Polymorphic Properties of Ionic Liquid of 1-Isopropyl-3-methylimidazolium Bromide

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The crystal structure of an ionic liquid, 1-isopropyl-3-methylimidazolium bromide ([*i*-C_3mim]Br), was studied using X-ray crystallographic analysis. The structures of three independent conformers of the isopropyl moiety were determined. Although the three conformers are classified into a group and their structures differ from the conformer described by Golovanov et al., the crystal structures are similar with respect to the inter-ionic interactions between [*i*-C_3mim]$^+$ and Br^-. This polymorphic property of the ionic liquid is interpreted as arising because the enthalpy gain from the stronger Coulomb interactions determines a tight framework for the arrangement of Br^- and the more positive moiety of the imidazolium ring. Thus, the isopropyl moiety is able to occupy the space within the framework in various conformations.

Ionic liquid (IL) is the common name for substances retaining their liquid state at ambient temperature despite the fact that they are salts composed only of ions.[1] This unique feature allows us to refer to these substances novel liquids.[2] Although IL crystallization is sometimes difficult to achieve, a large number of structural determinations have been performed. Among them, the report on the crystal of 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) by Holbrey et al. and independently Hamaguchi et al.[3] marked a turning point in the subject. Their papers proved that the polymorphic behavior is caused by the existence of plural stable conformations of the constituent ion, [C_4mim]$^+$, and that the variety of the conformational structures is one of the factors inhibiting easy crystallization of ILs. Although a crystal structure of 1-isopropyl-3-methylimidazolium bromide ([*i*-C_3mim]Br) has previously been reported by Golovanov et al.,[4] our experiment revealed another isomorphic crystal with three different conformers. In this paper, we explain its polymorphic properties relating to the characters and behaviors of ionic liquids.

The procedure of synthesizing [*i*-C_3mim]Br is described in a previous study.[5] Colorless needle crystals suitable for X-ray diffraction study were obtained by recrystallization from ethyl acetate. Data collections were performed using a Bruker SMART 1000 CCD area detector diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were resolved using direct methods, and refined through full-matrix least-squares refinements based on F^2. Structure solutions were performed using the SHELXS-97 and SHELXL-97.[6]

The parameters for the above mentioned crystal are shown in Table 1[7] for comparison with the results by Golovanov et al.[4] As shown in Table 1, the experiment by Golovanov et al. exhibits the orthorhombic space group $P2_12_12_1$ and a type of conformer for [*i*-C_3mim]$^+$ ($Z = 4$); whereas in our result three independent conformers are included in an asymmetric unit in the unit cell, and the crystal is in trigonal space group $P3_2$ and $Z = 9$.

Table 1. Comparison with these two crystals

	This work (**A**, **B**, and **C**)	Golovanov (**G**)
T/K	90	110
Crystal system	Trigonal	Orthorhombic
Space group	$P3_2$	$P2_12_12_1$
a/Å	18.1021(16)	7.5865(5)
b/Å	18.1021(16)	10.7364(7)
c/Å	7.4573(9)	11.1846(7)
V/Å^3	2116.3(4)	911.0(1)
Z, Z'	9, 3	4, 1
R_1, wR_2	4.88, 11.16	2.88, 6.32
GOF	1.061	0.978

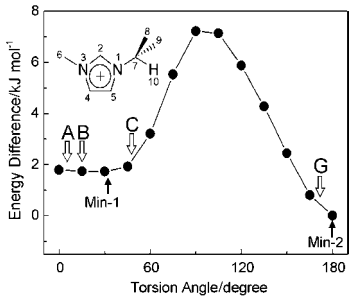

Figure 1. Correlation between torsion angle and potential energy.

All imidazolium rings of these conformers, including the results of Golovanov et al., exhibit flat planes and are identical. However, the conformations of the isopropyl group against the ring are significantly different.

For a free [*i*-C_3mim]$^+$, we calculated the potential energy for the isopropyl group rotation around the N1–C7 axis using density functional theory (DFT).[5] The dihedral angle of C5–N1–C7–H10 was defined as the torsion angle. Energy differences from the most stable conformer are shown in Figure 1. The calculation indicated two local minima at the torsion angles of ca. 30 and 180°, in which we named the two stable isomers Min-1 and Min-2, respectively. For three conformers **A**, **B**, and **C** (trigonal crystal system), the torsion angles were determined to be 0.32, 16.18, and 48.10°, respectively; whereas the torsion angle was 170.67° for the results of Golovanov et al. (**G**). These three independent [*i*-C_3mim]$^+$ molecules (**A**, **B**, and **C**) solved in this experiment are shown in Figure 2 with **G**.

The positions for **A**, **B**, **C**, and **G** are shown by arrows on the potential curve (Figure 1) with those of Min-1 and Min-2. As shown in Figure 1, there is a small energy difference between

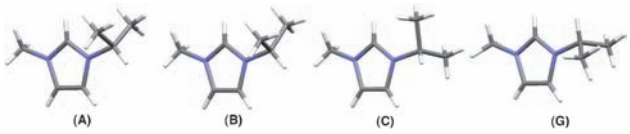

Figure 2. Three independent molecules (**A**, **B**, and **C**) and results of Golovanov et al. (**G**).

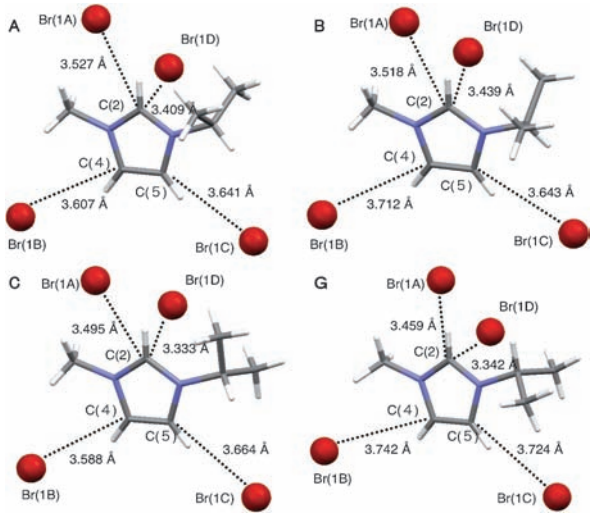

Figure 3. Three independent crystal structures (**A**, **B**, and **C**) and results of Golovanov et al. (**G**).

0 and 40° of the torsion angle. This means that various rotational isomers may possibly exist with slight rotation from Min-1. The small energy difference around Min-1 over a wide range is responsible for the present unique crystal structure.

The interaction between $[i\text{-}C_3mim]^+$ and Br^- in the crystal was examined. For each conformer, four symmetrically identical Br^- ions[8] are located near the imidazolium moiety (Figure 3). It is noted that two Br^- ions interact with C2. The reason believed is that the C2 atom in the imidazolium ring bears the highest positive charge.[9] As well as the above mentioned Br^- ions, a Br^- ion interacts with C5, and another Br^- ion interaction with C4. These interactions are reasonable because quantum mechanical calculations show that C4 and C5 bear the second highest positive charge in the imidazolium ring.[9] The C or N···Br distances in the respective imidazolium ring are summarized in Table 2. From the viewpoints of not only the positional relations but also the distances, almost identical interactions with Br^- ions were observed for these four independent conformers in the crystals. Despite the obvious difference in the conformational structures caused from the isopropyl moiety, the crystal structures with respect to the Br^- positions of each independent cation seem to be similar. This indicates that the most significant interaction determining the structure of the IL is, of course, the Coulomb interaction between the anion and the more positive moiety of the cation (imidazolium ring).

Therefore, it is concluded that the enthalpy gain from the stronger Coulomb interaction may determine the tight framework of the ionic arrangement. The van der Waals interaction between alkyl moieties, which would result in conformational uniformity, is too weak compared to the Coulomb interaction.[9] The isopropyl group may be able to occupy the space of the framework formed by Br^- and the more positive part of the cation. In turn, entropy gain may be obtained by taking plural conformations of the isopropyl group against the imidazolium ring.

Table 2. Cation–anion interaction: C or N–Br distance

	G	A	B	C
Br1A–N1	4.143	4.607	4.598	4.587
Br1A–C2	3.459	3.527	3.518	3.495
Br1A–N3	4.441	4.139	4.119	4.071
Br1B–N3	3.939	4.079	4.144	4.124
Br1B–C4	3.742	3.607	3.712	3.588
Br1B–C6	3.697	3.804	3.832	3.817
Br1C–Nl	4.482	4.239	4.234	4.312
Br1C–C5	3.724	3.641	3.643	3.664
Br1D–Nl	3.705	3.829	3.861	3.792
Br1D–C2	3.342	3.409	3.439	3.333
Br1D–N3	3.553	3.593	3.580	3.600

In conclusion, Coulomb forces strongly affect the crystallization process of ILs, leading to the formation of the ionic host-lattice with polymorphous domains. The present example of four conformers results in almost identical interactions with the Br^- ions, while the torsion angle of the isopropyl groups exhibits four different values. This may be because of a strong enthalpy gain responsible for the formation of the Br^- anion lattice. On the other hand, the entropy effect produces polymorphous conformers. It is well known that the plural conformers exist in liquid state for most ILs.[10] Regarding $[i\text{-}C_3mim]Br$, polymorphic crystals are also obtained as well as $[C_4mim]Cl$.[3]

References and Notes

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7 Crystallographic data: colorless needle $0.30 \times 0.20 \times 0.20\,mm^3$; $C_7H_{13}N_2Br$, $M_r = 205.10$; trigonal space group $P3_2$, $a = b = 18.1021(16)$ Å, $c = 7.4573(9)$ Å, $V = 2116.3(4)$ Å^3, $Z = 9$, $D_{calcd} = 1.448\,g\,cm^{-3}$, $T = 90$ K, 6259 unique and 5726 observed $[I > 2\sigma(I)]$ reflections, 281 parameters, final $[I > 2\sigma(I)]$ $R_1 = 0.0488$. $wR_2 = 0.1156$. $S = 1.061$. Two of three isopropyl groups were violentry disordered and refined with similarity restraints (SIMU). CCDC 715310 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.
8 Three asymmetric Br anions exist in the asymmetric unit ($Z' = 3$). Br(1A), Br(1B), and Br(1D) in Figure 3A are symmetrically "equivalent" and Br(1C) in Figure 3A are symmetrically "equivalent" with Br(1A) in Figure 3C.
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Published on the web (Advance View) October 31, 2009; doi:10.1246/cl.2009.1136