Crystal Structure of 1-Butyl-3-methylimidazolium Iodide

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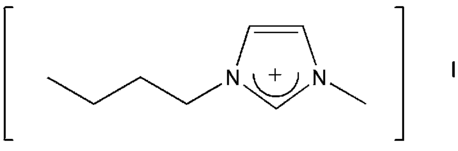
A crystal of 1-butyl-3-methylimidazolium iodide [bmim]I, a prototype ionic liquid, has been prepared and its crystal structure has been determined at the space group $P2_12_12_1$. The butyl-chain has *gauche* and *trans* configurations, and only one H atom of cation is linked to the iodide anion through a hydrogen bond. The weak hydrogen-bonded network involving the iodide anion is a characteristic feature of [bmim]I, which could be related to the observation that crystallization was accomplished under 233 K.

Ionic liquids are a new class of liquids with low melting points in spite of that they are solely composed of ions. The potential of ionic liquids to use as nonvolatile solvents for green chemistry and liquid electrolytes is of broad interest. The 1-butyl-3-methylimidazolium ($[\text{bmim}]^+$) cation is a prototype organic cation which is suitable to prepare a variety of ionic liquids when combined with different anions. Considering the characteristic properties of the $[\text{bmim}]^+$ cation, its structure determination is quite valuable to characterize ionic liquids. In the past studies, the crystal structures of polymorphs of 1-butyl-3-methylimidazolium chloride, [bmim]Cl,[1–3] and 1-butyl-3-methylimidazolium bromide, [bmim]Br[1,4,5] were determined. Since the crystallization of another [bmim] halide, [bmim]I (Scheme 1), had not been successful for several years, it was considered to be extremely hard. In the present study, crystallization was successfully accomplished in acetonitrile under 233 K.[6] The melting points of the chloride and bromide crystals were more than 313 K, whereas that of the [bmim]I crystal was estimated to be 270 K. The significantly low melting point is a distinctive property of the [bmim]I crystal, which is expected to reflect characteristic structural features. In this context, the crystal structure of 1-butyl-3-methylimidazolium iodide, [bmim]I, is presented here.

Two polymorphs, orthorhombic and monoclinic forms, were obtained in the [bmim]Cl crystals. Space group were $Pna2_1$ in the orthorhombic form and $P2_1/c$ and $P2_1/n$ in the monoclinic forms. Only an orthorhombic form (space group $Pna2_1$) was obtained in the [bmim]Br crystal. Although an orthorhombic form was also obtained in the [bmim]I crystal, its space group was $P2_12_12_1$.[7] The larger ionic radius of the iodide anion could have differentiated the space group.



Scheme 1. 1-Butyl-3-methylimidazolium iodide, [bmim]I.

In all crystal structures of 1-butyl-3-methylimidazolium halides, the butyl-chain is commonly twisted out of the plane of the imidazolium ring at the position of C5 (Figures 1 and 2), and the N1–C5–C6 bond angles are distributed in the narrow range 110–113°. The conformational feature of the cation that differentiates the crystal structures of 1-butyl-3-methylimidazolium halides is the torsion angles around C5–C6 in the butyl-chains. A comparison of the butyl-chain configurations is shown in Figure 2. In the [bmim]Cl crystals, the butyl-chain has both *trans* and *gauche* conformations around the C5–C6 bond and only *trans* conformation around the C6–C7 bond (abbreviated as *TT* and *GT*, respectively), whereas those in the [bmim]Br crystals have only *GT* conformations. In the [bmim]I crystal, the butyl-chain has *GT* conformation. The tendency of the torsion angle variation in the butyl-chain of $[\text{bmim}]^+$ cations based on the CCDC database implies that the butyl-chain is prone to be less flexible owing to the increase of ionic radii of anions. Currently, different crystalline polymorphs have not been obtained for [bmim]I, suggesting that the potential energy surface for [bmim]I contains one local conformational energy minimum.

The imidazolium ring is a planar pentagon, and the N1–C1 and C1–N2 bond lengths are 1.335(3) Å and the C2–C3 bond length is 1.367(3) Å, indicating the conjugated double-bond nature. The N1–C3 and N2–C2 bond lengths are 1.376(3) and 1.373(3) Å, respectively, which are shorter than that of a pure C–N single bond. It suggests that π electrons are broadly distributed in the imidazolium ring as previously described in the crystal structure of [bmim]Cl.[2] In the crystal structure of [bmim]Cl

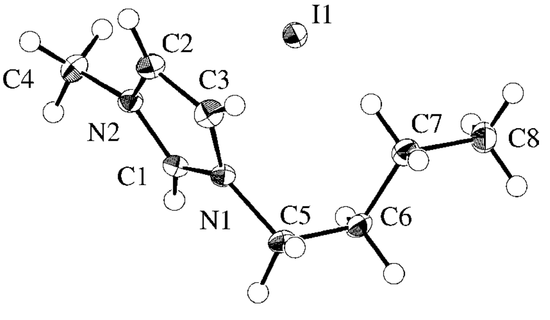


Figure 1. Molecular structure of [bmim]I along with the labeling atoms. Thermal ellipsoids of non-H atoms are drawn at the 50% probability level.

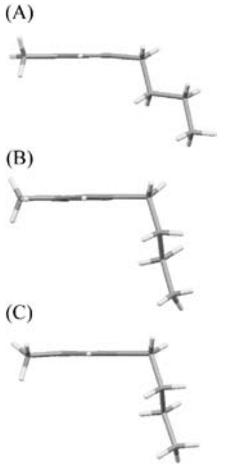


Figure 2. A comparison of the butyl-chain configurations of cations in the crystal structures of (A) [bmim]Cl (refcode TAJCUD02), (B) [bmim]Br (refcode TAJDAK01) and (C) [bmim]I as viewed on the side of the imidazolium ring.

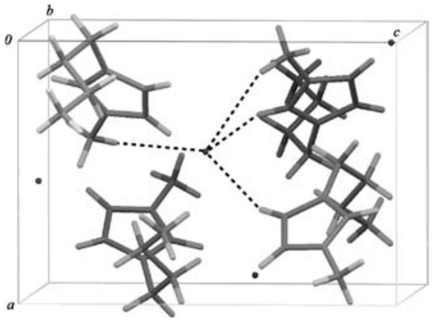


Figure 3. Part of the crystal structure of [bmim]I, showing the close contacts between H atoms of cations and the iodide anions. Only one iodide anion is shown for clarity.

(*TT* conformation) (refcode TAJCUD02[2]), the C1 proton and two C5 methylene protons are in the distance of hydrogen bond with the chloride anion. In the crystal structure of [bmim]Br (*GT* conformation) (refcode TAJDAK01[4]), the C1 proton and two C5 methylene protons are also in the distance of hydrogen bond with the bromide anion. In the crystal structure of [bmim]I (*GT* conformation), the C1 proton is the only candidate to form a hydrogen bond with the iodide anion in the aforesaid protons (Figure 3). Although the C–H···I angle is 132°, which is insufficient to form a hydrogen-bond, the distance between the C1 proton and the iodide anion is 2.979 Å. One of the reasons that that crystallization of [bmim]I was accomplished at the strikingly low temperature could be the weak or no hydrogen bonds of the C1 proton and C5 methylene protons with the iodide anion. Unexpectedly, the C3 proton can form a hydrogen bond with the iodide anion. The distance between the C3 proton and the iodide anion is 3.050 Å and the C–H···I angle is 156.48°.

The present study was supported by the Grant-in-Aid for Scientific Research (No. 17073002 for K. N. and No. 18045006 for M. N. and H. S.) in Priority Area "Science of Ionic Liquids" (Area Number: 452) and No. 18550082 (for M. T.) from Ministry of Education, Culture, Sports, Science and Technology.

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6 A solution of [bmim]I (18 g) in acetonitrile (2 mL) was cooled under 233 K for 24 h. The crystal was isolated by filtration under 253 K, washed with ethyl acetate (10 mL), dried in vacuum for 10 h at 203 K and recrystallized in acetonitrile under 233 K for 24 h (yield 64%, mp 270 K). Analysis, required for $C_8H_{15}N_2I\cdot 1/3H_2O$: C, 35.30; H, 5.80; N, 10.29%; Found: C, 35.40; H, 6.03; N, 10.59%.

7 A colorless block crystal having approximate dimensions of $0.35 \times 0.30 \times 0.25\,\text{mm}^3$ was mounted on dry ice in a loop. All measurements were carried out using a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71075$ Å) at 93 K. Formulae: $C_8H_{15}N_2I$. fw = 266.12. Orthorhombic system, space group: $P2_12_12_1$ with $a = 8.2806(3)$ Å, $b = 10.7885(3)$ Å, $c = 11.9985(4)$ Å. $V = 1071.89(6)\,\text{Å}^3$, $Z = 4$, $D_\text{calcd} = 1.649\,\text{g/cm}^3$. 3117 unique reflections with $R_\text{int} = 0.065$, 3044 reflections with $I > 2\sigma(I)$, $R(F_o)/R_W(F_o) = 0.0258/0.0266$. Data collection: RAPID-AUTO, cell refinement and data reduction: Crystal Structure 3.7.0, program(s) used to solve structure: SHELX97, program(s) used to refine structure: SHELX97, molecular graphics: Mercury 1.4.1. CCDC deposite number: 621179.

8 Supporting information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) November 11, 2006; doi:10.1246/cl.2006.1400