Halogen-bonded and Hydrogen-bonded Network Structures in Crystals of 1-Propyl- and 1-Butyl-4,5-dibromo-3-methylimidazolium Bromides

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Bromine substitutions in the 4 and 5 positions of 1-propyl- and 1-butyl-3-methylimidazolium ions provide characteristic layer organizations in the crystals through halogen bonding and hydrogen bonding. The network structures strongly affect the alkyl-chain conformations.

1-Alkyl-3-methylimidazolium-based cation (Im^+) is a representative cation composing ionic liquids.[1] A number of crystal structures of organic salts containing Im^+ have been analyzed for understanding the relationship between chemical structures and physicochemical properties of ionic liquids[2,3] and have given valuable information about hydrogen-bonding (HB) network structure and conformation of the flexible 1-alkyl group. We are furthering the design of Im^+s with halogen atoms to give some new functions to the ionic liquids by halogen bonding (XB). The present study belongs to this series and aims to develop the structural features of XB in ionic liquids and their crystals.

XB is the noncovalent intermolecular interaction between an antibonding orbital of an organic halide group and an electron donor site of a hetero atom. It is commonly known that the linearity of XB is generally stronger than that of HB.[4] In order to enhance the Lewis acidity of an organic halide group, it is necessary to associate the halogen with an electron-poor carbon. Logothetis et al. and Jones and Lozano have demonstrated that a pyridinium-based cation is an effective scaffold to promote the electron acceptability of an appended halogen atom.[5] In the case of an Im^+, the positive charge mainly locates at the 1, 2, and 3 positions. It is commonly known that the hydrogen atom in the 2 position has strong HB donor properties, and hydrogen atoms in the 4 and 5 positions are moderate HB donors. It can be expected that halogen substitution in the 4 and 5 positions of an Im^+ will provide a unique and rigid network structure. In this study, we have newly synthesized 1-propyl-4,5-dibromo-3-methylimidazolium bromide (**1**) and 1-butyl-4,5-dibromo-3-methylimidazolium bromide (**2**) and performed crystal structure analyses for both bromides in order to characterize the alkyl-chain conformation and interactions between the cation and anion.

4,5-Dibromo-1-methylimidazole prepared according to a previously reported procedure[6] was quaternized with 1-bromopropane and 1-bromobutane to give **1** and **2**. Single crystals of both salts were obtained by recrystallization from acetonitrile. The single-crystal X-ray diffraction data were collected at $-100\,°C$.

Figure 1 shows the asymmetric unit of **1** and coordinating anions. It is confirmed that not only $C–H\cdots Br^-$ HB but also $C–Br\cdots Br^-$ XB exists in this crystal. Both the Br1 and Br2 atoms act as electron acceptors. As shown in Table 1, the reduction percentages of the $Br\cdots Br^-$ distances against the sum of the van der Waals radius (1.85 Å)[7] and the ionic radius (1.96 Å)[8] are more than 15%, suggesting strong interactions. Both the $C2–Br1\cdots Br3i$ and $C3–Br2\cdots Br3ii$ angles are nearer to 180° than the $C–H\cdots Br^-$ HB angles, indicating strong linearity of the XB. The typical features of XB are clearly found in this crystal.

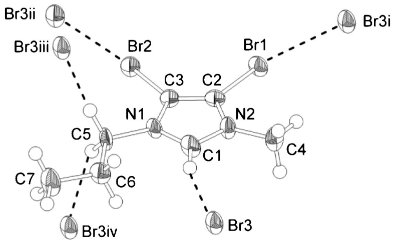

Figure 1. Asymmetry unit of **1** and coordinating anions, drawn at 50% ellipsoidal probability. H atoms are shown as spheres of arbitrary radius. Anion Br3i is at the symmetry position $(x, y, 1 + z)$, Br3ii is at $(-1/2 + x, 1/2 - y, 1.5 - z)$, Br3iii is at $(1 - x, 1 - y, 1 - z)$, and Br3iv is at $(1 - x, -1/2 + y, 1 - z)$. Other labeled atoms are those of the asymmetric unit. Interactions between the cation and anions are shown by dashed lines.

Table 1. Cation–anion interactions in the crystal of **1**

$A–B\cdots C$	$d_{B\cdots C}/Å$	$d_{A\cdots C}/Å$	$\angle_{A–B\cdots C}/°$
$C2–Br1\cdots Br3i$	3.220(1)		168.8(2)
$C3–Br2\cdots Br3ii$	3.209(1)		174.7(3)
$C1–H1\cdots Br3$	2.571	3.487(8)	162.9
$C5–H5A\cdots Br3iii$ $C5–H5B\cdots Br3iv$	2.856	3.740(2)	149.5

Figure 2 shows the packing diagrams of **1**. This salt crystallizes in the orthorhombic *Pnma* space group. The Br^- and all the atoms of the cation, except the hydrogen atoms in the methyl and the propyl group, lie in the crystallographic mirror plane. The cation structure is absolutely planar. The symmetry operations of this asymmetry unit reveal that **1** is organized in a completely planar layer structure (Figure 2a). The layer–layer interactions arise from the $H5A\cdots Br3iii$ and $H5B\cdots Br3iv$ HBs (dotted lines in Figure 2a). As can be seen in Figure 2b, the $H1\cdots Br3$ HB and both the XBs act as the intralayer interactions. A successive honeycomb-like structure is found in the layer. A unit of the honeycomb is composed of three pairs of the cation and the anion. The space inside one honeycomb unit is filled with the methyl and the propyl group.

The crystal structure of **2** is shown in Figure 3. Crystal **2** has static conformational disorder around the end of the butyl group. The occupancy of the C7–C8 and C9–C10 are 0.565 and 0.435, respectively. Except the C8, the entire carbon atoms of an asymmetry unit locate on the imidazolium plane. The cation structure in crystal **2** is planar-like.

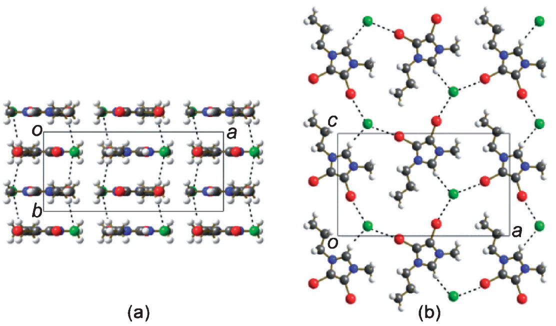

Figure 2. (a) Layer structure of **1**, projected along the *c* axis. (b) The packing diagram of the one layer (at $y = 1/4$), projected along the *b* axis. Inter- and intralayer interactions are shown as dotted lines in (a) and (b), respectively. The colors represent the following: C, grey; H, white; Br, red; N, blue; Br^-, green.

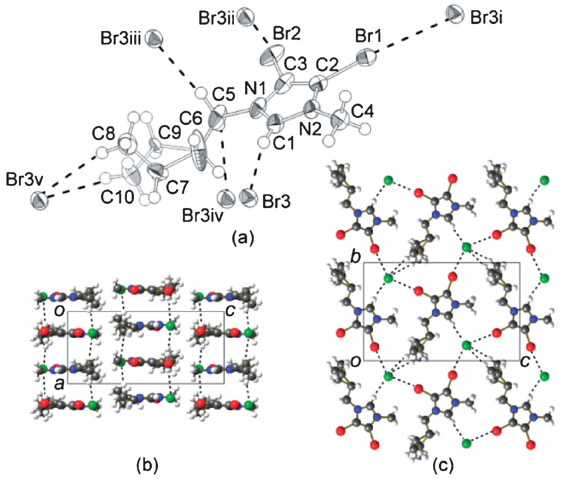

Figure 3. Crystal structure of **2**. (a) The asymmetric unit and coordinating anions, drawn at 50% ellipsoidal probability. The disordered C9 and C10 are displayed as translucent for image clarity. Anion Br3i is at the symmetry position $(x, 1 + y, z)$, Br3ii is at $(1/2 - x, 1 - y, -1/2 + z)$, Br3iii is at $(-1/2 + x, 1/2 - y, 1 - z)$, Br3iv is at $(1/2 + x, 1/2 - y, 1 - z)$, and Br3v is at $(1/2 - x, -y, -1/2 + z)$. (b) The layer structure projected along the *b* axis. (c) Packing diagram of the one layer (at $x = 0$–$1/2$), projected along the *a* axis.

XBs with strong linearity are also found in this crystal (see Supporting Information[9]). **2** crystallizes in the orthorhombic $P2_12_12_1$ space group. Although the planarity of the layer of **2** is not complete (Figure 3b) due to the C8 deviating from the imidazolium plane, the molecular orientation in the layer of **2** is quite similar to that of **1** (Figure 3c). We conclude that the tight honeycomb-like framework causes the irregular conformational disorder in the butyl group, and its steric effect, conversely, restricts the formation of completely planar layers. That is, the volume of the butyl group is too large to be positioned in the space inside the honeycomb-like framework. It is uncertain whether the short H8C···Br3v and H10B···Br3v indicate the presence of HBs.

As described above, bromine substitution at the 4 and 5 positions of the Im^+ provides the unique crystal structure via XBs and HBs. It is emphasized that the Im^+ with an alkyl chain of moderate length can only form a planar structure. The crystal structures of 1-propyl- and 1-butyl-3-methylimidazolium halides have been already reported.[3] Unlike the conformations of the present crystals, the 1-alkyl groups in these crystals are twisted out of the imidazolium plane. These facts indicate that the XB and HB network structures in the crystals of **1** and **2** are sufficiently tight frameworks.

From the results of the thermogravimetry and differential thermal analysis (TG-DTA), neither salt **1** nor salt **2** shows melting behavior up to the thermal decomposition temperatures. **1** and **2** show 10% weight losses at 226 and 193 °C, respectively.[9] In contrast, 3-methyl-1-propylimidazolium bromide and 1-butyl-3-methylimidazolium bromide melt at 36.2 and 79.2 °C, respectively.[3d] The rise in the melting temperature by the bromine substitution is due to the increased intermolecular interaction energy.

In conclusion, we have analyzed crystal structures of 1-propyl- and 1-butyl-4,5-dibromo-3-methylimidazolium bromides. The XB and HB network structures were clearly found in these crystals and gave rise to planar-layer structures with successive honeycomb-like frameworks that strongly affected the alkyl-chain conformations.

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9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html. Crystallographic data in CIF (CCDC 702091 and 702092) or other electronic format, experimental details, synthesis procedure, crystal, and refinement data for **1** and **2**, details of the interionic interactions in crystal **2**, TG-DTA curves are summarized.