Salts of 4-[(benzylamino)carbonyl]-1-methylpyridinium and iodide anions with different cation:iodine stoichiometric ratios

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The two iodide salts, 4-[(benzylamino)carbonyl]-1-methylpyridinium iodide–iodine (2/1), C_{14}H_{15}N_{2}O^{+}/C_{1}I^{−}−0.5I_{2}, I, and 4-[(benzylamino)carbonyl]-1-methylpyridinium triiodide, C_{14}H_{15}N_{2}O^{+}/II^{−}, II, with different cation:iodine atoms ratios were studied. Salt I contains one cation, one iodide anion and half of the neutral I_2 molecule in the asymmetric unit (cation:iodine atoms ratio is 1:2). Salt II contains two cations, one triiodide anion (I_3^{−}) and half triiodide anions (cation:iodine atoms ratio is 1:3). The NH group forms N—H—I hydrogen bonds with the I^{−} anion in the crystal of I or N—H···O hydrogen bonds in II where only triiodide anions are present.

1. Chemical context

4-[(Benzylamino)carbonyl]-1-methylpyridinium iodide, chemical formula C_{14}H_{15}N_{2}O^{+}I^{−}, is used as a multimodal antiviral drug (te Velthuis et al., 2020; Boltz et al., 2018; Buhtiarova et al., 2003; Frolov et al., 2004). Its molecular and crystal structure have been studied in detail by diffraction and spectroscopic methods (Drebushchak et al., 2017). The formation of different polymorphic modifications of an API is of great importance for the pharmaceutical industry (Bernstein, 2002; Brittain, 2009; Hilfiker, 2006). Unfortunately, all attempts to find polymorphic modifications of 4-[(benzylamino)carbonyl]-1-methylpyridinium iodide resulting from varying the solvents and crystallization conditions have failed. Only one crystal form with the P2_12_1_2 orthorhombic space group has been determined by single-crystal X-ray diffraction (Drebushchak et al., 2017).

In a continuation of this work, we attempted to obtain a new polymorphic form of this compound using not only different solvents (ethanol, methanol, 2-propanol, etc.), but also non-standard methods of activating the crystallization process. To do this, experiments on recrystallization from water under an ultrasonic field effect were carried out. It should be noted that under normal conditions, 4-[(benzyl-
Table 1
Selected geometrical parameters (Å, °) for the cations in salts I and II.

| Parameter | I      | II A     | II B     |
|-----------|--------|----------|----------|
| N1—C2     | 1.338 (10) | 1.327 (19) | 1.32 (2) |
| N1—C6     | 1.324 (11) | 1.35 (2)  | 1.313 (18) |
| N2—C7—C4—C3 | 18.1 (13) | 16 (2) | 18 (2) |
| C7—N2—C8—C9 | −75.0 (11) | −81 (2) | 178.3 (14) |
| N2—C8—C9—C10 | −77.6 (11) | −61.6 (18) | −53 (2) |
| H2···H3  | 2.09 | 2.14 | 2.11 |
| C3···H2  | 2.55 | 2.61 | 2.57 |

Table 2
Hydrogen-bond geometry (Å, °) for I.

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N2—H2···I2 | 0.86 | 2.84 | 3.632 (7) | 154 |
| C2—H2A···I2' | 0.93 | 3.18 | 4.053 (9) | 158 |
| C1—H1B···I2' | 0.96 | 3.11 | 3.992 (9) | 153 |
| C1—H1C···I2'' | 0.96 | 2.96 | 3.908 (9) | 171 |
| C1—H1A···I3'' | 0.96 | 3.00 | 3.824 (10) | 145 |
| C5—H5···O1'' | 0.93 | 2.59 | 3.328 (11) | 136 |
| C8—H8B···C11'' | 0.97 | 2.80 | 3.590 (15) | 140 |
| C8—H8B···C10'' | 0.97 | 2.76 | 3.694 (14) | 162 |

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

Table 3
Hydrogen-bond geometry (Å, °) for II.

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N2A—H2A···O1B | 0.86 | 2.02 | 2.846 (14) | 160 |
| C3A—H3A···O1B | 0.93 | 2.53 | 3.381 (18) | 152 |
| C2A—H2AA···I3 | 0.93 | 3.08 | 3.998 (17) | 169 |
| C1A—H1AC···C12A' | 0.96 | 2.72 | 3.62 (2) | 158 |
| C1A—H1AA···I7'' | 0.96 | 3.09 | 3.966 (19) | 153 |
| N2B—H2BB···O1A^a | 0.86 | 2.13 | 2.986 (14) | 176 |
| C3B—H3BB···O1A'' | 0.93 | 2.21 | 3.060 (17) | 151 |
| C2B—H2AA···C12A'' | 0.93 | 2.85 | 3.72 (2) | 156 |
| C1B—H1BB···C17'' | 0.96 | 3.07 | 3.819 (18) | 136 |
| C6B—H6B···C14'' | 0.93 | 3.12 | 4.019 (17) | 164 |

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

2. Structural commentary

The crystal structures of the salts under study consist of the same 4-[(benzylamino)carbonyl]-1-methylpyridinium cation (C14H15N2O+) and different anions. There is one cation, one iodide anion and half of the neutral I2 molecule in the asymmetric unit of compound I (Fig. 1, left). The neutral I2 molecule is located in a special position in relation to the symmetry centre coinciding with the midpoint of the I—I bond. Thus, the cation:iodine atoms ratio is 1:2 in compound I. The asymmetric unit of compound II contains two cations (A and B), one triiodide anion (I3−) and two halves of triiodide anions located on special positions in relation to the symmetry centre (Fig. 1, right). The cation:iodine atoms ratio is 1:3 in compound II.

The positive charge of the cation is localized at the quaternized nitrogen atom of the pyridine ring. This results in the N1—C6 and N1—C2 bond elongation (Table 1). The carbamide group is non-coplanar to the plane of the aromatic ring (as evidenced by the N2—C7—C4—C3 torsion angles; Table 1) as a result of steric repulsion between them [with short H2···H3 and H2···C3 contacts (as compared to the van der Waals radii sums; Zefirov, 1997) of 2.34 and 2.87 Å, respectively]. The cations in the two compounds under study differ in the conformation of the benzyl substituent. The phenyl fragment of the benzyl substituent is located in a −sc position relatively to the C7—N2 bond in I or in a +sc position in molecule A and an ap position in molecule B of II (cf the C7—N2—C8—C9 torsion angles in Table 1). The aromatic ring is turned relative to the carbamide fragment (see the N2—C8—C9—C10 torsion angles).

3. Supramolecular features

The main difference in the crystal structures of the studied salts is the participation of the carbamide group in inter-
molecular interactions. In the structure of I, the carbamide group participates in the N—H···I' hydrogen bond between the cation and the anion, while the carbonyl oxygen atom acts as an acceptor in the very weak C5—H···O1’ intermolecular interaction (Fig. 2, left; Table 2). In the structure of II, the carbamide group participates in the N—H···O hydrogen bonds between the cations (Fig. 2, right; Table 3). As a result, chains in the [100] crystallographic direction are formed. The triiodide anions occupy voids between neighbouring chains in the crystal. In addition, a set of weak C—H···I and C—H···π hydrogen bonds are found in both structures (Tables 2 and 3).

In the structure of II, the A and B cations form stacking dimers as a result of the interaction of the aromatic systems of the pyridine and benzene rings [the distance between the planes of aromatic cycles is 3.45 (1) Å, slippage 1.119 Å].

4. Hirshfeld surface analysis

Intermolecular interactions can be analyzed using Hirshfeld surface analysis and 2D fingerprint plots (Turner et al., 2017). The Hirshfeld surfaces were calculated for the cations found in two structures under study using a standard high surface resolution, mapped over d

\[d_{norm}\] (Fig. 3). 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. At the carbonyl group, red spots are found only in the cations of II. The two-dimensional fingerprint plots show that the hydrogen bonds in II are stronger (note the sharp spikes in Fig. 3).

To compare intermolecular interactions of different types in more quantitative way, their contributions to the total Hirshfeld surfaces were analysed (Fig. 4). The main contribution is provided by H···H short contacts (44.9% for I, 45% for cation A and 36.8% for cation B in II). The contribution of the I···H/ H···I short contacts is also significant [17.3% in I, 21.7% (molecule A) and 25.5% (molecule B) in II], as is that of the C···H/H···C interactions [17.2% in I, 15.5% (molecule A) and 10.7% (molecule B) in II]. Surprisingly, the contributions of the O···H/H···O interactions are very similar in the two structures [9.7% in I, 9.5% (molecule A) and 9.6% (molecule B) in II] despite the stronger N—H···O hydrogen bonds in the structure of II.

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 AmI salt with an equimolar cation:iodine atoms ratio (refcode BEBFIA; Drebushchak et al., 2017). A comparison of the cation conformations showed its flexibility resulting from rotation about the N—Csp³ and Csp³—Car bonds.
6. Synthesis and crystallization

Benzylation isonicotinic acid (124 g, 0.585 mol) and 270 mL of 90% ethanol were loaded into a glass flask. The obtained solution was heated to a temperature of 313–314 K, and then methyl iodide (91 g, 0.641 mol) was added dropwise. The reaction was stirred at a temperature of 313–314 K for 1 h, heated to boiling and boiled for 1 h. The reaction spontaneously cooled to a temperature of 313 K, then to a temperature of 283–288 K in a cooling water bath, and was stirred for 1.5 h at this temperature. The reaction mixture was filtered and the precipitate rinsed on the filter twice with 60 mL of cooled 96% ethanol. The product was dried at 313 K for 12 h. Yield: 145.5 g of crude 4-[(benzylamino)carbonyl]-1-methylpyridinium iodide (88%); yellow crystals.

45.5 g of crude 4-[(benzylamino)carbonyl]-1-methylpyridinium iodide were dissolved in 450 mL of water under ultrasonic activation. The reaction was heated to boiling temperature, stirred at boiling for 30 min and filtered. The obtained solution was cooled slowly and evaporated for three weeks. The rod-shaped crystals of I and block-shaped crystals of II crystallized almost simultaneously.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. Despite the presence of iodine atoms, crystals of salt II diffracted poorly due to their small size. All of the hydrogen atoms were located in difference-Fourier maps. Then, hydrogen atoms were refined as riding (AFIX 33 and 137 commands) with C—H = 0.96 Å, $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups (AFIX 43) and C—H = 0.93 Å, $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic rings (AFIX 23) and Csp$^2$—H = 0.97 Å, $U_{iso}(H) = 1.2U_{eq}(C)$ for the methylene fragment.

8. Powder diffraction characterization

A powder diffraction pattern of salt II was registered using a Siemens D500 powder diffractometer (Cu Kα radiation, Bragg–Brentano geometry, curved graphite monochromator on the counter arm, 4 < 2θ < 60°, $2D2θ = 0.02°$, time per step of 2 s). The Rietveld refinement of the obtained pattern (Fig. 5, left) was carried out with FULLPROF (Rodriguez-Carvajal, SHELXTL2014/5 (Sheldrick, 2015a), SHELXL2016/6 (Sheldrick, 2015b), Mercury (Macrae et al., 2020) and OLEX2 (Dolomanov et al., 2009).

Figure 5

Final Rietveld plots for II (on the left). Observed data points are indicated by red circles, the best-fit profile (black upper trace) and the difference pattern (blue lower trace) are shown as solid lines. The vertical green bars correspond to the Bragg positions of peaks. The calculated powder pattern for I is shown on the right.
2001) and WINPLOTR (Roisnel & Rodriguez-Carvajal, 2000) using an external standard (NIST SRM1976) for the calculation of the instrumental profile function and the single-crystal results as the structure model for the refinement. A powder pattern for salt I was not obtained because of the small amount of the crystal sample. For comparison, Fig. 5 (right) shows the pattern calculated for salt I.

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References
Bernstein, J. (2002). Polymorphism in Molecular Crystals. Oxford: Clarendon Press.
Boltz, D., Peng, X., Muzzio, M., Dash, P., Thomas, P. G. & Margitich, V. (2018). Antivir. Chem. Chemother. 26 https://doi.org/10.1177/2040206618811416.
Brittain, H. G. (2009). Polymorphism in pharmaceutical solids, 2nd ed. New York: Informa.
Buhtiarova, T. A., Danilenko, V. P., Homenko, V. S., Shatyrkina, T. V. & Yadlovsky, O. E. (2003). Ukrainian Med. J. 33, 72–74.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). J. Appl. Cryst. 42, 339–341.
Drebushchak, T. N., Kryukov, Y. A., Rogova, A. I. & Boldyreva, E. V. (2017). Acta Cryst. E73, 967–970.
Frolov, A. F., Frolov, V. M., Buhtiarova, T. A. & Danilenko, V. P. (2004). Ukrainian Med. J. 39, 69–74.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). Acta Cryst. B72, 171–179.
Hilfiker, R. (2006). Polymorphism in the Pharmaceutical Industry. Weinheim: John Wiley & Sons.
Macrae, C. E., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). J. Appl. Cryst. 53, 226–235.
Rigaku OD (2018). CrysAlis PRO. Rigaku Oxford Diffraction, Yarnton, England.
Rodríguez-Carvajal, J. (2001). Commission on Powder Diffraction (IUCr) Newsletter, 26, 12–19.
Roisnel, T. & Rodriguez-Carvajal, J. (2000). WinPLOTR, a Windows tool for powder diffraction patterns analysis. Mater. Sci. Forum, Proc. 7th Europ. Powder Diff. Conf. (EPDIC 7), edited by R. Delhez & E. J. Mittenmeijer, pp. 118–123.
Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.
Sheldrick, G. M. (2015b). Acta Cryst. A71, 3–8.
Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). CrystalExplorer17. University of Western Australia. http://Hirshfeldsurface.net
Velthuis, A. J. W. te, Zubkova, T. G., Shaw, M., Mehle, A., Boltz, D., Gmeinwieser, N., Stammer, H., Milde, J., Müller, L. & Margitich, V. (2020). Antimicrobial Agents and Chemotherapy, 64. https://doi.org/10.1128/AAC.02605-20.
Zefirov, Yu. V. (1997). Kristallografiya, 42, 936–958.
Salts of 4-[(benzylamino)carbonyl]-1-methylpyridinium and iodide anions with different cation:iodine stoichiometric ratios

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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 iodide–iodine (2/1) (I)

Crystal data
C_{14}H_{15}N_{2}O^{+}·I^{-}·0.5I_{2}
Mr = 481.08
Monoclinic, \textit{P}2_{1}/\textit{n}
a = 14.407 (3) Å
b = 8.8491 (10) Å
c = 14.555 (4) Å
\beta = 119.63 (3)°
V = 1613.0 (7) Å³
Z = 4

\(F(000) = 908\)
\(D_{c} = 1.981\) Mg m\(^{-3}\)
Mo \textit{Ka} radiation, \(\lambda = 0.71073\) Å
Cell parameters from 928 reflections
\(\theta = 3.6–21.8°\)
\(\mu = 3.89\) mm\(^{-1}\)
\(T = 293\) K
Stick, red

0.60 × 0.10 × 0.05 mm

Data collection
Xcalibur, Sapphire3
diffractometer
Radiation source: Enhance (Mo) X-ray Source
Detector resolution: 16.1827 pixels mm\(^{-1}\)
\(\omega\) scans
Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2018)
\(T_{\text{min}} = 0.159, T_{\text{max}} = 1.000\)
11491 measured reflections
3698 independent reflections
1941 reflections with \(I > 2\sigma(I)\)

\(R_{\text{int}} = 0.083\)
\(\theta_{\text{max}} = 27.5°, \theta_{\text{min}} = 3.2°\)
\(h = -18\rightarrow18\)
\(k = -11\rightarrow11\)
\(l = -18\rightarrow18\)

Refinement
Refinement on \(F^2\)
Least-squares matrix: full
\(R[F^2 > 2\sigma(F^2)] = 0.053\)
\(wR(F^2) = 0.157\)
\(S = 1.03\)
3698 reflections
173 parameters
0 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
\(w = 1/[\sigma(F^2) + (0.0416P)^2]\)
where \(P = (F^2 + 2F_c^2)/3\)

\((\Delta/\sigma)_{\text{max}} = 0.001\)
\(\Delta\rho_{\text{max}} = 0.90\) e Å\(^{-3}\)
\(\Delta\rho_{\text{min}} = -0.89\) 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)**

| Atom | x         | y         | z         | Uiso* / Ueq |
|------|-----------|-----------|-----------|-------------|
| I1   | 0.51630 (5) | 0.11900 (6) | 0.57075 (6) | 0.0696 (2)   |
| I2   | 0.55433 (5) | 0.39112 (7) | 0.74152 (6) | 0.0738 (3)   |
| O1   | 0.1044 (5)  | 0.3003 (8)  | 0.5772 (6)  | 0.090 (2)    |
| N1   | 0.1782 (6)  | 0.6060 (7)  | 0.3371 (6)  | 0.0614 (18)  |
| N2   | 0.2820 (6)  | 0.2698 (8)  | 0.6521 (6)  | 0.0652 (19)  |
| H2   | 0.338519    | 0.295372    | 0.650010    | 0.078*       |
| C1   | 0.1732 (8)  | 0.7074 (10) | 0.2544 (8)  | 0.075 (3)    |
| H1A  | 0.127757    | 0.663816    | 0.186085    | 0.113*       |
| H1B  | 0.243679    | 0.720760    | 0.264125    | 0.113*       |
| H1C  | 0.145051    | 0.803613    | 0.259012    | 0.113*       |
| C2   | 0.2636 (7)  | 0.5182 (10) | 0.3929 (8)  | 0.069 (3)    |
| H2A  | 0.320082    | 0.521097    | 0.379074    | 0.083*       |
| C3   | 0.2692 (7)  | 0.4235 (10) | 0.4707 (8)  | 0.067 (2)    |
| H3   | 0.327838    | 0.360259    | 0.506976    | 0.081*       |
| C4   | 0.1885 (6)  | 0.4224 (9)  | 0.4944 (8)  | 0.062 (2)    |
| C5   | 0.1012 (7)  | 0.5127 (12) | 0.4336 (8)  | 0.078 (3)    |
| H5   | 0.043510    | 0.511632    | 0.445534    | 0.093*       |
| C6   | 0.0979 (7)  | 0.6028 (10) | 0.3569 (8)  | 0.070 (3)    |
| H6   | 0.038316    | 0.663303    | 0.317556    | 0.084*       |
| C7   | 0.1885 (6)  | 0.3260 (10) | 0.5791 (7)  | 0.057 (2)    |
| C8   | 0.2932 (8)  | 0.1666 (10) | 0.7357 (8)  | 0.073 (3)    |
| H8A  | 0.362531    | 0.117925    | 0.766315    | 0.087*       |
| H8B  | 0.239142    | 0.088488    | 0.704706    | 0.087*       |
| C9   | 0.2828 (7)  | 0.2439 (8)  | 0.8213 (7)  | 0.057 (2)    |
| C10  | 0.3668 (7)  | 0.3281 (10) | 0.8984 (8)  | 0.068 (2)    |
| H10  | 0.433231    | 0.333813    | 0.895876    | 0.089*       |
| C11  | 0.3548 (9)  | 0.4014 (10) | 0.9732 (9)  | 0.081 (3)    |
| H11  | 0.410137    | 0.461576    | 1.022065    | 0.097*       |
| C12  | 0.2622 (9)  | 0.3890 (10) | 0.9788 (9)  | 0.078 (3)    |
| H12  | 0.255082    | 0.439378    | 1.031040    | 0.094*       |
| C13  | 0.1810 (9)  | 0.3010 (13) | 0.9058 (9)  | 0.083 (3)    |
| H13  | 0.118664    | 0.289920    | 0.909431    | 0.099*       |
| C14  | 0.1904 (7)  | 0.2294 (10) | 0.8280 (9)  | 0.071 (3)    |
| H14  | 0.134482    | 0.170291    | 0.778882    | 0.085*       |

**Atomic displacement parameters (Å²)**

|        | U^11     | U^22     | U^33     | U^12     | U^13     | U^23     |
|--------|----------|----------|----------|----------|----------|----------|
| I1     | 0.0651 (4)| 0.0655 (4)| 0.0790 (5)| 0.0033 (3)| 0.0364 (4)| -0.0008 (3)|

Acta Cryst. (2021). E77, 1219-1223
I2 0.0669 (4) 0.0799 (4) 0.0809 (5) −0.0121 (3) 0.0413 (4) −0.0181 (3)
O1 0.050 (3) 0.118 (5) 0.100 (6) −0.008 (3) 0.036 (4) 0.012 (5)
N1 0.060 (4) 0.060 (4) 0.056 (5) 0.006 (3) 0.023 (4) −0.002 (3)
N2 0.058 (4) 0.068 (4) 0.074 (6) −0.007 (3) 0.036 (4) 0.003 (4)
C1 0.081 (6) 0.070 (6) 0.062 (7) 0.008 (5) 0.025 (5) 0.008 (5)
C2 0.066 (6) 0.070 (6) 0.080 (8) 0.013 (4) 0.042 (6) −0.002 (5)
C3 0.057 (5) 0.083 (6) 0.073 (7) 0.018 (4) 0.040 (5) 0.006 (5)
C4 0.051 (5) 0.066 (5) 0.060 (6) 0.003 (4) 0.021 (4) −0.019 (4)
C5 0.048 (5) 0.121 (8) 0.067 (7) 0.008 (5) 0.030 (5) 0.004 (6)
C6 0.059 (5) 0.075 (6) 0.073 (7) 0.017 (4) 0.031 (5) 0.005 (5)
C7 0.050 (4) 0.063 (5) 0.060 (6) −0.006 (4) 0.029 (4) −0.002 (4)
C8 0.075 (6) 0.066 (5) 0.077 (7) 0.001 (5) 0.037 (6) 0.013 (5)
C9 0.067 (5) 0.048 (4) 0.060 (6) 0.005 (4) 0.035 (5) 0.006 (4)
C10 0.059 (5) 0.072 (6) 0.072 (7) −0.004 (4) 0.033 (5) 0.010 (5)
C11 0.086 (7) 0.068 (6) 0.074 (8) −0.012 (5) 0.028 (6) −0.002 (5)
C12 0.092 (8) 0.072 (6) 0.073 (8) 0.027 (5) 0.043 (7) 0.017 (5)
C13 0.075 (6) 0.106 (8) 0.070 (7) 0.014 (6) 0.039 (6) 0.019 (6)
C14 0.053 (5) 0.075 (6) 0.083 (8) −0.003 (4) 0.032 (5) 0.016 (5)

Geometric parameters (Å, °)

I1—IIi 2.8182 (13) C5—C6 1.353 (13)
O1—C7 1.221 (9) C5—H5 0.9300
N1—C6 1.324 (11) C6—H6 0.9300
N1—C2 1.338 (10) C8—C9 1.494 (12)
N1—C1 1.475 (11) C8—H8A 0.9700
N2—C7 1.332 (11) C8—H8B 0.9700
N2—C8 1.465 (11) C9—C14 1.387 (11)
N2—H2 0.8600 C9—C10 1.391 (12)
C1—H1A 0.9600 C10—C11 1.350 (14)
C1—H1B 0.9600 C10—H10 0.9300
C1—H1C 0.9600 C11—C12 1.381 (14)
C2—C3 1.378 (12) C11—H11 0.9300
C2—H2A 0.9300 C12—C13 1.369 (15)
C3—C4 1.366 (11) C12—H12 0.9300
C3—H3 0.9300 C13—C14 1.362 (14)
C4—C5 1.380 (12) C13—H13 0.9300
C4—C7 1.499 (13) C14—H14 0.9300
C6—N1—C2 119.8 (8) O1—C7—N2 123.3 (8)
C6—N1—C1 119.7 (7) O1—C7—C4 119.4 (8)
C2—N1—C1 120.5 (8) N2—C7—C4 117.2 (7)
C7—N2—C8 123.3 (7) N2—C8—C9 113.1 (7)
C7—N2—H2 118.4 N2—C8—H8A 109.0
C8—N2—H2 118.4 C9—C8—H8A 109.0
N1—C1—H1A 109.5 N2—C8—H8B 109.0
N1—C1—H1B 109.5 C9—C8—H8B 109.0
H1A—C1—H1B 109.5 H8A—C8—H8B 107.8

Acta Cryst. (2021). E77, 1219-1223

sup-3
### Chemical Structure

| Bond/angle | Value | Bond/angle | Value |
|------------|-------|------------|-------|
| N1—C1—H1C | 109.5 | C14—C9—C10 | 118.4 (9) |
| H1A—C1—H1C | 109.5 | C14—C9—C8 | 120.8 (9) |
| H1B—C1—H1C | 109.5 | C10—C9—C8 | 120.8 (8) |
| N1—C2—C3 | 120.9 (8) | C11—C10—C9 | 120.0 (9) |
| N1—C2—H2A | 119.5 | C11—C10—H10 | 120.0 |
| C3—C2—H2A | 119.5 | C9—C10—H10 | 120.0 |
| C4—C3—C2 | 120.0 (8) | C10—C11—C12 | 121.5 (10) |
| C4—C3—H3 | 120.0 | C10—C11—H11 | 119.3 |
| C2—C3—H3 | 120.0 | C12—C11—H11 | 119.3 |
| C3—C4—C5 | 116.9 (9) | C13—C12—C11 | 118.7 (10) |
| C3—C4—C7 | 123.9 (8) | C13—C12—H12 | 120.7 |
| C5—C4—C7 | 119.1 (8) | C11—C12—H12 | 120.7 |
| C6—C5—C4 | 121.4 (8) | C14—C13—C12 | 120.7 (10) |
| C6—C5—H5 | 119.3 | C14—C13—H13 | 119.6 |
| C4—C5—H5 | 119.3 | C12—C13—H13 | 119.6 |
| N1—C6—C5 | 120.9 (8) | C13—C14—C9 | 120.6 (10) |
| N1—C6—H6 | 119.6 | C13—C14—H14 | 119.7 |
| C5—C6—H6 | 119.6 | C9—C14—H14 | 119.7 |
| C6—N1—C2—C3 | 0.4 (14) | C3—C4—C7—N2 | 18.1 (13) |
| C1—N1—C2—C3 | 179.7 (9) | C5—C4—C7—N2 | −164.0 (9) |
| N1—C2—C3—C4 | −2.5 (14) | C7—N2—C8—C9 | −75.0 (11) |
| C2—C3—C4—C5 | 3.5 (13) | N2—C8—C9—C14 | 104.6 (9) |
| C2—C3—C4—C7 | −178.6 (9) | N2—C8—C9—C10 | −77.6 (11) |
| C3—C4—C5—C6 | −2.7 (14) | C14—C9—C10—C11 | −4.3 (13) |
| C7—C4—C5—C6 | 179.3 (9) | C8—C9—C10—C11 | 177.8 (9) |
| C2—N1—C6—C5 | 0.5 (14) | C9—C10—C11—C12 | 3.4 (15) |
| C1—N1—C6—C5 | −178.9 (9) | C10—C11—C12—C13 | −0.5 (15) |
| C4—C5—C6—N1 | 0.7 (16) | C11—C12—C13—C14 | −1.3 (15) |
| C8—N2—C7—O1 | 2.3 (14) | C12—C13—C14—C9 | 0.2 (15) |
| C8—N2—C7—C4 | −176.2 (8) | C10—C9—C14—C13 | 2.6 (13) |
| C3—C4—C7—O1 | −160.5 (9) | C8—C9—C14—C13 | −179.5 (9) |
| C5—C4—C7—O1 | 17.4 (13) |

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

### Hydrogen-Bond Geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|--------|-----|-------|-------|---------|
| N2—H2···I2 | 0.86 | 2.84 | 3.632 (7) | 154 |
| C2—H2A···I2a | 0.93 | 3.18 | 4.053 (9) | 158 |
| C1—H1B···I2a | 0.96 | 3.11 | 3.992 (9) | 153 |
| C1—H1C···I2ii | 0.96 | 2.96 | 3.908 (9) | 171 |
| C1—H1A···I1vi | 0.96 | 3.00 | 3.824 (10) | 145 |
| C5—H5···O1v | 0.93 | 2.59 | 3.328 (11) | 136 |
| C8—H8B···C11vi | 0.97 | 2.80 | 3.590 (15) | 140 |
| C8—H8B···C10vi | 0.97 | 2.76 | 3.694 (14) | 162 |

**Symmetry codes:** (ii) −x+1, −y+1, −z+1; (iii) x−1/2, −y+3/2, z−1/2; (iv) x−1/2, −y+1/2, z−1/2; (v) −x, −y+1, −z+1; (vi) −x+1/2, y−1/2, −z+3/2.
4-[(Benzylamino)carbonyl]-1-methylpyridinium triiodide (II)

Crystal data

$C_{14}H_{15}N_2O^+\cdot I_3^-$

$F(000) = 2242$

$D_r = 2.183$ Mg m$^{-3}$

Monoclinic, $P2_1/c$$

$\alpha = 9.914$ (2) Å

$\beta = 107.83$ (2)$^\circ$

$\theta = 3.1$–$18.1^\circ$

$\mu = 5.07$ mm$^{-1}$

$T = 293$ K

Cell parameters from 1078 reflections

$\theta = 3.1$–$18.1^\circ$

$\mu = 5.07$ mm$^{-1}$

$T = 293$ K

$0.03 \times 0.03 \times 0.02$ mm

Data collection

$X$-calibur, Sapphire3

diffractometer

Radiation source: Enhance (Mo) X-ray Source

Detector resolution: $16.1827$ pixels mm$^{-1}$

$\omega$ scans

Absorption correction: multi-scan

$\theta_{	ext{max}} = 25.0^\circ$, $\theta_{	ext{min}} = 3.0^\circ$

$T_{\text{min}} = 0.347$, $T_{\text{max}} = 1.000$

21040 measured reflections

6496 independent reflections

2548 reflections with $I > 2\sigma(I)$

$R_{	ext{int}} = 0.124$

$\theta = 3.1$–$18.1^\circ$

$\omega = 0.71073$ Å

$\lambda = 0.71073$ Å

Cell parameters from 1078 reflections

$\theta = 3.1$–$18.1^\circ$

$\mu = 5.07$ mm$^{-1}$

$T = 293$ K

$0.03 \times 0.03 \times 0.02$ mm

Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.065$

$wR(F^2) = 0.187$

$S = 0.97$

6496 reflections

371 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

$\Delta\rho_{\text{max}} = 0.70$ e Å$^{-3}$

$\Delta\rho_{\text{min}} = -0.77$ 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 ($\AA^2$)

|    | $x$    | $y$    | $z$    | $U_{	ext{eq}}$ | Occ. (<1) |
|----|--------|--------|--------|----------------|-----------|
| I1 | 0.45921 (12) | 0.79328 (4) | 0.65364 (9) | 0.0868 (4) |
| I2 | 0.46503 (14) | 0.71598 (5) | 0.78702 (11) | 0.1072 (4) |
| I3 | 0.45434 (15) | 0.87375 (4) | 0.50883 (10) | 0.1061 (5) |
| I4 | 0.000000 | 1.000000 | 0.500000 | 0.1048 (6) |
| I5 | −0.09620 (18) | 0.93095 (5) | 0.62111 (13) | 0.1313 (6) |
| I6 | −0.4785 (8) | 0.5112 (2) | 0.5262 (5) | 0.130 (2) | 0.5 |
| I7 | −0.3252 (7) | 0.5746 (2) | 0.6849 (5) | 0.1504 (17) | 0.5 |
| I7A | −0.3531 (7) | 0.5527 (2) | 0.6302 (5) | 0.1504 (17) | 0.5 |
| O1A | −0.1281 (11) | 0.6399 (4) | 0.3910 (8) | 0.092 (3) |
| N1A | 0.0042 (18) | 0.8083 (4) | 0.3781 (10) | 0.081 (4) |
### Supporting Information

| Atom | x    | y    | z    | Uiso |
|------|------|------|------|------|
| N2A  | 0.0997 (12) | 0.6306 (4) | 0.4111 (9) | 0.078 (4) |
| H2A  | 0.175586 | 0.643198 | 0.404694 | 0.094* |
| C1A  | 0.004 (2) | 0.8621 (5) | 0.3785 (13) | 0.110 (6) |
| H1AA | −0.091508 | 0.873532 | 0.349446 | 0.165* |
| H1AB | 0.039744 | 0.873527 | 0.445762 | 0.165* |
| H1AC | 0.062284 | 0.873811 | 0.340557 | 0.165* |
| C2A  | 0.1245 (19) | 0.7843 (6) | 0.4148 (13) | 0.096 (5) |
| H2AA | 0.209343 | 0.801051 | 0.438759 | 0.115* |
| C3A  | 0.1251 (16) | 0.7345 (6) | 0.4178 (12) | 0.088 (5) |
| H3A  | 0.210205 | 0.717786 | 0.440984 | 0.106* |
| C4A  | 0.0012 (16) | 0.7105 (6) | 0.3867 (12) | 0.079 (4) |
| C5A  | −0.1202 (19) | 0.7349 (6) | 0.3482 (12) | 0.089 (5) |
| H5A  | −0.205655 | 0.718459 | 0.324995 | 0.107* |
| C6A  | −0.1183 (19) | 0.7837 (7) | 0.3431 (13) | 0.095 (5) |
| H6A  | −0.202505 | 0.800379 | 0.315060 | 0.114* |
| C7A  | −0.0134 (16) | 0.6579 (6) | 0.3940 (11) | 0.079 (4) |
| C8A  | 0.1044 (17) | 0.5796 (5) | 0.4403 (13) | 0.092 (5) |
| H8AA | 0.181584 | 0.564057 | 0.423495 | 0.110* |
| H8AB | 0.016959 | 0.564255 | 0.401688 | 0.110* |
| C9A  | 0.1238 (18) | 0.5715 (5) | 0.5504 (12) | 0.074 (4) |
| C10A | 0.252 (2) | 0.5902 (6) | 0.6130 (16) | 0.097 (6) |
| H10A | 0.316106 | 0.605499 | 0.587126 | 0.117* |
| C11A | 0.279 (2) | 0.5848 (6) | 0.7157 (17) | 0.106 (6) |
| H11A | 0.360108 | 0.597669 | 0.760162 | 0.128* |
| C12A | 0.184 (2) | 0.5606 (7) | 0.7493 (16) | 0.106 (6) |
| H12A | 0.203600 | 0.554933 | 0.817130 | 0.127* |
| C13A | 0.060 (2) | 0.5444 (6) | 0.685 (2) | 0.107 (7) |
| H13A | −0.005324 | 0.529527 | 0.710907 | 0.128* |
| C14A | 0.027 (2) | 0.5491 (7) | 0.5838 (17) | 0.121 (7) |
| H14A | −0.057924 | 0.537576 | 0.540700 | 0.145* |
| O1B  | 0.3841 (10) | 0.6543 (4) | 0.4242 (8) | 0.086 (3) |
| N1B  | 0.4543 (16) | 0.5322 (5) | 0.1922 (12) | 0.088 (4) |
| N2B  | 0.6125 (12) | 0.6628 (4) | 0.4475 (8) | 0.076 (4) |
| H2B  | 0.684595 | 0.655003 | 0.429131 | 0.091* |
| C1B  | 0.4388 (19) | 0.4928 (6) | 0.1164 (14) | 0.108 (6) |
| H1BA | 0.530747 | 0.480708 | 0.119642 | 0.162* |
| H1BB | 0.382401 | 0.467282 | 0.130134 | 0.162* |
| H1BC | 0.393375 | 0.505462 | 0.051088 | 0.162* |
| C2B  | 0.581 (2) | 0.5433 (6) | 0.2527 (16) | 0.102 (6) |
| H2BA | 0.658994 | 0.525293 | 0.250589 | 0.123* |
| C3B  | 0.5997 (15) | 0.5805 (5) | 0.3180 (12) | 0.074 (4) |
| H3B  | 0.690985 | 0.589253 | 0.355599 | 0.088* |
| C4B  | 0.4836 (14) | 0.6059 (5) | 0.3296 (11) | 0.069 (4) |
| C5B  | 0.356 (2) | 0.5904 (6) | 0.2686 (12) | 0.089 (5) |
| H5B  | 0.273994 | 0.605203 | 0.272963 | 0.107* |
| C6B  | 0.3436 (18) | 0.5548 (6) | 0.2030 (12) | 0.090 (5) |
| H6B  | 0.253572 | 0.545749 | 0.163528 | 0.107* |
| C7B  | 0.4904 (17) | 0.6428 (5) | 0.4034 (11) | 0.071 (4) |
|      |      |      |      |      |      |      |
|------|------|------|------|------|------|------|
| C8B  | 0.6312 (18) | 0.6988 (5) | 0.5285 (12) | 0.085 (5) |      |      |
| H8BA | 0.569928 | 0.726128 | 0.502782 | 0.102* |      |      |
| H8BB | 0.601106 | 0.684595 | 0.581491 | 0.102* |      |      |
| C9B  | 0.7765 (16) | 0.7161 (6) | 0.5702 (11) | 0.072 (4) |      |      |
| C10B | 0.8890 (17) | 0.6853 (6) | 0.6049 (12) | 0.084 (4) |      |      |
| H10B | 0.872179 | 0.652312 | 0.601274 | 0.100* |      |      |
| C11B | 1.024 (2) | 0.7013 (7) | 0.6443 (13) | 0.097 (5) |      |      |
| H11B | 1.097443 | 0.679375 | 0.668821 | 0.116* |      |      |
| C12B | 1.0525 (19) | 0.7495 (8) | 0.6480 (11) | 0.094 (5) |      |      |
| H12B | 1.144660 | 0.760430 | 0.676679 | 0.112* |      |      |
| C13B | 0.946 (2) | 0.7812 (7) | 0.6098 (13) | 0.096 (5) |      |      |
| H13B | 0.966127 | 0.813824 | 0.608168 | 0.115* |      |      |
| C14B | 0.8040 (16) | 0.7646 (6) | 0.5720 (11) | 0.081 (5) |      |      |
| H14B | 0.730116 | 0.786363 | 0.548735 | 0.097* |      |      |

Atomic displacement parameters (Å²)

|      | U¹¹ | U¹² | U¹³ | U¹² | U¹³ | U¹³ |
|------|-----|-----|-----|-----|-----|-----|
| I1   | 0.0752 (7) | 0.0882 (8) | 0.0963 (8) | −0.0041 (6) | 0.0254 (6) | −0.0169 (6) |
| I2   | 0.0868 (9) | 0.0985 (9) | 0.1316 (11) | −0.0025 (7) | 0.0264 (8) | 0.0075 (8) |
| I3   | 0.1210 (11) | 0.0961 (9) | 0.0995 (9) | −0.0168 (8) | 0.0312 (8) | −0.0034 (7) |
| I4   | 0.0852 (12) | 0.0960 (13) | 0.1177 (14) | 0.0118 (10) | 0.0082 (10) | −0.0004 (10) |
| I5   | 0.1384 (14) | 0.1108 (11) | 0.1504 (14) | 0.0019 (10) | 0.0526 (12) | 0.0023 (9) |
| I6   | 0.099 (4) | 0.131 (5) | 0.180 (7) | 0.027 (3) | 0.072 (5) | 0.077 (4) |
| I7   | 0.117 (3) | 0.148 (4) | 0.200 (6) | −0.001 (3) | 0.069 (4) | 0.048 (3) |
| I7A  | 0.117 (3) | 0.148 (4) | 0.200 (6) | −0.001 (3) | 0.069 (4) | 0.048 (3) |
| O1A  | 0.068 (7) | 0.091 (8) | 0.123 (10) | −0.009 (6) | 0.039 (7) | −0.023 (6) |
| N1A  | 0.106 (11) | 0.062 (8) | 0.085 (9) | 0.004 (8) | 0.043 (9) | 0.012 (7) |
| N2A  | 0.048 (7) | 0.080 (9) | 0.105 (10) | −0.015 (7) | 0.022 (7) | −0.018 (7) |
| C1A  | 0.137 (18) | 0.073 (11) | 0.116 (15) | −0.004 (11) | 0.031 (13) | 0.013 (10) |
| C2A  | 0.071 (12) | 0.091 (13) | 0.124 (15) | −0.013 (10) | 0.029 (11) | 0.002 (11) |
| C3A  | 0.058 (10) | 0.079 (11) | 0.115 (14) | −0.002 (9) | 0.008 (9) | 0.013 (9) |
| C4A  | 0.048 (9) | 0.093 (12) | 0.086 (11) | −0.011 (9) | 0.005 (8) | −0.001 (9) |
| C5A  | 0.085 (13) | 0.089 (13) | 0.087 (12) | −0.024 (11) | 0.018 (10) | −0.002 (9) |
| C6A  | 0.069 (11) | 0.121 (16) | 0.098 (13) | 0.017 (12) | 0.031 (10) | 0.017 (11) |
| C7A  | 0.050 (9) | 0.110 (14) | 0.076 (11) | −0.004 (10) | 0.021 (8) | −0.010 (9) |
| C8A  | 0.078 (12) | 0.075 (11) | 0.125 (16) | −0.011 (9) | 0.035 (11) | −0.017 (10) |
| C9A  | 0.080 (11) | 0.064 (10) | 0.067 (11) | −0.006 (8) | 0.009 (9) | −0.018 (8) |
| C10A | 0.108 (15) | 0.081 (12) | 0.122 (16) | −0.001 (11) | 0.063 (14) | −0.017 (11) |
| C11A | 0.087 (14) | 0.105 (15) | 0.125 (18) | −0.001 (11) | 0.029 (13) | −0.021 (12) |
| C12A | 0.094 (15) | 0.113 (16) | 0.112 (16) | 0.024 (13) | 0.034 (14) | 0.002 (12) |
| C13A | 0.114 (17) | 0.074 (12) | 0.16 (2) | 0.003 (12) | 0.084 (17) | 0.024 (13) |
| C14A | 0.125 (18) | 0.140 (18) | 0.120 (19) | −0.011 (15) | 0.072 (16) | −0.011 (14) |
| O1B  | 0.058 (7) | 0.107 (8) | 0.098 (8) | −0.007 (6) | 0.029 (6) | −0.016 (6) |
| N1B  | 0.087 (10) | 0.073 (9) | 0.120 (12) | 0.009 (8) | 0.058 (10) | −0.002 (8) |
| N2B  | 0.042 (7) | 0.105 (10) | 0.078 (9) | −0.011 (7) | 0.014 (6) | −0.018 (7) |
| C1B  | 0.105 (15) | 0.101 (13) | 0.120 (15) | −0.017 (11) | 0.036 (13) | −0.017 (12) |
| C2B  | 0.075 (13) | 0.060 (11) | 0.18 (2) | −0.006 (10) | 0.048 (14) | 0.007 (12) |
### Geometric parameters (Å, °)

| Bond/Symmetry   | Distance (Å) |  Angle (°) |
|-----------------|--------------|------------|
| I1—I2           | 2.8459 (18)  | 93.00      |
| I1—I3           | 3.0206 (17)  | 137.00     |
| I4—I5           | 2.9181 (15)  | 93.00      |
| I4—I5\textsuperscript{i} | 2.9181 (15)  | 93.00      |
| I6—I6\textsuperscript{ii} | 0.962 (9)    | 122.00     |
| I6—I7A          | 1.977 (7)    | 131.3 (18) |
| I6—I7           | 2.890 (7)    | 132.00     |
| I6—I7A\textsuperscript{a} | 2.925 (7)    | 1504.00    |
| I7—I7A          | 0.957 (7)    | 1305.00    |
| O1A—C7A         | 1.231 (16)   | 1488.00    |
| N1A—C2A         | 1.327 (19)   | 860.00     |
| N1A—C6A         | 1.35 (2)     | 960.00     |
| N1A—C1A         | 1.495 (17)   | 960.00     |
| N2A—C7A         | 1.315 (17)   | 960.00     |
| N2A—C8A         | 1.472 (17)   | 36.00      |
| N2A—H2A         | 0.8600       | 930.00     |
| C1A—H1AA        | 0.9600       | 1403.00    |
| C1A—H1AB        | 0.9600       | 930.00     |
| C1A—H1AC        | 0.9600       | 136.00     |
| C2A—C3A         | 1.39 (2)     | 1447.00    |
| C2A—H2AA        | 0.9300       | 1335.00    |
| C3A—C4A         | 1.348 (19)   | 930.00     |
| C3A—H3A         | 0.9300       | 930.00     |
| C4A—C5A         | 1.34 (2)     | 146.00     |
| C4A—C7A         | 1.48 (2)     | 970.00     |
| C5A—C6A         | 1.36 (2)     | 970.00     |
| C5A—H5A         | 0.9300       | 1372.00    |
| C6A—H6A         | 0.9300       | 1374.00    |
| C8A—C9A         | 1.52 (2)     | 136.00     |
| C8A—H8AA        | 0.9700       | 930.00     |
| C8A—H8AB        | 0.9700       | 137.00     |
| C9A—C14A        | 1.35 (2)     | 930.00     |
| C9A—C10A        | 1.40 (2)     | 135.00     |

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**Supported by information**

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**Acta Cryst. (2021). E77, 1219-1223 sup-8**
C10A—C11A 1.40 (2)  C12B—H12B 0.9300
C10A—H10A 0.9300  C13B—C14B 1.42 (2)
C11A—C12A 1.35 (2)  C13B—H13B 0.9300
C11A—H11A 0.9300  C14B—H14B 0.9300
C12A—C13A 1.36 (3)

I2—I1—I3 178.72 (5)  C12A—C13A—C14A 122.8 (18)
I5—I4—I5i 180.0  C12A—C13A—H13A 118.6
I6i—I6—I7A 168.1 (11)  C14A—C13A—H13A 118.6
I6i—I6—I7 174.9 (11)  C9A—C14A—C13A 116 (2)
I7A—I6—I7 6.9 (3)  C9A—C14A—H14A 121.9
I6i—I6—I7Ai 8.0 (8)  C13A—C14A—H14A 121.9
I7A—I6—I7Ai 176.1 (4)  C6B—N1B—C2B 118.4 (15)
I7—I6—I7Ai 176.9 (4)  C6B—N1B—C1B 121.6 (16)
I7A—I7—I6 14.4 (7)  C2B—N1B—C1B 120.0 (15)
I7—I7A—I6 158.7 (10)  C2B—N1B—C1B 120.0 (15)
I7—I7A—I6i 162.5 (9)  C7B—N2B—H2B 118.9
I6—I7A—I6i 3.9 (4)  C8B—N2B—H2B 118.9
C2A—N1A—C6A 119.2 (14)  N1B—C1B—H1BA 109.5
C2A—N1A—C1A 120.4 (16)  N1B—C1B—H1BB 109.5
C6A—N1A—C1A 120.3 (16)  H1BA—C1B—H1BB 109.5
C7A—N2A—C8A 124.0 (13)  N1B—C1B—H1BC 109.5
C7A—N2A—H2A 118.0  H1BA—C1B—H1BC 109.5
C8A—N2A—H2A 118.0  H1BB—C1B—H1BC 109.5
N1A—C1A—H1AA 109.5  N1B—C2B—C3B 121.5 (16)
N1A—C1A—H1AB 109.5  N1B—C2B—H2BA 119.3
H1AA—C1A—H1AB 109.5  C3B—C2B—H2BA 119.3
N1A—C1A—H1AC 109.5  C2B—C3B—C4B 121.0 (15)
H1AA—C1A—H1AC 109.5  C2B—C3B—H3B 119.5
H1AB—C1A—H1AC 109.5  C4B—C3B—H3B 119.5
N1A—C2A—C3A 120.7 (16)  C5B—C4B—C3B 113.7 (14)
N1A—C2A—H2AA 109.5  C4B—C3B—H3B 119.5
C3A—C2A—H2AA 119.6  C5B—C4B—C7B 120.6 (14)
C4A—C3A—C2A 119.3 (16)  C3B—C4B—C7B 125.5 (14)
C4A—C3A—H3A 120.3  C6B—C5B—C4B 122.9 (16)
C2A—C3A—H3A 120.3  C6B—C5B—H5B 118.5
C5A—C4A—C3A 119.7 (16)  C4B—C5B—H5B 118.5
C5A—C4A—C7A 115.8 (14)  N1B—C6B—C5B 122.2 (17)
C3A—C4A—C7A 124.5 (15)  N1B—C6B—H6B 118.9
C4A—C5A—C6A 120.1 (17)  C5B—C6B—H6B 118.9
C4A—C5A—H5A 120.0  O1B—C7B—N2B 121.1 (14)
C6A—C5A—H5A 120.0  O1B—C7B—C4B 120.4 (15)
N1A—C6A—C5A 120.8 (17)  N2B—C7B—C4B 118.6 (13)
N1A—C6A—H6A 119.6  C9B—C8B—N2B 113.9 (13)
C5A—C6A—H6A 119.6  C9B—C8B—H8BA 108.8
O1A—C7A—N2A 119.8 (16)  N2B—C8B—H8BA 108.8
O1A—C7A—C4A 120.7 (14)  N2B—C8B—H8BB 108.8
N2A—C7A—C4A 119.3 (14)  H8BA—C8B—H8BB 107.7
| Bond                  | Angle (deg)    | Bond                  | Angle (deg)    |
|----------------------|----------------|----------------------|----------------|
| N2A—C8A—C9A         | 114.4 (12)     | C10B—C9B—C14B       | 118.1 (15)     |
| N2A—C8A—H8AA        | 108.7          | C10B—C9B—C8B        | 122.2 (15)     |
| C9A—C8A—H8AA        | 108.7          | C14B—C9B—C8B        | 119.6 (15)     |
| N2A—C8A—H8AB        | 108.7          | C11B—C10B—C9B       | 122.2 (17)     |
| C9A—C8A—H8AB        | 107.6          | C9B—C10B—H10B       | 118.9          |
| H8AA—C8A—H8AB       | 121.3          | C13B—C12B—C11B      | 120.1          |
| C14A—C9A—C10A       | 123.7 (18)     | C10B—C11B—C12B      | 120.2 (18)     |
| C14A—C9A—C8A        | 123.0 (17)     | C10B—C11B—H11B      | 119.9          |
| C10A—C9A—C8A        | 113.2 (16)     | C12B—C11B—H11B      | 119.9          |
| C11A—C10A—C9A       | 117.4 (17)     | C12B—C13B—C14B      | 119.9 (17)     |
| C11A—C10A—H10A      | 121.3          | C12B—C13B—H13B      | 120.1          |
| C9A—C10A—H10A       | 121.3          | C14B—C13B—H13B      | 120.1          |
| C12A—C11A—C10A      | 119.2          | C12B—C13B—C14B      | 119.9 (17)     |
| C12A—C11A—H11A      | 120.5          | C12B—C13B—H13B      | 120.1          |
| C10A—C11A—H11A      | 120.5          | C14B—C13B—H13B      | 120.1          |
| C11A—C12A—C13A      | 121 (2)        | C9B—C14B—C13B       | 119.6 (16)     |
| C11A—C12A—H12A      | 119.6          | C9B—C14B—H14B       | 120.2          |
| C13A—C12A—H12A      | 119.6          | C13B—C14B—H14B      | 120.2          |

I6—I7—I7A—I6ii: -2.0 (11)

| Bond                  | Angle (deg)    | Bond                  | Angle (deg)    |
|----------------------|----------------|----------------------|----------------|
| I6—I7—I7A—I6ii      | -2.0 (11)      | C6B—N1B—C2B—C3B     | -7 (3)         |
| C6A—N1A—C2A—C3A     | 0 (2)          | C1B—N1B—C2B—C3B     | 176.0 (14)     |
| C1A—N1A—C2A—C3A     | 177.8 (15)     | N1B—C2B—C3B—C4B     | 6 (3)          |
| N1A—C2A—C3A—C4A     | -3 (3)         | C2B—C3B—C4B—C5B     | -2 (2)         |
| C2A—C3A—C4A—C5A     | 4 (3)          | C2B—C3B—C4B—C7B     | 173.6 (15)     |
| C2A—C3A—C4A—C7A     | -174.6 (15)    | C3B—C4B—C5B—C6B     | -1 (2)         |
| C3A—C4A—C5A—C6A     | -2 (3)         | C7B—C4B—C5B—C6B     | -176.4 (14)    |
| C7A—C4A—C5A—C6A     | 176.7 (14)     | C2B—N1B—C6B—C5B     | 4 (3)          |
| C2A—N1A—C6A—C5A     | 2 (2)          | C1B—N1B—C6B—C5B     | -178.7 (15)    |
| C1A—N1A—C6A—C5A     | -175.8 (14)    | C4B—C5B—C6B—N1B     | 0 (3)          |
| C4A—C5A—C6A—N1A     | -1 (2)         | C8B—N2B—C7B—O1B     | 3 (2)          |
| C8A—N2A—C7A—O1A     | -8 (2)         | C8B—N2B—C7B—C4B     | -176.2 (13)    |
| C8A—N2A—C7A—C4A     | 166.8 (14)     | C5B—C4B—C7B—O1B     | 13 (2)         |
| C5A—C4A—C7A—O1A     | -19 (2)        | C3B—C4B—C7B—O1B     | -161.8 (15)    |
| C3A—C4A—C7A—O1A     | 159.5 (17)     | C5B—C4B—C7B—N2B     | -167.7 (14)    |
| C5A—C4A—C7A—N2A     | 166.0 (15)     | C3B—C4B—C7B—N2B     | 18 (2)         |
| C3A—C4A—C7A—N2A     | -16 (2)        | C7B—N2B—C8B—C9B     | 178.3 (14)     |
| C7A—N2A—C8A—C9A     | -81 (2)        | N2B—C8B—C9B—C10B    | -53 (2)        |
| N2A—C8A—C9A—C14A    | 117.5 (17)     | N2B—C8B—C9B—C14B    | 124.6 (15)     |
| N2A—C8A—C9A—C10A    | -61.6 (18)     | C14B—C9B—C10B—C11B  | 3 (2)          |
| C14A—C9A—C10A—C11A  | 0 (3)          | C8B—C9B—C10B—C11B   | -179.5 (15)    |
| C8A—C9A—C10A—C11A   | 179.4 (14)     | C9B—C10B—C11B—C12B  | -2 (3)         |
| C9A—C10A—C11A—C12A  | 2 (3)          | C10B—C11B—C12B—C13B | -2 (3)         |
| C10A—C11A—C12A—C13A | -4 (3)         | C11B—C12B—C13B—C14B | 4 (2)          |
| C11A—C12A—C13A—C14A | 4 (3)          | C10B—C9B—C14B—C13B  | 0 (2)          |
| C10A—C9A—C14A—C13A  | -1 (3)         | C8B—C9B—C14B—C13B   | -178.0 (14)    |
C8A—C9A—C14A—C13A 179.8 (15)  C12B—C13B—C14B—C9B 3 (2)
C12A—C13A—C14A—C9A −1 (3)

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

Hydrogen-bond geometry (Å, °)

| D—H···A     | D—H | H···A | D···A  | D—H···A |
|-------------|------|-------|--------|---------|
| N2A—H2A···O1B | 0.86 | 2.02  | 2.846 (14) | 160 |
| C3A—H3A···O1B | 0.93 | 2.53  | 3.381 (18) | 152 |
| C2A—H2A···I3  | 0.93 | 3.08  | 3.998 (17) | 169 |
| C1A···C12A  | 0.96 | 2.72  | 3.62 (2)  | 158 |
| C1A···C12A  | 0.96 | 3.09  | 3.966 (19) | 153 |
| N2A···O1A  | 0.86 | 2.13  | 2.986 (14) | 176 |
| C3B···O1A  | 0.93 | 2.21  | 3.060 (17) | 151 |
| C2B···C12A  | 0.93 | 2.85  | 3.72 (2)  | 156 |
| C1B···I7B  | 0.96 | 3.07  | 3.819 (18) | 136 |
| C6B···I4B  | 0.93 | 3.12  | 4.019 (17) | 164 |

Symmetry codes: (iii) x, −y+3/2, z-1/2; (iv) x+1, y, z; (v) −x+1, −y+1, −z+1; (vi) −x, −y+1, −z+1; (vii) −x, −y+1/2, −z+1/2.