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PII: S0022-2860(17)30008-X

DOI: 10.1016/j.molstruc.2017.01.008

Reference: MOLSTR 23313

To appear in: Journal of Molecular Structure

Received Date: 5 September 2016

Revised Date: 29 December 2016

Accepted Date: 2 January 2017

Please cite this article as: B. Haddad, D. Mokhtar, M. Goussem, E.-h. Belarbi, D. Villemin, S. Bresson, M. Rahmouni, N.R. Dhumal, H.J. Kim, J. Kiefer, Influence of methyl and propyl groups on the vibrational spectra of two imidazolium ionic liquids and their non-ionic precursors, *Journal of Molecular Structure* (2017), doi: 10.1016/j.molstruc.2017.01.008.

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### Influence of methyl and propyl groups on the vibrational spectra of two imidazolium ionic liquids and their non-ionic precursors

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#### Abstract

Imidazolium-based ionic liquids (ILs) are usually synthesized using non-ionic imidazole compounds as precursors. While the ILs have been extensively studied in the past, the precursors was not paid much attention to. The structural analysis of the precursors, however, may offer an opportunity to better understand the behavior of the ionic compounds of interest. In this paper, a comparative study of two ionic liquids and their imidazole precursors is presented. The precursors 1-methylimidazole [1-MIM] and 1,2-dimethylimidazole [1,2-DMIM] are compared in order to explain the influences of the methyl group at the C(2)position (methylation). Since the imidazole compounds are non-ionic, the spectroscopic properties of [1-MIM] and [1,2-DMIM] are not affected by cation-anion interactions. In addition, the products obtained by alkylation using propyl iodide leading to the corresponding IL compounds 1-methyl-3-propylimidazolium iodide [1-MPrIM<sup>+</sup>][[] and 1,2-dimethyl-3propylimidazolium iodide [1,2-DMPrIM<sup>+</sup>][I] were studied. For this purpose, vibrational spectroscopy in terms of FT-Raman and FTIR in the wavenumber range from [45 to 3500cm<sup>-</sup> <sup>1</sup>] and from [600 to 4000 cm<sup>-1</sup>], respectively, was performed. Moreover, to aid the spectral assignment, density functional theory (DFT) calculations were carried out. The aim was to investigate the vibrational structure, to understand the effects of the propyl group at the N(3)and of the methyl group at the C(2) position, and to analyze the resulting cation-anion interactions. The data indicate that the iodide ion predominantly interacts with the C(2)-H group via hydrogen bonding. Upon methylation, the C(4/5)-H moiety becomes the main interaction site. However, an interaction takes place only with one of the two hydrogen atoms resulting in a split of the initially degenerate CH stretching modes.

Keywords: Ionic liquids ILs; FT-Raman, FTIR/ATR, imidazolium, methylation, propylation.

#### 1. Introduction

1-Methylimidazole (or N-methylimidazole) and 1,2-dimethylimidazole are heterocyclic aromatic compounds having the chemical formula  $CH_3C_3H_3N_2$  and  $CH_3CH_3C_3H_2N_2$ , respectively. They are colourless liquids that are used as specialty solvents [1], bases, and as precursors in the synthesis of ionic liquids (ILs) [2]. Furthermore, the properties of these important compounds make them a very promising class of materials for a wide range of applications such as in pharmaceuticals [3] and pesticides [4]. In addition, they are widely utilized in corrosion inhibitors [5] and as catalytic deprotonation reagents [6].

The chemical reaction of these two precursors with alkyl halides yields transfer of the alkyl group to the imidazolium ring and results in an imidazolium halide ionic liquid [7]. The large variety of possible combinations of cations and anions leads to ionic compounds with a wide range of physicochemical properties [8]. For example, ILs based on dialkylimidazolium cations like 1-methyl-3-propylimidazolium combined with the iodide anion provide excellent efficiency and good stability in dye-sensitized solar cells [9]. They have also been extensively studied as electrolytes because of their outstanding thermal and electrochemical stability [10]. Besides the cation-anion combination, simple changes in the length of the spacer or the aliphatic chains of the cation allows for tailoring the physical properties of these ILs for specific applications. With this objective, several studies have been done to control the vibrational spectroscopic properties of ILs through the design of their cations and anions for practical use [11-12].

Recent studies have been performed to elucidate the relation between the structure of ILs and their physicochemical properties, especially, the thermophysical properties including the viscosity, density, and melting point. These properties determine whether or not an IL is suitable for a given application [14]. Previous reports indicate that the methylation of the C2 position [N-C-N site in the aromatic ring] of 1,3-dialkylimidazolium-based ILs disrupts the predominant hydrogen-bonding interaction between cation and anion leading to unexpected changes of the physicochemical properties [15-16]. The intermolecular cation-anion interactions have been studied by several groups [17-18]. These interionic interactions determine the macroscopic (chemical and thermophysical) properties [19].

The present work focuses on the synthesis and vibrational properties of two ionic liquids and their precursors. The alkylation reaction of 1-methylimidazole and 1,2-dimethylimidazole with propyl iodide using a microwave process yields the ionic liquids [1-MPrIM<sup>+</sup>][I<sup>-</sup>] and [1,2-DMPrIM<sup>+</sup>][I<sup>-</sup>]. The obtained ILs are confirmed by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and FTIR

spectroscopy. In the first step of our work, the precursors, 1-methylimidazole and 1,2dimethylimidazole, are studied. To date, only few experimental studies have been dedicated to illustrate the vibrational mode assignments of methylimidazoles. For example, Carter and Pemberton have reviewed and discussed the Raman and SERS (Surface-enhanced Raman scattering) spectra as well as the vibrational assignments of 1- and 2-methylimidazole [13]. A vibrational analysis of 1,2-dimethylimidazole has not been published, to the best of our knowledge. The understanding of the vibrational structures is important to explain the influences of the methyl group at the C2 position (effect of methylation) in the two resulting ILs. For this purpose, the Raman and attenuated total reflection Fourier transform infrared (ATR/FTIR) spectra are analysed. In the second stage, the 1-methyl-3-propylimidazolium iodide [1-MPrIM<sup>+</sup>][T] and 1,2-dimethyl-3-propylimidazolium iodide [1,2-DMPrIM<sup>+</sup>][T] ionic liquids are studied to unravel the impact of propylating the N3 position and converting the precursors into ionic compounds. Their inter- and intramolecular interactions are analyzed utilizing the Raman and IR spectra.

#### 2. Experimental

#### 2.1 Materials, synthesis, and characterization

The reagents used in this study are 1-methylimidazole (>99%), 1,2-dimethylimidazole (98%), and propyl iodide (98%). They were purchased from Fluka and used as received.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a DRX 400 MHz NMR instrument. The chemical shifts ( $\delta$ ) are given in ppm and referenced to the internal solvent signal from TMS and CFCl<sub>3</sub>, respectively. The IR spectra were recorded on a FT-IR Perkin-Elmer Spectrum BX spectrophotometer (using KBr pellets) with a resolution of 4 cm<sup>-1</sup> in the range 4000-650 cm<sup>-1</sup>.

The synthesis of 1-methyl-3-propylimidazolium iodide  $[1-MPrIM^+][\Gamma]$  is depicted in scheme 1. Under microwave exposure, a mixture of 1-methylimidazole (7.78 mL, 100 mmol) and propyl iodide (9.74 mL, 50 mmol) was heated for 3 min at 120°C. The yield of this reaction was 87%. The reaction mixture was evaporated at reduced pressure and the product was washed repeatedly with diethyl ether (5 × 20 mL) to remove any excess propyl iodide. Then the solvent was removed and the product was dried under vacuum for 8 h to obtain a product with high purity. The resulting 1-methyl-3-propylimidazolium iodide was obtained as a yellowish viscous liquid. 1,2-Dimethyl-3-propylimidazolium iodide [1,2-DMPrIM<sup>+</sup>][ $\Gamma$ ] was synthesized in a similar way as the  $[1-MPrIM^+][\Gamma]$  ionic liquid. The yield of the synthesis was 92%. The compound was obtained as a slightly yellow liquid at room temperature.



Scheme 1. General synthesis of [1-MPrIM<sup>+</sup>][I<sup>-</sup>] and [1,2-DMPrIM<sup>+</sup>][I<sup>-</sup>] and numbering of atoms. MW = microwave.

The structures of the obtained products are confirmed using <sup>1</sup>H-, <sup>13</sup>C-NMR, and FTIR spectroscopy, which also confirms the absence of any major impurities. The spectroscopic data are given below and the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra are presented in Fig. S1 and S2 of the supplementary material:

**[1-MPrIM<sup>+</sup>][I<sup>-</sup>]**: <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta_{\rm H}$  (ppm): 9.08 (1H, s, N<sub>3</sub><sup>+</sup>C<sub>2</sub><u>HN</u>), 7.72 (1H, s, N<sub>3</sub><sup>+</sup>C<sub>4</sub><u>H</u>), 7.67 (1H, s, N<sub>1</sub>C<sub>5</sub>H), 4.11-4.14 (2H, t, J=4 Hz, N<sub>3</sub><sup>+</sup>C<sub>8</sub><u>H2</u>), 3.86 (3H, s, N<sub>1</sub>C<u>H</u><sub>3</sub>), 1.79-1.84 (2H, m, J=8 Hz, N<sub>3</sub><sup>+</sup>C<sub>8</sub>H<sub>2</sub>C<sub>9</sub><u>H<sub>2</sub></u>), 0.85-0.88 (3H, t, J=8 Hz, N<sub>3</sub><sup>+</sup>C<sub>8</sub>H<sub>2</sub>C<sub>9</sub>H<sub>2</sub>C<sub>10</sub><u>H<sub>3</sub></u>); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta_{\rm C}$  (ppm): 10.4, 23.3, 36.8, 51.1, 122.2, 123.5, 136.0; IR ( $\tilde{\nu}$  /cm<sup>-1</sup>): 3071 [ $\nu$ (=C-H)], 2962,2875 [ $\nu$  (C-H)], 1567 [ $\nu$ (C=C)], 1455 [ $\delta$ (C-H)], 1189 [ $\nu$ (C-N)], 747 [ $\nu$ (C-H)].

**[1,2-DMPrIM<sup>+</sup>][I**]: <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta_{\rm H}$  (ppm): 7.63(1H, s, N<sub>3</sub><sup>+</sup>C<sub>4</sub><u>H</u>), 7.60 (1H, s, N<sub>1</sub>C<sub>5</sub>H), 4.06-4.09 (2H, t, J= 4 Hz, N<sub>3</sub><sup>+</sup>C<sub>8</sub><u>H</u><sub>2</sub>), 3.75 (3H, s, N<sub>5</sub>C<u>H</u><sub>3</sub>), 2.58 (3H, s, N<sub>3</sub><sup>+</sup>C<sub>2</sub>C<u>H</u><sub>3</sub>N), 1.71-1.77 (2H, m, J=4 Hz, N<sub>3</sub><sup>+</sup>C<sub>8</sub>H<sub>2</sub>C<sub>9</sub><u>H</u><sub>2</sub>), 0.86-0.89 (3H, t, J=4 Hz, N<sub>3</sub><sup>+</sup>C<sub>8</sub>H<sub>2</sub>C<sub>9</sub>H<sub>2</sub>C<sub>10</sub><u>H</u><sub>3</sub>); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta_{\rm C}$  (ppm): 10.9, 11.7, 23.2, 36.7, 50.4, 121.3, 122.8, 143.7; IR ( $\tilde{\nu}$  /cm<sup>-1</sup>): 3074 [ $\nu$ (=C-H)], 2963,2876 [ $\nu$ (C–H)], 1586 [ $\nu$ (C=C)], 1456 [ $\delta$ (C-H)], 1135 [ $\nu$ (C-N)], 751 [ $\nu$ (C-H)].

### 2.2. FTIR/ATR and FT-RAMAN measurements

The measurements for the structural analysis were performed in the Walloon Agricultural Research Center (Craw) Belgium. The FTIR/ATR measurements were acquired on a Bruker Vertex II-70RAM Spectrometer (Bruker Analytical, Madison, WI) operating with a Golden Gate diamond ATR accessory (Specac Ltd, Slough, United Kingdom). The FTIR/ATR spectra [600-4000 cm<sup>-1</sup>] were collected with 1 cm<sup>-1</sup> nominal resolution by co-adding 64 scans for each spectrum. The OPUS 6.0 Software for Windows was used for the management of the instrument.

FT-Raman spectra were acquired on a Vertex 70-RAM II Bruker FT-Raman spectrometer. This instrument is equipped with a Nd:YAG laser (yttrium aluminium garnet crystal doped with triply ionized neodymium) with a wavelength of 1064 nm and a maximum power of 1.5 W. The measurement accessory is pre-aligned, only the Z-axis of the scattered light is adjusted to set the sample in the appropriate position regarding the local measurement point. The RAM II spectrometer is equipped with a liquid-nitrogen-cooled Ge detector. FT-Raman spectra [45-4000 cm<sup>-1</sup>] were collected with 1 cm<sup>-1</sup> resolution by co-adding 128 scans for each spectrum at room temperature. The OPUS 6.0 software was used for the spectral acquisition, manipulation, and transformation.

#### 2.3. DFT calculations

In order to aid the spectral assignments, the state-of-the-art density functional theory (DFT) calculations of the four compounds were carried out. For this purpose, isolated molecules or ion pairs were considered. Hybrid density functional theory, which incorporates Becke's three-parameter exchange with the Lee, Yang, and Parr correlation functional [20-21] method (B3LYP) in the GAUSSIAN-09 program [22] were performed on the four compounds by employing the 6-31(d, p) basis set for C, N H and LANL2DZ for I. Vibrational frequencies were calculated for confirmation of local minima on the potential energy surface, which were found to have no imaginary components.

#### 3. Results and discussion

In general, the vibrational structure of ILs is determined by the characteristics of the counterions and their molecular interactions. Therefore, the spectra of ILs are frequently studied. However, only few studies have been reported on the neutral (non-ionic) precursors [23-24]. In the present case, the precursors are [1-MIM] and [1,2-DMIM]. These species carry no net charges. Hence, the molecular complexity is significantly reduced compared to an IL as only a single species is present in the sample. The vibrational analysis may therefore provide interesting insights into the local structure and intramolecular interactions in these substances. Moreover, it can aid the interpretation of the IL compounds.

Figure 1 shows the IR spectra of 1-methylimidazole [1-MIM], 1,2-dimethylimidazole [1,2-DMIM], 1-methyl-3-propylimidazolium iodide [1-MPrIM<sup>+</sup>][ $\Gamma$ ], and 1,2-dimethyl-3-propylimidazolium iodide [1,2-DMPrIM<sup>+</sup>][ $\Gamma$ ]. The individual panels show the enlarged spectra in the ranges 600-1000 cm<sup>-1</sup>, 1000-1700 cm<sup>-1</sup>, and 2800-3200 cm<sup>-1</sup>. The observed IR

bands and their assignments are listed in Table 1. The Raman spectra of [1-MIM], [1,2-DMIM], [1-MPrIM<sup>+</sup>][I<sup>-</sup>], and [1,2-DMPrIM<sup>+</sup>][I<sup>-</sup>] are illustrated in Fig. 2, and the observed Raman bands and their assignments are summarized in Table 2. For an overview, the full IR and Raman spectra are shown in Figs. S3 and S4 of the supplementary material, respectively.



**Figure 1.** FTIR/ATR spectra of [1-MIM], [1,2-DMIM] (a, b and c), [1-MPrIM<sup>+</sup>][I<sup>-</sup>], [1,2-DMPrIM<sup>+</sup>][I<sup>-</sup>] (a', b' and c') in the spectral range: 600-1000 cm<sup>-1</sup>, 1000-1700 cm<sup>-1</sup> and 2800-3200 cm<sup>-1</sup>.



**Figure 2.** FT-Raman Spectra of [1-MIM], [1,2-DMIM] (a, b, c and d), [1-MPrIM<sup>+</sup>][I], and [1,2-DMPrIM<sup>+</sup>][I<sup>-</sup>] (a', b' c' and d') in the spectral ranges 0-600 cm<sup>-1</sup> (a), 600-1000 cm<sup>-1</sup>(b), 1000-1700 cm<sup>-1</sup>(c), and 2800-3200 cm<sup>-1</sup>(d).

3.1 Non-ionic Precursors

The observed peak wavenumbers in the computational and experimental data of the precursors are summarized in Table 1. The assignments are made on the basis of the DFT results and the literature [23-39].

#### <u>Region 0-600 cm<sup>-1</sup></u>

Unlike FTIR/ATR, the Raman instrument allows recording the vibrational spectrum in the low wavenumber region down to  $45 \text{ cm}^{-1}$  (the spectra of [1-MIM] and [1,2-DMIM] are shown in Fig. 2a). Below 200 cm<sup>-1</sup>, however, the spectra are dominated by a strong interference from elastically scattered light and thus the features observed should not be over-interpreted. Beyond 200 cm<sup>-1</sup>, the spectra show predominantly peaks that can be assigned to N-CH<sub>3</sub> vibrations.

### <u>Region 600-1000 cm<sup>-1</sup></u>

The bands between 600 and 1000 cm<sup>-1</sup> can be mainly ascribed to contributions from ring deformation modes of the imidazole (Fig 1a). The very strong band at 615 cm<sup>-1</sup> in [1-MIM] is assigned to the CN bond oscillation. The DFT suggests a very weak peak for this mode and no intensity at all for methylated species. The latter is confirmed by the absence of this peak in the spectrum of [1,2-DMIM]. The IR bands at 734 cm<sup>-1</sup> for [1-MIM] and 723/725 cm<sup>-1</sup> (IR/Raman) for [1,2-DMIM] are related to N-C-H wagging modes. The peak at 815 cm<sup>-1</sup> for [1-MIM] is assigned to the wagging contribution of the N-C2-H moiety. The rather strong [1-MIM] peak at 906/907 cm<sup>-1</sup> is attributed to the bending vibration of the N-C2-N moiety. The corresponding band in the methylated species [1,2-DMIM] is weak and observed at 925/920 cm<sup>-1</sup>.

### <u>Region 1000-1700 cm<sup>-1</sup></u>

In this spectral region, the methylation has further characteristic effects. For instance, the IR band at 1438 cm<sup>-1</sup> can be assigned to  $(CH_3)C2$  scissoring in [1,2-DMIM] does not have a corresponding mode in the spectrum of [1-MIM]. On the other hand, [1-MIM] exhibits an N-C2-H rocking mode at 1230/1231 cm<sup>-1</sup>, which is absent in the methylated precursor.

#### **Region 2800-3200 cm<sup>-1</sup>**

The spectral range 2800-3200 cm<sup>-1</sup> contains the CH-stretching vibrations of the alkyl groups as well as those of the imidazole ring. The IR and Raman spectra in this range are shown in Fig.1c and 2d, respectively. The signals are relatively weak in the IR owing to the selection

rules for absorption. The bands at low wavenumber are assigned to CH stretching in the aliphatic groups. The two weak bands at 2950/2953 and 2952/2953 cm<sup>-1</sup> in the spectra of the precursors, [1-MIM] and [1,2-DMIM], are likely due to the N1-methyl groups. The bands at higher wavenumber, i.e. around 3130 and 3178 cm<sup>-1</sup>, are a result of CH vibrations of the aromatic ring.

Figure 1(c) shows that the IR spectra of the two precursors [1-MIM] and [1-DMIM] are very similar in the CH stretching region between 2800 and 3200 cm<sup>-1</sup>. On the other hand, the bands at the highest frequency,  $3132 \text{ cm}^{-1}$  for [1,2-DMIM] and  $3134 \text{ cm}^{-1}$  for [1-MIM], are assigned to the symmetric stretching modes of C-H at the 4 and 5 positions of the imidazole ring. The C(2)-H stretching mode in [1-MIM] is not observed as an individual peak as the frequency is rather similar to that of the C4,5-H modes.

The weak Raman peaks at 2816 and 2803 cm<sup>-1</sup> for [1-MIM] and [1-DMIM], respectively, are likely due to overtone vibrations methyl rocking modes at 1420 and 1412 cm<sup>-1</sup>. Their appearance at a wavenumber that is slightly below the doubled values of the fundamental modes can be explained by anharmonicity effects.

Table 1. Computational and experimentally ob	served wavenumbers (in cm <sup>-1</sup> ) of the imidazole
precursors and their vibrational assignments.	

1-methylimidazole		1,2-dimethylimidazole			Assignment	
DFT	FTIR	Raman	DFT	FTIR	Raman	
3184 (3)	3178		3182 (5)	3179		H-C4-C5-H symmetric stretch
3155 (3)	3134	3135	3154 (7)	3132	3135	H-C4-C5-H asymmetric stretch
3153 (3)						C2-H stretch
			3065 (4)			CH <sub>3</sub> (C2) asymmetric stretch
3056 (10)	3105	3109	3056 (11)	3108	3109	CH <sub>3</sub> asymmetric stretch
3022 (20)	3014		3023 (18)			CH <sub>3</sub> asymmetric stretch
			2989 (23)	2999		CH <sub>3</sub> (C2) asymmetric stretch
			2942 (28)	2952	2953	CH <sub>3</sub> (C2) symmetric stretch
2959 (47)	2950	2953				CH <sub>3</sub> symmetric stretch
		2917			2928	
		2816			2803	overtone
			1535 (21)	1527		CN stretch
1511 (7)	1515	1516	1480 (6)			CH <sub>3</sub> scissor
			1502 (24)	1504	1504	N3-C4-H rock + CH3 rock
			1460 (13)	1469	1465	CH <sub>3</sub> (C2) rocking
1451 (7)		1467	1452 (1)			
			1451 (3)			$CH_3$ (C2) scissor

			1438 (22)	1438		CH <sub>3</sub> (C2) scissor + CH <sub>3</sub> rocking
1418	1419	1420	1408 (43)	1411	1412	CH <sub>3</sub> rock
(19)						
			1375 (1)			CH <sub>3</sub> (C2) rock
1366 (1)						N1-C2-N3 asymmetric stretch
1349 (3)	1350	1378	1348 (6)	1350	1345	CN stretch + CH <sub>3</sub> rocking
1276	1284	1285	1280 (35)	1280	1284	H-C4-C5-H rock
(27)						
1236	1230	1231				N1-C2-H rock
(20)						
	1186		1189 (2)	1186	1202	
1116	1135		1148 (10)	1132	1143	N1-C5-H rock
(15)						
	1107	1109				
1070	1076	1077	1075 (9)	1083	1084	H-C4-C5-H scissor
(11)						
1047	1054			1054		CH <sub>3</sub> scissor
(11)						
1014 (9)	1027	1029				N1-C2-N3 symmetric stretch
			971 (14)	985		CH3 wag
888 (11)	906	907	900 (2)	925	920	N1-C2-N3 bend
831 (2)			822 (5)			H-C4-C5-H twist
782 (25)	815					N1-C2-H wag
699 (18)	734		702 (21)	723	725	N3-C4-H wag
660 (4)	663	668		/		
654 (13)			663 (15)	675		CN bond oscillation
604 (4)	615		608 (0)	640	642	CN bond oscillation

### **3.2 Ionic liquids**

The observed peak wavenumbers in the computational and experimental data of the ionic liquids are summarized in Table 2. The assignments are made on the basis of the DFT results and the literature [23-39].

Table 2. Computational and experimentally observed wavenumbers (in cm<sup>-1</sup>) of the imidazole precursors and their vibrational assignments.

1-methyl-3-		1,2-dimethyl-3-			Assignment	
propylimidazolium iodide		propylimidazolium iodide				
DFT	FTIR	Raman	DFT	FTIR	Raman	
3316 (2)			3222 (2)	3174	3171	H-C-C-H symmetric stretch
3198 (6)	3138	3145	3204 (5)	3121	3122	H-C-C-H asymmetric stretch
3086 (1)			3094 (0)			CH <sub>3</sub> asymmetric stretch
3060 (6)			3079 (7)			CH <sub>3</sub> asymmetric stretch
3043 (11)	3071	3076	3056 (7)	3074	3074	CH <sub>3</sub> (propyl chain) asymmetric
						stretch
3035 (10)			3040 (21)			CH <sub>2</sub> (propyl chain) asymmetric

						stretch
3024 (25)			3038 (7)			CH <sub>3</sub> (propyl chain) asymmetric
						stretch
3000 (4)			3037 (13)			CH <sub>2</sub> (propyl chain) asymmetric
						stretch
			3015 (19)			$CH_2$ (propyl chain) asymmetric
			2002 (10)			stretch
			2993 (10)			CH <sub>2</sub> (propyl chain) asymmetric
2083 (22)			2075 (42)		2072	CH symmetric stratch
2983(22)	2062	2072	2973(42)	2062	2972	CH <sub>3</sub> symmetric stretch
2974 (47)	2962	2973	2937 (13)	2962		stretch
2954 (27)		2945	2948 (39)		2944	CH <sub>2</sub> (propyl chain) symmetric
2751(27)		2343	2910(39)		2344	stretch
2945 (38)	2933	2927				CH <sub>2</sub> (propyl chain) symmetric
		_				stretch
			2939 (41)	2933		$CH_3$ ( $C_2$ ) symmetric stretch
			2925 (98)			$CH_3$ (C <sub>2</sub> ) symmetric stretch
	2875			2875		CH <sub>2</sub> (propyl chain) symmetric
						stretch
		2826			2826	overtone
2758 (1140)	2849					C2-H stretch
1566 (16)	1585	1564	1580 (26)	1567		$C_4$ - $C_5$ + C-N stretch
1552 (80)	1535			,		N <sub>1</sub> -C <sub>2</sub> -H rock
			1522 (76)	1515		N1-C2-N3 stretch + $CH_3$ ( $C_2$ )
						rock
1476 (13)						CH <sub>3</sub> (propyl chain) scissor
1474 (15)			1504 (24)			CH <sub>3</sub> scissor
1471 (7)			1481 (8)			CH <sub>2</sub> (propyl chain) scissor
1458 (3)						CH <sub>2</sub> (propyl chain) scissor
1455 (13)	1456		1472 (8)			CH <sub>3</sub> scissor
			1470 (10)	r		CH <sub>3</sub> (propyl chain) scissor
1449 (6)		1446	1467 (4)			CH <sub>2</sub> (propyl chain) scissor
			1462 (6)			CH <sub>2</sub> (propyl chain) scissor
			1454 (4)	1456		CH <sub>3</sub> scissor
			1433 (8)		1446	$CH_3$ (C <sub>2</sub> ) scissor
			1424 (27)	1419		CH <sub>3</sub> scissor
1425 (8)	1429		1401 (8)			CH <sub>3</sub> rocking
1413 (21)		1416	1388 (1)			CH <sub>2</sub> (propyl chain) rocking + C-N
						stretch
1387 (7)		1386				CH <sub>3</sub> (propyl chain) rock
			1385 (6)			$CH_3(C_2)$ rock
1380 (6)	1382		1379 (10)	1382	1378	CH <sub>2</sub> (propyl chain) rock
1364 (5)	1351		1368 (4)	1351		$CH_2$ (propyl chain) rock
	1328	1337	1332 (9)	1328	1242	N1-C2-N3 bend
1324 (1)			1304 (2)		1303	CH <sub>2</sub> (propyl chain) rock
1305 (2)			1299 (8)			CH <sub>2</sub> (propyl chain) rock
1292 (5)						CH <sub>2</sub> (propyl chain) rock
1276 (25)	1267	1271	1253 (6), 1227 (17)	1243		$H-C_4-C_5-H$ rock
		1235	,			

1231 (4)	1189		1187 (12)	1186		CH <sub>2</sub> (propyl chain) twist
1231(+) 1163(102)	1164		1107 (12)	1100		N. C. H rock
1103 (102)	1104					
1124 (4)						CH <sub>3</sub> rock
			1123 (17)	1135		$CH_3$ (C <sub>2</sub> ) rock
1120 (7)		1113	1117 (4)		1114	CH <sub>2</sub> (propyl chain) twist
1099 (4)						
1084 (1)	1087		1095 (7)			H-C <sub>4</sub> -C <sub>5</sub> -H scissor
1074 (29)	1056					CH <sub>3</sub> rock
1020 (1)	1043		1091 (5)			C-C (propyl chain) stretch
			1020 (48)	1056	1058	CH <sub>3</sub> (C <sub>2</sub> ) wag
1008 (3)						
999 (24)		1021				Ring breathing
920 (39)		904				N <sub>1</sub> -C <sub>2</sub> -H wag
884 (6)			880 (6)		880	CH <sub>3</sub> (propyl chain) wag
735 (12)			737 (2)			CH <sub>2</sub> (propyl chain) wag
723 (15)	748		747 (12)	752	760	CN stretch
				724		G
712 (38)	696	696	708 (16),	703	704	H-C <sub>4</sub> -C <sub>5</sub> -H wag
			703 (10)			
652 (12)	646	659	634 (53)	663	667	CN bond oscillation
609 (1)	615	619	598 (103)			CN bond oscillation

### **Region 0-600 cm**<sup>-1</sup>

The Raman spectra in the low wavenumber region down to 45 cm<sup>-1</sup> are shown in Fig. 2a'. Below 200 cm<sup>-1</sup>, the IL spectra are dominated by a strong interference from elastically scattered light like for the non-ionic precursors. Beyond 200 cm<sup>-1</sup>, the spectra show predominantly peaks that can be assigned to N-CH<sub>3</sub> vibrations.

### <u>Region 600-1000 cm<sup>-1</sup></u>

The bands between 600 and 1000 cm<sup>-1</sup> can be mainly ascribed to contributions imidazolium cation (Fig 1.a'). Like in [1-MIM], we noticed a very strong band at 615/619 cm<sup>-1</sup> in [1-MPrIM<sup>+</sup>][I<sup>-</sup>]. This band is assigned to CN bond oscillations. The corresponding mode in the species with a methylated C2 position is absent. However, according to the DFT simulations, it is likely located outside the range accessible by the IR instrument. The IR bands of the precursors at 734 cm<sup>-1</sup> for [1-MIM] and 723/725 cm<sup>-1</sup> for [1,2-DMIM] are shifted after propylation to 748 cm<sup>-1</sup> for [1-MPrIM<sup>+</sup>][I<sup>-</sup>] and at 752 cm<sup>-1</sup> for [1,2-DMPrIM<sup>+</sup>][I<sup>-</sup>], respectively. These bands are assigned to vibrations of the N-C-N moiety and therefore are strongly affected by methylation at C2 and propylation at C3.

### <u>Region 1000-1700 cm<sup>-1</sup></u>

As for the precursors, the methylation has some characteristic effects in this spectral range. For instance, the strong band at 1164 cm<sup>-1</sup> for  $[1-MPrIM^+][\Gamma]$  can be assigned to (N)-C2-H rocking. The IR modes at 1351 cm<sup>-1</sup> are assigned to CH<sub>2</sub> rocking in the propyl chain. In this range, the Raman spectrum exhibits also bands at 1350/1348 cm<sup>-1</sup> for [1-MIM], at 1350/1345 cm<sup>-1</sup> for [1,2-DMIM], which are due to CN stretching and CH<sub>3</sub> rocking. The corresponding bands in the ionic compounds are observed at 1337 cm<sup>-1</sup> for  $[1-MPrIM^+][\Gamma]$ , and at 1342 cm<sup>-1</sup> for  $[1,2-DMPrIM^+][\Gamma]$ . The medium intensity bands centered around 1456 cm<sup>-1</sup> in the IR spectra of both propylated compounds  $[1-MPrIM^+][\Gamma]$  and  $[1,2-DMPrIM^+][\Gamma]$  can be assigned to CH<sub>3</sub> scissoring vibrations. Moreover, the strong band centered around 1515 cm<sup>-1</sup> in the Raman spectrum of  $[1,2-DMPrIM^+][\Gamma]$  is assigned to a NC(2)N stretching band.

#### <u>Region 2800-3200 cm<sup>-1</sup></u>

Again, the spectral range 2800-3200 cm<sup>-1</sup> contains the CH-stretching vibrations of the alkyl groups as well as those of the imidazolium ring. The latter are likely carrying information about possible interionic hydrogen bonding interactions if present. The IR and Raman spectra in this range are shown in Fig. 1c' and 2d', respectively. Both IL compounds exhibit bands at 2875 and 2933 cm<sup>-1</sup>, which can be assigned to CH vibrations in the propyl chain. Moreover, the ILs exhibit a strong band at 2962 cm<sup>-1</sup>, which is again a contribution of the propyl chain. The bands at higher wavenumber, i.e. beyond 3100 cm<sup>-1</sup>, is a result of CH vibrations of the aromatic ring. Only the C2-H stretching mode is significantly shifted to 2849 cm<sup>-1</sup> as a result of interionic interactions. A detailed discussion is provided in the next section.

#### **3.3 Effects of interionic interactions**

After propylation, the spectra in the region 2800-3200 cm<sup>-1</sup> become more distinctly divided into two regions (see Figure 1c'). The presence of the propyl side chains results in three joint peaks in the region below 3000 cm<sup>-1</sup>. These bands can be attributed to antisymmetric and symmetric vibrations of the methyl and methylene groups. The bands at wavenumbers above  $3100 \text{ cm}^{-1}$  can be assigned to the aromatic CH stretching modes, which may be influenced by anion-cation interactions via C(2,4,5)-H…T. For example, the band at 3138 cm<sup>-1</sup> in the spectrum [1-MPrIM<sup>+</sup>][T] was assigned to C(4,5)-H stretching. In the methylated IL [1,2-DMPrIM<sup>+</sup>][T], this band virtually disappears, while a very weak mode at 3174 cm<sup>-1</sup> and a shoulder band at 3121 cm<sup>-1</sup> appear. These bands are marked by arrows in Fig. 1c'. A similar effect can be observed in the Raman spectra, see Fig. 2d'. This observation can be explained

in terms of the interionic interactions. In [1-MPrIM<sup>+</sup>][I<sup>-</sup>], the C2-H is the predominant interaction site due to the polarization of this bond and the resulting slightly acidic character. Consequently, it is significantly red-shifted to 2849 cm<sup>-1</sup> in [1-MPrIM<sup>+</sup>][I<sup>-</sup>] while it has virtually the same frequency as the C(4,5)-H modes in the non-ionic precursor [1-MIM], where no hydrogen bond acceptor is present and the C2-H bond is not acidic. This interaction site is removed, when the IL is methylated (see Fig. 3). As a consequence, interionic interactions at C(4,5)-H become favorable. When the iodide ion forms a C-H $\cdots$ I hydrogen bond at either the C4 or the C5 position, the interactions will result in two distinguishable C-H bonds [30]. One will interact with the iodide and hence the corresponding C-H stretching mode will be red-shifted (3121 cm<sup>-1</sup>). The other hydrogen atom will not (or at least less) be involved in the interactions. This, combined with the induced re-distribution of charge in the imidazolium ring leads to a blue-shift that manifests as the peak at 3174 cm<sup>-1</sup>. Endo et al. [40] observed a similar behavior in the Raman spectra of the ILs [BMIM<sup>+</sup>][I] and [1,2-DMBuIM<sup>+</sup>][ $\Gamma$ ]. The red-shift was also attributed to the interionic interactions at the C4 and C5 position, but the weak blue-shifted band was not assigned. The peak-split mechanism proposed above could be a possible explanation for their data.

The experimental results presented in this study reveal that propylating the precursors [1-MIM] and [1,2-DMIM] and converting them into ionic liquids has a significant impact on the vibrational structure. This is particularly true for the modes in the fingerprint region 600-1700  $cm^{-1}$ . On the other hand, replacing the C(2) proton with a methyl group shows the most significant effects in the high frequency region, where the vibrational bands of the C(2)-H and C(4/5)-H groups of the imidazolium ring have their stretching modes. The methylation at the C(2) position removes the predominant site for interionic hydrogen bonding. As a consequence, the imidazolium CH groups at C(4) and C(5) become more involved in the interactions. It was found that when the  $\Gamma$  anion interacts with one of the two initially very similar and vibrationally degenerate CH groups, a split of the vibrational band can be observed. This results in a red-shifted contribution for the hydrogen-bonded group and a blueshifted one for the non-hydrogen-bonded group. Other studies also reported similar effects upon methylation of the C2 position in imidazolium ILs. Noack et al. studied imidazolium NTf<sub>2</sub>-ILs with and without a methyl group at the C2 position using vibrational and NMR spectroscopy [25]. They found that the methylation removes the strong positive partial charge of the hydrogen atom leading to a decrease of the electron density at the C2 atom, which is not compensated by the +I-effect of the methyl group or stronger hydrogen bonding at C4/C5-

H. Namboodiri et al. studied the same set of ILs by femtosecond coherent anti-Stokes Raman scattering (CARS) spectroscopy [41]. They observed that the ILs exhibiting a proton at the C2 position can transfer vibrational energy between the cation and the anion via hydrogen bonds. This ultrafast energy transfer was disabled when the C2 position was methylated. In a follow-up study, however, they showed for 1-ethyl-3-methylimidazolium ethylsulfate that the presence of a C2-H group is not the only pre-requisite for this energy transfer and that the underlying mechanisms are yet to be fully understood [42]. Furthermore, Lehmann and coworkers also observed the importance of the C(2) position in two important co-conformers in IL [1-MEIM<sup>+</sup>][Cl<sup>-</sup>] (on-top and in-plane) [26]. They found an increase in intensity and a large red-shift of the C2-H stretching frequency for the in-plane compared to the on-top conformation. Our experimental IR data suggest that a significant fraction of ion pairs interact via hydrogen bonds, hence arrange themselves in-plane. The existence of on-top conformers however cannot be excluded.



Figure 3. C2,4,5-H positions of H-bond abilities in two investigated ILs.

#### 4. Conclusion

Two ionic liquids, 1-methyl-3-propylimidazolium iodide  $[1-MPrIM^+][\Gamma]$  and 1,2-dimethyl-3propylimidazolium iodide  $[1,2-DMPrIM^+][\Gamma]$ , were successfully synthesized from the precursors 1-methylimidazole [1-MIM] and 1,2-dimethylimidazole [1-DMIM], respectively. The structures of the synthesized ILs were confirmed by <sup>1</sup>H, <sup>13</sup>C-NMR, and IR spectroscopy. A detailed structural study of the ILs and their precursors was carried out using Raman and IR spectroscopy in the wavenumber ranges  $[45 \text{ to } 3500 \text{ cm}^{-1}]$  and  $[600 \text{ to } 4000 \text{ cm}^{-1}]$ , respectively. The spectra allowed unraveling the effects of (1) methylation of the C2 position

in the imidazolium ring, and of (2) converting the neutral compound into an ionic species with a propyl side chain. The chemical conversion via propylation adds significant complexity to the vibrational spectra, in particular, to the Raman spectrum. This can be attributed to the high Raman activity of the additional CH bending and stretching modes in the propyl side chain. Moreover, it was found that blocking the predominant interaction site at C2 with a methyl group removed the possibility for hydrogen bonding interactions at this position. The iodide ion is then interacting with the hydrogen atoms at C4 and C5. The spectra suggest that this interaction is basically the formation of a hydrogen bond with one of the two C-H groups. This was evidenced by a splitting of an initially degenerate C4,5-H stretching vibration into a red- and a blue-shifted peak. The red-shift indicates the formation of a hydrogen-bonded C-H bond.

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Highlights:

- The vibrational analysis of nonionic precursors can aid the understanding of ionic liquids.
- Methylation of the C2 position in imidazolium ILs triggers interionic hydrogen bonding at C4/5.
- Iodide interactions with either C4-H or C5-H are evident as a split of the initially degenerate stretching modes.