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1,3-Dibenzylimidazolium salts: A paradigm of water and anion effect on the supramolecular H-bonds network

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ABSTRACT

Two crystals of 1,3-dibenzylimidazolium salts with chloride (crystal **I**) and hexafluorophosphate (crystal **III**) have been obtained by slow evaporation of a saturated aqueous solution for **I** and saturated chloroform solution for **III**. The two structures are described and compared to the corresponding bromide salt (crystal **II**). The X-ray diffraction studies on single crystals revealed that the three crystalline materials are monoclinic with $P2_1/n$ or $P2_1/c$ space group. The structures of **I** and **III** are completely different compared to that of the analogous bromide salt (**II**): no C—H···π or π–π interactions were observed and only very weak H-bonds occur between the acidic protons of the imidazolium ring and the halogenated atoms of the anion for compound **III**. For **I** and **II**, water molecules are included in the crystal lattice. Water molecules link the chloride anions in the case of **I**, but there are no direct interactions between the protons of the imidazolium ring and water molecules, as in the case of compound **II**. The hydrogen bond network in the case of compound **II** is formed *via* water molecules between the cations and the anions. In the case of the hexafluorophosphate salt, classical organization in an extended network of cations and anions connected together by hydrogen bond was observed.

1. Introduction

Ionic liquids (ILs) are an attractive field in chemistry. These salts are defined as "molten salts" with melting points below 100 °C. The significant interest in ILs is due to their chemical characteristics and potentially useful solvent properties [1,2]. The most common ILs are members of the 1,3-disubstituted imidazolium family, which generally have been used as green solvents in organic synthesis, organometallic catalysis and enzymatic catalysis [3–11]. Many applications also exist in separation processes, nano-chemistry, electrochemistry and as new materials [12–14]. Recent studies have demonstrated that pure 1,3-disubstituted imidazolium salts form a hydrogen-bonded supramolecular network in the solid phase. The H-bonds are proposed to be maintained, to a great extent, in the liquid or gas phase [15]. The imidazolium salts possess pre-organized structures: through the three acidic protons localized on the imidazolium ring that can act as H-bond donors, and *via* π-stacking in the third dimension (Fig. 1) [15]. In fact, an overview of the X-ray studies reported in the past decade on the structure of 1,3-dialkylimidazolium salts [16–20], reveals that they form an extended network of cations and anions connected together by hydrogen bonds. The monomeric unit is always composed of one imidazolium cation surrounded by at least three anions and each anion is surrounded by at least three imidazolium cations [21]. The strongest hydrogen bond always involves the most acidic H_2 ($pK_a = 23.0$ for the 1,3-dimethylimidazolium cation) [22,23] followed by H_4 and H_5 of the imidazolium ring. These hydrogen bonds are weak to moderate (with H···X bond lengths > 2.2 Å; C—H···X bond angles between 100° and 180°) [24]. The number of anions that surround the cation (and vice-versa) varies according to the anion size and the nature of the imidazolium residues.

We have recently reported the self-assembly of 1,3-dibenzylimidazolium halides in solution and in gas phase, on the basis of NMR titrations, mass spectrometry data and theoretical calculations [25]. The benzyl groups impose additional π-stacking interactions with the imidazolium rings by aromatic stacking (T or π). In solution, the chloride salt has a similar organization to its bromide analogue. The crystal structure of 1,3-dibenzylimidazolium bromide revealed an atypical organization when compared to previously observed structures of ILs [25]. Since water molecules participate directly in the formation of the supramolecular network, a fact very unusual for imidazolium salts, we were inspired to perform a crystallographic study of the 1,3-dibenzylimidazolium analogs, namely the chloride and the hexafluorophosphate. To simplify the notation, the crystals of the 1,3-dbenzylimidazolium salts are referred to as **I**, **II** and **III**, for chloride, bromide and hexafluorophosphate anions, respectively (Fig. 2).

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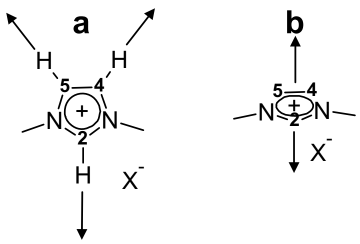

Fig. 1. (a) The three T-stacking and H-bond donors of an imidazolium ring and their directionality, and (b) π-stacking.

2. Experimental

2.1. Materials

All reactions were carried out in oven-dried glassware under nitrogen, using standard Schlenk and vacuum line techniques. The ^{1}H and ^{13}C NMR spectra were recorded using an Advance 300 Brucker, at 300.13 and 75.49 MHz, respectively. Chemical shifts are given in ppm (δ) and measured relative to residual solvent. Elemental analyses were performed by the “Université de Montréal” facility. $CDCl_3$ and all other chemicals were purchased from Aldrich and used without further purification. “Distilled” solvents were obtained using a GlassContour system (Irvine, CA).

2.2. Synthesis of 1,3-dibenzylimidazolium chloride (**I**)

A dry flask (250 mL), equipped with a magnetic stir bar and a septum-inlet for nitrogen, was charged with a solution of (chloromethyl) benzene (1.06 g, 8.42 mmol) in toluene (50 mL). In a Schlenk, a solution of 1-benzylimidazole (1.60 g, 10.1 mmol) in toluene (10 mL) was added to the other flask in a dropwise fashion by cannulation at 0 °C. The reaction mixture was stirred for 20 min at room temperature, then filtered under gravity. The solid was washed with diethylether to remove unreacted 1-benzylimidazole. The white solid was dried overnight at 120 °C in a vacuum. The product was stored under dry nitrogen (90%).

^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): δ = 5.41 (s, 4H, NCH_2), 7.23 (m, 6H, $H_{aro(ortho)}$, $H_{aro(para)}$ and imidazolium CH=CH), 7.34 (d, 2H, CH=CH, $^{3}J_{H-H}$ = 1.3 Hz), 7.41 (dd, 4H, $H_{aro(meta)}$, $^{3}J_{H-H}$ = 6.3 Hz and $^{3}J_{H-H}$ = 6.7 Hz), 10.92 ppm (s, 1H, N=CHN); ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ = 53.0 ppm (NCH_2), 122.0 ppm (CH=CH), 128.7 ppm (C_m), 129.1 ppm (C_o), 129.2 ppm (C_p), 133.0 ppm (N=CHN), 137.0 ppm ($C_{aro}CH_2$). Anal. Calc. for $C_{17}H_{17}ClN_2$: C, 71.70%; H, 6.02%; N, 9.84%. Found: C, 69.89%; H, 6.01%; N, 9.75%. ESI/HRMS *m/z* found: 249.1582 $(M-Cl)^+$, calc.: 249.1391. MP: 63 °C.

2.3. Synthesis of 1,3-dibenzylimidazolium bromide (**II**)

The procedure is identical to the one which presented above.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 5.52 (s, 4H, NCH_2), 7.23 (d, 2H, CH=CH, $^{3}J_{H-H}$ = 1.4 Hz), 7.31–7.39 (m, 10H; H_{aro}), 10.51 (s, 1H; N=CHN); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ (ppm) = 53.2 (NCH_2), 121.8 (CH=CH), 128.9 (C_m),129.3 (C_o), 129.3 (C_p), 132.7 (NCHN), 136.6 ($C_{aro}CH_2$). Anal. Calc. for $C_{17}H_{17}BrN_2$; $2H_2O$: C, 55.90%; H, 5.79%; N, 7.67%. Found: C, 54.84%; H, 5.77%; N, 7.87%. ESI/HRMS *m/z* found: 249.1376 $(M-Br)^+$, calc.: 249.1391. MP: 85 °C.

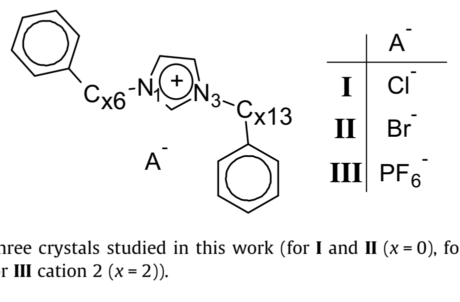

Fig. 2. The three crystals studied in this work (for **I** and **II** (x = 0), for **III** cation 1 (x = 1) and for **III** cation 2 (x = 2)).

2.4. Synthesis of 1,3-dibenzylimidazolium hexafluorophosphate (***III***)

The 1,3-dibenzylimidazolium bromide salt was dissolved in water (5 mmol L^{-1}) and a NH_4PF_6 aqueous solution (5 mmol L^{-1}) was added. The imidazolium hexafluorophosphate salt precipitates (95%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 5.23 (s, 4H, NCH_2), 7.24 (m, 2H, CH=CH, $^{3}J_{H-H}$ = 1.3 Hz), 7.3–7.4 (m, 10H; H_{aro}), 9.63 (s, 1H; N=CHN); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ (ppm) = 53.2 (NCH_2), 121.4 (CH=CH), 128.6 (C_m),129.1 (C_o), 129.3 ppm (C_p), 132.5 (N=CHN), 136.2 ($C_{aro}CH_2$). Anal. Calc. for $C_{17}H_{17}F_6N_2P$: C, 51.78%; H, 4.35%; N, 7.10%. Found: C, 51.82%; H, 5.41%; N, 7.11%. ESI/HRMS *m/z* found: 249.1264 $(M-PF_6)^+$, calc.: 249.1391. MP: 93 °C.

2.5. Crystallization and X-ray diffraction

All the crystallizations are performed in an open flask by dissolving the 1,3-dibenzylimidazolium cation (33 wt.%) in 10 mL of hot water (for **I** and **II**) or in 10 mL of hot chloroform (for **III**). After a week at room temperature, single crystals suitable for X-ray diffraction were obtained. All X-ray data were collected at T = 150 K and the structures were solved by the direct method with ShelxS-97. All non-H atoms were refined by full-matrix least-squares with anisotropic displacement parameters while hydrogen atoms were placed in idealized position. Hydrogen atoms from the water molecules were initially located from a difference Fourier map, then their location were adjusted using restrains at idealized distances (0.84 Å) and angles (104.5°) in the direction of the hydrogen bonding acceptors, either chloride (compound **I**) or bromide (compound **II**) anions.

X-ray crystallographic data for **I** and **III** were collected from a single crystal sample, which was mounted on a loop fiber. Data were collected using a Bruker microstar diffractometer equipped with a Platinum 135 CCD Detector, Helios optics and Kappa goniometer. The crystal-to-detector distance was 4.0 cm, and the data collection was carried out in 512 × 512 pixel mode. The initial unit cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 10.0° scan in 33 frames over three different parts of the reciprocal space (99 frames total). One complete sphere of data was collected.

X-ray crystallographic data for **II** were collected from a single crystal sample, which was mounted on a loop fiber. Data were collected using a Bruker Platform diffractometer, equipped with a Bruker SMART 4K Charged-Coupled Device (CCD) Area Detector using the program APEX II and a Nonius FR591 rotating anode equipped with Montel 200 optics. The crystal-to-detector distance was 5.0 cm, and the data collection was carried out in 512 × 512 pixel mode. The initial unit cell parameters were determined by the same procedure (see above). One complete sphere of data was collected, to better than 0.80 Å resolution.

In each case, the refinement was on F^2 using all reflections. The weighted R-factor (wR) and goodness-of-fit S are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors (gt) etc. and is not relevant to the choice of reflections for refinement. All esds (except the eds in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix.