Rotational Isomerism and Structure of the 1-Butyl-3-methylimidazolium Cation in the Ionic Liquid State

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The crystal structures of 1-butyl-3-methylimidazolium chloride [bmim]Cl and 1-butyl-3-methylimidazolium bromide [bmim]Br show that two rotational isomers, the *TT* form and the *GT* form, of the $[bmim]^+$ cation exist in the crystalline state. A vibrational analysis based on a DFT calculation indicates that two characterstic Raman bands of crystalline [bmim]Cl and three of crystalline [bmim]Br can be used as marker bands of the rotational isomerism around the C_7–C_8 bond of the *n*-butyl group. The Raman spectra of liquid $[bmim]BF_4$, in which both sets of marker bands are simultaneously observed, then prove that at least two rotational isomers of the $[bmim]^+$ cation coexist in the ionic liquid state.

Ionic liquids, a new class of liquids that are solely composed of ions, are stimulating much interest among chemists.[1–3] Recent discovery of the crystal polymorphism of a prototype ionic liquid [bmim]Cl[4] and subsequent crystal-structure determination of [bmim]Cl[5,6] and [bmim]Br[5,7] have provided a new firm basis for examining the ionic liquid structures in terms of the corresponding crystal structures. The existence of the two polymorphs of [bmim]Cl, Crystal (1) (mp 41 °C)[5] and Crystal (2) (mp 66 °C),[5] was first reported by us on the basis of their distinct X-ray powder patterns and Raman spectra.[4] Subsequently, the crystal structures of [bmim]Cl Crystal (1) and [bmim]Br (mp >70 °C) at room temperature were determined.[6,7] Just after our first paper was published, Holbrey et al. reported the crystal structures of the two polymorphs of [bmim]Cl and that of [bmim]Br at −100 °C and showed that the structure of the $[bmim]^+$ cation in [bmim]Cl Crystal (2) is essentially the same as that in [bmim]Br.[5] The crystal structures determined independently at different temperatures agree excellently with each other.

The $[bmim]^+$ cation is a prototype organic cation that generates a variety of ionic liquids when combined with different anions. Therefore, structure determination of the cation both in the crystalline and liquid states is highly important in the structural studies of ionic liquids. The structure of the $[bmim]^+$ cation in [bmim]Cl Crystal (1)[6] and that in [bmim]Br[7] at room temperature are shown in Figure 1 together with their Raman spectra. Raman spectra were recorded at room temperature on a laboratory made near-infrared Raman spectroscopic system employing the 1064-nm line of a Nd:YAG laser as the excitation light source. The $[bmim]^+$ cation in [bmim]Cl Crystal (1) (Figure 1a, left) has an *n*-butyl group with the *TT* conformation, where the first *T* indicates the *trans* conformation around the C_7–C_8 bond and the second *T* the *trans* conformation around the C_8–C_9 bond. On the other hand, the $[bmim]^+$ cation in [bmim]Br (Figure 1b, left) has an *n*-butyl group with the *GT* conformation, where *G* stands for the *gauche* conformation around the C_7–C_8 bond. The Raman spectrum of [bmim]Cl Crystal (1) (Figure 1a, right) shows two characteristic bands at 625 and 730 cm^{-1}, while that of crystalline [bmim]Br (Figure 1b, right) shows three at 500, 603, and 701 cm^{-1}.

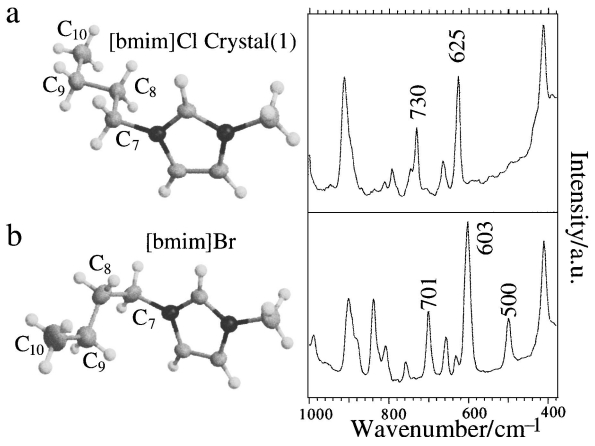

Figure 1. Structures of (a) [bmim]Cl Crystal (1) and (b) [bmim]Br together with their Raman spectra.

In order to confirm that the Raman spectral differences in Figure 1 reflect the structural variation of the $[bmim]^+$ cation and not the difference in the crystal environment, we carried out a DFT calculation (Gaussian 98,[8] B3LYP/6-31G+** level) of the $[bmim]^+$ cation with energy optimization at the *TT* and *GT* conformations. The results are shown in Figure 2. The calculation reproduces the spectral patterns very well both for the *TT* and *GT* forms. In particular, the two characteristic bands of [bmim]Cl Crystal (1) at 625 and 730 cm^{-1}, and the corresponding three bands of [bmim]Br at 500, 603, and 701 cm^{-1} are reproduced very well by the calculation. Not only the calculated peak positions but also the calculated intensities of those characteristic bands agree excellently with the observed ones. The calculation reveals that the 625 cm^{-1} band of the *TT* form and the 603 cm^{-1} band of the *GT* form arise from analogous deformation vibrations of the imidazolium ring but that they differ in the coupling scheme with the CH_2 rocking vibration of the C_8 methylene group, on account of the different conformation around the C_7–C_8 bond. The same is true for the 730 cm^{-1} band of the *TT* form and the 700 cm^{-1} band of the *GT* form. Thus, the 625 and 730 cm^{-1} bands of the $[bmim]^+$ cation can be used as marker bands of the *trans* conformation around the C_7–C_8 bond, while the 603 and 701 cm^{-1} bands those of the *gauche* confor-

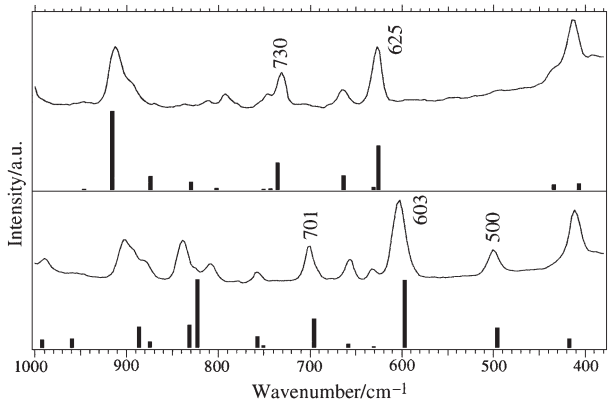

Figure 2. Experimental (continuous lines) and calculated (solid bars) Raman spectra of [bmim]Cl Crystal (1) (above) and [bmim]Br (below).

mation. The 500 cm^{-1} band of the *GT* form is ascribed to the C_7–C_8–C_9 deformation and again reflect the *gauche* conformation around the C_7–C_8 bond.

With these pieces information on the normal modes, we discuss the structure of the $[bmim]^+$ cation in the ionic liquid state. Figure 3 compares the Raman spectrum of a room temperature ionic liquid $[bmim]BF_4$ (Figure 3a) with those of [bmim]Cl Crystal (1) (Figure 3b) and [bmim]Br (Figure 3c). The bands marked by asterisks are due to the BF_4^- anion. The remaining bands in Figure 3a are ascribed to the $[bimim]^+$ cation in the ionic liquid state. The *trans* marker at 625 cm^{-1} and the *gauche* markers at 600 and 700 cm^{-1} are clearly observed in the spectrum of $[bmim]BF_4$, as shown by the arrows. The 730 cm^{-1} band of the *trans* conformation and the 500 cm^{-1} band of the *gauche* conformation are also observed weakly, though partially overlapped with nearby strong BF_4^- bands. Therefore, at least two rotational isomers of the $[bmim]^+$ cation, one having the *trans* conformation around the C_7–C_8 bond and the other having the *gauche* conformation, coexist in the ionic liquid state. With regard to the rotational isomerism around the C_8–C_9 bond, we have yet to obtain decisive evidence. A preliminary calculation on the *TG* conformer suggests that this

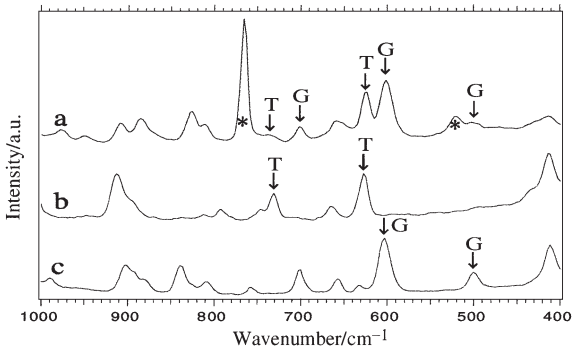

Figure 3. Raman spectra of (a) $[bmim]BF_4$ (liquid), (b) [bmim]Cl Crystal (1) (solid) and (c) [bmim]Br (solid). Asterisks indicate anion bands.

form may also exist in the liquid state in addition to the *TT* and *GT* form. However, we need further detailed vibrational analysis of the butyl vibrations, perhaps based on deuteriation experiments, in order to make this point clear.

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References and Notes

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