Crystal Structure of 1-Butyl-3-methylimidazolium Chloride. A Clue to the Elucidation of the Ionic Liquid Structure[1]

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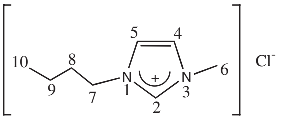
A single crystal of 1-butyl-3-methylimidazolium chloride [bmim]Cl, a prototype ionic liquid, has successfully been prepared and an X-ray crystallographic analysis has been performed. It reveals the presence of a hydrogen bonding network involving the chloride anion and the ring as well as the *n*-butyl hydrogen atoms, a strong hydrophobic interaction between the two *n*-butyl groups of the [bmim] cations, and a unique corrugated sheets structure of the imidazolium rings. Considering the similarity of the Raman spectra of crystalline and liquid states, we suspect that the three dimensional structure determined in the present study also exist, at least partially, in the ionic liquid state.

Ionic liquids (ILs) have been attracting much attention of chemists owing to their many interesting and useful characteristics.[2–4] Nevertheless, only little has so far been known for their crystal and liquid structures.[5–8] In a previous paper, we reported on the crystal polymorphism of a prototype IL, 1-butyl-3-methylimidazolium chloride, [bmim]Cl (Scheme 1).[9] Two different types of crystals, Crystal (1) and Crystal (2), were found and shown to have distinct X-ray powder patterns and Raman spectra. In addition, it was suggested from the Raman spectra of the crystalline as well as the liquid state that two distinct structures of the $[bmim]^+$ ion, one corresponding to that in Crystal (1) and the other to that in Crystal (2), coexist in the liquid state. The $[bmim]^+$ ion generates a variety of ILs having distinctly different properties when combined with different anions. Hence it is important to know the details of the structure of the $[bmim]^+$ ion in the liquid state as well as in the crystalline state.



Scheme 1. 1-butyl-3-methylimidazolium chloride, [bmim]Cl.

[bmim]Cl was synthesized following the general procedure.[10] White rectangular-shaped crystals, suitable for single crystal X-ray crystallographic study, were obtained from dry acetonitrile. The X-ray diffraction experiment was carried out by using a Rigaku/MSC Mercury CCD system with graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) at 293 K.

[bmim]Cl Crystal (1) crystallizes in monoclinic space group $P2_1/n$ with $a = 9.982(10)$, $b = 11.590(12)$, $c = 10.077(11)$ Å, $\beta = 121.80(2)°$, $V = 990.8(18)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.17$ g/cm^3.[11] The asymmetric unit consists of one $[bmim]^+$ and one Cl^- while the unit cell contains four of each.

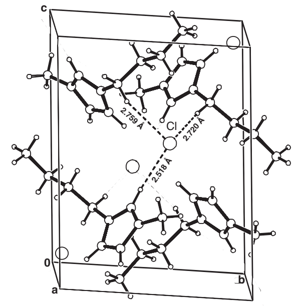


Figure 1. A view of [bmim]Cl Crystal (1). Only one chloride anion is shown hydrogen bonded to three different imidazolium cations for clarity.

The solved crystal structure has revealed several interesting features of [bmim]Cl Crystal (1) (Figure 1). The imidazolium ring is a planar pentagon. The average bond length of 1.32 Å for the N1–C2 and C2–N3 bonds indicates the conjugated double-bond nature of these two bonds. The C4–C5 bond length of 1.34 Å also indicates the same as expected. Furthermore, the average bond length of the N1–C5 and N3–C4 bonds is 1.37 Å and is considerably shorter than that of a pure C–N single bond (typically 1.47 Å). It seems that the π electrons are highly delocalized in the imidazolium ring. The carbon atom of the methyl group attached to N3 is on the plane of the imidazolium ring. The C7 carbon, which is the jointing carbon of the *n*-butyl group, has a little deviation (about $\approx 1.8°$) from the imidazolium ring plane. The other carbon atoms in the *n*-butyl group are considerably out of plane and they all take the *trans* configuration. Because of the all-*trans* configuration, two cations can interact through the hydrophobic interaction between the *n*-butyl groups.

The chloride anion is away from the methyl group and rather close to the hydrophobic region produced by the *n*-butyl groups. Of the three protons of the imidazolium ring, *only* the C2 proton is within the distance of hydrogen bonding with the chloride anion. The observed H–Cl^- distance is 2.52 Å (C–H–Cl^- angle 157.5°), while typical hydrogen-bonded H–Cl^- distance is less than 3.0 Å.[12] This finding is in contrast to the cases of the 1-ethyl-3-methylimidazolium salts, [emim]Cl, in which all of the three protons of the imidazolium ring are hydrogen-bonded with the chloride ion.[7] There are other two hydrogen bonds involving the chloride anion. Two C7 methylene protons of two different cation moieties are in the distance of hydrogen bonding (2.72 Å (168.0°) and 2.76 Å (147.6°)). Hence, each chloride anion is hydrogen-bonded to three different imidazolium cations and vice versa.

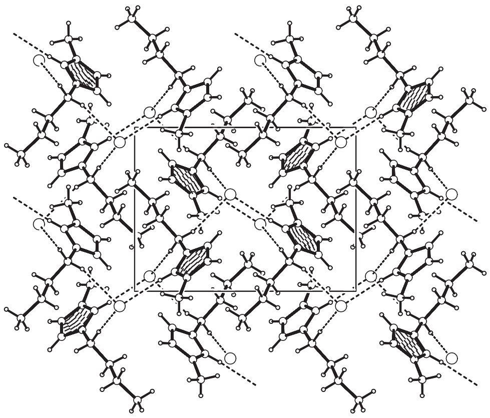


Figure 2. A view of the molecular arrangement in [bmim]Cl Crystal (1) showing the hydrogen bonding interaction between the chloride anion and $[bmim]^+$ cation.

The molecular arrangements in [bmim]Cl Crystal (1) is quite interesting (Figure 2). There are two corrugated sheets of imidazolium rings in Crystal (1) as marked differently in Figure 2. The angle between the two imidazolium rings belonging to the two different sheets is 69.49°. There is no indication of any π–π stacking interaction among imidazolium rings, contrary to what was found for $[emim]CF_3SO_3$.[8] The out of plane all *trans* configuration of the *n*-butyl group is probably the reason for the large separation distance between the two imidazolium rings. It is interesting to observe that two *n*-butyl groups are closely associated with each other, creating a hydrophobic region. The methyl group attached to the imidazolium ring seems to have no dominant role in the crystal structure.

Figure 3 gives another view of the molecular arrangements, which shows the channels in which chloride anions are accommodated as chains. The distance between the two chloride anions is 4.84 Å and is too long to assume any specific interaction between them.

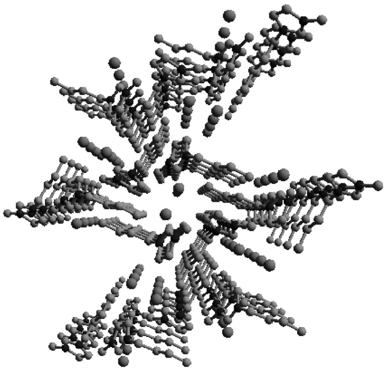


Figure 3. A view of molecular arrangements of [bmim]Cl Crystal (1) showing the channels in which chloride anions are accommodated. Hydrogen bonds are not shown for clarity.

It seems that the crystal structure of [bmim]Cl Crystal (1) results from a delicate balance of three interactions: The electrostatic interactions among the cations and the anions, the hydrogen-bonding interactions among the chloride anions and the ring as well as the *n*-butyl hydrogens, and the hydrophobic interaction between the two *n*-butyl groups of the [bmim] cations. As we have already shown in a previous paper,[9] the Raman spectrum of liquid [bmim]Cl consists of two groups of Raman bands characteristic of Crystals (1) and (2), indicating that the imidazolium structure that we determined here for Crystal (1) also exists in the liquid state. Furthermore, from the unusually long equilibration time observed for liquid [bmim]Cl, we suggested that some local three-dimensional structures exist in the ionic liquid state. Combining these results, we conjecture that the three dominant interactions that determine the crystal structure of [bmim]Cl Crystals (1) are also effective in the liquid state and that the structure determined in the present study exists, at least partially, in the ionic liquid state. Ionic liquids seem to be unique in that they have definite local structures despite their homogeneous appearance.

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References and Notes

1 After the present manuscript was submitted for publication, we came to know that the same structure was independently obtained by J. D. Holbrey et al., (Chem. Commun., in press). The authors thank Professor K. R. Seddon for informing us of their results prior to publication.

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10 Synthesis and crystal preparation: Under dry N_2 atmosphere, redistilled *N*-methylimidazole and 1-chlorobutane (1:1.3 mole ratio) were mixed in dry acetonitrile at room temperature followed by gentle reflux (ca. 75 °C) for 36 h. After cooling to room temperature, volatile material was removed at reduced pressure. The resultant dry white solid was redissolved in minimum quantity of dry acetonitrile and kept at ca. 10 °C for 4 days. Needle shaped white crystals were obtained on solid white mass. Liquid portion was decanted out and the crystals were carefully separated from the white mass. They were identified as Crystal (2) by Raman spectroscopy. (Although we were able to obtain apparently good single crystals of Crystal (2), our repeated efforts to get reasonable X-ray data failed mainly because of inherent unstable nature of Crystal (2). We are continuing our efforts to obtain X-ray data for Crystal (2)). The mother liquor was again kept with a very small seed crystal without any disturbance at ca. 20 °C for 2 days. White rectangular shaped clear crystals were formed. These crystals were identified as Crystal (1). It is important to mention at this point that if we try to dry these crystals completely by high vacuum, they lose their crystalline nature. All operations, including cutting to an appropriate size, mounting of a single crystal into 0.5 mm capillary, were done in an N_2 filled glove box. At no point of the experiment, either solution or crystal was allowed to expose to air or moisture.

11 Crystallographic data: A crystal with a dimension of $0.30 \times 0.20 \times 0.10$ mm was mounted in a glass capillary sealed with N_2. Formulae: $C_8H_{15}ClN_2$, fw: 174.67. 2234 Unique reflections with $R_{int} = 0.032$, 1394 observed reflections with $I > 3.00\ \sigma(I)$, $R(F_0)/R_w(F_0) = 0.044/0.051$. The structure was solved by direct methods (SIR97) and refined by a full-matrix least squares treatment. The nonhydrogen atoms were refined anisotropically. CCDC 213959.

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