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

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The hemihydrate of 4-[(benzylamino)carbonyl]-1-methylpyridinium bromide, C₁₄H₁₅N₂O⁺Br⁻·0.5H₂O, was studied by single-crystal and powder X-ray diffraction methods. In the asymmetric unit, two organic cations of similar conformation, two bromide anions and one water molecule are present. In the crystal, N—H···Br hydrogen bonds link the cations and anions. The formation of a set of intermolecular C—H···Br and C—H···π interactions result in double chains extending parallel to [011]. A Hirshfeld surface analysis showed high contributions of H···H and C···H/H···C short contacts to the total Hirshfeld surfaces of the cations.

1. Chemical context

The 4-[(benzylamino)carbonyl]-1-methylpyridinium cation (Am⁺) has been shown to possess antiviral activity (Buhtiarova et al., 2003; Frolov et al., 2004; Boltz et al., 2018; te Velthuis et al., 2021). Being charged due to quaternization of the pyridine N atom, this type of cation is more stable than its protonated analogue formed by H-atom transition in the form of an acid–base pair. Halogenide anions can be used as simple counter-ions of the organic cation. In fact, the iodide salt of 4-[(benzylamino)carbonyl]-1-methylpyridinium (AmI) is known as a multimodal antiviral drug and has been studied by single-crystal X-ray diffraction, powder diffraction, IR spectroscopy, and DSC methods (Drebushchak et al., 2017). The search for polymorphic modifications, hydrates or solvates is of great importance for the pharmaceutical industry to improve the quality of a drug and to protect intellectual property. However, polymorphic screening performed for the AmI salt did not reveal any other crystalline form.
The 4-[(benzylamino)carbonyl]-1-methylpyridinium bromide (AmBr) salt is the closest analogue of AmI. Polymorphic screening for this salt resulted in the crystallization of a hemihydrate. In this communication we present the molecular and crystal structures of 4-[(benzylamino)carbonyl]-1-methylpyridinium bromide hemihydrate, \((\text{C}_{14}\text{H}_{15}\text{N}_{2}\text{O})^{+}\text{Br}^{-}\cdot0.5\text{H}_{2}\text{O}\).

### Table 1

| Parameter | Cation A | Cation B |
|-----------|----------|----------|
| N1—C2    | 1.343 (6) | 1.323 (7) |
| N1—C6    | 1.330 (7) | 1.329 (7) |
| N2—C7—C4—C3 | 17.1 (7) | –1.4 (9) |
| C7—N2—C8—C9 | –102.6 (6) | –107.0 (6) |
| N2—C8—C9—C10 | –168.9 (5) | –167.4 (5) |
| H2—H3    | 2.11     | 2.04     |
| H2—C3    | 2.59     | 2.54     |

2. **Structural commentary**

The asymmetric unit contains two molecules of the cation (denoted \(A\) and \(B\)), two bromide anions (\(A\) and \(B\)) and one water molecule (Fig. 1). The positive charge of the cation is located at the quaternized nitrogen atom of the pyridine ring.

![Figure 1](image)

**Figure 1**
Molecular structure of the title compound, AmBr hemihydrate. Displacement ellipsoids are shown at the 50% probability level. \(\text{C—H} \cdot \cdot \cdot \text{Br}\) and \(\text{N—H} \cdot \cdot \cdot \text{Br}\) hydrogen bonds are indicated by dotted lines.

![Figure 2](image)

**Figure 2**
Molecular overlay plot of cations \(A\) and \(B\).

### Table 2

| D–H–A      | D–H–A  | D–H–A  | D–H–A  |
|------------|-------|-------|-------|
| N2A—H2A—Br1A | 0.86  | 2.53  | 3.339 (5) | 158  |
| C3A—H3A—Br1A | 0.93  | 2.98  | 3.814 (5) | 150  |
| C2A—H2AA—Br1A′ | 0.93  | 2.84  | 3.725 (6) | 159  |
| C1A—H1AA—Br1A′ | 0.96  | 2.88  | 3.784 (6) | 157  |
| C6A—H6A—CgB° | 0.93  | 2.65  | 3.510 (7) | 154  |
| N2B—H2B—Br1B | 0.86  | 2.60  | 3.419 (5) | 159  |
| C3B—H3B—Br1B | 0.93  | 2.83  | 3.753 (5) | 175  |
| C6B—H6B—CgB° | 0.93  | 2.71  | 3.400 (7) | 132  |
| O1W—H1WA—Br1B° | 0.85  | 3.03  | 3.473 (7) | 115  |
| C1A—H1AC—O1W° | 0.96  | 2.89  | 3.794 (10) | 157  |

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

The carbamide group is slightly non-planar with the plane of the aromatic ring, as shown by the N2—C7—C4—C3 torsion angles given in Table 1. The non-planarity is caused by steric repulsion between the two constituents as revealed by the am иде\(\text{H}_{2} \cdot \cdot \cdot \text{H}_{3}\)pyridine and am иде\(\text{H}_{2} \cdot \cdot \cdot \text{C}_{3}\)pyridine short contacts (Table 1) as compared to the van der Waals radii sums (Zefirov, 1997) of 2.34 and 2.87 Å, respectively. The cations \(A\) and \(B\) have similar conformations of the benzyl substituent (Fig. 2). The phenyl fragment of the benzyl substituent is located in an \(–ac\) position in relation to the \(C7—N2\) bond and is twisted in relation to the carbamide fragment in both cations \(A\) and \(B\), as seen in the \(C7—N2—C8—C9\) and \(N2—C8—C9—C10\) torsion angles (Table 1).

3. **Supramolecular features**

In the crystal, cations \(A\) and \(B\) interact with the bromide anions by \(\text{N—H} \cdot \cdot \cdot \text{Br}\) hydrogen bonds. In addition, a set of \(\text{C—H} \cdot \cdot \cdot \text{O}\) hydrogen bond as a proton acceptor and \(\text{O—H} \cdot \cdot \cdot \text{Br}\) and \(\text{O—H} \cdot \cdot \cdot \text{O}\) hydrogen bonds as a proton donor (Table 2). All these hydrogen-bonding interactions result in the formation of double chains extending parallel to [011] (Fig. 3).

![Figure 3](image)

**Figure 3**
Crystal packing of AmBr hemihydrate in a view along [100]. Hydrogen-bonding interactions are shown by dashed lines.
4. Hirshfeld surface analysis

Intermolecular interactions were analysed using Hirshfeld surface analysis and two-dimensional fingerprint plots by using CrystalExplorer17 (Turner et al., 2017). The Hirshfeld surfaces were calculated separately for cations A and B using a standard high surface resolution, mapped over $d_{\text{norm}}$ (Fig. 4). The red spots corresponding to contacts that are shorter than the van der Waals radii sum of the closest atoms are observed at the hydrogen atom of the amino group and at some phenyl and methyl hydrogen atoms. The two-dimensional fingerprint plots showed the absence of strong hydrogen bonds in the structure under study. To compare intermolecular interactions of different types in a more quantitative way, their contributions to the total Hirshfeld surfaces were analysed (Fig. 5). The main contribution is provided by H/C1/C1/C1 H short contacts (Fig. 5g,h). The contribution of C···H/C1/C1/C1 short contacts is also significant (Fig. 5i,j). The Br···H/C1/C1/C1 Br and O···H/C1/C1/C1 O interactions contribute to the total Hirshfeld surface in the same way (Fig. 5c,d and 5e,f).

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 anhydrous AmI salt with an equimolar cation:iodine ratio (refcode BEBFIA; Drebushchak et al., 2017). A comparison of the molecular conformation of the cation showed its flexibility due to rotation about the N—Csp\(^{3}\) and Csp\(^{3}\)—Caryl bonds.

6. Powder diffraction characterization

An X-ray powder diffraction pattern of the title compound was registered using a Siemens D500 powder diffractometer (Cu Ka radiation, Bragg–Brentano geometry, curved graphite monochromator on the counter arm, $4 < 2\theta < 60^\circ$, $D2\theta = 0.02^\circ$). A Rietveld refinement (Fig. 6) on the basis of the obtained pattern was carried out with Fullprof and WinPLOTR (Rodriguez-Carvajal & Roisnel, 1998) using data of an external standard (NIST SRM1976) for the calculation of the instrumental profile function and the single-crystal data as the structure model for refinement. The main results of the Rietveld refinement are shown in Table 3. On the basis of the Rietveld refinement, the experimental powder X-ray diffraction pattern coincides with the theoretical one calculated from the X-ray single crystal study.

7. Synthesis and crystallization

4-[(Benzylationocarbonyl]-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, and the resulting precipitate was filtered off. The solvent was evaporated under reduced pressure. To the precipitate were added 300 ml of acetonitrile and refluxed for 2 h. The reaction then was spontaneously cooled to a temperature of 303 K and the precipitate filtered off and rinsed on the filter with 50 ml of cooled acetonitrile. The product was dried at 313 K for 12 h. Yield: 14 g of 4-[[benzylamino)carbonyl]-1-methylpyridinium bromide (28%); colourless crystals.

8. Refinement
Crystal data, data collection and structure refinement details are summarized in Table 4. All of the hydrogen atoms were placed in calculated positions and treated as riding with C—H = 0.96 Å, Uiso(H) = 1.5Ueq for methyl groups and with Csp²—H = 0.93 Å, Csp—H = 0.97 Å, Uiso(H) = 1.2Ueq for all other hydrogen atoms.

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Table 4
Experimental details.

| Crystal data | Chemical formula | Chemical composition | M | Crystal system, space group | Temperature (K) | α, β, γ (°) | V (Å³) | Z | Radiation type | μ (mm⁻¹) | Crystal size (mm) |
|--------------|------------------|----------------------|---|-----------------------------|----------------|------------|------|----|---------------|---------|------------------|
| C₁₄H₁₅N₂O⁺Br⁻·0.5H₂O | 316.19 | Triclinic, P T | 293 | 5.8891 (4), 14.7565 (10), 17.8090 (11) | 65.773 (6), 85.396 (6), 85.544 (6) | 4 | Mo K | 2.92 | 0.30 × 0.15 × 0.10 |

Data collection

| Diffractionometer | Xcalibur, Atlas |
|-------------------|----------------|
| Absorption correction | Multi-scan (CrysAlis PRO; Rigaku OD, 2021) |
| No. of measured, independent and observed | 4925, 3547 |
| F[2 > 2σ(I)] | 0.069, 0.175, 1.06 |
| No. of reflections | 4925 |
| No. of parameters | 339 |
| H-atom treatment | H-atom parameters constrained |
| Δρmax, Δρmin (e Å⁻³) | 1.12, –0.45 |

Computer programs: CrysAlis PRO (Rigaku OD, 2021), SHELXT (Sheldrick, 2015a), SHELXL (Sheldrick, 2015b), Mercury (Macrae et al., 2020), OLEX2 (Dolomanov et al., 2009).

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4-[(Benzy lamino)carbonyl]-1-methylpyridinium bromide hemihydrate: X-ray diffraction study and Hirshfeld surface analysis

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2021); cell refinement: *CrysAlis PRO* (Rigaku OD, 2021); data reduction: *CrysAlis PRO* (Rigaku OD, 2021); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae et al., 2020); software used to prepare material for publication: *OLEX2* (Dolomanov et al., 2009).

4-[(Benzy lamino)carbonyl]-1-methylpyridinium bromide hemihydrate

Crystal data

\[
\begin{align*}
C_{14}H_{15}N_2O^+ \cdot Br^- \cdot 0.5H_2O & \quad Z = 4 \\
M_r = 316.19 & \quad F(000) = 644 \\
Triclinic, \ P\bar{T} & \quad D_e = 1.495 \text{ Mg m}^{-3} \\
a = 5.8891 (4) \AA & \quad \text{Mo } K\alpha \text{ radiation, } \lambda = 0.71073 \AA \\
b = 14.7565 (10) \AA & \quad \text{Cell parameters from 4991 reflections} \\
c = 17.8090 (11) \AA & \quad \theta = 3.6^\circ - 25.4^\circ \\
a = 65.773 (6)^\circ & \quad \mu = 2.92 \text{ mm}^{-1} \\
\beta = 85.396 (6)^\circ & \quad T = 293 \text{ K} \\
\gamma = 85.544 (6)^\circ & \quad \text{Plate, colorless} \\
V = 1405.08 (17) \text{ \AA}^3 & \quad 0.30 \times 0.15 \times 0.10 \text{ mm} \\
\end{align*}
\]

Data collection

Xcalibur, Atlas diffractometer
Radiation source: Enhance (Mo) X-ray Source
Detector resolution: 10.3779 pixels mm\(^{-1}\)
\(\omega\) scans
Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2021)
\(T_{\text{min}} = 0.634, T_{\text{max}} = 1.000\)

14465 measured reflections
4925 independent reflections
3547 reflections with \(I > 2\sigma(I)\)
\(R_{\text{int}} = 0.075\)
\(\theta_{\text{max}} = 25.0^\circ, \theta_{\text{min}} = 3.4^\circ\)
\(h = -6\rightarrow 6\)
\(k = -16\rightarrow 17\)
\(l = -21\rightarrow 20\)

Refinement

Refinement on \(F^2\)
Least-squares matrix: full
\(R[F^2 > 2\sigma(F^2)] = 0.060\)
\(wR(F^2) = 0.175\)
\(S = 1.06\)
4925 reflections
339 parameters
0 restraints

Hydrogen site location: mixed
H-atom parameters constrained
\(w = 1/[\sigma^2(F_o^2) + (0.0802P)^2 + 0.8154P]\)
where \(P = (F_o^2 + 2F_c^2)/3\)
$(\Delta/\sigma)_{\text{max}} = 0.001$
$\Delta \rho_{\text{max}} = 1.12 \text{ e Å}^{-3}$

**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 |
|-----|----------|----------|----------|-----------|
| Br1A| 0.68503 (10) | 1.06475 (4) | 0.84634 (4) | 0.0614 (2) |
| Br1B| 0.37067 (11) | 0.44764 (5) | 0.67323 (4) | 0.0621 (2) |
| O1A | 0.3136 (7) | 0.6956 (3) | 0.9887 (2) | 0.0611 (11) |
| N1A | 0.9794 (7) | 0.7007 (3) | 1.1351 (2) | 0.0438 (10) |
| N1B | 0.6285 (7) | 0.7967 (3) | 0.3685 (3) | 0.0496 (11) |
| N2A | 0.3986 (7) | 0.8566 (3) | 0.9181 (3) | 0.0493 (11) |
| H2A | 0.486736 | 0.902420 | 0.913909 | 0.059* |
| O1B | 0.0287 (8) | 0.6602 (4) | 0.5982 (3) | 0.0518 (11) |
| H2B | 0.133971 | 0.614443 | 0.605368 | 0.062* |
| C9B | 0.06246 (8) | 0.7400 (3) | 0.7500 (3) | 0.0432 (12) |
| C9C | 0.09195 (9) | 0.7968 (4) | 0.10910 (3) | 0.0473 (13) |
| C5A | 0.996826 | 0.846374 | 0.926125 | 0.057* |
| C10B | −0.2902 (9) | 0.5848 (4) | 0.8037 (3) | 0.0505 (14) |
| H6A | 0.4317 (8) | 0.7654 (4) | 0.9765 (3) | 0.0431 (12) |
| C14A | 0.5157 (9) | 0.8564 (4) | 0.7586 (3) | 0.0484 (13) |
| H14A | 0.618478 | 0.829285 | 0.800112 | 0.058* |
| C3A | 0.7436 (9) | 0.8223 (4) | 1.0381 (3) | 0.0471 (13) |
| H3A | 0.701404 | 0.88839 | 1.007835 | 0.057* |
| C8A | 0.2168 (9) | 0.8807 (4) | 0.8609 (3) | 0.0516 (14) |
| H8AA | 0.141562 | 0.943815 | 0.855334 | 0.062* |
| H8AB | 0.104777 | 0.830227 | 0.883854 | 0.062* |
| C4B | 0.2677 (9) | 0.8763 (4) | 0.4813 (3) | 0.0435 (12) |
| C6B | 0.4700 (10) | 0.8688 (4) | 0.3605 (4) | 0.0576 (15) |
| H6B | 0.481705 | 0.930081 | 0.315903 | 0.069* |
| C13A | 0.5825 (10) | 0.8647 (4) | 0.6799 (4) | 0.0572 (15) |
| C14A | 0.730428 | 0.845033 | 0.668565 | 0.069* |
| C5A | 0.6988 (9) | 0.6501 (4) | 1.0763 (3) | 0.0456 (12) |
| H5A | 0.626632 | 0.598873 | 1.071699 | 0.055* |
| C8B | −0.1697 (9) | 0.6367 (4) | 0.6549 (3) | 0.0517 (14) |
| H8BA | −0.226852 | 0.574898 | 0.658879 | 0.062* |
| Atomic displacement parameters ($\mathbf{A}^2$) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                  | $U^1$           | $U^2$           | $U^3$           | $U^{12}$        | $U^{13}$        | $U^{23}$        |
| Br1A             | 0.0648 (4)      | 0.0476 (4)      | 0.0676 (4)      | −0.0142 (3)     | −0.0086 (3)     | −0.0165 (3)     |
| Br1B             | 0.0719 (4)      | 0.0510 (4)      | 0.0559 (4)      | −0.0091 (3)     | −0.0022 (3)     | −0.0133 (3)     |
| O1A              | 0.068 (3)       | 0.049 (2)       | 0.061 (2)       | −0.0199 (19)    | −0.0167 (19)    | −0.0110 (19)    |
| N1A              | 0.050 (2)       | 0.047 (3)       | 0.033 (2)       | −0.0052 (19)    | −0.0020 (17)    | −0.015 (2)      |
| N1B              | 0.056 (3)       | 0.052 (3)       | 0.041 (2)       | −0.016 (2)      | 0.0023 (19)     | −0.018 (2)      |
| N2A              | 0.054 (3)       | 0.045 (3)       | 0.045 (2)       | −0.0116 (19)    | −0.0074 (19)    | −0.011 (2)      |
| O1B              | 0.069 (3)       | 0.059 (3)       | 0.075 (3)       | 0.002 (2)       | 0.018 (2)       | −0.005 (2)      |
| N2B              | 0.058 (3)       | 0.052 (3)       | 0.040 (2)       | −0.003 (2)      | 0.0033 (19)     | −0.015 (2)      |
| C9B              | 0.044 (3)       | 0.038 (3)       | 0.039 (3)       | −0.007 (2)      | −0.002 (2)      | −0.011 (2)      |
| C9A              | 0.046 (3)       | 0.033 (3)       | 0.046 (3)       | −0.007 (2)      | −0.008 (2)      | −0.009 (2)      |
| C2A              | 0.062 (3)       | 0.036 (3)       | 0.043 (3)       | −0.008 (2)      | −0.009 (2)      | −0.012 (2)      |

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| Atomic  | U^11 | U^22 | U^33 | U^12 | U^13 | U^23 |
|---------|------|------|------|------|------|------|
| C10B    | 0.043(3) | 0.054(4) | 0.053(3) | -0.015(2) | 0.007(2) | -0.020(3) |
| C4A     | 0.049(3) | 0.041(3) | 0.032(3) | -0.007(2) | 0.001(2) | -0.015(2) |
| C6A     | 0.053(3) | 0.033(3) | 0.039(3) | -0.003(2) | -0.004(2) | -0.008(2) |
| C7A     | 0.049(3) | 0.045(3) | 0.036(3) | -0.009(2) | 0.002(2) | -0.016(2) |
| C14A    | 0.048(3) | 0.041(3) | 0.052(3) | -0.002(2) | -0.011(2) | -0.013(2) |
| C3A     | 0.057(3) | 0.034(3) | 0.048(3) | -0.006(2) | -0.007(2) | -0.013(2) |
| C8A     | 0.045(3) | 0.051(4) | 0.052(3) | 0.001(2)  | -0.011(2) | -0.013(3) |
| C4B     | 0.054(3) | 0.043(3) | 0.033(3) | -0.005(2) | -0.005(2) | -0.015(2) |
| C6B     | 0.064(4) | 0.040(3) | 0.054(3) | -0.007(3) | 0.003(3)  | -0.005(3) |
| C13A    | 0.058(3) | 0.051(4) | 0.062(4) | 0.000(3)  | -0.004(3) | -0.023(3) |
| C5A     | 0.057(3) | 0.037(3) | 0.043(3) | -0.012(2) | 0.003(2)  | -0.016(2) |
| C8B     | 0.058(3) | 0.049(3) | 0.043(3) | -0.009(2) | 0.000(2)  | -0.012(3) |
| C14B    | 0.050(3) | 0.043(3) | 0.048(3) | -0.010(2) | 0.005(2)  | -0.012(3) |
| C10A    | 0.043(3) | 0.050(3) | 0.052(3) | -0.001(2) | -0.013(2) | -0.011(3) |
| C13B    | 0.060(3) | 0.058(4) | 0.055(4) | -0.009(3) | -0.007(3) | -0.025(3) |
| C11B    | 0.064(4) | 0.063(4) | 0.050(3) | -0.019(3) | 0.018(3)  | -0.021(3) |
| C1A     | 0.047(3) | 0.060(4) | 0.049(3) | 0.000(3)  | -0.014(2) | -0.016(3) |
| C12B    | 0.072(4) | 0.062(4) | 0.046(3) | -0.004(3) | -0.002(3) | -0.025(3) |
| C7B     | 0.051(3) | 0.051(4) | 0.039(3) | -0.001(3) | -0.003(2) | -0.013(3) |
| C2B     | 0.065(4) | 0.045(4) | 0.056(4) | 0.000(3)  | 0.002(3)  | -0.015(3) |
| C12A    | 0.079(4) | 0.061(4) | 0.061(4) | -0.012(3) | 0.000(3)  | -0.029(3) |
| C3B     | 0.063(3) | 0.045(3) | 0.042(3) | -0.003(3) | 0.004(2)  | -0.007(3) |
| C5B     | 0.058(3) | 0.045(3) | 0.054(3) | 0.001(3)  | 0.004(3)  | -0.011(3) |
| C11A    | 0.068(4) | 0.063(4) | 0.062(4) | 0.002(3)  | -0.022(3) | -0.019(3) |
| C1B     | 0.067(4) | 0.072(5) | 0.062(4) | -0.012(3) | 0.019(3)  | -0.021(3) |
| O1W     | 0.103(5) | 0.189(8) | 0.132(6) | 0.013(5)  | -0.021(4) | -0.095(6) |

**Geometric parameters (Å, °)**

| Bond                  | Distance (Å) | Angle (°)  |
|-----------------------|--------------|------------|
| O1A—C7A               | 1.223 (6)    | C4B—C5B    | 1.373 (7)  |
| N1A—C6A               | 1.330 (7)    | C4B—C3B    | 1.382 (7)  |
| N1A—C2A               | 1.343 (6)    | C4B—C7B    | 1.514 (7)  |
| N1A—C1A               | 1.491 (7)    | C6B—C5B    | 1.357 (8)  |
| N1B—C2B               | 1.323 (7)    | C6B—H6B    | 0.9300     |
| N1B—C6B               | 1.329 (7)    | C13A—C12A  | 1.372 (9)  |
| N1B—C1B               | 1.480 (7)    | C13A—H13A  | 0.9300     |
| N2A—C7A               | 1.332 (6)    | C5A—H5A    | 0.9300     |
| N2A—C8A               | 1.459 (7)    | C8B—H8BA   | 0.9700     |
| N2A—H2A               | 0.8600       | C8B—H8BB   | 0.9700     |
| O1B—C7B               | 1.231 (6)    | C14B—C13B  | 1.386 (8)  |
| N2B—C7B               | 1.326 (7)    | C14B—H14B  | 0.9300     |
| N2B—C8B               | 1.446 (7)    | C10A—C11A  | 1.382 (8)  |
| N2B—H2B               | 0.8600       | C10A—H10A  | 0.9300     |
| C9B—C14B              | 1.373 (7)    | C13B—C12B  | 1.384 (8)  |
| C9B—C10B              | 1.397 (7)    | C13B—H13B  | 0.9300     |
| C9B—C8B               | 1.502 (7)    | C11B—C12B  | 1.375 (9)  |
| C9A—C14A              | 1.376 (7)    | C11B—H11B  | 0.9300     |
| C9A—C10A              | 1.381 (7)    | C1A—H1AA   | 0.9600     |
C9A—C8A 1.507 (8)  C1A—H1AB 0.9600  
C2A—C3A 1.381 (8)  C1A—H1AC 0.9600  
C2A—H2AA 0.9300  C12B—H12B 0.9300  
C10B—C11B 1.370 (8)  C2B—C3B 1.370 (8)  
C10B—H10B 0.9300  C2B—H2BA 0.9300  
C4A—C5A 1.379 (7)  C12A—C11A 1.372 (9)  
C4A—C3A 1.385 (7)  C12A—H12A 0.9300  
C4A—C7A 1.515 (7)  C3B—H3B 0.9300  
C6A—C5A 1.365 (8)  C5B—H5B 0.9300  
C6A—H6A 0.9300  C11A—H11A 0.9300  
C14A—C13A 1.383 (8)  C1B—H1BA 0.9600  
C14A—H14A 0.9300  C1B—H1BB 0.9600  
C3A—H3A 0.9700  O1W—H1WA 0.8506  
C8A—H8AA 0.9700  O1W—H1WB 0.8502  
C6A—N1A—C2A 120.9 (4)  C6A—C5A—H5A 120.0  
C6A—N1A—C1A 119.3 (4)  C4A—C5A—H5A 120.0  
C2A—N1A—C1A 119.9 (5)  N2B—C8B—C9B 114.0 (5)  
C2B—N1B—C6B 120.5 (5)  N2B—C8B—H8BA 108.8  
C2B—N1B—C1B 119.4 (5)  C9B—C8B—H8BA 108.8  
C6B—N1B—C1B 120.0 (5)  N2B—C8B—H8BB 108.8  
C7A—N2A—C8A 121.7 (5)  C9B—C8B—H8BB 108.8  
C7A—N2A—H2A 119.1  H8BA—C8B—H8BB 107.6  
C8A—N2A—H2A 119.1  C9A—C10A—C11A 120.6 (5)  
C7B—N2B—C8B 122.7 (5)  C9B—C10A—C11A 120.6 (5)  
C7B—N2B—H2B 118.6  C13B—C14B—H14B 119.0  
C8B—N2B—H2B 118.6  C9B—C14B—C13B 122.1 (5)  
C14B—C9B—C10B 117.7 (5)  C9A—C10A—H10A 119.7  
C14B—C9B—C8B 123.6 (4)  C11A—C10A—H10A 119.7  
C10B—C9B—C8B 118.7 (5)  C12B—C13B—C14B 119.1 (6)  
C14A—C9A—C10A 118.3 (5)  C12B—C13B—H13B 120.5  
C14A—C9A—C8A 123.7 (4)  C14B—C13B—H13B 120.5  
C10A—C9A—C8A 118.0 (5)  C10B—C11B—C12B 120.7 (5)  
N1A—C2A—C3A 120.4 (5)  C10B—C11B—H11B 119.7  
N1A—C2A—H2AA 119.8  C12B—C11B—H11B 119.7  
C3A—C2A—H2AA 119.8  N1A—C1A—H1AA 109.5  
C11B—C10B—C9B 120.8 (5)  N1A—C1A—H1AB 109.5  
C11B—C10B—H10B 119.6  N1A—C1A—H1AC 109.5  
C9B—C10B—H10B 119.6  H1AA—C1A—H1AC 109.5  
C5A—C4A—C3A 118.6 (5)  H1AA—C1A—H1AC 109.5  
C5A—C4A—C7A 116.8 (5)  H1AB—C1A—H1AC 109.5  
C3A—C4A—C7A 124.7 (5)  C11B—C12B—C13B 119.7 (6)  
N1A—C6A—C5A 120.9 (5)  C11B—C12B—H12B 120.2  
N1A—C6A—H6A 119.5  C13B—C12B—H12B 120.2  
C5A—C6A—H6A 119.5  O1B—C7B—N2B 123.4 (5)  
O1A—C7A—N2A 124.3 (5)  O1B—C7B—C4B 119.2 (5)  
O1A—C7A—C4A 118.4 (5)  N2B—C7B—C4B 117.4 (5)
| Bond                     | Angle (°) | Bond                     | Angle (°) | Bond                     | Angle (°) |
|--------------------------|-----------|--------------------------|-----------|--------------------------|-----------|
| N2A—C7A—C4A             | 117.2 (5) | N1B—C2B—C3B             | 120.8 (5) |
| C9A—C14A—C13A           | 121.1 (5) | N1B—C2B—H2BA            | 119.6     |
| C9A—C14A—H14A           | 119.4     | C3B—C2B—H2BA            | 119.6     |
| C13A—C14A—H14A          | 119.4     | C13A—C12A—C11A          | 119.2 (6) |
| C2A—C3A—C4A             | 119.3 (5) | C13A—C12A—H12A          | 120.4     |
| C2A—C3A—H3A             | 120.4     | C11A—C12A—H12A          | 120.4     |
| C4A—C3A—H3A             | 120.4     | C2B—C3B—C4B             | 119.6 (5) |
| N2A—C8A—C9A             | 113.5 (4) | C2B—C3B—H3B             | 120.2     |
| N2A—C8A—H8AA            | 108.9     | C4B—C3B—H3B             | 120.2     |
| N2A—C8A—C9A             | 113.5 (4) | C6B—C5B—C4B             | 120.2 (5) |
| N2A—C8A—H8AB            | 108.9     | C6B—C5B—H5B             | 119.9     |
| C9A—C8A—H8AB            | 108.9     | C4B—C5B—H5B             | 119.9     |
| H8AA—C8A—H8AB           | 107.7     | C12A—C11A—C10A          | 120.6 (5) |
| C5B—C4B—C3B             | 117.8 (5) | C12A—C11A—H11A          | 119.7     |
| C5B—C4B—C7B             | 117.6 (5) | C10A—C11A—H11A          | 119.7     |
| C3B—C4B—C7B             | 124.6 (5) | N1B—C1B—H1BA            | 109.5     |
| N1B—C6B—C5B             | 121.0 (5) | N1B—C1B—H1BB            | 109.5     |
| N1B—C6B—H6B             | 119.5     | C11A—C12A—H12A          | 109.5     |
| C5B—C6B—H6B             | 119.5     | C12A—C13A—C12B          | 109.5     |
| C5B—C6B—C11B            | 137.5 (6) | C12A—C13A—H13A          | 109.5     |
| C12A—C13A—C14A          | 120.2 (6) | C14A—C13A—H13A          | 109.5     |
| C14A—C13A—C14A          | 119.9     | C6A—C5A—C4A             | 120.0 (5) |
| C6A—N1A—C2A—C3A         | 0.3 (8)   | C6B—C5B—C4B—O1B         | 178.7 (6) |
| C1A—N1A—C2A—C3A         | 0.3 (8)   | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C14B—C9B—C10B—C11B      | 0.7 (8)   | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C8B—C9B—C10B—C11B       | 0.7 (8)   | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C2A—C1A—C6A—C5A         | 0.4 (8)   | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C1A—N1A—C6A—C5A         | 0.4 (8)   | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C8A—C9B—C10B—C11B       | 0.4 (8)   | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C2A—N1A—C6A—C5A         | 0.4 (8)   | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C8A—N2A—C7A—C4A         | 177.9 (5) | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C8A—N2A—C7A—C4A         | 177.9 (5) | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C5A—C4A—C7A—C1A         | 15.0 (7)  | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C3A—C4A—C7A—C1A         | 15.0 (7)  | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C5A—C4A—C7A—N2A         | -164.4 (5)| C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C3A—C4A—C7A—N2A         | -164.4 (5)| C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C10A—C9A—C14A—C13A      | 0.5 (8)   | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C8A—C9A—C14A—C13A       | -179.8 (6)| C1A—N1A—C2A—C3A         | 0.3 (8)   |
| N1A—C2A—C3A—C4A         | -0.5 (8)  | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C5A—C4A—C3A—C2A         | -0.1 (8)  | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C7A—C4A—C3A—C2A         | 178.4 (5) | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C7A—N2A—C8A—C9A         | -102.6 (6)| C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C14A—C9A—C8A—N2A        | 11.4 (8)  | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C10A—C9A—C8A—N2A        | -168.9 (5)| C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C2B—N1B—C6B—C5B         | -0.3 (9)  | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C1B—N1B—C6B—C5B         | 176.6 (6) | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| C9A—C14A—C13A—C12A      | -1.8 (9)  | C1A—N1A—C2A—C3A         | 0.3 (8)   |
| N1A—C6A—C5A—C4A         | -1.0 (8)  | C1A—N1A—C2A—C3A         | 0.3 (8)   |
Hydrogen-bond geometry (Å, °)

CgA and CgB are the centroids of the C9A–C14A and C9B–C14B rings, respectively.

| D—H···A          | D—H  | H···A | D···A     | D—H···A |
|------------------|-------|-------|-----------|---------|
| N2A—H2A···Br1A   | 0.86  | 2.53  | 3.339 (5) | 158     |
| C3A—H3A···Br1A   | 0.93  | 2.98  | 3.814 (5) | 150     |
| C2A—H2A···Br1Ai  | 0.93  | 2.84  | 3.725 (6) | 159     |
| C1A—H1A···Br1Ai  | 0.96  | 2.88  | 3.784 (6) | 157     |
| C6A—H6A···CgBii  | 0.93  | 2.65  | 3.510 (7) | 154     |
| N2B—H2B···Br1B   | 0.86  | 2.60  | 3.419 (5) | 159     |
| C3B—H3B···Br1B   | 0.93  | 2.83  | 3.753 (5) | 175     |
| C6B—H6B···CgAiii | 0.93  | 2.71  | 3.400 (7) | 132     |
| O1W—H1WA···Br1Biv| 0.85  | 3.03  | 3.473 (7) | 115     |
| C1A—H1AC···O1Wv  | 0.96  | 2.89  | 3.794 (10)| 157     |

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