 0.561 (5)   | 0.5990 (10) | 0.063 (10)* |
| C1  | 0.7545 (4)  | 0.6081 (6)  | 0.37003 (9) | 0.0661 (10) |
| H1A | 0.822085    | 0.742522    | 0.367808   | 0.099*      |
| H1B | 0.652886    | 0.646109    | 0.356333   | 0.099*      |
| H1C | 0.798499    | 0.479503    | 0.352058   | 0.099*      |
| C2  | 0.8023 (4)  | 0.6758 (5)  | 0.45742 (10) | 0.0586 (9) |
| H2A | 0.855209    | 0.812634    | 0.449031   | 0.070*      |
| C3  | 0.7896 (4)  | 0.6142 (5)  | 0.50613 (10) | 0.0594 (9) |
| H3  | 0.833718    | 0.709994    | 0.530460   | 0.071*      |
| C4  | 0.7124 (3)  | 0.4127 (5)  | 0.51914 (10) | 0.0469 (7) |
| C5  | 0.6493 (4)  | 0.2765 (5)  | 0.48176 (10) | 0.0551 (8) |
| H5  | 0.595346    | 0.139381    | 0.489249   | 0.066*      |
| C6  | 0.6655 (4)  | 0.3418 (5)  | 0.43357 (11) | 0.0575 (9) |
| H6  | 0.624699    | 0.246639    | 0.408589   | 0.069*      |
| C7  | 0.6881 (4)  | 0.3322 (5)  | 0.57169 (11) | 0.0535 (8) |
| C8  | 0.7728 (4)  | 0.3762 (5)  | 0.65733 (9) | 0.0603 (9)  |
| H8A | 0.875072    | 0.408118    | 0.672190   | 0.072*      |
| H8B | 0.754012    | 0.208480    | 0.659881   | 0.072*      |
| C9  | 0.6503 (4)  | 0.5038 (5)  | 0.68622 (9) | 0.0492 (8)  |
| C10 | 0.5909 (4)  | 0.67194 (5) | 0.67180 (11) | 0.0589 (9) |
| H10 | 0.626455    | 0.789378    | 0.643179   | 0.071*      |
| C11 | 0.4807 (5)  | 0.8315 (6)  | 0.69903 (12) | 0.0763 (11) |
| H11 | 0.441586    | 0.976239    | 0.688610   | 0.092*      |
| C12 | 0.4267 (5)  | 0.7325 (7)  | 0.74176 (13) | 0.0789 (11) |
| H12 | 0.349989    | 0.808053    | 0.759759   | 0.095*      |
| C13 | 0.4875 (4)  | 0.5203 (7)  | 0.75753 (11) | 0.0732 (11) |
| H13 | 0.454056    | 0.453721    | 0.786750   | 0.088*      |
| C14 | 0.5986 (4)  | 0.4067 (6)  | 0.72969 (10) | 0.0587 (9)  |
| H14 | 0.638986    | 0.263078    | 0.740336   | 0.070*      |

Atomic displacement parameters (Å²)

|     | U¹¹  | U²²  | U³³  | U¹²  | U¹³  | U²³  |
|-----|------|------|------|------|------|------|
| Cl1 | 0.0722 (6) | 0.0577 (5) | 0.0636 (5) | −0.0109 (5) | 0.0095 (4) | −0.0002 (4) |
| O1  | 0.0690 (16) | 0.0706 (15) | 0.0660 (14) | −0.0208 (14) | 0.0031 (12) | 0.0193 (11) |

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### Supporting Information

#### Geometric parameters (Å, °)

|    | N1    | N2    | C1    | C2    | C3    | C4    | C5    | C6    | C7    | C8    | N2—C8 | C9    | C10   | C11   | C12   | C13   | C14   |
|----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|-------|-------|-------|-------|-------|-------|
|    | 0.0510 (16) | 0.0512 (15) | 0.0500 (14) | 0.0014 (14) | 0.0027 (12) | 0.0026 (12) |       |       |       |       |        |       |       |       |       |       |
|    | 0.0646 (19) | 0.0573 (17) | 0.0487 (15) | −0.0013 (16) | 0.0033 (14) | 0.0087 (13) |       |       |       |       |        |       |       |       |       |       |
|    | 0.078 (3) | 0.075 (2) | 0.0447 (16) | −0.0112 (2) | −0.0035 (16) | 0.0126 (15) |       |       |       |       |        |       |       |       |       |       |
|    | 0.070 (2) | 0.0507 (19) | 0.0552 (19) | −0.0110 (18) | −0.0021 (17) | 0.0057 (15) |       |       |       |       |        |       |       |       |       |       |
|    | 0.075 (2) | 0.0558 (19) | 0.0472 (17) | −0.0142 (19) | −0.0018 (16) | 0.0038 (14) |       |       |       |       |        |       |       |       |       |       |
|    | 0.0444 (18) | 0.0435 (17) | 0.0531 (16) | 0.0006 (15) | 0.0054 (14) | 0.0046 (14) |       |       |       |       |        |       |       |       |       |       |
|    | 0.055 (2) | 0.0516 (18) | 0.0588 (18) | −0.0087 (17) | 0.0112 (16) | 0.0044 (15) |       |       |       |       |        |       |       |       |       |       |
|    | 0.062 (2) | 0.0515 (19) | 0.0585 (19) | −0.0118 (18) | 0.0027 (16) | −0.0034 (15) |       |       |       |       |        |       |       |       |       |       |
|    | 0.055 (2) | 0.0516 (19) | 0.0544 (18) | 0.0023 (18) | 0.0086 (17) | 0.0095 (15) |       |       |       |       |        |       |       |       |       |       |
|    | 0.064 (2) | 0.068 (2) | 0.0480 (17) | −0.0007 (19) | −0.0025 (16) | 0.0127 (15) |       |       |       |       |        |       |       |       |       |       |
|    | 0.056 (2) | 0.0489 (18) | 0.0422 (15) | −0.0129 (16) | −0.0083 (14) | 0.0022 (13) |       |       |       |       |        |       |       |       |       |       |
|    | 0.078 (3) | 0.0464 (18) | 0.0523 (17) | −0.0067 (19) | −0.0081 (17) | 0.0038 (15) |       |       |       |       |        |       |       |       |       |       |
|    | 0.098 (3) | 0.057 (2) | 0.073 (2) | 0.012 (2) | −0.020 (2) | −0.0109 (18) |       |       |       |       |        |       |       |       |       |       |
|    | 0.078 (3) | 0.095 (3) | 0.064 (2) | 0.012 (2) | −0.003 (2) | −0.027 (2) |       |       |       |       |        |       |       |       |       |       |
|    | 0.077 (3) | 0.094 (3) | 0.0485 (18) | −0.012 (2) | 0.0034 (19) | −0.0030 (19) |       |       |       |       |        |       |       |       |       |       |
|    | 0.069 (2) | 0.062 (2) | 0.0453 (16) | −0.0060 (19) | −0.0047 (16) | 0.0079 (15) |       |       |       |       |        |       |       |       |       |       |

#### Geometric parameters (Å, °)

|    | C1—C7 | C5—H5 | O1—C7—N2 | C6—H6 | N1—C2 | C8—C9 | N2—C8 | C9—C10 | C1—H1A | C10—C11 | C1—C12 | C2—C3 | C11—C12 | C2—H2A | C12—C13 | C3—C4 | C13—C14 | C4—C5 | C13—H13 | C4—C7 | C14—H14 | C5—C6 |
|----|-------|-------|-----------|-------|-------|-------|-------|--------|-------|--------|--------|-------|--------|--------|--------|-------|--------|-------|--------|-------|--------|-------|
|    | 1.230 (3) |       | 1.332 (3) |       | 1.332 (4) |       | 1.450 (3) |       | 0.9600 |       | 0.9600 |       | 1.376 (4) |       | 0.9300 |       | 1.377 (4) |       | 0.9300 |       | 1.371 (4) |       |       |
|    |       | C5—H5 |       | O1—C7—N2 | C6—H6 | N1—C2 | C8—C9 | N2—C8 | C9—C10 | C1—H1A | C10—C11 | C1—C12 | C2—C3 | C11—C12 | C2—H2A | C12—C13 | C3—C4 | C13—C14 | C4—C5 | C13—H13 | C4—C7 | C14—H14 | C5—C6 |       |
|    |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |

#### Geometric parameters (Å, °)

|    | C6—N1—C2 | O1—C7—N2 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|----|-----------|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|    | 120.6 (2) | 125.0 (3) |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|    | 119.7 (3) | 119.5 (3) |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|    | 119.7 (3) | 115.5 (3) |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|    | 122.5 (3) | 114.5 (2) |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|    | 123.7 (17) | 108.6 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|    | 113.8 (17) | 108.6 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|    | 109.5 | 108.6 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|    | 109.5 | 108.6 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|    | 109.5 | 108.6 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |

**Note:** The table includes geometric parameters for the structure, with bond lengths and angles specified. The values are given in ångstroms (Å) and degrees (°).
Hydrogen-bond geometry (Å, °)

| D—H···A   | D—H | H···A | D···A | D—H···A |
|-----------|------|-------|-------|---------|
| N2—H2···Cl1 | 0.92 (3) | 2.26 (3) | 3.16 (3) | 165 (2) |
| C1—H1C···Cl1\(^i\) | 0.96 | 2.89 | 3.51 (3) | 124 |
| C1—H1A···Cl1\(^u\) | 0.96 | 2.72 | 3.63 (3) | 160 |
| C2—H2A···Cl1\(^u\) | 0.93 | 2.59 | 3.47 (3) | 160 |
| C3—H3···Cl1 | 0.93 | 2.63 | 3.53 (3) | 165 |

Symmetry codes: (i) \(-x+2, -y+1, -z+1\); (ii) \(-x+2, -y+2, -z+1\).

4-[(Benzylamino)carbonyl]-1-methylpyridinium bromide (AmBr)

Crystal data

| C\(_{14}\)H\(_{15}\)N\(_{2}\)O\(^+\)·Br\(^-\) | a = 9.417 (3) Å |
| M\(_f\) = 307.19 | b = 11.099 (5) Å |
| Orthorhombic, P2\(_{1}\)2\(_{1}\)2\(_{1}\) | c = 14.363 (6) Å |
\[ V = 1501.2 \text{ (10) Å}^3 \]
\[ Z = 4 \]
\[ F(000) = 624 \]
\[ D_x = 1.359 \text{ Mg m}^{-3} \]
\[ \text{Mo } K\alpha \text{ radiation, } \lambda = 0.71073 \text{ Å} \]
\[ \theta = 3.2\text{–}24.8^\circ \]
\[ \mu = 2.73 \text{ mm}^{-1} \]
\[ T = 293 \text{ K} \]

Cell parameters from 748 reflections

| \( \theta \text{ max} \) | \( \theta \text{ min} \) |
|-----------------|-----------------|
| 25.0\(^\circ\)  | 3.4\(^\circ\)  |

\( h = -11\rightarrow11 \)
\( k = -13\rightarrow13 \)
\( l = -17\rightarrow16 \)

Data collection

Xcalibur, Sapphire3 diffractometer

Radiation source: Enhance (Mo) X-ray Source

Detector resolution: 16.1827 pixels mm\(^{-1}\)

Absorption correction: multi-scan

\( T_{\text{min}} = 0.068, T_{\text{max}} = 1.000 \)

Refinement

Refinement on \( F^2 \)

\[ R[F^2 > 2\sigma(F^2)] = 0.063 \]

\[ wR(F^2) = 0.150 \]

| \( S \) | 1.00 |

2635 reflections

164 parameters

0 restraints

H-atom parameters constrained

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

| \( x \) | \( y \) | \( z \) | \( U_{iso}^{*}/U_{eq} \) |
|--------|--------|--------|-----------------|
| Br1 0.91899 (12) 0.26554 (10) 0.17853 (8) 0.0849 (5) |
| O1 0.5589 (10) 0.6049 (7) 0.3657 (5) 0.091 (3) |
| N2 0.7250 (9) 0.4630 (7) 0.3158 (7) 0.073 (2) |
| H2 0.743714 0.406610 0.276630 0.088* |
| N1 0.3088 (10) 0.4355 (9) 0.0832 (7) 0.073 (2) |
| C7 0.5970 (12) 0.5238 (9) 0.3083 (7) 0.070 (3) |
| C3 0.5277 (11) 0.3994 (10) 0.1584 (8) 0.071 (3) |
| H3 0.612742 0.356784 0.159577 0.085* |
| C2 0.4254 (14) 0.3763 (9) 0.0884 (9) 0.078 (3) |
| H2A 0.445066 0.317583 0.043984 0.093* |
| C5 0.3663 (13) 0.5481 (12) 0.2211 (9) 0.090 (4) |
| H5 0.343497 0.606658 0.264908 0.108* |
| C4 0.4986 (13) 0.4888 (10) 0.2269 (8) 0.071 (3) |
| C6 0.2692 (14) 0.5207 (11) 0.1512 (10) 0.095 (4) |

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\(^2\))

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### Atomic displacement parameters (\(\AA^2\))

|    | \(U^{11}\) | \(U^{22}\) | \(U^{33}\) | \(U^{12}\) | \(U^{13}\) | \(U^{23}\) |
|----|------------|------------|------------|-----------|-----------|-----------|
| Br1 | 0.0782 (7) | 0.0895 (8) | 0.0868 (8) | 0.0122 (7) | 0.0041 (7) | 0.0018 (7) |
| O1  | 0.106 (6)  | 0.085 (5)  | 0.083 (6)  | 0.013 (5)  | -0.001 (6) | -0.023 (4) |
| N2  | 0.077 (6)  | 0.074 (6)  | 0.068 (6)  | -0.001 (5) | -0.002 (6) | -0.003 (5) |
| N1  | 0.063 (6)  | 0.077 (7)  | 0.080 (7)  | 0.004 (5)  | -0.002 (5) | 0.000 (5)  |
| C7  | 0.084 (7)  | 0.066 (7)  | 0.060 (7)  | 0.000 (6)  | 0.011 (7)  | 0.014 (5)  |
| C3  | 0.071 (7)  | 0.072 (7)  | 0.071 (8)  | 0.006 (5)  | -0.005 (6) | 0.005 (5)  |
| C2  | 0.077 (7)  | 0.069 (7)  | 0.087 (8)  | -0.003 (7) | 0.020 (8)  | -0.004 (5) |
| C5  | 0.086 (8)  | 0.098 (10) | 0.086 (9)  | 0.027 (7)  | -0.006 (8) | -0.027 (7) |
| C4  | 0.075 (7)  | 0.071 (8)  | 0.066 (9)  | -0.006 (6) | 0.005 (7)  | 0.004 (6)  |
| C6  | 0.072 (8)  | 0.103 (10) | 0.111 (12) | 0.025 (7)  | 0.001 (8)  | -0.007 (8) |
| C9  | 0.078 (8)  | 0.066 (7)  | 0.074 (8)  | 0.000 (6)  | -0.012 (7) | 0.001 (6)  |
| C8  | 0.074 (7)  | 0.102 (10) | 0.094 (10) | -0.019 (7) | 0.005 (7)  | 0.000 (7)  |
| C13 | 0.084 (8)  | 0.104 (10) | 0.065 (8)  | -0.015 (8) | 0.007 (7)  | -0.008 (7) |
| C14 | 0.064 (7)  | 0.082 (8)  | 0.075 (8)  | 0.004 (6)  | -0.010 (7) | -0.009 (7) |
| C12 | 0.126 (10) | 0.095 (10) | 0.073 (8)  | -0.011 (9) | -0.024 (8) | 0.007 (8)  |
| C1  | 0.082 (8)  | 0.140 (12) | 0.095 (10) | -0.004 (9) | -0.009 (8) | -0.014 (9) |
| C10 | 0.095 (9)  | 0.104 (9)  | 0.088 (9)  | 0.032 (9)  | -0.004 (9) | 0.006 (7)  |
| C11 | 0.178 (15) | 0.099 (10) | 0.091 (9)  | 0.059 (12) | -0.027 (11) | -0.014 (8) |

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

|    | \(O1—C7\) | 1.273 (12) | \(C9—C14\) | 1.423 (14) |
|----|------------|------------|------------|-----------|
| N2—C7 | 1.386 (12) | \(C9—C8\) | 1.536 (15) |
| N2—C8 | 1.498 (14) | \(C8—H8A\) | 0.9700 |
| N2—H2 | 0.8600 | \(C8—H8B\) | 0.9700 |
| Bond          | Length (Å) | Bond          | Length (Å) | Bond          | Length (Å) |
|--------------|------------|--------------|------------|--------------|------------|
| N1—C2        | 1.347 (14) | C13—C14      | 1.392 (15) | N1—C6        | 1.392 (14) |
| N1—C6        | 1.392 (14) | C13—C12      | 1.433 (16) | N1—C1        | 1.521 (13) |
| C7—C4        | 1.540 (15) | C14—H14      | 0.930      | C3—C2        | 1.416 (15) |
| C3—C2        | 1.416 (15) | C12—C11      | 1.404 (18) | C3—C4        | 1.425 (14) |
| C3—H3        | 0.930      | C1—H1A       | 0.960      | C2—H2A       | 0.930      |
| C2—H2A       | 0.930      | C1—H1B       | 0.960      | C5—C6        | 1.392 (16) |
| C5—C6        | 1.392 (16) | C1—H1C       | 0.960      | C5—C4        | 1.412 (14) |
| C5—C4        | 1.412 (14) | C10—C11      | 1.404 (17) | C5—H5        | 0.9300     |
| C6—H6        | 0.9300     | C10—H10      | 0.930      | C6—H6        | 0.9300     |
| C9—C10       | 1.422 (15) | C11—H11      | 0.930      | C7—N2—C8     | 122.4 (9)  |
|              |            |              |            | N2—C8—C9     | 113.2 (9)  |
| C7—N2—H2     | 118.8      | N2—C8—H8A    | 108.9      | C8—N2—H2     | 118.8      |
| C2—N1—C6     | 118.6 (11) | N2—C8—H8B    | 108.9      | C2—N1—C6     | 121.3 (10) |
| C6—N1—C1     | 120.0 (10) | C9—C8—H8B    | 108.9      | C6—N1—C1     | 120.0 (11) |
| O1—C7—N2     | 122.6 (11) | H8A—C8—H8B   | 107.7      | O1—C7—N2     | 120.0 (10) |
| O1—C7—C4     | 120.0 (10) | C14—C13—C12  | 118.6 (11) | O1—C7—C4     | 117.4 (10) |
| N2—C7—C4     | 119.1 (10) | C14—C13—H13  | 120.7      | N2—C7—C4     | 117.4 (10) |
| C2—C3—C4     | 120.5      | C13—C14—H14  | 118.4      | C2—C3—C4     | 120.5      |
| C4—C3—H3     | 120.5      | C9—C14—H14   | 118.4      | C4—C3—H3     | 120.5      |
| N1—C2—C3     | 122.9 (10) | C11—C12—C13  | 118.9 (12) | N1—C2—C3     | 122.9 (10) |
| N1—C2—H2A    | 118.5      | C11—C12—H12  | 120.6      | N1—C2—H2A    | 118.5      |
| C3—C2—H2A    | 118.5      | C13—C12—H12  | 120.6      | C3—C2—H2A    | 118.5      |
| C6—C5—C4     | 121.4 (11) | N1—C1—H1A    | 109.5      | C6—C5—C4     | 121.4 (11) |
| C6—C5—H5     | 119.3      | N1—C1—H1B    | 109.5      | C6—C5—H5     | 119.3      |
| C4—C5—H5     | 119.3      | H1A—C1—H1B   | 109.5      | C4—C5—H5     | 119.3      |
| C5—C4—C3     | 117.0 (11) | N1—C1—H1C    | 109.5      | C5—C4—C3     | 117.0 (11) |
| C5—C4—C7     | 117.3 (10) | H1A—C1—H1C   | 109.5      | C5—C4—C7     | 117.3 (10) |
| C3—C4—C7     | 125.7 (11) | H1B—C1—H1C   | 109.5      | C3—C4—C7     | 125.7 (11) |
| C5—C6—N1     | 121.0 (11) | C11—C10—C9   | 120.4 (12) | C5—C6—N1     | 121.0 (11) |
| C5—C6—H6     | 119.5      | C11—C10—H10  | 119.8      | C5—C6—H6     | 119.5      |
| N1—C6—H6     | 119.5      | C9—C10—H10   | 119.8      | N1—C6—H6     | 119.5      |
| C10—C9—C14   | 117.0 (11) | C10—C11—C12  | 121.7 (13) | C10—C9—C14   | 117.0 (11) |
| C10—C9—C8    | 121.2 (11) | C10—C11—H11  | 119.2      | C10—C9—C8    | 121.2 (11) |
| C14—C9—C8    | 121.8 (10) | C12—C11—H11  | 119.2      | C14—C9—C8    | 121.8 (10) |
| C8—N2—C7—O1  | -2.8 (15)  | C2—N1—C6—C5  | 2.6 (18)   | C8—N2—C7—C4  | 177.7 (9)  |
| C6—N1—C2—C3  | -2.0 (17)  | C7—N2—C8—C9  | 93.5 (12)  | C6—N1—C2—C3  | -2.0 (17)  |
| C1—N1—C2—C3  | -179.7 (10)| C10—C9—C8—N2 | 103.8 (12) | C1—N1—C2—C3  | -179.7 (10) |
| C4—C3—C2—N1  | 0.2 (16)   | C14—C9—C8—N2 | -76.9 (13) | C4—C3—C2—N1  | 0.2 (16)   |
| C6—C5—C4—C3  | -0.3 (19)  | C12—C13—C14—C9 | 1.1 (17)  | C6—C5—C4—C3  | -0.3 (19)  |
C6—C5—C4—C7  −178.7 (11)  C10—C9—C14—C13  −1.4 (16)
C2—C3—C4—C5  0.9 (16)  C8—C9—C14—C13  179.3 (10)
C2—C3—C4—C7  179.1 (10)  C14—C13—C12—C11  0.9 (17)
O1—C7—C4—C5  −1.4 (16)  C14—C9—C10—C11  −0.3 (18)
N2—C7—C4—C5  178.0 (10)  C8—C9—C10—C11  179.1 (12)
O1—C7—C4—C3  −179.6 (10)  C9—C10—C11—C12  2 (2)
N2—C7—C4—C3  −0.2 (15)  C13—C12—C11—C10  −3 (2)
C4—C5—C6—N1  −1 (2)  

Hydrogen-bond geometry (Å, °)

| D—H···A        | D—H | H···A | D···A   | D—H···A |
|---------------|-----|-------|---------|---------|
| N2—H2···Br1    | 0.86| 2.68  | 3.468 (9)| 154     |
| C1—H1'A···Br1i| 0.96| 3.04  | 3.913 (13)| 152    |
| C1—H1'C···Br1ii| 0.96| 3.01  | 3.901 (13)| 154    |

Symmetry codes: (i) x−1/2, −y+1/2, −z; (ii) x−1, y, z.