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Cocrystal of an Ionic Liquid with Organic Molecules as a Mimic of Ionic Liquid Solution

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ABSTRACT: The cocrystal of organic compound dissolved in the ionic liquid (1-methyl-3-*n*-butyl imidazolium bromide) has been investigated for the first time using single crystal X-ray diffraction. The interactions between ionic solvent and solute were examined. It was shown that the general features of supramolecular organization of the solvent part remain the same as in the crystal of the pure ionic liquid.

Ionic liquids (ILs) are low melting (<100 °C) salts representing a new type of nonmolecular, ionic solvents.[1] Owing to their unique chemical and physical properties, ILs have received recent attention for applications as solvent alternatives,[2] where, for example, ILs can be used instead of organic solvents in synthesis, catalysis, electrochemistry, and liquid/liquid extractions.[3]

The principal possibility of polycondensation processes in ionic liquids was early demonstrated upon the formulation of high performance polymers, such as polyimides.[4a] High molecular weight polyimides including ones containing six-membered naphthoyleneimide rings and functional (sulfonated) ones have been obtained in the absence of any added catalyst. However, the solvation mechanism and catalytic effects of ILs have not been investigated so far and seem to be a question of scientific interest.

Although single crystal X-ray diffraction data cannot give the direct information about intermolecular interactions in solution, the study of a sufficiently high number of series of compounds and especially their solvates and cocrystals can give insight to the nature and dominance of specific self-assembling forces and the most stable specific interactions.[5] We have started investigation of cocrystals of ILs with organic molecules to mimic the interactions between solvent (anion and cation of ionic liquid) and solute.

p-Phenylenediamine is one of the simplest diamines widely used in polymer synthesis. Taking this into account, we carried out X-ray diffraction study of the cocrystal of 1,4-phenylenediamine (PD) with the ionic liquid 1-*n*-butyl-3-methyl imidazolium bromide (**1**). The choice of these particular compounds was based on DSC measurements[6] according to which PD and **1** form cocrystals with the melting point 83.19–83.38 °C (Figure 1). For comparison, the melting points of individual compounds **1** and PD are 69–70 and 147 °C, respectively.[7]

Analysis of available crystal data shows that PD has a tendency to form cocrystals with different mono- and dihydroxyaryls. In these cocrystals and especially in the case of bishydroxyarenes (see, i.e., ref 8), the PD

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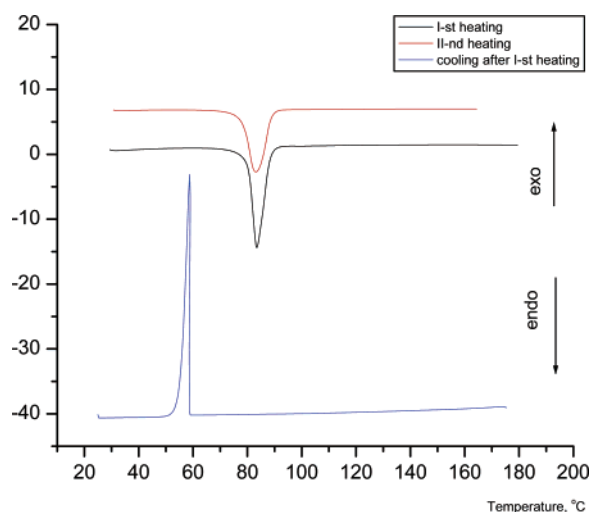
Figure 1. DSC data of cocrystal of **1** and 1,4-diaminobenzene.
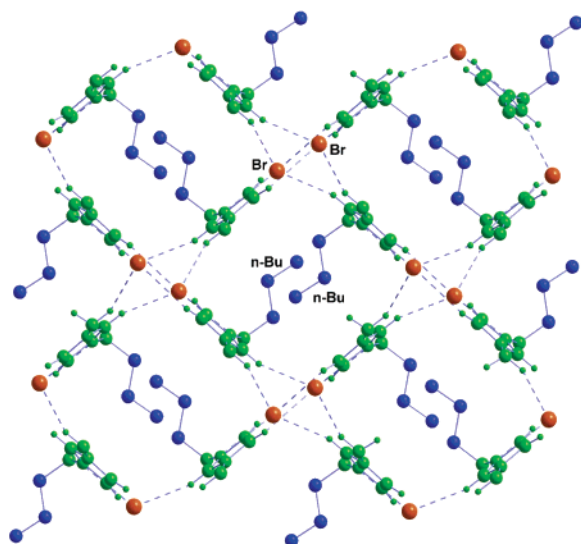
molecules are assembled by the O—H···N and N—H···O H-bonds into layers composed from the alternating strips of PD and hydroxyarenes.

Because it concerns the supramolecular organization of bromide salts of imidazolium, the recent X-ray diffraction analysis of the 1-*n*-butyl-3-methyl imidazolium (**1**), 1,3-di(*n*-propyl) imidazolium (**2**), and 1,3-di-(i-propyl) imidazolium (**3**) has revealed that in all these structures the organic cations are assembled into a 3-D network by mean of the Br···H—C contacts.[4a] The specific feature of self-assembling the imidazolium cations in the crystal of **1** is that they serve as the walls of nanosized (10 × 11.8 Å) orthorhombic channels directed along the crystallographic *c* axis.[4b] These channels are filled in by the butyl substituents that do not participate in specific interactions with bromine anions (Figure 2).

It should be noted that according to the MP2/6-31+G* calculation, variation in energy for different types of Br⁻···imidazolium close contact ion pairs is not so high (3.6–12.4 kcal/mol)[9]; thus, in the case of the competitive H-bonding N—H···Br⁻ and C—H···Br⁻ types, it is difficult to predict the overall supramolecular organization for cocrystals.

X-ray diffraction study of the single crystal obtained from the solution of PD in **1** has revealed the formation

Figure 2. Orthorhombic channels (10 × 11.8 Å) formed by imidazolium cations (green) and bromine anions in the IL **1**, filled in by *n*-butyl groups (blue). Hydrogen atoms that do not participate in Br···H—C contacts are omitted for clarity.
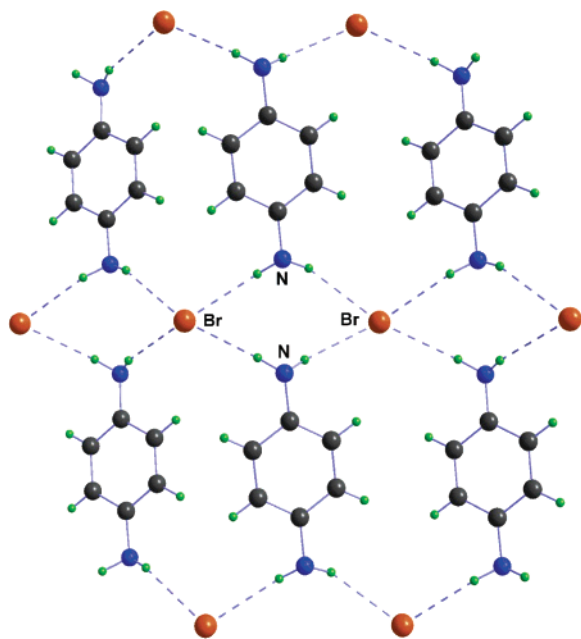
Figure 3. N—H···Br linked corrugated layers in the cocrystal of IL with **PD**.

of the cocrystal with a 1:1 ratio.[10] It was found, surprisingly, that crystal packing of PD·**1** encompass the general features of the aforementioned cocrystals of PD with aromatic molecules (Figure 3) as well as of pure ionic liquids (see Figures 2 and 4 for comparison). It is noteworthy that although the crystal system for **1** (orthorhombic) and PD·**1** (monoclinic) is different, both crystallize in noncentrosymmetric space groups *Pca*2₁ and *Cc*, respectively.

The bond lengths and bond angles in the imidazolium ring in the cocrystal of PD·**1** are similar to those in the crystal of **1**. In contrast, the conformation of the butyl substituent with respect to imidazolium in **1** and PD·**1** is different (Figure 5). Although both butyl substituents are characterized by an all-trans conformation, in the crystal of **1**, it is directed approximately perpendicular
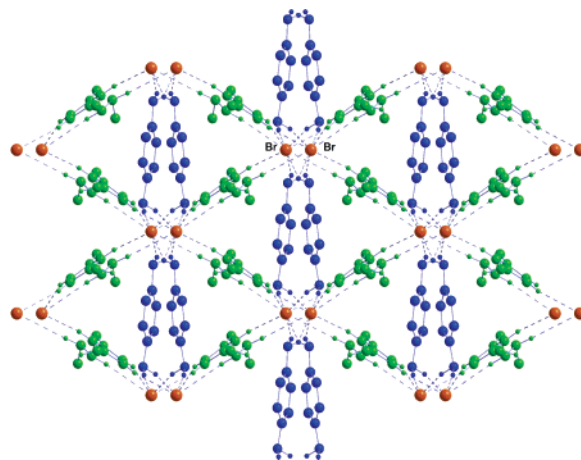

Figure 4. Orthorhombic channels (8.9 × 15.3 Å) formed by imidazolium cations (green) and bromine anions in the cocrystal, filled in by **PD** molecules (blue).

to the imidazolium ring while in the PD·**1** it is almost coplanar with the five-membered ring. Corresponding torsion angles N(1)C(6)C(7)C(8) in **1** and ····**1** are equal to 65 and 171.4°. This difference in the torsion angle probably resulted from the formation of the additional weak C—H···Br contact C(8)—H(8A)···Br(1) (3.03 Å) (Figure 5A).

Analysis of the crystal packing has revealed that the main type of interactions between solute and solvent are N—H···Br hydrogen bonds. These bonds assemble molecules into corrugated layers parallel to the crystallographic plane *ac*, which is quite close to the mentioned layers in the cocrystal of PD with dihydroxyarenes (Figure 3). It should be noted that Br···H—N bonds in the cocrystal are relatively weak. According to analysis of the intermolecular C—NH₂···Br contacts in CCDC, the Br···N distances vary in the range of 3.25—3.70 Å with the mean value equal to 3.45 Å. Corresponding Br···N distances in PD·**1** are 3.535(4)—3.606(4) Å. Surprisingly, the H···Br distances (2.66—2.72 Å) for the N—H···Br hydrogen bonds in the cocrystal are comparable or slightly longer than those for C—H···Br bonds with the imidazolium ring (2.46—2.95 Å) in the previously studied ILs **1**—**3**.[4]

The ionic liquid part in the cocrystal of PD·**1** is remarkably identical to the crystal of **1**. As it can be seen, cations are assembled by C—H···Br contacts into a 3-D network with the rhombus channels (Figure 4). The increase of the size of filling of channels leads to elongation of one of diagonals up to 15.31 Å and to a decrease of the opposite down to 8.96 Å.

Despite the similarity of supramolecular organization of cations and bromine anions, the number and strengths of the C—H···Br contacts in the cocrystal and **1** are different. In the cocrystal, each imidazolium cation is surrounded by four bromine anions and a bromine anion with the account that N—H···Br contacts participate in the nine contacts (Figure 5A). For comparison, in the crystal of **1**, the imidazolium is surrounded by five bromine atoms and the bromines form only eight contacts (Figure 5B). The strength of the C—H···Br contacts in PD·**1** is weaker than in **1**, but the relative strengths of the C—H···Br contacts for alkyl and hydrogens atoms of imidazolium ring is the same.
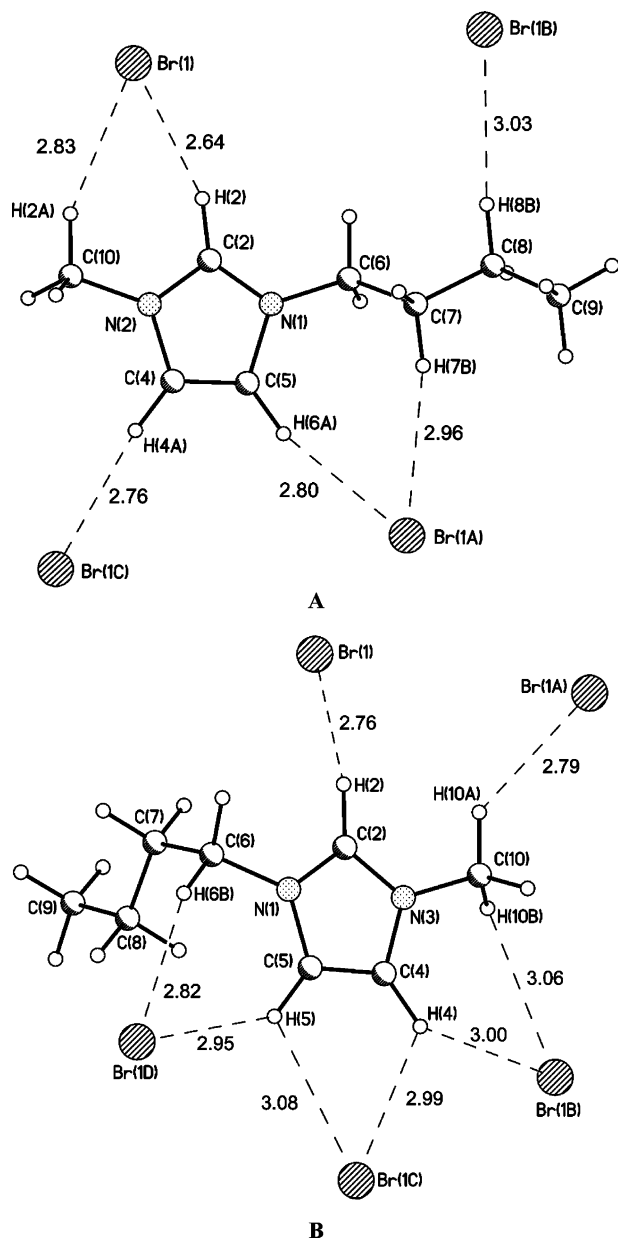
Figure 5. Surrounding of imidazolium cation by bromine anions in the cocrystal of IL with PD (A) and in pure IL (B). The C–H···Br contacts are depicted. All C–H lengths are normalized at ideal value of 1.08 Å.

Thus, the first X-ray diffraction analysis of the cocrystal of 1-*n*-butyl-3-methyl imidazolium bromide and 1,4-phenylenediamine has revealed that despite the N–H···Br hydrogen bonds, formation of the 3-D network of imidazolium cations and bromine anions is practically the same as in the crystal of pure ionic liquid. Further investigations will give insight if such types of cocrystallization are the general feature or are just a specific situation for this pair of compounds.

Supporting Information Available: CIF files for **1** and cocrystal of PD·**1** are available free of charge via the Internet at http://pubs.acs.org.

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(6) 1,4-Phenylenediamine (PD, mp 143−145 °C) was purified by vacuum sublimation. 1-Methylimidazole and *n*-bromobutane were purchased from Aldrich. 1-Methylimidazole was distilled over KOH under vacuum. *n*-Bromobutane was distilled under inert atmosphere over CaCl₂. Procedure for the preparation of IL 1-methyl-3-butyl imidazolium bromide [1-Me-3-Bu im]Br: 1-methylimidazole (15.84 mL, 0.2 mol) and bromobutane (21.48 mL, 0.2 mol) were refluxed for 5−6 h under stirring. The resultant viscous 1-butyl-3-methyl-imidazolium bromide was dried in vacuo for 5 h; yield was 33.5 g (76.5%). 1-Methyl-3-butylimidazolium bromide: Anal. Calcd for $C_8H_{15}N_2Br$ (219.14): C, 43.81%; H, 6.84%; N, 12.89%; Br, 36.46%. Found: C, 43.14%; H, 6.61%; N, 12.61%; Br, 36.96%. IR (KBr pellet): 3170 (m), 3120 (m), 2980 (m), 2950 (m), 2890 (m), 1580 (s), 1472 (s), 1390 (m), 1350 (m), 1180 (s), 1040 (s), 770 (m) cm⁻¹. ¹H NMR (CDCl₃): δ = 0.90 (t, 3 H, CH₂CH₂CH₂CH₃, J(HH) = 7.1 Hz), 1.34 (m, 2 H, CH₂CH₂CH₂CH₃, J(HH) = 7.3 Hz), 1.93 (m, 2 H, CH₂CH₂CH₂CH₃, J(HH) = 7.2 Hz), 4.23 (s, 3 H, NCH₃, J(HH) = 7.2 Hz), 4.52 (t, 2 H, NCH₂, J(HH) = 7.2 Hz), 8.28 (s, 1 H, H5 (Im)), 8.38 (s, 1 H, H4 (Im)), 10.02 (s, 1 H, H2 (Im)). Procedure for the preparation of cocrystal of PD 1: 1-methyl-3-*n*-butyl imidazolium bromide (0.30 g, 0.0014 mol) and 1,4-phenylenediamine (0.15 g, 0.0014 mol) were put into the three-necked flask. The mixture was heated to 140 °C under inert flow with stirring. After complete dilution of components, the reaction mass was cooled to room temperature forming brown crystals. DSC measurements were carried out using Mettler 822 with heat grade equal to 10 °C/min.

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(10) Crystallographic data for cocrystal *PD·1*: at 120 K, the crystal of $C_{14}H_{23}BrN_4$, $M = 327.27$, monoclinic space group *Cc*, $a = 8.956(3)$ Å, $b = 15.313(5)$ Å, $c = 11.660(4)$ Å, $\beta = 94.62(2)$, $V = 1594.0(9)$ Å^3, $Z = 4$ $d_{calc} = 1.364$ g cm^{-3}, $\mu(MoK\alpha) = 25.73$ cm^{-1}, and $F(000) = 680$. Intensities of 4901 reflections were measured with a SMART 1000 CCD diffractometer at 120 K ($\lambda(MoK\alpha) = 0.71072$ Å, ω-scans with 0.3 step in ω and 10 s per frame exposure, $2\theta < 54°$), and 3300 independent reflections ($R_{int} = 0.0376$) were used in further refinement. The absorption correction was applied semiempirically using the equivalent reflections. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. The hydrogen atoms were located in Fourier density synthesis and refined in the riding model. The refinement converged to $wR_2 = 0.1000$ and GOF = 1.028 for all independent reflections ($R1 = 0.0487$ was calculated against F for 2506 observed reflections with $I > 2\sigma(I)$). All calculations were performed using SHELXTL PLUS 5.1.