Effect of Temperature on the Purity of Product in the Preparation of 1-Butyl-3-methylimidazolium-Based Ionic Liquids

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The preparation of room-temperature ionic liquids 1-butyl-3-methylimidazolium chloride, hexafluorophosphate, and dicyanamide by microwave-assisted reaction in non-solvent and solvent conditions has been studied in this contribution. A special emphasis is put on the effect of the reaction temperature on the purity of ionic liquids that was monitored by electrospray ionisation mass spectrometry and ^{1}H NMR. The X-ray structure of 1-butyl-3-methylimidazolium chloride is presented.

Key words: RTIL, Purity, Side Products, Electrospray Mass Spectrum

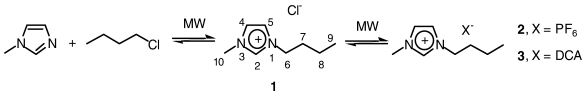
Introduction

Ionic liquids are organic salts that are liquids at temperatures below 100 °C. While the first room temperature ionic liquid was discovered as early as 1914 [1], early literature is sparse [2 – 4] and ionic liquids were largely ignored until the work of Seddon [5] and Hussey [6 – 8] in the 1980's. Since then these species have seen extensive research activity (for excellent reviews on the wide variety of the use of ionic liquids, see Refs. [9 – 16].

Quaternisation of appropriate amines is a general method to prepare ionic liquids [13, 15]. This method has been used to prepare 1-alkyl-3-methylimidazolium salts. Halides can be made by a reaction of *N*-methylimidazole with an appropriate haloalkane [17]. Various anions can be introduced by anion exchange of the halides [14, 16]. This can be done by the addition of a metal salt or by displacement of a halide ion by a strong acid [17 – 20].

One of the recent research interests is concerned with the purity and quality of ionic liquids prepared by various methods [21, 22]. A pure ionic liquid should be colourless [23]. However, early work methods often afforded coloured products that were impure and laborious to purify.

In this paper, we explore the formation of ionic liquids by using microwave-assisted methods for which the information is still sparse [24 – 29]. Interestingly, we also encountered coloured products depending on the reaction conditions. In particular, temperature



Scheme 1.

seems to play an important role in the purity of some commonly used ionic liquids, 1-butyl-3-methylimidazolium chloride (**1**), hexafluorophosphate (**2**), and dicyanamide (**3**) (Scheme 1).

Results and Discussion

1-Butyl-3-methylimidazolium chloride

1-Butyl-3-methylimidazolium chloride [BMIM]Cl (**1**) is a common precursor for many ionic liquids. Its preparation by the literature method [18] produced coloured products the purification of which was a complicated and laborious process, especially when an excess butyl chloride was used. Consequently, the desired product crystallized poorly. Recent studies have reported the preparation of **1** in a microwave digester [26, 27]. We explored further the microwave-assisted preparation of **1** with the objective to minimize the formation of coloured side products and to shorten the reaction time. A special attention was directed to the reaction temperature and the molar ratio of the reactants. The reaction between *N*-methylimidazole and butyl chloride was performed in the molar ratio range 1:1 – 1:1.5 in a closed microwave reactor [30] designed for synthetic purposes. The reaction temperature was kept at 150 °C by the automatic regulation of the ir-

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Table 1. The effect of temperature on the preparation of 1-butyl-3-methylimidazolium chloride (**1**) assisted by microwaves.

T [°C]	Colour of the reaction mixture	Yield of **1** [%]	Purity by ^{1}H NMR	MS(ESI$^+$), *m/z*	Colour of the crystalline **1**
80	colourless	7	–	–	white
90	colourless	9	–	–	white
100	colourless	14	–	–	white
110	colourless	29	–	–	white
120	yellowish	61	pure **1**	M^+ 139	white
130	light yellow	77	pure **1**	M^+ 139	milky white
140	light yellow	83	impurities	M^+ 139, 181	milky white
150	light yellow	84	impurities	M^+ 139, 97, 181	
160	yellowish	94	impurities	–	yellowish

Reaction conditions: 3.2 mmol of **1** and butylchloride, reaction time 15 min, microwave radiation power normal.

radiation power and the reaction time varied from 5 to 10 min. The best crude yield of **1** (90%) was obtained when the molar ratio was 1:1.1 and the reaction time was at least 10 min. A higher molar ratio than 1:1.1 reduced the yield. Equimolar amounts of the reagents produced 85% of white 1-butyl-3-methylimidazolium chloride (**1**) in 10 min. After workup the ^{1}H NMR spectrum of **1** did not show resonances due to starting materials. While many ionic liquids are thermally stable at high temperatures [18], the preparation of **1** at 160 °C resulted in partial scrambling of the side chains in the five membered C_3N_2 ring, as indicated by ^{1}H NMR spectroscopy.

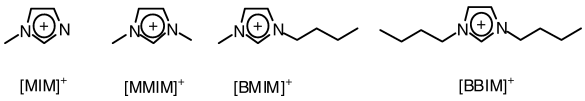
To study the effect of the reaction temperature on the product formation and scrambling, we carried out the synthesis of [BMIM]Cl at nine temperatures ranging from 80 to 160 °C. Equimolar amounts of the starting compounds were allowed to react 15 min in every experiment. The reaction mixture remained colourless below 110 °C, but at higher temperatures, it became yellowish. The highest yield of pure **1** was produced at 130 °C (77%). According to the ^{1}H NMR spectrum, rearrangement reactions of 1-butyl-3-methylimidazolium chloride began to occur at 140 °C. The reactions at higher temperatures than 130 °C gave a better yield of **1**, but the product contained impurities (see Table 1).

The reaction mixtures formed at different temperatures were analysed by ^{1}H NMR and electrospray ionization mass spectrometry MS(ESI$^+$ and ESI$^-$) [31]. ESI-MS is the softest available technique to transfer positive or negative ions from solution to the gas phase, from which the ions can be subjected to MS analysis. One can define the softness of the ion-transfer method as the degree to which fragmentation of the ions is avoided. The ESI mass spectrum is simple and ions can be unambiquously identified. The method is a particularly suitable technique for the detection of ionic liquids, because they are already in the ionic form [31 – 34].

Table 2. Electrospray ionization mass spectra of crude products of 1-butyl-3-methylimidazolium chloride (**1**) from separate reaction temperatures.

T [°C]	MS (ESI$^+$), *m/z* (rel. int. %) of detected components in crude **1**
130	83 (20) $[MIM]^+$, 139 (100) $[BMIM]^+$
140	83 (55) $[MIM]^+$, 139 (100) $[BMIM]^+$, 181(5) $[BBIM]^+$
150	83 (70) $[MIM]^+$, 97 (15) $[MMIM]^+$, 139 (100) $[BMIM]^+$, 181(55) $[BBIM]^+$

$[MIM]^+$ = methylimidazolium cation, $[MMIM]^+$ = dimethylimidazolium cation, $[BMIM]^+$ = butyl-methylimidazolium cation, $[BBIM]^+$ = dibutylimidazolium cation.



Scheme 2.

The peaks in ESI mass spectra of the product mixtures at different temperatures are shown in Table 2. The crude product derived from the reaction at 140 °C contained an additional peak at *m/z* 181 and that from the reaction at 150 °C showed yet another peak at *m/z* 97. The former probably arose from the 1,3-dibutylimidazolium cation $[BBIM]^+$ and the latter from the 1,3-dimethylimidazolium cation $[MMIM]^+$ (see Scheme 2). The molecular peak *m/z* 83 $[MIM]^+$ was obviously formed in the mass spectrometer during ionization depending upon a used electron potential.

The ^{1}H NMR spectra also contained other resonances in addition to those of **1**. The scrambled products ($\geq$ 140 °C) showed signals at 4.10 and 4.11 ppm (the methyl groups of $[MMIM]^+$). Small resonances were observed near to the multiplets at 7.33 and 7.44 ppm (ring protons H-4 and H-5, respectively). The crude product from the reaction at 150 °C showed three singlets for the methine group between N atoms, indicating the presence of three different imidazolium cations. The ^{1}H NMR spectra indicated that approximately 7% of the product had rearranged at 140 °C, 20% at 150 °C, and 35% at 160 °C.

We also studied the influence of the heating on pure **1**. A sample of **1** was heated by microwaves in acetone and without the solvent at 150 °C for 10 min up to 1 h. The heated samples were analyzed by ^{1}H NMR and MS(ESI$^+$). Both spectra indicated that the heating

Table 3. Selected bond lengths (Å) and angles (°) of 1-butyl-3-methylimidazolium chloride (**1**).

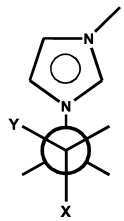
N(1)-C(2)	1.382(2)	N(1)-C(5)	1.473(2)
N(1)-C(6)	1.473(2)	N(3)-C(2)	1.328(2)
N(3)-C(10)	1.466(2)	C(4)-C(5)	1.354(2)
C(6)-C(7)	1.521(2)	C(7)-C(8)	1.523(2)
C(8)-C(9)	1.524(2)		
N(1)-C(2)-N(3)	108.7(1)	N(1)-C(5)-C(4)	106.9(1)
N(1)-C(6)-C(7)	110.4(1)	N(3)-C(4)-C(5)	106.9(1)
C(2)-N(1)-C(5)	108.7(1)	C(2)-N(1)-C(6)	125.9(1)
C(5)-N(1)-C(6)	125.0(1)	C(2)-N(3)-C(4)	108.7(1)
C(2)-N(3)-C(10)	124.7(1)	C(4)-N(3)-C(10)	126.5(1)
C(6)-C(7)-C(8)	112.2(1)	C(7)-C(8)-C(9)	111.8(1)
C(5)-N(1)-C(2)-N(3)	−0.4(2)	N(1)-C(2)-N(3)-C(4)	0.3(2)
C(2)-N(3)-C(4)-C(5)	−0.1(2)	N(3)-C(4)-C(5)-N(1)	−0.2(2)
C(4)-C(5)-N(1)-C(2)	0.4(2)	C(4)-C(5)-N(1)-C(6)	173.3(1)
C(4)-C(5)-N(3)-C(10)	−179.5(1)	N(1)-C(2)-N(3)-C(10)	179.7(1)
N(3)-C(2)-N(1)-C(6)	−173.2(1)	C(2)-N(1)-C(6)-C(7)	82.9(2)
C(5)-N(1)-C(6)-C(7)	−88.8(2)	N(1)-C(6)-C(7)-C(8)	174.2(1)
C(6)-C(7)-C(8)-C(9)	174.8(1)		

does not cause rearrangement in [BMIM]Cl (**1**). The formation of impurities is therefore dependent on the temperature during the actual synthesis.

A maximum useful reaction temperature for the microwave-assisted synthesis of 1-butyl-3-methylimidazolium chloride (**1**) is 130 °C. Higher temperature leads to the formation of a product mixture. The purification of these impurities by washing with the solvent was not successful.

Structural information about ionic liquids is rather sparse with few crystal structures reported for the *N,N'*-dialkylimidazolium cation with different counterions [35 – 44]. The X-ray structure of **1** is shown in Figure 1 together with the numbering of the atoms [44]. The bond lengths and angles are presented in Table 3.

It can be seen from Table 3 that all bond lengths in the cation of **1** are quite normal and agree with those of other related salts [35 – 43]. There are several alternative conformations for the butyl side chain depending on the mutual orientations of the carbon atoms in the butyl side chain. This can be exemplified as follows:



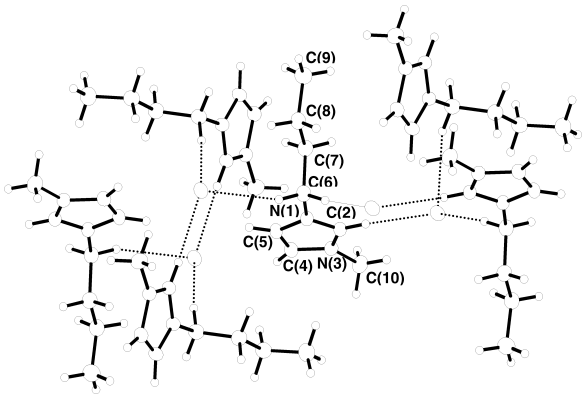


Fig. 1. The crystal structure of 1-butyl-3-methylimidazolium chloride (**1**) indicating the numbering of atoms. The thermal ellipsoids have been drawn at 50% propability level. Hydrogen bonds involving three short H···Cl contacts connect the cations and anions into a three-dimensional network.

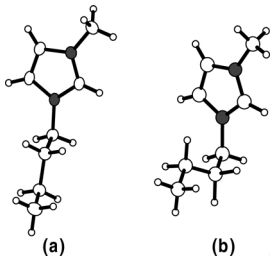


Fig. 2. The conformation of the 1-butyl-3-methylimidazolium cation in (a) the chloride salt (**1**), (b) the tetraphenylborate salt [36, 39].

For steric reasons, the *N*-methylimidazole ring is generally approximately perpendicular to the C(6)-C(7) bond (for the numbering of the atoms, see Fig. 1). The terminal ethyl fragment involving the carbon atoms C(7) and C(8) has two alternative orientations **X** and **Y** that could be energetically equally favourable. Indeed, it can be seen from Fig. 2 that the ethyl group in the cation of **1** adopts the **X** orientation and that in 1-butyl-3-methylimidazolium tetraphenylborate [36, 39] adopts the **Y** orientation. Similar alternative orientations can be conceived to exist for the methyl group {carbon atom C(9)} at the end of the butyl chain. The structural characterization of several 1-butyl-3-methylimidazolium cations [35 – 43] has demonstrated that packing effects seem to be the determining factor in deciding the actual conformation in the cation.

The 1-butyl-3-methylimidazolium cations and the chloride anions are joined together by a hydrogen bonding network, as shown in Fig. 1. The shortest H···Cl contacts of 2.485, 2.653, and 2.688 Å in-

volve hydrogen atoms H(2), H(6A), and H(6B), respectively. These hydrogen atoms are expected to be most acidic in the cation. The respective C-H···Cl angles are 157.9, 166.0, and 145.6°.

1-Butyl-3-methylimidazolium hexafluorophosphate

1-Butyl-3-methylimidazolium hexafluorophosphate [BMIM]PF_6 (**2**) was prepared from pure **1** [43]. The starting compound was weighted in a reactor vessel, and acetone was added. [BMIM]Cl does not dissolve noticeably in acetone at room temperature. However, the presence of some [BMIM]Cl could be inferred from the ^{1}H NMR spectrum of a pure sample of [BMIM]Cl recorded in d_6-acetone. An equimolar amount of $NaPF_6$ was subsequently added. The reaction was performed at 80 °C for 5 to 15 min. After cooling, solid NaCl was separated by filtration through Celite. Neutral alumina or Silica Gel could also be used for the filtration. The yield of **2** was 95–99%. The yellow/orange colour of the product was due to the presence of traces of acetone, which can sometimes result in colouration during the quaternisation step [21]. However, the reaction without the solvent was not possible because of high melting points of [BMIM]Cl and $NaPF_6$.

For comparison, the above reaction was repeated at room temperature without microwave heating. The reagents were mixed together and allowed to react for 4.5 h. The crude product was filtered through Celite. After removal of the solvent by evaporation and drying in vacuum the yield of brown [BMIM]PF_6 was 83%. The ^{1}H NMR spectrum indicated a pure product.

We also studied the effect of temperature on the preparation of [BMIM]PF_6 promoted by microwave heating. The increase in temperature from 80 to 100 °C did not essentially improve the yield. The reaction time needs to be long enough for a good yield (see Table 4). The products from the separate reaction temperatures were analysed by ^{1}H NMR and MS(ESI^+ and ESI^-). NMR spectra were all similar. Every MS (ESI^+) spectrum contained *m/z*'s due to $[BMIM]^+$ and $[MIM]^+$, and MS(ESI^-) showed a peak due to $[PF_6]^-$. In addition, positive as well as negative electrospray MS spectrum contained double ions, which occasionally were induced by the MS recording conditions.

The best way to prepare [BMIM]PF_6 (**2**) by a microwave-assisted reaction was to allow equimolar amounts of starting compounds to react together in acetone for 10 min at 80 °C. In that time all starting material was consumed. When the reaction time was sufficient, the filtration through a sintered glass funnel was adequate to remove completely the precipitated NaCl. If the reaction was not complete, some [BMIM]Cl remained in the solution and it could not be separated from **2**.

Table 4. The effect of the reaction temperature on a microwave-assisted preparation of 1-butyl-3-methylimidazolium hexafluorophosphate (**2**) in acetone.

T [°C]	Reaction time [min]	Colour of the product	Yield of **2** [%]
80	5	orange	87
80	10	yellow	99
90	5	orange	87
100	10	orange	92

Reaction conditions: 1 mmol of [BMIM]Cl and $NaPF_6$ in acetone, microwave radiation power high.

A preparation of ionic liquids of alkylimidazolium fluoroanions has also been performed in water [19]. We studied the preparation of [BMIM]PF_6 in water by microwave heating. The reaction was carried out in a similar fashion as in acetone. After 5 min at 80 °C a cloudy, orange reaction mixture was cooled and washed three times with distilled water. Drying overnight in vacuum at 90 °C afforded 75% of a yellow product. The crude product was analysed by MS(ESI^+) and ^{1}H NMR. The MS spectrum was similar to that of [BMIM]PF_6 from the reaction in acetone. The ^{1}H NMR spectrum was also similar, but we could not observe the resonance due to H-2.

1-Butyl-3-methylimidazolium dicyanamide

1-Butyl-3-methylimidazolium dicyanamide [BMIM]CA (**3**) is a low viscosity ionic liquid which is a suitable solvent for a wide variety of inorganic and organic compounds [45–46]. We prepared [BMIM]DCA by using microwave heating directly from pure **1** and $NaN(CN)_2$. [BMIM]Cl was weighted in a reactor vessel, and acetone and $NaN(CN)_2$ were added. The solid starting compounds did not noticeably dissolve in acetone at room temperature. The reaction was performed at three temperatures 80, 90 and 100 °C and the reaction time was 10 min. After cooling, solid NaCl was separated from the yellow product mixture by filtration through Celite. The evaporation of the solvent and the overnight drying in vacuum yielded 89% (reaction temperature 80 °C) of crude **3** (see Table 5). The increase in the reaction temperature in fact decreased the crude yield, because the product then contained unreacted [BMIM]Cl. The products

Table 5. Preparation of 1-butyl-3-methylimidazolium dicyanamide (**3**) at separate reaction temperatures assisted by microwave irradiation.

T [°C]	Colour of the product	Yield of crude **3** [%]	Remarks
80	yellow	89	
90	yellow	90	contains some [BMIM]Cl
100	yellow	92	contains some [BMIM]Cl

Reaction conditions: 1 mmol of [BMIM]Cl and $NaN(CN)_2$ in acetone, reaction time 10 min, microwave irradiation power high.

Table 6. Electrospray ionization mass spectra of the crude products of 1-butyl-3-methylimidazolium dicyanamide (**3**) from separate reaction temperatures.

T [°C]	MS (ESI^+), *m/z* (rel. int. %) of detected components in crude **3**
80	83 (90) $[MIM]^+$, 139 (100) $[BMIM]^+$
90	83 (35) $[MIM]^+$, 139 (100) $[BMIM]^+$, 313(15) $[BMIM]_2{}^+Cl$
100	83 (75) $[MIM]^+$, 139 (100) $[BMIM]^+$, 313(30) $[BMIM]_2{}^+Cl$

$[MIM]^+$ = methylimidazolium cation, $[MMIM]^+$ = butyl-methylimidazolium cation.

from all three reaction temperatures were characterized by ^{1}H NMR and MS(ESI^+ and ESI^-). While all NMR spectra were identical, the MS(ESI^+) spectra were different (see Table 6). It could be inferred that the product contained small amounts of unreacted [BMIM]Cl. The optimal reaction temperature is 80 °C.

Conclusions

Microwave technique is a fast and simple procedure to produce 1-butyl-3-methylimidazolium salts. For the successful preparation of 1-butyl-3-methylimidazolium hexafluorophosphate and dicyanamide it is essential that the starting compound 1-butyl-3-methylimidazolium chloride is pure. The removal of impurities from the product by washing or by multiple recrystallisation is laborious, if not impossible. We have shown that coloured side products can be avoided by using a low enough reaction temperature during the preparation of the ionic liquid. The optimum temperatures during the preparation were 130, 80 and 80 °C for 1-butyl-3-methylimidazolium chloride, hexafluorophosphate and dicyanamide, respectively. The higher reaction temperatures led to the formation of product mixtures. However, pure ionic liquids do not rearrange upon heating.

Reaction time during the synthesis was also a crucial factor. For a successful high-yield preparation of ionic liquids by the microwave-assisted reaction it is important that the reaction time is sufficiently long to allow the reaction to complete. The advantages of the microwave-assisted method compared to conventional heating involve the saving of chemicals, reaction time, and work and facilitates high yields of pure ionic liquids.

MS(ESI^+) is a very sensitive and useful technique for the rapid determination of the purity of ionic liquids, since minor, potentionally undesirable side products can conveniently be detected and identified. The presence of additional anions in the product can be detected by MS(ESI^-) even when their content is small. The disadvantage in the anion mode is the variation of the sensitivity from anion to anion. The quantitative estimation of the content of impurities is also difficult.

The assignment of the NMR spectra is hampered by widely varying solubilities of different ionic liquids that necessitates the recording of the ^{1}H NMR spectra of each individual compound in different solvents. It is well-known that positions of resonances in NMR spectra are influenced by a solvent [47] and therefore direct comparison of ^{1}H NMR spectra of different ionic liquids can be misleading. In addition, non-protonic anions cannot be detected by ^{1}H NMR. It can be concluded that the reliable estimation of the side products and impurities during the formation of ionic liquids is best carried out by combined use of ESIMS and ^{1}H NMR spectroscopy.

Experimental Section

General

N-Methylimidazole and $NaPF_6$ (Aldrich), butyl chloride (Fluka), and $NaN(CN)_2$ (Fluka) were used without further purification. Ethyl acetate (Lab-Scan) was distilled over CaH_2 and acetone (J. T. Baker) stored on a Molecular Sieve (4 Å).

The microwave reactor was the single mode Emrys™ Creator (Personal Chemistry AB) [30] designed for synthetic use and equipped with a magnetic stirrer, and a temperature and pressure control and adjustment system. Reactor vessels were Emrys Process Vials™

for 0.5 – 2.0 ml. ^{1}H NMR spectra were recorded on a Bruker DBX 200 instrument at 200 MHz. Electrospray ionisation mass spectra were recorded on a Micromass, LCT mass spectrometer.

*Preparation of 3-butyl-1-methylimidazolium chloride [BMIM]Cl (**1**)*

N-Methylimidazole (3.2 mmol) and butylchloride (3.5 mmol) were mixed in a sealed microwave reactor and irradiated for 15 min at 130 °C. The crude product of **1** was washed few times with dry EtOAc and dried overnight in a

vacuum at 70 °C. The yield of a white [BMIM]Cl was 77%. The product was analyzed by ^{1}H NMR and MS(ESI$^+$). ^{1}H NMR spectrum of **1** ($CDCl_3$, 200 MHz): $\delta = 0.97$ (t, 3H, $J = 7.3$ Hz, 9-CH_3) 1.37 (m, 2H, $J = 7.4$ Hz, 8-CH_2), 1.90 (m, 2H, $J = 7.4$ Hz, 7-CH_2), 4.13 (s, 3H, 10-CH_3), 4.33 (t, 2H, $J = 7.3$ Hz, 6-CH_2), 7.33 (t, 1H, $J = 1.8$ Hz, 5-CH), 7.44 (t, 1H, $J = 1.8$ Hz, 4-CH), 10.9 (s, 1H, 2-CH). Lit. [23]. MS(ESI$^+$) [*m/z* (rel. int.,%)]: $M^{+\cdot}$ 139 (100) $[BMIM]^+$, 83(20) $[MIM]^+$.

*Preparation of 3-butyl-1-methylimidazolium hexafluorophosphate [BMIM]PF_6 (**2**) in acetone*

[BMIM]Cl (**1**) (1 mmol) was weighted into a microwave reactor, 1 ml of acetone and $NaPF_6$ (1 mmol) added. The reaction mixture was heated by microwaves for 10 min at 80 °C. The cooled reaction mixture was filtered through Celite to remove solid NaCl. After the evaporation of acetone the yield of [BMIM]PF_6 was 99%. The product was analyzed by ^{1}H NMR and MS(ESI$^+$ and ESI$^-$). ^{1}H NMR spectrum of **2** (MeOD, 200 MHz): $\delta = 0.99$ (t, 3H, $J = 7.3$ Hz, 9-CH_3) 1.38 (m, 2H, $J = 7.4$ Hz, 8-CH_2), 1.86 (m, 2H, $J = 7.4$ Hz, 7-CH_2), 3.92 (s, 3H, 10-CH_3), 4.20 (t, 2H, $J = 7.4$ Hz, 6-CH_2), 7.54 (t, 1H, $J = 1.8$ Hz, 5-CH), 7.61 (t, 1H, $J = 1.8$ Hz, 4-CH), 8.85 (s, 1H, 2-CH). MS(ESI$^+$) [*m/z* (rel. int.,%)]: M^+ 139 (100) $[BMIM]^+$, 83 (45) $[MIM]^+$. MS (ESI$^-$) [*m/z* (rel. int.,%)]: $M^{-\cdot}$ 145 (100) $[PF_6]^-$.

*Preparation of 3-butyl-1-methylimidazolium hexafluorophosphate [BMIM]PF_6 (**2**) in water*

[BMIM]Cl (**1**) (1 mmol), $NaPF_6$ (1 mmol) and 1 ml of distilled water were heated in a microwave reactor for 5 min at 80 °C. An orange ionic liquid settled down. After cooling the crude product was washed three times with distilled water and dried overnight in a vacuum. The yield of a yellow **2** was 75%. According to ^{1}H NMR the product was pure.

*Preparation of 3-butyl-1-methylimidazolium hexafluorophosphate [BMIM]PF_6 (**2**) at room temperature*

[BMIM]Cl (**1**) (2 mmol), $NaPF_6$ (2 mmol) and 1 ml of acetone were mixed at room temperature for 4.5 h. After filtration through Celite, the solvent was evaporated and the brown product dried in a vacuum. The yield was 83%. The ^{1}H NMR indicated that the product was pure.

*Preparation of 3-butyl-1-methylimidazoliumcc dicyanamide [BMIM]DCA (**3**)*

[BMIM]Cl (**1**) (1 mmol) was weighted into a microwave reactor, 1 ml of acetone and $NaPF_6$ (1 mmol) were added. The reaction mixture was irradiated for 10 min at 80 °C. The product mixture was filtered through Celite to remove solid NaCl. After the evaporation of acetone the yield of **3** was 89%. The product was analyzed by ^{1}H NMR and MS(ESI$^+$ and ESI$^-$). ^{1}H NMR spectrum of **3** ($CDCl_3$, 200 MHz) $\delta = 0.99$ (t, 3H, $J = 7.4$ Hz, 9-CH_3) 1.41 (m, 2H, $J = 7.5$ Hz, 8-CH_2), 1.92 (m, 2H, $J = 7.5$ Hz, 7-CH_2), 4.10 (s, 3H, 10-CH_3), 4.30 (t, 2H, $J = 7.4$ Hz, 6-CH_2), 7.37 (t, 1H, $J = 1.8$ Hz, 5-CH), 7.43 (t, 1H, $J = 1.8$ Hz, 4-CH), 10.15 (s, 1H, 2-CH). MS(ESI$^+$) [*m/z* (rel. int.,%)]: M^+ 139 (100) $[BMIM]^+$, 83 (90) $[MIM]^+$. MS(ESI$^-$) [*m/z* (rel. int.,%)]: $M^{-\cdot}$ 66 (100) $[N(CN)_2]^-$, 97 (10).

Table 7. Details of the crystal structure determination of **1**.

Empirical Formula	$C_8H_{15}ClN_2$
Relative molecular mass	174.67
T [K]	150 K
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	9.920(2)
b [Å]	11.453(2)
c [Å]	9.649(2)
β [°]	118.81(3)
V [Å^3]	960.6(3)
Z	4
$F(000)$	376
D_c [g cm^{-3}]	1.208
μ(Mo-K$_\alpha$) [mm^{-1}]	0.341
Crystal size [mm]	$0.15 \times 0.10 \times 0.05$
θ Range (deg.)	4.22 – 25.99
Number of reflections collected	12068
Number of unique reflections	1881
Number of observed reflections[a]	1675
Number of refined parameters	103
R_{INT}	0.0465
R_1 (all data)[a]	0.0387
wR_2 (all data)[a]	0.0797
GOOF	1.112
Max. and min. heights in final difference Fourier synthesis (e Å^{-3})	0.201, −0.255

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2] / [\Sigma w(F_o^2)^2]\}^{1/2}$.

X-ray crystallography

Diffraction data of **1** were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) by recording 360 frames *via* φ-rotation ($\delta\varphi = 1°$; twice 20 s per frame). Crystal data and details of structure determination are given in Table 7.

The structure was solved by direct methods using SHELXS-97 [48] and refined using SHELXL-97 [49]. After the full-matrix least-squares refinement of non-hydrogen atoms with anisotropic displacement parameters, the hydrogen atoms were placed in calculated positions (C-H=0.95, 0.99, and 0.98 Å in the case of aromatic hydrogen atoms, methylene hydrogen atoms, and methyl hydrogen atoms, respectively).

In the final refinement the hydrogen atoms were riding with the carbon atom they were bonded to. The isotropic dis-

placement parameters of the aromatic hydrogen atoms were fixed at 1.2 times to those of the corresponding carbon atoms, and those of the aliphatic hydrogen atoms at 1.5 times to those of the corresponding carbon atoms. The scattering factors for the neutral atoms were those incorporated with the programs.

Supplementary material available

Crystallographic information for **1** (excluding tables of structure factors) has been deposited with the Cambridge Crystallographic Data Center as the supplementary publication number CCDC 208726. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax. +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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