

REGULAR ARTICLE

# Synthesis, experimental and theoretical vibrational studies of 1-methyl and 1,2-dimethyl, 3-propyl imidazolium bis(trifluoromethanesulfonyl) imide

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**Abstract.** In this study, two ionic liquids containing the bis(trifluoromethanesulfonyl)imide ( $[(CF_3SO_2)_2N^-]$ ) anion are synthesized. The syntheses are based on an alkylation reaction of 1-methyl imidazole and 1,2-dimethyl imidazole followed by anion exchange. The obtained ILs are characterized by  $^1H$ -NMR,  $^{13}C$ -NMR,  $^{19}F$ -NMR and FT-IR spectroscopy. Vibrational spectroscopy studies were conducted by infrared (FTIR/ATR), Raman spectroscopy and DFT calculations. The presence of methylation in the C2 position gives rise to specific marker bands in the Raman and IR spectra. In order to ascertain whether cation conformers are present in our ionic liquids, a computational study was performed using the density functional theory. The comparison of the experimental data and the computed spectra shows that three conformers of the imidazolium ions are present in both ionic liquids.

**Keywords.** Ionic liquids ILs; FT-Raman; FT IR/ATR; imidazolium; density functional theory; conformers.

## 1. Introduction

In the past few decades, new compounds, named ionic liquids, have displayed improved thermal, chemical and electrochemical properties in comparison with the volatile organic compounds (VOCs)<sup>1</sup>. Because of their interesting properties, they have been considered for promising applications in various fields such as electrochemistry<sup>2</sup> inorganic chemistry,<sup>3</sup> catalysis,<sup>4</sup> engineering,<sup>5</sup> spectroscopy<sup>6–8</sup> and material science.<sup>9</sup> For these reasons, the physicochemical properties of ionic liquids have been largely investigated.<sup>8</sup>

The properties of ionic liquids are generally influenced by the nature of cations and anions. Among these compounds, ionic liquids (ILs) based on the bis(trifluoromethanesulfonyl) imide  $[(CF_3SO_2)_2N^-]$  anion represent a new generation of ILs; they have special properties that make them very attractive,<sup>10</sup> such

as their high ionic conductivity, low melting points and low viscosity compared to other ILs.<sup>11</sup> For these reasons they are expected to have several application opportunities in the field of lithium batteries.<sup>12</sup>

Recently, many studies investigated the spectroscopic properties of ionic liquids;<sup>13–18</sup> generally, the aim of these works is to elucidate the relationship between the structures of ILs and their physicochemical properties; that is to say, a better comprehensive interpretation of the spectroscopic properties can be reached if physicochemical investigations are correlated with structural ones.

In this framework, detailed spectroscopic studies indicate that replacing hydrogen by a methyl group at C2 position in the imidazolium ring leads to a very significant variation of the macroscopic properties. Therefore, the comprehension of a relationship between macroscopic properties (i.e., melting point, viscosity, conductivity, *etc.*) and structural properties is

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essential for designing ILs with desirable properties. In this regard, several studies have been reported in the literature. For example, Bonhote *et al.*,<sup>19</sup> and others<sup>20–26</sup> found that methylation of the C(2) position of 1,3-dialkylimidazolium based ionic liquids disrupts the predominant hydrogen bonding interaction between cation and anion leading to unexpected changes of the physicochemical properties. For example, to reveal the impact of extra methyl substitution at the C2 position and getting information on their effect on the properties of imidazolium ionic liquids, Chen *et al.*,<sup>27</sup> found the viscosity of cationic C2-methylated 1,2-dimethyl 1,3-propyl imidazolium bis(trifluoromethane-sulfonyl) imide ( $\eta = 88.9$  cP) to be about twice higher than that of their cationic C2-protonated 1-methyl,3-propyl imidazolium bis(trifluoromethane sulfonyl) imide ( $\eta = 43.7$  cP) at  $T = 25^\circ\text{C}$ . In the same way, many studies were devoted to the spectroscopic properties of various ionic liquids by using DFT calculations and *ab initio* MD simulations in order to investigate the hydrogen bonding between cation and anion in these compounds.<sup>28–32</sup>

Inspired by the previous research, the present work focuses on the synthesis and vibrational properties of two ionic liquids, namely: 1-methyl,3-propyl imidazolium bis(trifluoromethane-sulfonyl) imide ( $[1\text{-MPrIM}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ ) and 1,2-dimethyl,3-propyl imidazolium bis(trifluoromethane-sulfonyl) imide ( $[1,2\text{-DMPrIM}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ ). The understanding of the vibrational structures is important to explain the influence of the methyl group at C2 position (effect of methylation) between the two synthesized ILs. For this purpose, experimental and computational study of both  $[1\text{-MPrIM}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$  and  $[1,2\text{-DMPrIM}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$  were performed using the infrared (FTIR/ATR) and Raman spectroscopy and DFT calculations.

## 2. Experimental

### 2.1 Materials, synthesis and preliminary characterization

The reagents used in this study are: 1-methylimidazole (>99%), 1,2-dimethylimidazole (98%), propyl iodide (98%), lithium bis(trifluoromethylsulfonyl) Imide (99%). They were purchased from Fluka and used as received. Deionized  $\text{H}_2\text{O}$  was obtained with a Millipore ion-exchange resin deionizer.

$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR spectra were recorded on a DRX 400 MHz spectrometer. The chemical shifts ( $\delta$ ) are given in ppm and referred to the internal solvent signal, namely, tetramethylsilane (TMS) and trichlorofluoromethane ( $\text{CFCl}_3$ ). Preliminary IR spectra were recorded on a FT-IR Perkin-Elmer BX spectrophotometer with a resolution of  $4\text{ cm}^{-1}$  in the range  $4000\text{--}650\text{ cm}^{-1}$  in order to check the

occurrence of the expected chemical reactions and the production of the ionic liquids.

### 2.2 General procedure for the synthesis of two ILs

1-methyl-3-propylimidazolium bis(trifluoromethane-sulfonyl) imide  $[1\text{-MPrIM}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$  and 1,2-dimethyl, 3-propyl imidazolium bis(trifluoromethane-sulfonyl) imide  $[1,2\text{-DMPrIM}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$  were synthesized following the procedures described in the literature.<sup>33</sup> Briefly, the chemical reaction of 1-methylimidazole and 1,2-dimethylimidazole with propyl iodide results in transfer of the propyl group to the imidazolium ring and results in 1-methyl,3-propyl imidazolium and 1,2-dimethyl,3-propyl imidazolium combined with iodide anion, respectively. Both iodide ILs were subjected to anion exchange from iodide to bis(trifluoromethane-sulfonyl) imide. The reaction of lithium bis(trifluoromethanesulfonyl) imide with these two iodide ILs in water leads to the corresponding ionic liquids,  $[1\text{-MPrIM}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$  and  $[1,2\text{-DMPrIM}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ . The resulting 1-methyl,3-propyl imidazolium bis(trifluoromethane-sulfonyl) imide and 1,2-dimethyl,3-propyl imidazolium bis(trifluoromethane-sulfonyl) imide were obtained as yellowish viscous liquids. Scheme 1 shows the general synthesis of  $[1\text{-MPrIM}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$  and  $[1,2\text{-DMPrIM}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ .

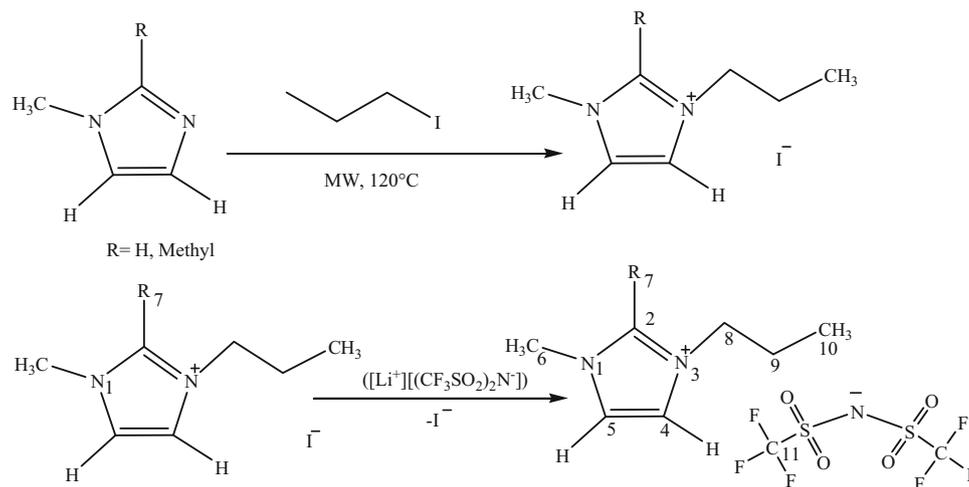
To confirm the absence of any major impurity in the two investigated ILs, their structures were ascertained using  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ -NMR and FT-IR spectroscopy. The spectroscopic data are given below and the  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$ -NMR spectra are presented in Figures S1 and S2 (see Supplementary Information).

2.2a  $[1\text{-MPrIM}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ :  $^1\text{H}$  NMR (DMSO, 400 MHz)  $\delta$ : 9.75 (1H, s), 7.55 (1H, s), 7.52 (1H, s), 4.17–4.21 (2H, t,  $J = 8$  Hz), 3.99 (3H, s), 1.82–1.87 (2H, m,  $J = 8$  Hz), 0.83–0.87 (3H, t,  $J = 8$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz)  $\delta$ : 10.4, 11.6, 22.6, 49.9, 120.8, 122.2, 122.2, 144.2;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz)  $\delta$ :  $-79.0$  (s,  $\text{CF}_3\text{SO}_2)_2\text{N}^-$ ). IR ( $\tilde{\nu}/\text{cm}^{-1}$ ): 3123 [ $\nu$  (=C-H)], 2978, 2887 [ $\nu$  (C-H)], 1461 [ $\delta$ (C-H)], 1347, 1329 [ $\nu$ (S=O)], 1179 [ $\nu$ (C-F)], 1132 [ $\delta$ (S=O)], 1051 [ $\delta$ (C-F)].

2.2b  $[1,2\text{-DMPrIM}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ :  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.32 (1H, d), 7.24 (1H, d), 3.85–3.89 (2H, q,  $J = 8$  Hz), 3.67 (3H, s), 2.50 (3H, s), 1.54–1.59 (2H, m,  $J = 4$  Hz), 0.66–0.69 (3H, t,  $J = 8$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz)  $\delta$ : 9.4, 10.5, 14.8, 36.3, 50.0, 120.9, 122.3, 122.4, 143, 2–143.3;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz)  $\delta$ :  $-78.82$  (s,  $\text{CF}_3\text{SO}_2)_2\text{N}^-$ ). IR ( $\tilde{\nu}/\text{cm}^{-1}$ ): 3152 [ $\nu$  (=C-H)], 2974, 2885 [ $\nu$  (C-H)], 1540, 1462 [ $\delta$ (C-H)], 1347, 1329 [ $\nu$  (S=O)], 1176 [ $\nu$ (C-F)], 1132 [ $\delta$ (S=O)], 1054 [ $\delta$ (C-F)].

### 2.3 FTIR/ATR and FT-RAMAN measurements

The Infrared ATR spectra and Raman spectra, reported in the following Sections 3.1 and 3.2, were performed in the



**Scheme 1.** General synthesis of ionic liquids, [1-MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and [1, 2-DMPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>]. MW = microwave.

Walloon Agricultural Research Center (Craw) Belgium. For both kind of measurements the as-synthesized samples were used without further purification.

The FTIR/Attenuated Total Reflectance (FTIR/ATR) measurements were acquired on a Bruker Vertex II-70RAM Spectrometer (Bruker Analytical, Madison, WI) operating with a Golden Gate diamond ATR accessory TM (Specac Ltd, Slough, uk). A drop of the synthesized ionic liquids was placed directly on the ATR crystal. 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 Software 6.0 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. A drop of the as-synthesized samples was placed in a quartz cell and maximization of the Raman scattered light was performed. 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.

### 3. Results and discussion

#### 3.1 IR spectroscopy

The FTIR/ATR [600–3400 cm<sup>-1</sup>] spectra of the two investigated ILs, namely, [1-MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and [1, 2-DMPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] are shown in

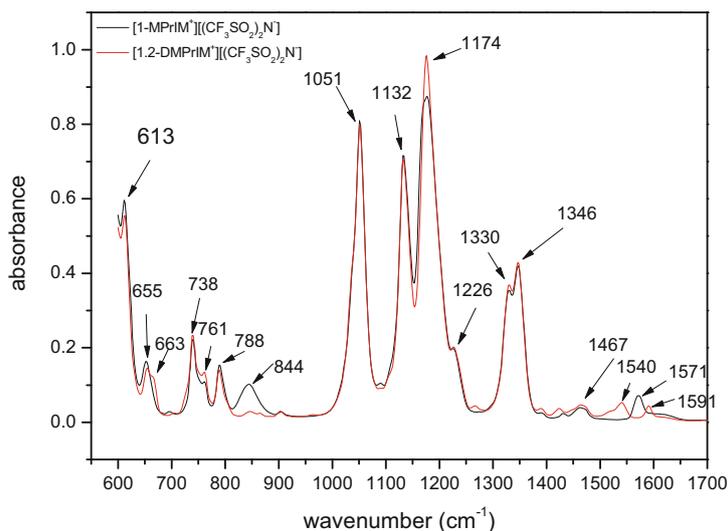
Figures 1 and 2, divided in two spectral regions: 600–1700 cm<sup>-1</sup> and 2800–3400 cm<sup>-1</sup>.

**3.1a The 600–1700 cm<sup>-1</sup> region:** The spectra of the two ILs look similar. However, two peaks observed in this region are important indication for the methylation effect in C2 position. A first difference between the spectra of methylated [1, 2-DMPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and non-methylated [1MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] ILs occurs at 844 cm<sup>-1</sup>; this band is assigned to CH bending vibration in the ring NC(H)N. The absence of this mode in the methylated [1, 2-DMPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] supports this assignment (this band is observed at 846 cm<sup>-1</sup> in the study by Noack *et al.*<sup>24</sup>).

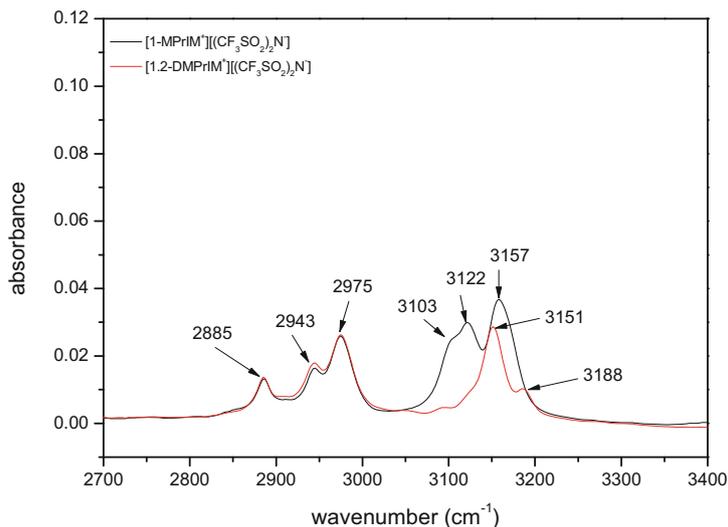
Furthermore, the presence of a characteristic band at 1540 cm<sup>-1</sup> in [1, 2-DMPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and at 1571 cm<sup>-1</sup> in [1-MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>], can be attributed to a CC stretching in NC(CH<sub>3</sub>)N ring and NC<sub>2</sub>(H)N ring; here, again the methylation effect is clearly observed. These vibrational mode assignment agrees also with that proposed by Noack *et al.*, who also found that there is a broad peak around 1540 cm<sup>-1</sup> assigned to CC stretching in NC(CH<sub>3</sub>)N ring.<sup>24</sup>

As indicated in Table 1, all bands in the FTIR/ATR spectra appearing in this region can be mainly ascribed to contributions from ring bending modes of the imidazolium cation and to modes of [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] anion. For example, the most intense IR bands at 1051, 1132, 1174, 1226, 1330, 1346 and 1446 cm<sup>-1</sup> are common in both ILs, as they are dominated by vibrations of the [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] anion.<sup>34–39</sup>

**3.1b The 2800–3400 cm<sup>-1</sup> region:** In this region, the same absorption bands can be observed in the



**Figure 1.** FTIR/ATR spectra of [1-MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and [1, 2-DMPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] in the spectral range 550–1700 cm<sup>-1</sup>.



**Figure 2.** FTIR/ATR spectra of [1-MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and [1, 2-DMPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] in the spectral range 2800–3400 cm<sup>-1</sup>.

FTIR/ATR spectra of the two ILs below 3000 cm<sup>-1</sup>. The bands at low wavenumber are assigned to CH stretching in the propyl groups. Both ILs exhibit bands at 2885 and 2943 cm<sup>-1</sup>, which can be assigned to CH vibrations in the propyl chain.<sup>40,41</sup> Moreover, the spectra in this region exhibit a strong band at 2975 cm<sup>-1</sup>, which is again a contribution of the propyl chain.<sup>41</sup> Concerning the bands above 3000 cm<sup>-1</sup>, all the spectroscopic literature mentioned that the vibrational bands at higher wavenumbers correspond to C(4/5)-H stretching modes, whereas those at lower wavenumbers can be assigned to C(2)-H stretching modes.<sup>40–42</sup> In [1-MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>], absorption bands occur at 3103, 3122 and 3157 cm<sup>-1</sup>,

which can be attributed to the C(2)-H and H-C(4)-C(5)-H stretching vibration of the imidazolium ring respectively.<sup>40,41</sup> On the contrary, in the methylated IL, [1, 2-DMPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>], two important bands are observed at 3151 and 3188 cm<sup>-1</sup> and they can be assigned to anti-symmetric and symmetric vibrations mode of H-C(4)-C(5)-H stretching vibration.

In the case of non-methylated IL, [1-MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>], three interaction positions are possible: C(2)-H and C(4/5)-H. As reported by Fumino *et al.*,<sup>23</sup> when the H atom at C(2) is replaced by a CH<sub>3</sub> group, the cation–anion interaction at this position is switched off. So, when we look in our spectra,

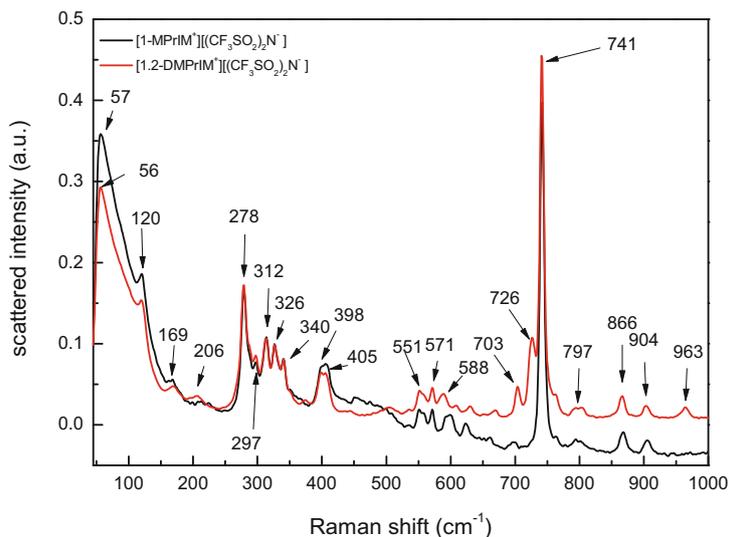
**Table 1.** Observed FTIR/ATR and RAMAN bands and their assignment for [1-MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and [1, 2-DMPPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] (vw = very weak, w = weak, m = medium, s = strong, sh = shoulder, str = stretch, δ = deformation, bend = bending deformation, γ = out-of-plane deformation, ω = wagging, ρ = rocking, sym = symmetric, asym = antisymmetric).

FTIR/ATR		Raman		Vibrational assignment	Refs.
[1-MPrIM <sup>+</sup> ] [(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N <sup>-</sup> ]	[1, 2-DMPPrIM <sup>+</sup> ] [(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N <sup>-</sup> ]	[1-MPrIM <sup>+</sup> ] [(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N <sup>-</sup> ]	[1, 2-DMPPrIM <sup>+</sup> ] [(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N <sup>-</sup> ]		
613 (s)		57 (s)	56 (s)	Intermolecular vibration	14/34
655 (w)		121 (m)	120 (m)	Intermolecular vibration	14/34
		170 (vw)	169 (vw)	Intermolecular vibration	14/34
			206 (vw)	γ N-CH <sub>3</sub>	
		278 (m)	278 (m)	Trans-TFSI: ρ CF <sub>3</sub>	34/35/36
		296 (w)	296 (w)	CH <sub>2</sub> (N), CH <sub>3</sub> (N)CH bend, Trans-TFSI: ρ(CF <sub>3</sub> ), νas(CS)	35/36
		312 (w)	312 (w)	Trans-TFSI: ρ(SO <sub>2</sub> ), ρ(CF <sub>3</sub> )	35/36
		327 (w)	326 (w)	SC Str	35/36
		340 (w)	339 (w)	Trans-TFSI: τ (SO <sub>2</sub> )	36/37
		398 (w)	398 (w)	CH <sub>2</sub> (N), CH <sub>3</sub> (N)CH bend, Trans-TFSI: ω(SO <sub>2</sub> )	35/36
		405 (vw)	405 (vw)	Trans-TFSI: ω(SO <sub>2</sub> )	35/36/37
		553 (vw)	551 (vw)	Trans-TFSI: δs(SO <sub>2</sub> )	35/36/37
		573 (vw)	571 (vw)	Trans-TFSI: δas(CF <sub>3</sub> )	35/36/37
		594 (vw)	588 (vw)	Trans-TFSI: δas(CF <sub>3</sub> ), δip as(SO <sub>2</sub> ), δs(NSO <sub>2</sub> )	35/36/37
	613 (s)			Trans-TFSI: δSNS,	35/36/37
	657 (w)		703 (w)	CH <sub>2</sub> (N) str, CH <sub>3</sub> (N)CN str/ν N-CH <sub>3</sub>	35/36
	663 (sh)		726 (m)	Ring HCCH sym bend, CH <sub>2</sub> (N) and CH <sub>3</sub> (N) CN	35/36
	738 (m)	742 (s)	741 (s)	Trans TFSI: δs(CF <sub>3</sub> )	35/36/37
	764 (w)			ring HCCH asym bend/ω(CH <sub>2</sub> ) rocking.	35/36
	788 (w)		797 (vw)	Trans-TFSI: νas SN + vs CF	35/36/37
788 (w)				Trans TFSI: δs(CF <sub>3</sub> )	35/36/37
844 (w)		864 (vw)	866 (vw)	NC2(H)N CH bending	35/36/37
		906 (vw)	904 (vw)	NC(H) N/propylchain CCC symstr propylchain CCC symstr	35/36/37
			963 (vw)	ν <sub>sym</sub> CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub> CCC	35/36
		1023 (vw)	1035 (vw)	ν(C-C)/CH <sub>2</sub> (N)/CH <sub>3</sub> (N)CN Str.	45
					35/37
					35/37

Table 1. (contd.)

FTIR/ATR		Raman		Vibrational assignment	Refs
[1-MPrIM <sup>+</sup> ] [(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N <sup>-</sup> ]	[1, 2-DMPriM <sup>+</sup> ] [(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N <sup>-</sup> ]	[1-MPrIM <sup>+</sup> ] [(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N <sup>-</sup> ]	[1, 2-DMPriM <sup>+</sup> ] [(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N <sup>-</sup> ]		
1051 (s)	1051 (s)		1076 (vw)	Trans TFSI: $\nu_s(\text{SO}_2)/\nu_{\text{sym}}(\text{chain CCC})$	24/35/45 35/36
1132 (s)	1132 (s)	1135 (vw)	1137 (w)	Trans TFSI: $\nu_s(\text{SO}_2)/\nu_{\text{sym}}(\text{chain CCC})$	35/45
1174 (s)	1174 (s)			Trans-TFSI $\nu_s(\text{SO}_2)$	24/37
1226 (sh)	1226 (sh)	1242 (m)	1242 (vw)	CC Str, Trans TFSI: $\nu_s(\text{SO}_2)$	35/37
1330 (m)	1330 (m)	1336 (vw)	1338 (vw)	Trans TFSI: $\nu_s(\text{CF}_3)$	24/36
1346 (m)	1346 (m)	1388 (vw)	1389 (vw)	Trans TFSI: $\nu_{\text{as}}(\text{SO}_2)$ , CH <sub>2</sub> (N)/CH <sub>3</sub> (N)CN Str	35/36
		1418 (vw)	1418 (vw)	Trans TFSI: $\nu_{\text{as}}(\text{SO}_2)$ , CH <sub>2</sub> (N)/CH <sub>3</sub> (N)CN Str	36/37
		1452 (w)	1449 (w)	$\delta_s\text{CH}_3/\nu_{\text{as}}(\text{C}(2)\text{N}(1)\text{C}(5))$	35/36
1467 (w)	1467 (w)		1462 (w)	$\delta_s\text{CH}_3/\text{CH}_2(\text{N})/\text{CH}_3(\text{N})\text{CN Str}$ , $\delta(\text{CH}_2)$	35/36
			1516 (m)	$\nu\text{C-C}$ , $\nu\text{CH}_3\text{-N-CN}$	35/36
				(N)CH <sub>3</sub> HCH symbend, (N)CH <sub>3</sub> CN str	35/36
1571 (w)	1540 (w)			Ring CH <sub>3</sub> HCH asym bend	24/36
				NC(CH <sub>3</sub> )NCC	35/36
				NC2(H)N CH bending	35/36
				CCH HCH asym bend/CH <sub>3</sub> (N) CN str	24/36
			2764 (vw)	propyl C-H	45/36
			2837 (vw)	propyl C-H	40/46
			2885 (sh)	Propyl CH <sub>3</sub>	32/40/41
2885 (w)	2885 (w)	2883 (vw)	2885 (sh)	$\nu_{\text{sym}}\text{CH}_3/\text{propyl C-H}$	40/41/45
2943 (w)	2943 (w)	2943 (vw)	2945 (sh)	$\nu_s(\text{CH}_3)/\text{propyl C-H}$	40/43/45
2975 (w)	2975 (w)	2969 (w)	2969 (m)	$\nu_{\text{asym}}\text{CH}_3$	40/41/44
3103 (w)			3091 (vw)	$\nu\text{C}(2)\text{-H}/\nu_{\text{as}}(\text{N})\text{CH}_3$	40/41/43
3122 (m)				$\nu\text{C}(4,5)\text{-H}$	40/41/43
3157 (m)	3151 (m)		3151 (w)	$\nu_{\text{as}}\text{C}(4,5)\text{-H}$	21/40/47
		3173 (vw)		$\nu\text{C}(2)\text{-H}$	21/40/41
			3188 (vw)	$\nu_s\text{C}(4, 5)\text{-H}$	21/40/41

TFSI is the acronym for [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>].



**Figure 3.** FT-RAMAN Spectra of [1-MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and [1,2-DMPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] in the spectral range of 45–1000 cm<sup>-1</sup>.

the stretching modes between 3103 and 3122 cm<sup>-1</sup> are completely missing in the FTIR/ATR spectra of methylated IL. For [1-MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] IL, the band at 3157 cm<sup>-1</sup>, is assigned to the C(4)-H/C(5)-H symmetric stretching mode, while the same band in [1,2-DMPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] is blue shifted to a frequency of 3188 cm<sup>-1</sup>. This finding indicates that interaction cation-anion by C(4)-H/C(5)-H position in methylated IL can take place only through these positions.

### 3.2 FT-Raman spectroscopy

The FT-RAMAN spectra [45–3500 cm<sup>-1</sup>] of [1-MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and [1,2-DMPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] are illustrated in Figures 3, 4, 5, and the observed FT-RAMAN bands and their assignment are listed in Table 1.

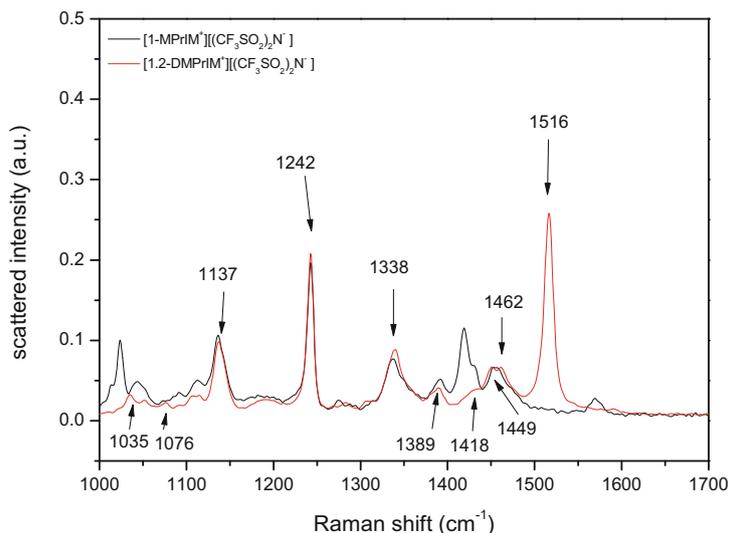
**3.2a The 45–500 cm<sup>-1</sup> region:** In the range 45–200 cm<sup>-1</sup>, no significant difference between the two ILs were observed; three bands are seen for both ILs. These lines arise primarily from the intramolecular vibrations. These interactions are affected by the presence of [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] anion.<sup>34</sup> The Raman modes at 56 cm<sup>-1</sup> and 57 cm<sup>-1</sup> are attributed to acoustic excitations, while the mode at 120 cm<sup>-1</sup> is assigned to an intramolecular normal mode of [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] anion, and the mode at 204 cm<sup>-1</sup> is related to vibrational motion of the imidazolium ring.<sup>34</sup> In the second region between 500 and 1000 cm<sup>-1</sup> (Figure 3), small differences around 700 cm<sup>-1</sup> are observed between the spectra of the two

ILs, which will be further exploited in the subsequent Section 3.3.

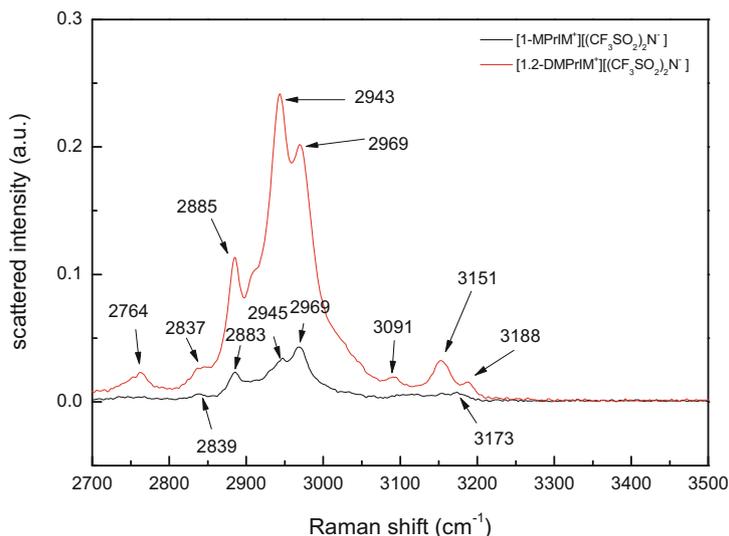
**3.2b The 1000–1700 cm<sup>-1</sup> region:** Concerning Raman spectra in [1-MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and [1,2-DMPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>], recent studies mentioned that the Raman bands at 278, 312, 326, 340, 398, 405, 551, 571, 588, 726, 741, 797, 866, 904, 1035, 1137, 1242 and 1338 cm<sup>-1</sup> can be assigned to the [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] anion, and these bands were also found in our measurements.<sup>34–36</sup> Previous literature provided evidence that the bands at 278, 297, 312, and 398 cm<sup>-1</sup> are due to both trans- and cis-conformer of [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>];<sup>43,44</sup> however, the band at 326 cm<sup>-1</sup> was assigned to cis-conformer, while the line at 340 cm<sup>-1</sup> can be associated only to trans-[(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>]. In our experimental spectra we observe the bands expected for both conformers of [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>]. At higher Raman shift, both ILs display bands at 742 and 1242 cm<sup>-1</sup>, which according to the literature,<sup>42</sup> are due to the symmetric CF<sub>3</sub> stretching and deformation bands in the [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] anion.

As shown in Table 1 and Figure 4, the methylated IL [1,2-DMPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>], having an additional methyl group (CH<sub>3</sub> at C<sub>2</sub> position), shows an intense band around 1516 cm<sup>-1</sup>, which is not observable in [1-MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>]; this band is probably assigned to C2-CH<sub>3</sub> group, this group being absent in the non-methylated IL.<sup>24</sup>

**3.2c The 2700–3500 cm<sup>-1</sup> region:** Figure 5 shows high frequency Raman spectra of [1-MPrIM<sup>+</sup>]



**Figure 4.** FT-RAMAN Spectra of [1-MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and [1,2-DMPriM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] in the spectral range of 1000–1700 cm<sup>-1</sup>.

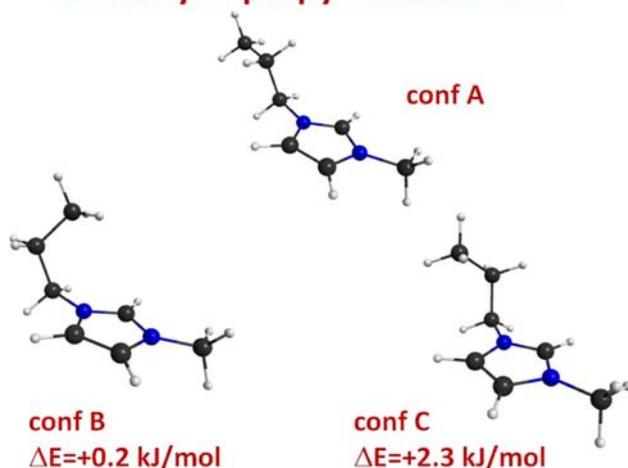


**Figure 5.** FT-RAMAN Spectra of [1-MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and [1,2-DMPriM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] in the spectral range of 2700–3500 cm<sup>-1</sup>.

[(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and [1,2-DMPriM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>]. In this region, we observe many differences in the vibrational spectra of the ILs. The Raman modes are located at 2839, 2883, 2945, 2969 cm<sup>-1</sup> for [1-MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and at 2764, 2837, 2885, 2943, 2969 cm<sup>-1</sup> for [1,2-DMPriM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>]. All of them can be assigned to the CH stretching vibration of the [1-MPrIM<sup>+</sup>] and [1,2-DMPriM<sup>+</sup>] chains.<sup>40</sup> Furthermore, three bands are detected at 3091, 3151, 3188 cm<sup>-1</sup> for [1,2-DMPriM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>], while only a very weak Raman band at 3173 cm<sup>-1</sup> is observed for the non-methylated case. The first band at 3091 cm<sup>-1</sup>

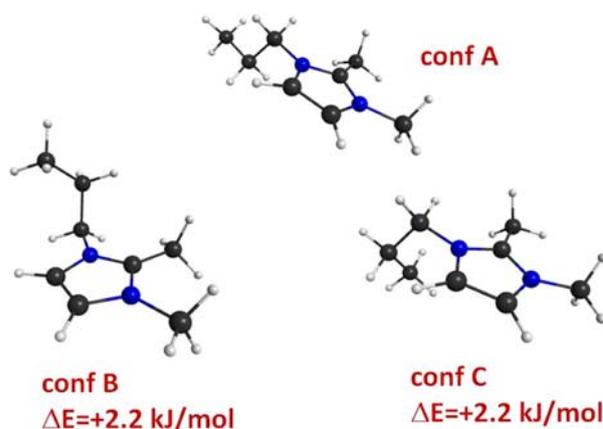
originates from asymmetric stretch of (N)CH<sub>3</sub>, while bands at 3151, 3188 cm<sup>-1</sup> are attributed to the anti-symmetric and symmetric vibrations of C(4)-H/C(5)-H, respectively. C(2)-H vibration for non-methylated [1-MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] is found at 3171 cm<sup>-1</sup>; this demonstrates that the interaction between [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and the imidazolium ring is totally different in the two ILs. The fact that the Raman bands undergo a blue shift after methylation suggests that the hydrogen bonds through the C(4/5)-H position are stronger in the methylated IL.

## 1-methyl 3-propyl imidazolium



**Figure 6.** Schematic view of the three conformers of 1-methyl, 3-propyl imidazolium, with the relative energy difference with conformer A. Blue, black and light gray balls represent N, C and H atoms, respectively.

## 1, 2-dimethyl 3-propyl imidazolium



**Figure 7.** Schematic view of the three conformers of 1,2-dimethyl 3-propyl imidazolium, with the relative energy difference with conformer A. Blue, black and light gray balls represent N, C and H atoms, respectively.

### 3.3 A study of the conformers of the imidazolium ions

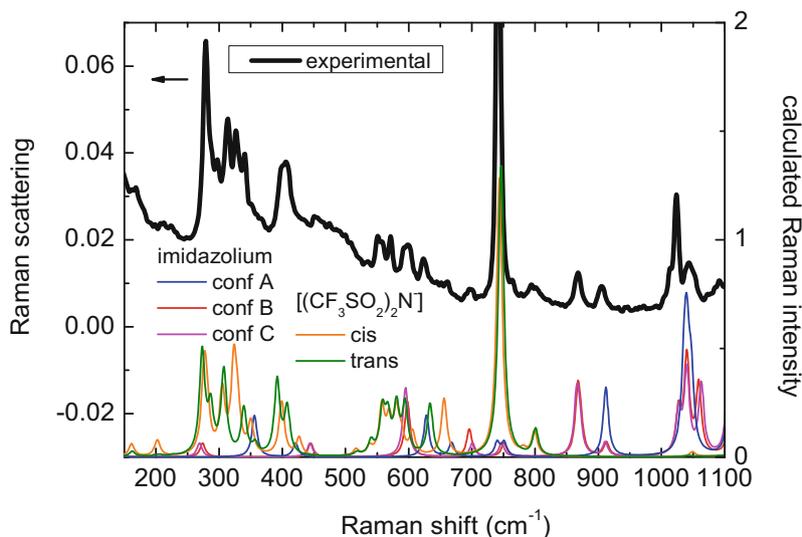
In this part, our discussion is focused on the comparison between the calculated Raman spectra of the conformers of both imidazolium cations and  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$  anions and their presence in the experimental spectra of both ILs. The existence of two conformers of  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$  has been largely reported in the literature.<sup>37,38,43,44</sup> Previous studies have shown that imidazolium ions can show the existence of conformers due to the flexibility of the alkyl chain attached to the ring.<sup>21,45</sup> In the present study we investigated the possible existence of conformers by a systematic computational investigation of the two cations, using Spartan software for the computational study,<sup>48,49</sup> which is able to perform a systematic variation of the angles between chemical bonds. A preliminary screening was performed at the molecular mechanics level and three possible geometries for each cation were found. Starting from these geometries, a minimization of the energy of each candidate was performed using the density functional theory.

Figures 6 and 7 present a schematic view of the three conformers of each cation, together with the energy difference ( $\Delta E$ ) with respect to the lowest energy one (conf. A). The atomic positions for all the conformers are reported in Tables S1–S6 in the Supporting Information. In the case of 1-methyl,3-propyl imidazolium, Conf. B and C show a  $\Delta E$  of +0.2 and +2.3 kJ/mol, respectively. For 1,2-dimethyl,3-propyl imidazolium, both conf. B and C possess an energy 2.2 kJ/mol higher than that of the lowest energy conformer (Conf. A). Even though Conf. B and C of 1,2-dimethyl,3-propyl imidazolium

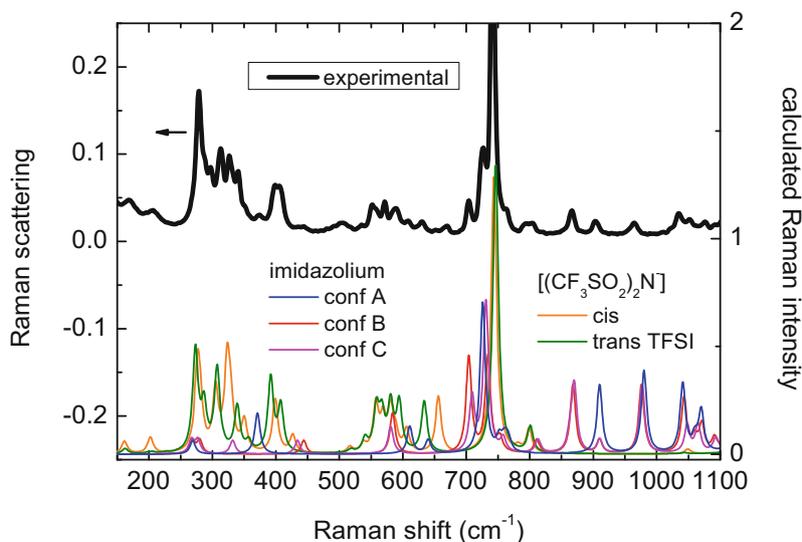
have the same energy difference with respect to Conf. A, it must be kept in mind that they are different. One can note that for both cations, the energy difference between the conformers is extremely small, so that at room temperature all the conformational states can be populated with a non-negligible population. For example, with an energy difference of 2.2 kJ/mol, the higher energy state has a population of 30%, while 70% of ions are in the lowest energy level.

In view of the fact that the calculations suggest that the energy difference between the conformers of the two imidazolium ions is extremely low, we checked whether any signature of the occurrence of more than one rotamer can be found in the vibrational spectra of the two ionic liquids. Therefore, we calculated the vibrational frequencies and their Raman intensity for the conformers of both 1-methyl,3-propyl imidazolium and 1,2-dimethyl,3-propyl imidazolium, using the B3LYP functional and the 6-31G\*\* basis set. The list of the frequencies and Raman intensities is reported in Tables S7 and S8 in the Supporting Information. The Raman frequencies and intensities of the two conformers of  $[(\text{CF}_3\text{SO}_2)_2\text{N}^-]$  have been previously reported and a scaling factor of 1.04 for the calculated frequencies gave the best agreement with the position of the experimental bands.<sup>43,44</sup> The Raman spectrum of each ion was simulated by summing Gaussian curves centered at each calculated vibration frequency with a fixed peak width of  $10\text{ cm}^{-1}$ .

Figures 8 and 9 present the comparison of the experimental Raman spectrum of the two ionic liquids with the Raman intensity calculated for each conformer of



**Figure 8.** Experimental Raman spectrum of 1-methyl, 3-propyl imidazolium bis(trifluoromethane-sulfonyl) imide and calculated Raman intensity of the three conformers of 1-methyl 3-propyl imidazolium and of the two conformers of  $[(CF_3SO_2)_2N^-]$ . A scaling factor 1.04 is considered for  $[(CF_3SO_2)_2N^-]$  frequencies.



**Figure 9.** Experimental Raman spectrum of 1,2-dimethyl,3-propyl imidazolium bis(trifluoromethane-sulfonyl) imide and calculated Raman intensity of the three conformers of 1,2-dimethyl 3-propyl imidazolium and of the two conformers of  $[(CF_3SO_2)_2N^-]$ . A scaling factor 1.04 is considered for  $[(CF_3SO_2)_2N^-]$  frequencies.

the imidazolium ions and for the two conformers of  $[(CF_3SO_2)_2N^-]$ . Concerning 1-methyl,3-propyl imidazolium bis(trifluoromethane-sulfonyl) imide, one can note that Conf. B and C of the imidazolium ion give similar Raman spectra, which, however, are quite different from that of Conf. A (Figure 8). The line centered around  $700\text{ cm}^{-1}$  is attributable to conformers B and C, while it is not present in the spectrum of conformer A.

The band around  $867\text{ cm}^{-1}$  is expected for Conf. B and C, but it should not occur in Conf. A. Finally, the line at  $905\text{ cm}^{-1}$  should be present for all the three conformers, but it should have a much lower intensity in Conf. B and C than in Conf. A. Experimentally, the intensity of this line is comparable to that centered around  $867\text{ cm}^{-1}$ , suggesting the presence of a large concentration of Conf. A in the ionic liquid.

The occurrence of more than one conformer is even more clear in 1,2-dimethyl,3-propyl imidazolium bis(trifluoromethane-sulfonyl) imide. In fact, it presents clear bands centered at 704 and 726  $\text{cm}^{-1}$ ; the lower frequency band is attributable to Conf. B and C, while the higher frequency band occurs in the calculated spectra of Conf. A and C. The experimental line centered around 374  $\text{cm}^{-1}$  should be attributed to Conf. A. As for 1-methyl, 3-propyl imidazolium bis(trifluoromethane-sulfonyl) imide, the band around 867  $\text{cm}^{-1}$  is expected for Conf. B and C, but it should not occur in Conf. A. Moreover, the line at 903  $\text{cm}^{-1}$  should be present for all the three conformers, but it should have a much lower intensity in Conf. B and C than in Conf. A. The comparable intensity of the line centered at 867 and 903  $\text{cm}^{-1}$  indicates the presence of a large concentration of Conf. A in the ionic liquid.

In conclusion, the DFT calculations suggest that various conformers of the imidazolium ions are present in both ionic liquids.

#### 4. Conclusions

In this work, two imidazolium ionic liquids having bis(trifluoromethane sulfonyl)imide anions, differing in the atoms attached to C2 positions, were successfully synthesized. The obtained ILs were identified by means of  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ -NMR and FT-IR spectroscopy. The FTIR/ATR and Raman spectra of the synthesized ILs are reported. Also, Density Functional Theoretical study of the conformers of the imidazolium ions was performed at the B3LYP/6-31G\*\* level. Experimentally, it was found that the methylation at the C(2) position can be demonstrated in the IR spectrum below 1700  $\text{cm}^{-1}$  by the two bands centered at 844, 1571  $\text{cm}^{-1}$  and a single intense band centered at 1516  $\text{cm}^{-1}$  in the Raman spectrum. Moreover, we observed a blue shift in the C4/C5-H stretching modes in the IR spectra, suggesting stronger interactions between the cation and anion through these positions in the case of methylated IL. Finally, the comparison between calculated and experimental Raman spectra suggests the existence of three conformers of the imidazolium cation in each IL. The most stable geometries of the conformers were obtained for both ILs.

#### Supplementary Information (SI)

All additional information pertaining to experimental data and characterization of the ionic liquids [1-MPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and [1, 2-DMPPrIM<sup>+</sup>][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] using  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$ -NMR are given in Supplementary Information (Figures S1 and S2); the atomic positions for all the conformers are

given in (Tables S1–S6); also, the list of the frequencies and Raman intensities (Tables S7 and S8) are given. Supporting Information is available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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