

REGULAR ARTICLE

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

M DRAI^{a,b}, A MOSTEFAI^c, A PAOLONE^{d,*} , B HADDAD^{b,c,e}, E BELARBI^b,
D VILLEMINE^c, S BRESSON^f, O ABBAS^g, Y CHAKER^b and M RAHMOUNI^b

^aLaboratoire de Matériaux & Catalyse, Université Djillali Liabès, BP 89, 22000 Sidi-Bel-Abbès, Algeria

^bSynthesis and Catalysis Laboratory LSCT, Tiaret University, Tiaret, Algeria

^cDepartment of Chemistry, Dr Moulay Tahar University of Saida, Saida, Algeria

^dCNR-ISC, U.O.S. La Sapienza, Piazzale A Moro 5, 00185 Rome, Italy

^eLCMT, ENSICAEN, UMR 6507 CNRS, University of Caen, 6 bd Ml Juin, 14050 Caen, France

^fLaboratoire de Physique des Systèmes Complexes, Université Picardie Jules Verne, 33 rue St Leu,
80039 Amiens Cedex, France

^gCentre Wallon de Recherche Agronomique, CRA-W, Bâtiment Maurice Henseval, Chaussée de Namur, 24,
50030 Gembloux, Belgium

E-mail: Annalisa.Paolone@roma1.infn.it

MS received 2 December 2016; accepted 10 April 2017

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)¹. Because of their interesting properties, they have been considered for promising applications in various fields such as electrochemistry² inorganic chemistry,³ catalysis,⁴ engineering,⁵ spectroscopy^{6–8} and material science.⁹ For these reasons, the physicochemical properties of ionic liquids have been largely investigated.⁸

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,¹⁰ such

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

Recently, many studies investigated the spectroscopic properties of ionic liquids;^{13–18} 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

*For correspondence

essential for designing ILs with desirable properties. In this regard, several studies have been reported in the literature. For example, Bonhote *et al.*,¹⁹ and others^{20–26} 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.*,²⁷ 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.^{28–32}

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 H_2O was obtained with a Millipore ion-exchange resin deionizer.

^1H NMR (400 MHz) and ^{13}C NMR spectra were recorded on a DRX 400 MHz spectrometer. The chemical shifts (δ) are given in ppm and referred to the internal solvent signal, namely, tetramethylsilane (TMS) and trichlorofluoromethane (CFCl_3). Preliminary IR spectra were recorded on a FT-IR Perkin-Elmer BX spectrophotometer with a resolution of 4 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.³³ 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 $[1,2\text{-DMPrIM}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$.

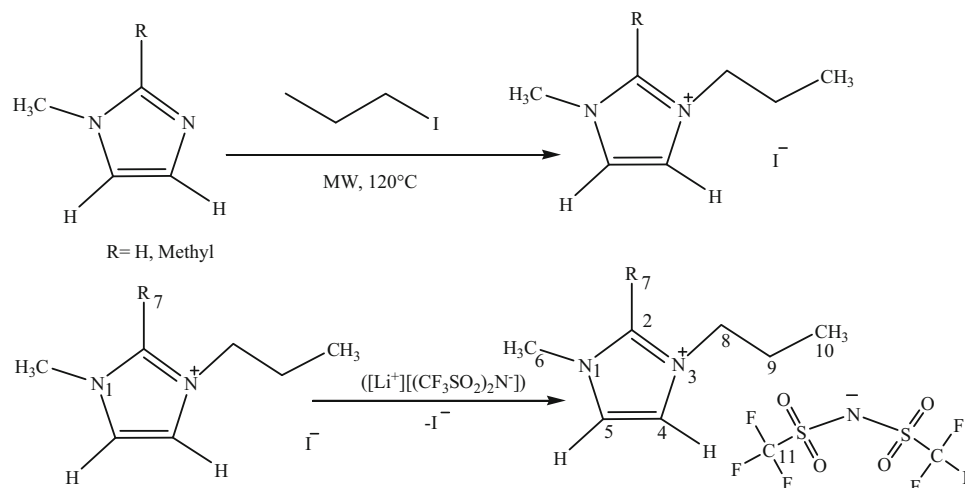
To confirm the absence of any major impurity in the two investigated ILs, their structures were ascertained using ^1H , ^{13}C , ^{19}F -NMR and FT-IR spectroscopy. The spectroscopic data are given below and the ^1H , ^{13}C and ^{19}F -NMR spectra are presented in Figures S1 and S2 (see Supplementary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

2.2a $[1\text{-MPrIM}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$: ^1H NMR (DMSO, 400 MHz) δ : 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}C NMR (CDCl_3 , 100.6 MHz) δ : 10.4, 11.6, 22.6, 49.9, 120.8, 122.2, 122.2, 144.2; ^{19}F NMR (CDCl_3 , 100.6 MHz) δ : -79.0 (s, $\text{CF}_3\text{SO}_2)_2\text{N}^-$). IR ($\tilde{\nu}/\text{cm}^{-1}$): 3123 [ν (=C-H)], 2978, 2887 [ν (C-H)], 1461 [δ (C-H)], 1347, 1329 [ν (S=O)], 1179 [ν (C-F)], 1132 [δ (S=O)], 1051 [δ (C-F)].

2.2b $[1,2\text{-DMPrIM}^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]$: ^1H NMR (CDCl_3 , 400 MHz) δ : 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}C NMR (CDCl_3 , 100.6 MHz) δ : 9.4, 10.5, 14.8, 36.3, 50.0, 120.9, 122.3, 122.4, 143, 2–143.3; ^{19}F NMR (CDCl_3 , 100.6 MHz) δ : -78.82 (s, $\text{CF}_3\text{SO}_2)_2\text{N}^-$). IR ($\tilde{\nu}/\text{cm}^{-1}$): 3152 [ν (=C-H)], 2974, 2885 [ν (C-H)], 1540, 1462 [δ (C-H)], 1347, 1329 [ν (S=O)], 1176 [ν (C-F)], 1132 [δ (S=O)], 1054 [δ (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⁺][(CF₃SO₂)₂N⁻] and [1, 2-DMPrIM⁺][(CF₃SO₂)₂N⁻]. 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⁻¹] were collected with 1 cm⁻¹ 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⁻¹] were collected with 1 cm⁻¹ 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⁻¹] spectra of the two investigated ILs, namely, [1-MPrIM⁺][(CF₃SO₂)₂N⁻] and [1, 2-DMPrIM⁺][(CF₃SO₂)₂N⁻] are shown in

Figures 1 and 2, divided in two spectral regions: 600–1700 cm⁻¹ and 2800–3400 cm⁻¹.

3.1a The 600–1700 cm⁻¹ 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⁺][(CF₃SO₂)₂N⁻] and non-methylated [1MPrIM⁺][(CF₃SO₂)₂N⁻] ILs occurs at 844 cm⁻¹; 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⁺][(CF₃SO₂)₂N⁻] supports this assignment (this band is observed at 846 cm⁻¹ in the study by Noack *et al.*²⁴).

Furthermore, the presence of a characteristic band at 1540 cm⁻¹ in [1, 2-DMPrIM⁺][(CF₃SO₂)₂N⁻] and at 1571 cm⁻¹ in [1-MPrIM⁺][(CF₃SO₂)₂N⁻], can be attributed to a CC stretching in NC(CH₃)N ring and NC₂(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⁻¹ assigned to CC stretching in NC(CH₃)N ring.²⁴

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 [(CF₃SO₂)₂N⁻] anion. For example, the most intense IR bands at 1051, 1132, 1174, 1226, 1330, 1346 and 1446 cm⁻¹ are common in both ILs, as they are dominated by vibrations of the [(CF₃SO₂)₂N⁻] anion.^{34–39}

3.1b The 2800–3400 cm⁻¹ region: In this region, the same absorption bands can be observed in the

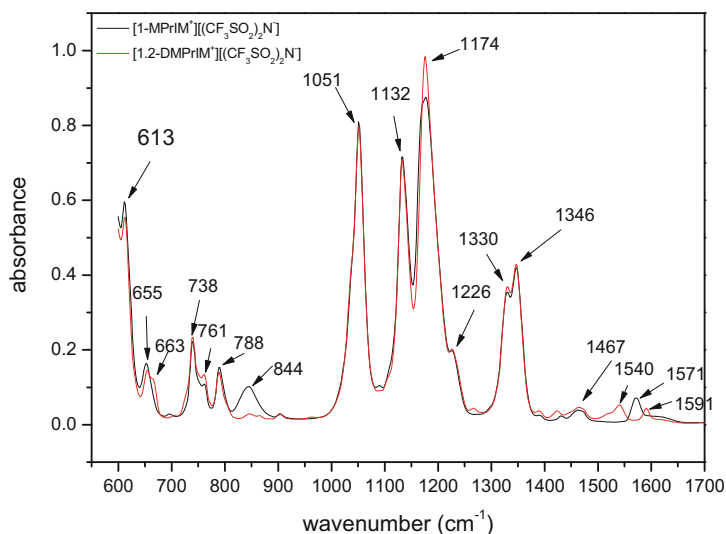


Figure 1. FTIR/ATR spectra of [1-MPrIM⁺][(CF₃SO₂)₂N⁻] and [1, 2-DMPrIM⁺][(CF₃SO₂)₂N⁻] in the spectral range 550–1700 cm⁻¹.

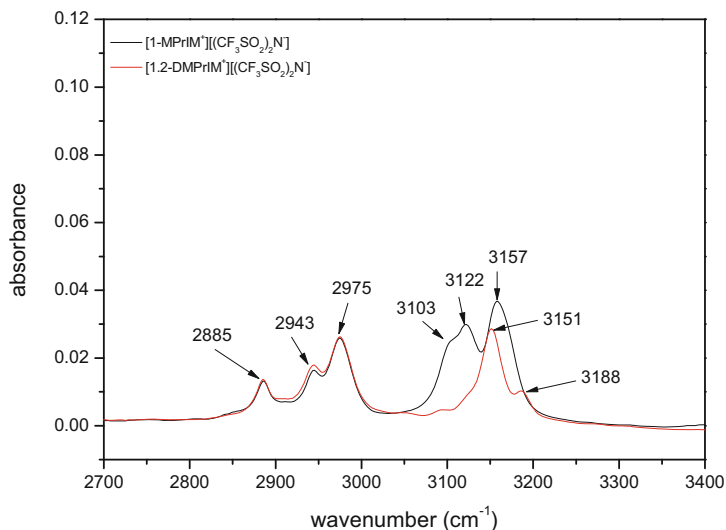


Figure 2. FTIR/ATR spectra of [1-MPrIM⁺][(CF₃SO₂)₂N⁻] and [1, 2-DMPrIM⁺][(CF₃SO₂)₂N⁻] in the spectral range 2800–3400 cm⁻¹.

FTIR/ATR spectra of the two ILs below 3000 cm⁻¹. The bands at low wavenumber are assigned to CH stretching in the propyl groups. Both ILs exhibit bands at 2885 and 2943 cm⁻¹, which can be assigned to CH vibrations in the propyl chain.^{40,41} Moreover, the spectra in this region exhibit a strong band at 2975 cm⁻¹, which is again a contribution of the propyl chain.⁴¹ Concerning the bands above 3000 cm⁻¹, 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.^{40–42} In [1-MPrIM⁺][(CF₃SO₂)₂N⁻], absorption bands occur at 3103, 3122 and 3157 cm⁻¹,

which can be attributed to the C(2)-H and H-C(4)-C(5)-H stretching vibration of the imidazolium ring respectively.^{40,41} On the contrary, in the methylated IL, [1, 2-DMPrIM⁺][(CF₃SO₂)₂N⁻], two important bands are observed at 3151 and 3188 cm⁻¹ 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⁺][(CF₃SO₂)₂N⁻], three interaction positions are possible: C(2)-H and C(4/5)-H. As reported by Fumino *et al.*,²³ when the H atom at C(2) is replaced by a CH₃ 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⁺][(CF₃SO₂)₂N⁻] and [1, 2-DMPPrIM⁺][(CF₃SO₂)₂N⁻] (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 ⁺] [(CF ₃ SO ₂) ₂ N ⁻]	[1, 2-DMPPrIM ⁺] [(CF ₃ SO ₂) ₂ N ⁻]	[1-MPrIM ⁺] [(CF ₃ SO ₂) ₂ N ⁻]	[1, 2-DMPPrIM ⁺] [(CF ₃ SO ₂) ₂ N ⁻]		
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 ₃	
		278 (m)	278 (m)	Trans-TFSI: ρ CF ₃	34/35/36
		296 (w)	296 (w)	CH ₂ (N), CH ₃ (N)CH bend, Trans-TFSI: ρ(CF ₃), νas(CS)	35/36
		312 (w)	312 (w)	Trans-TFSI: ρ(SO ₂), ρ(CF ₃)	35/36
		327 (w)	326 (w)	SC Str	35/36
		340 (w)	339 (w)	Trans-TFSI: τ (SO ₂)	36/37
		398 (w)	398 (w)	CH ₂ (N), CH ₃ (N)CH bend, Trans-TFSI: ω(SO ₂)	35/36
		405 (vw)	405 (vw)	Trans-TFSI: ω(SO ₂)	35/36/37
		553 (vw)	551 (vw)	Trans-TFSI: δs(SO ₂)	35/36/37
		573 (vw)	571 (vw)	Trans-TFSI: δas(CF ₃)	35/36/37
		594 (vw)	588 (vw)	Trans-TFSI: δas(CF ₃), δip as(SO ₂), δs(NSO ₂)	35/36/37
	613 (s)			Trans-TFSI: δSNS,	35/36/37
	657 (w)		703 (w)	CH ₂ (N) str, CH ₃ (N)CN str/ν N-CH ₃	35/36
	663 (sh)		726 (m)	Ring HCCH sym bend, CH ₂ (N) and CH ₃ (N) CN	35/36
	738 (m)	742 (s)	741 (s)	Trans TFSI: δs(CF ₃)	35/36/37
	764 (w)			ring HCCH asym bend/ω(CH ₂) rocking.	35/36
			797 (vw)	Trans-TFSI: νas SN + vs CF	35/36/37
	788 (w)			Trans TFSI: δs(CF ₃)	35/36/37
788 (w)		864 (vw)	866 (vw)	NC2(H)N CH bending	35/36/37
844 (w)		906 (vw)	904 (vw)	NC(H) N/propylchain CCC symstr propylchain CCC symstr	35/36/37
			963 (vw)	ν _{sym} CH ₂ -CH ₂ -CH ₃ CCC	35/36
		1023 (vw)	1035 (vw)	ν(C-C)/CH ₂ (N)/CH ₃ (N)CN Str.	45
					35/37
					35/37

Table 1. (contd.)

FTIR/ATR		Raman		Vibrational assignment	Refs
[1-MPrIM ⁺] [(CF ₃ SO ₂) ₂ N ⁻]	[1, 2-DMPriM ⁺] [(CF ₃ SO ₂) ₂ N ⁻]	[1-MPrIM ⁺] [(CF ₃ SO ₂) ₂ N ⁻]	[1, 2-DMPriM ⁺] [(CF ₃ SO ₂) ₂ N ⁻]		
1051 (s)	1051 (s)			Trans TFSI: $\nu_s(\text{SO}_2)/\nu_{\text{sym}}(\text{chain CCC})$	24/35/45 35/36
1132 (s)	1132 (s)	1135 (vw)	1076 (vw)	Trans TFSI: $\nu_s(\text{SO}_2)/\nu_{\text{sym}}(\text{chain CCC})$	35/45
1174 (s)	1174 (s)		1137 (w)	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 ₂ (N)/CH ₃ (N)CN Str	35/36
		1418 (vw)	1418 (vw)	Trans TFSI: $\nu_{\text{as}}(\text{SO}_2)$, CH ₂ (N)/CH ₃ (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 ₃ HCH symbend, (N)CH ₃ CN str	35/36
1571 (w)	1540 (w)			Ring CH ₃ HCH asym bend	24/36
				NC(CH ₃)NCC	35/36
				NC2(H)N CH bending	35/36
				CCH HCH asym bend/CH ₃ (N) CN str	24/36
			2764 (vw)	propyl C-H	45/36
			2837 (vw)	propyl C-H	40/46
			2885 (sh)	Propyl CH ₃	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 [(CF₃SO₂)₂N⁻].

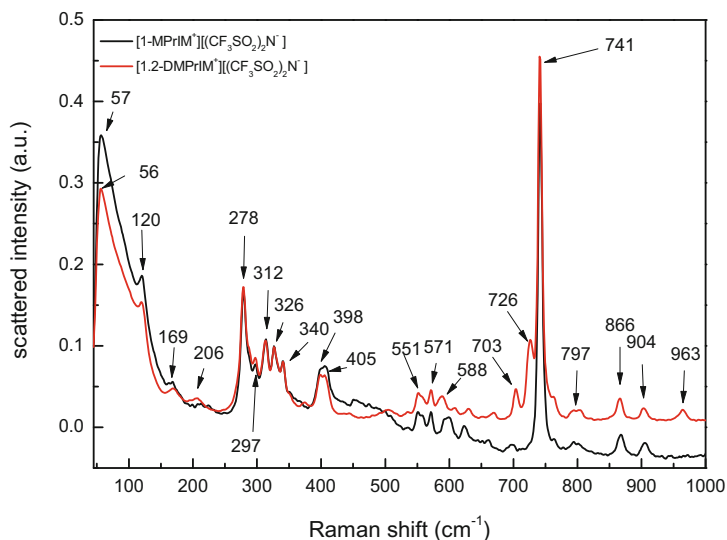


Figure 3. FT-RAMAN Spectra of [1-MPrIM⁺][(CF₃SO₂)₂N⁻] and [1,2-DMPrIM⁺][(CF₃SO₂)₂N⁻] in the spectral range of 45–1000 cm⁻¹.

the stretching modes between 3103 and 3122 cm⁻¹ are completely missing in the FTIR/ATR spectra of methylated IL. For [1-MPrIM⁺][(CF₃SO₂)₂N⁻] IL, the band at 3157 cm⁻¹, is assigned to the C(4)-H/C(5)-H symmetric stretching mode, while the same band in [1,2-DMPrIM⁺][(CF₃SO₂)₂N⁻] is blue shifted to a frequency of 3188 cm⁻¹. 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⁻¹] of [1-MPrIM⁺][(CF₃SO₂)₂N⁻] and [1,2-DMPrIM⁺][(CF₃SO₂)₂N⁻] 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⁻¹ region: In the range 45–200 cm⁻¹, 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 [(CF₃SO₂)₂N⁻] anion.³⁴ The Raman modes at 56 cm⁻¹ and 57 cm⁻¹ are attributed to acoustic excitations, while the mode at 120 cm⁻¹ is assigned to an intramolecular normal mode of [(CF₃SO₂)₂N⁻] anion, and the mode at 204 cm⁻¹ is related to vibrational motion of the imidazolium ring.³⁴ In the second region between 500 and 1000 cm⁻¹ (Figure 3), small differences around 700 cm⁻¹ 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⁻¹ region: Concerning Raman spectra in [1-MPrIM⁺][(CF₃SO₂)₂N⁻] and [1,2-DMPrIM⁺][(CF₃SO₂)₂N⁻], 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⁻¹ can be assigned to the [(CF₃SO₂)₂N⁻] anion, and these bands were also found in our measurements.^{34–36} Previous literature provided evidence that the bands at 278, 297, 312, and 398 cm⁻¹ are due to both trans- and cis-conformer of [(CF₃SO₂)₂N⁻];^{43,44} however, the band at 326 cm⁻¹ was assigned to cis-conformer, while the line at 340 cm⁻¹ can be associated only to trans-[(CF₃SO₂)₂N⁻]. In our experimental spectra we observe the bands expected for both conformers of [(CF₃SO₂)₂N⁻]. At higher Raman shift, both ILs display bands at 742 and 1242 cm⁻¹, which according to the literature,⁴² are due to the symmetric CF₃ stretching and deformation bands in the [(CF₃SO₂)₂N⁻] anion.

As shown in Table 1 and Figure 4, the methylated IL [1,2-DMPrIM⁺][(CF₃SO₂)₂N⁻], having an additional methyl group (CH₃ at C₂ position), shows an intense band around 1516 cm⁻¹, which is not observable in [1-MPrIM⁺][(CF₃SO₂)₂N⁻]; this band is probably assigned to C2-CH₃ group, this group being absent in the non-methylated IL.²⁴

3.2c The 2700–3500 cm⁻¹ region: Figure 5 shows high frequency Raman spectra of [1-MPrIM⁺]

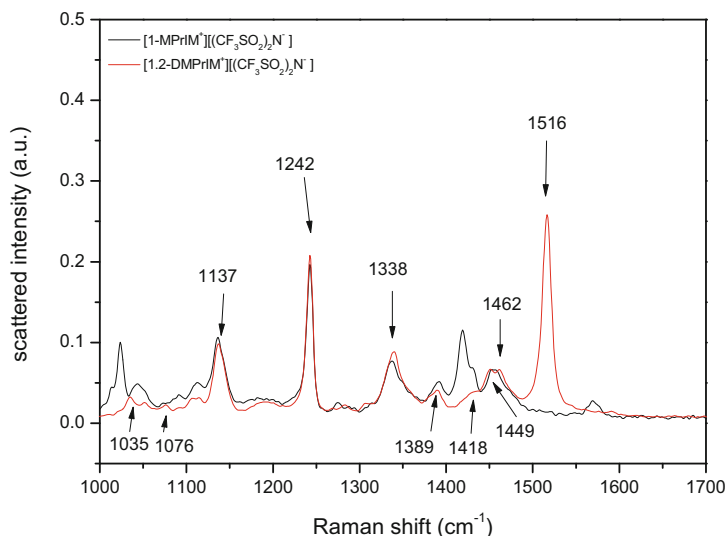


Figure 4. FT-RAMAN Spectra of [1-MPrIM⁺][(CF₃SO₂)₂N⁻] and [1,2-DMPriM⁺][(CF₃SO₂)₂N⁻] in the spectral range of 1000–1700 cm⁻¹.

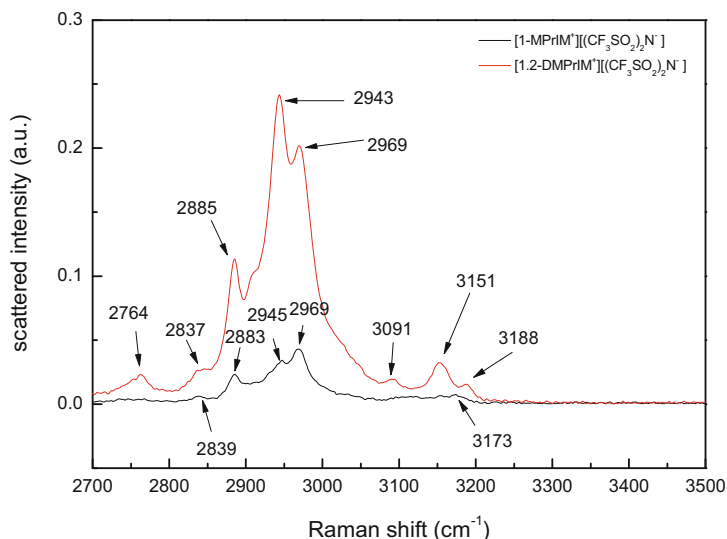


Figure 5. FT-RAMAN Spectra of [1-MPrIM⁺][(CF₃SO₂)₂N⁻] and [1,2-DMPriM⁺][(CF₃SO₂)₂N⁻] in the spectral range of 2700–3500 cm⁻¹.

[(CF₃SO₂)₂N⁻] and [1,2-DMPriM⁺][(CF₃SO₂)₂N⁻]. 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⁻¹ for [1-MPrIM⁺][(CF₃SO₂)₂N⁻] and at 2764, 2837, 2885, 2943, 2969 cm⁻¹ for [1,2-DMPriM⁺][(CF₃SO₂)₂N⁻]. All of them can be assigned to the CH stretching vibration of the [1-MPrIM⁺] and [1,2-DMPriM⁺] chains.⁴⁰ Furthermore, three bands are detected at 3091, 3151, 3188 cm⁻¹ for [1,2-DMPriM⁺][(CF₃SO₂)₂N⁻], while only a very weak Raman band at 3173 cm⁻¹ is observed for the non-methylated case. The first band at 3091 cm⁻¹

originates from asymmetric stretch of (N)CH₃, while bands at 3151, 3188 cm⁻¹ 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⁺][(CF₃SO₂)₂N⁻] is found at 3171 cm⁻¹; this demonstrates that the interaction between [(CF₃SO₂)₂N⁻] 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

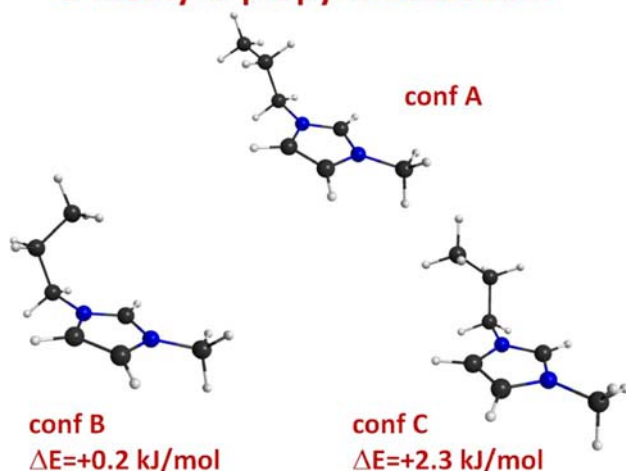


Figure 6. Schematic view of the three conformers of 1-methyl, 3-propyl imidazolium, with the relative energy difference with conformer A. Blue, black and light gray balls represent N, C and H atoms, respectively.

1, 2-dimethyl 3-propyl imidazolium

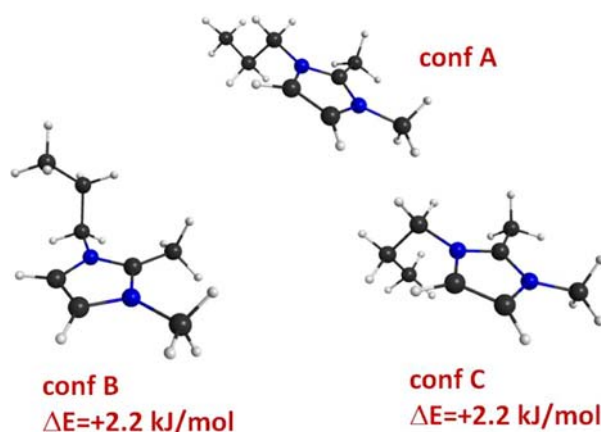


Figure 7. Schematic view of the three conformers of 1,2-dimethyl 3-propyl imidazolium, with the relative energy difference with conformer A. Blue, black and light gray balls represent N, C and H atoms, respectively.

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.^{37,38,43,44} 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.^{21,45} 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,^{48,49} 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 (ΔE) 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 ΔE 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.^{43,44} 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 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

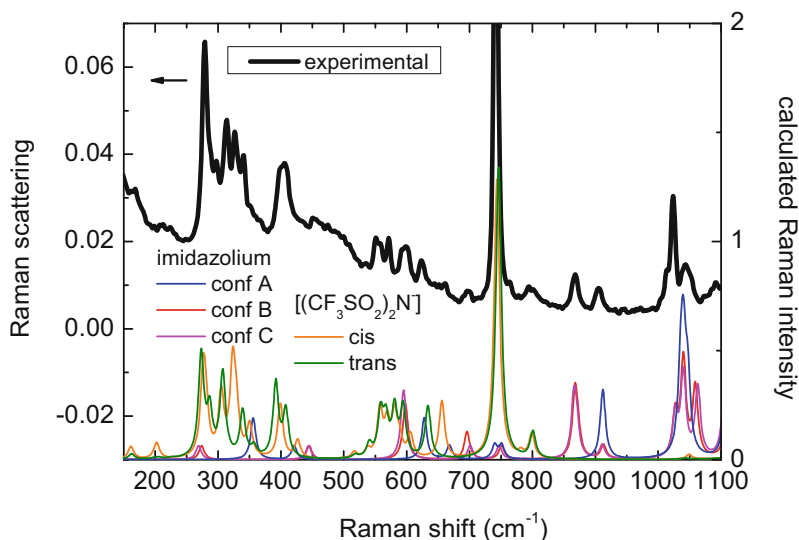


Figure 8. Experimental Raman spectrum of 1-methyl, 3-propyl imidazolium bis(trifluoromethane-sulfonyl) imide and calculated Raman intensity of the three conformers of 1-methyl 3-propyl imidazolium and of the two conformers of $[(CF_3SO_2)_2N^-]$. A scaling factor 1.04 is considered for $[(CF_3SO_2)_2N^-]$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

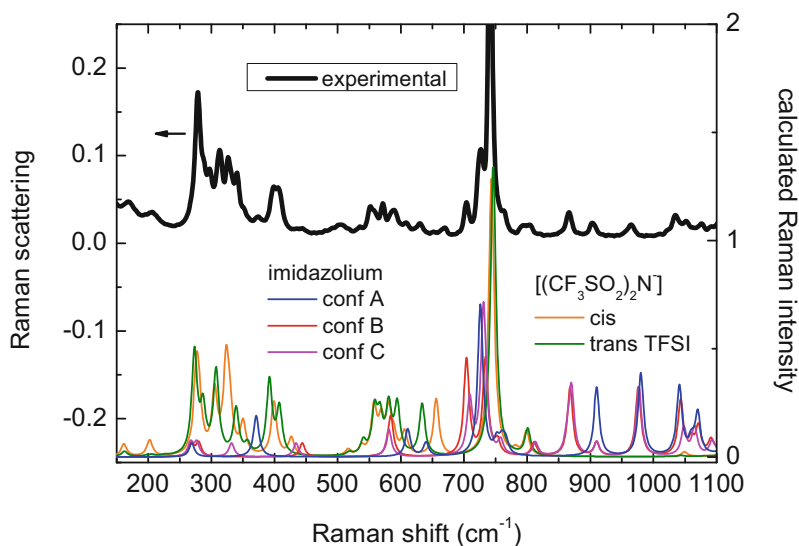


Figure 9. Experimental Raman spectrum of 1,2-dimethyl,3-propyl imidazolium bis(trifluoromethane-sulfonyl) imide and calculated Raman intensity of the three conformers of 1,2-dimethyl 3-propyl imidazolium and of the two conformers of $[(CF_3SO_2)_2N^-]$. A scaling factor 1.04 is considered for $[(CF_3SO_2)_2N^-]$ 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 cm^{-1} is attributable to conformers B and C, while it is not present in the spectrum of conformer A.

The band around 867 cm^{-1} is expected for Conf. B and C, but it should not occur in Conf. A. Finally, the line at 905 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 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 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 cm^{-1} should be attributed to Conf. A. As for 1-methyl, 3-propyl imidazolium bis(trifluoromethane-sulfonyl) imide, the band around 867 cm^{-1} is expected for Conf. B and C, but it should not occur in Conf. A. Moreover, the line at 903 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 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 ^1H , ^{13}C , ^{19}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 cm^{-1} by the two bands centered at 844, 1571 cm^{-1} and a single intense band centered at 1516 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⁺][(CF₃SO₂)₂N⁻] and [1, 2-DMPPrIM⁺][(CF₃SO₂)₂N⁻] using ^1H , ^{13}C and ^{19}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.

Acknowledgements

The authors gratefully acknowledge the financial support by MESRS, Univ-Saida, Algeria. H. B. also thanks Pr. Didier Villemin from LCMT-Caen for the helpful collaboration since 2008. We would like to thank Quentin Arnould, technician of Walloon Agricultural Research Centre (CRAW, Belgium), who participated in FT-Raman and FTIR/ATR measurements.

References

- Lane G H 2012 Electrochemical reduction mechanisms and stabilities of some cation types used in ionic liquids and other organic salts *Electrochim. Acta* **83** 513
- Chakrabarti M H, Mjalli F S, AlNashef I M, Hashim M A, Hussain M A, Bahadori L and Low C T J 2014 Prospects of applying ionic liquids and deep eutectic solvents for renewable energy storage by means of redox flow batteries *Renewable Sustainable Energy Rev.* **30** 254
- Smith A M, Lovelock K R J, Gosvami N N, Licence P, Dolan A, Welton T and Perkin S 2013 Monolayer to bilayer structural transition in confined pyrrolidinium-based ionic liquids *J. Phys. Chem. Lett.* **4** 378
- Precht M 2016 In *Nanocatalysis in Ionic Liquids* (Germany: John Wiley)
- Lei Z, Dai C and Chen B 2014 Gas solubility in ionic liquids *Chem. Rev.* **114** 1289
- Palgunadi J and Sik K H 2010 The vibrational infrared spectra of 1-methyl-3-methylimidazolium dimethylphosphate. Is the dispersion-corrected functional important in intermolecular DFT calculation of ionic liquids? *Spectrosc. Lett.* **43** 513
- Smiglak M, Pringle J M, Lu X, Han L, Zhang S, Gao H, MacFarlane D R and Rogers R D 2014 Ionic liquids for energy, materials, and medicine *Chem. Commun.* **50** 9228
- Singh M P, Singh R K and Chandra S 2014 Ionic liquids confined in porous matrices: Physicochemical properties and applications *Prog. Mater. Sci.* **64** 73
- Geppert-Rybczyńska M, Lehmann J K and Heintz A 2014 Physicochemical properties of two 1-alkyl-1-methylpyrrolidinium bis [(trifluoromethyl) sulfonyl] imide ionic liquids and of binary mixtures of 1-butyl-1-methylpyrrolidinium bis [(trifluoromethyl) sulfonyl] imide with methanol or acetonitrile *J. Chem. Thermodyn.* **71** 171
- Couadou E, Jacquemin J, Galiano H, Hardacre C and Anouti M 2013 A comparative study on the thermophysical properties for two bis [(trifluoromethyl) sulfonyl] imide-based ionic liquids containing the trimethyl-sulfonium or the trimethyl-ammonium cation in molecular solvents *J. Phys. Chem. B* **117** 1389
- Neale A R, Li P, Jacquemin J, Goodrich P, Ball S C, Compton R G and Hardacre C 2016 Effect of cation structure on the oxygen solubility and diffusivity in a range of bis (trifluoromethyl) sulfonyl imide anion based

- ionic liquids for lithium–air battery electrolytes *Phys. Chem. Chem. Phys.* **18** 11251
12. Katsyuba S A, Vener M V, Zvereva E E, Fei Z, Scopelitti R, Laurency G, Yan N, Paunescu E and Dyson P J 2013 How strong is hydrogen bonding in ionic liquids? Combined X-ray crystallographic, infrared/Raman spectroscopic, and density functional theory study *J. Phys. Chem. B* **117** 9094
 13. Roth C, Peppel T, Fumino K, Köckerling M and Ludwig R 2010 The importance of hydrogen bonds for the structure of ionic liquids: Single-crystal X-ray diffraction and transmission and attenuated total reflection spectroscopy in the terahertz region *Angew. Chem. Int. Ed.* **49** 10221
 14. Penna T C, Faria L F O, Matos J R and Ribeiro M C C 2013 Pressure and temperature effects on intermolecular vibrational dynamics of ionic liquids *J. Chem. Phys.* **138** 104503
 15. Binetti E, Panniello A, Triggiani L, Tommasi R, Agostiano A, Curri M L and Striccoli M 2012 Spectroscopic study on imidazolium-based ionic liquids: Effect of alkyl chain length and anion *J. Phys. Chem. B* **116** 3512
 16. Moumene T, Belarbi E H, Haddad B, Villemin D, Abbas O, Khelifa B and Bresson S 2014 Vibrational spectroscopic study of ionic liquids: Comparison between monocationic and dicationic imidazolium ionic liquids *J. Mol. Struct.* **1065-1066** 86
 17. Matthews R P, Welton T and Hunt P A 2015 Hydrogen bonding and π - π interactions in imidazolium-chloride ionic liquid clusters *Phys. Chem. Chem. Phys.* **17** 14437
 18. Clough M T, Geyer K, Hunt P A, McIntosh A J S, Rowe R, Welton T and White A J P 2016 Azoniaspiro salts: Towards bridging the gap between room-temperature ionic liquids and molten salts *Phys. Chem. Chem. Phys.* **18** 3339
 19. Bonhôte P, Dias A-P, Papageorgiou N, Kalyanasundaram K and Grätzel M 1996 Hydrophobic, highly conductive ambient-temperature molten salts *Inorg. Chem.* **35** 1168
 20. Hunt P A 2007 Why does a reduction in hydrogen bonding lead to an increase in viscosity for the 1-butyl-2,3-dimethyl-imidazolium-based ionic liquids? *J. Phys. Chem. B* **111** 4844
 21. Endo T, Kato T and Nishikawa K 2010 Effects of methylation at the 2 position of the cation ring on phase behaviors and conformational structures of imidazolium-based ionic liquids *J. Phys. Chem. B* **114** 9201
 22. Zhang Y and Maginn E J 2012 The effect of C2 substitution on melting point and liquid phase dynamics of imidazolium based-ionic liquids: Insights from molecular dynamics simulations *Phys. Chem. Chem. Phys.* **14** 12157
 23. Fumino K, Wulf A and Ludwig R 2008 Starke, lokalisierte und gerichtete H-Brücken machen ionische Flüssigkeiten beweglicher *Angew. Chem.* **120** 8859
 24. Noack K, Schulz P S, Paape N, Kiefer J, Wasserscheid P and Leipertz A 2010 The role of the C2 position in interionic interactions of imidazolium based ionic liquids: A vibrational and NMR spectroscopic study *Phys. Chem. Chem. Phys.* **12** 14153
 25. Izgorodina E I, Maganti R, Armel V, Dean P M, Pringle J M, Seddon K R and MacFarlane R 2011 Understanding the effect of the C2 proton in promoting low viscosities and high conductivities in imidazolium-based ionic liquids: part I. weakly coordinating anions *J. Phys. Chem. B* **115** 14688
 26. Haddad B, Mokhtar D, Gousseem M, Belarbi E H, Villemin D, Bresson S, Rahmouni M, Dhumal N R, Kim H J and Kiefer J 2017 Influence of methyl and propyl groups on the vibrational spectra of two imidazolium ionic liquids and their non-ionic precursors *J. Mol. Struct.* **1134** 582
 27. Chen Z J and Lee J M 2014 Free volume model for the unexpected effect of C2-methylation on the properties of imidazolium ionic liquids *J. Phys. Chem. B* **118** 2712
 28. Chen S, Vijayaraghavan R, MacFarlane D R and Izgorodina E I 2013 Ab initio prediction of proton NMR chemical shifts in imidazolium ionic liquids *J. Phys. Chem. B* **117** 3186
 29. Fumino K, Wulf A and Ludwig R 2009 The potential role of hydrogen bonding in aprotic and protic ionic liquids *Phys. Chem. Chem. Phys.* **11** 8790
 30. Lassègues J-C, Grondin J, Cavagnat D and Johansson P 2009 New interpretation of the CH stretching vibrations in imidazolium-based ionic liquids *J. Phys. Chem. A* **113** 6419
 31. Huang J-F, Chen P-Y, Sun I-W and Wang S P 2001 NMR Evidence of hydrogen bond in 1-ethyl-3-methylimidazolium-tetrafluoroborate room temperature ionic liquid *Spectrosc. Lett.* **34** 591
 32. Dong K, Zhang S, Wang D and Yao X 2006 Hydrogen bonds in imidazolium ionic liquids *J. Phys. Chem. A* **110** 9775
 33. Holbrey J D, Reichert W M and Rogers R D 2004 Crystal structures of imidazolium bis (trifluoromethanesulfonyl) imide 'ionic liquid' salts: The first organic salt with a cis-TFSI anion conformation *Dalton Trans.* **2004** 2267
 34. Moumene T, Belarbi E H, Haddad B, Villemin D, Abbas O, Khelifa B and Bresson S 2015 Study of imidazolium dicationic ionic liquids by Raman and FTIR spectroscopies: The effect of the nature of the anion *J. Mol. Struct.* **1083** 179
 35. Moschovi A M, Ntais S, Dracopoulos V and Nikolakis V 2012 Vibrational spectroscopic study of the protic ionic liquid 1-H-3-methylimidazolium bis (trifluoromethanesulfonyl) imide *Vib. Spec.* **63** 350
 36. Fujii K, Fujimori T, Takamuku T, Kanzaki R, Umebayashi Y and Ishiguro S 2006 Conformational equilibrium of bis (trifluoromethanesulfonyl) imide anion of a room-temperature ionic liquid: Raman spectroscopic study and DFT calculations *J. Phys. Chem. B* **110** 8179
 37. Lassègues J C, Grondin J, Holomb R and Johansson P 2007 Raman and ab initio study of the conformational isomerism in the 1-ethyl-3-methyl-imidazolium bis (trifluoromethanesulfonyl) imide ionic liquid *J. Raman Spectrosc.* **38** 551
 38. Capitani F, Gatto S, Postorino P, Palumbo O, Trequatrini F, Deutsch M, Brubach J-B, Roy P and Paolone A 2016 The complex dance of the two conformers of bis (trifluoromethanesulfonyl) imide as a function of pressure and temperature *J. Phys. Chem. B* **120** 1312
 39. Roth C, Chatzipapadopoulos S, Kerlé D, Friedriszik F, Lütgens M, Lochbrunner S, Kühn and Ludwig R 2012 Hydrogen bonding in ionic liquids probed by linear and nonlinear vibrational spectroscopy *New J. Phys.* **14** 105026

40. Cha S, Ao M, Sung W, Moon B, Ahlström B, Johansson P, Ouchi Y and Kim D 2014 Structures of ionic liquid–water mixtures investigated by IR and NMR spectroscopy *Phys. Chem. Chem. Phys.* **16** 9591
41. Jeon Y, Sung J, Seo C, Lim H, Cheong H, Kang M, Moon B, Ouchi Y and Kim D 2008 Structures of ionic liquids with different anions studied by infrared vibration spectroscopy *J. Phys. Chem. B* **112** 4735
42. Berg R W 2007 Raman spectroscopy and ab-initio model calculations on ionic liquids *Monatsch. Chem.* **138** 1045
43. Capitani F, Trequatrini F, Palumbo O, Paolone A and Postorino P 2016 Phase transitions of PYR₁₄-TFSI as a function of pressure and temperature: the competition between smaller volume and lower energy conformer *J. Phys. Chem. B* **120** 2921
44. Herstedt M, Smirnov M, Johansson P, Chami M, Grondin J, Servant L and Lassègues J C 2005 Spectroscopic characterization of the conformational states of the bis (trifluoromethanesulfonyl) imide anion (TFSI-) *J. Raman Spectrosc.* **36** 762
45. Holomb R, Martinelli A, Albinsson I, Lassègues J C, Johansson P and Jacobsson P 2008 Ionic liquid structure: the conformational isomerism in 1-butyl-3-methyl-imidazolium tetrafluoroborate ([bmim][BF₄]). *J. Raman Spectrosc.* **39** 793.
46. Heimer N E, Del Sesto R E, Meng Z, Wilkes J S and Carper W R 2006 Vibrational spectra of imidazolium tetrafluoroborate ionic liquids. *J. Mol. Liq.* **124** 84
47. Chang H-C, Jiang J-C, Su J-C, Chang C-Y and Lin S H 2007 Evidence of rotational isomerism in 1-butyl-3-methylimidazolium halides: A combined high-pressure infrared and Raman spectroscopic study *J. Phys. Chem. A* **111** 9201
48. Shao Y, Molnar L F, Jung Y, Kussmann J, Ochsenfeld C, Brown S T, Gilbert A T B, Slipchenko L V, Levchenko S V, O'Neill D P, DiStasio R A Jr., Lochan R C, Wang T, Beran G J O, Besley N A, Herbert J M, Lin C Y, Van Voorhis T, Chien S H, Sodt A, Steele R P, Rassolov V A, Maslen P E, Korambath P P, Adamson R D, Austin B, Baker J, Byrd E F C, Dachsel H, Doerksen R J, Dreuw A, Dunietz B D, Dutoi A D, Furlani T R, Gwaltney S R, Heyden A, Hirata S, Hsu C-P, Kedziora G, Khalliulin R Z, Klunzinger P, Lee A M, Lee M S, Liang W Z, Lotan I, Nair N, Peters B, Proynov E I, Pieniazek P A, Rhee Y M, Ritchie J, Rosta E, Sherrill C D, Simmonett A C, Subotnik J E, Woodcock H L III, Zhang W, Bell A T, Chakraborty A K, Chipman D M, Keil F J, Warshel A, Hehre W J, Schaefer H F, Kong J, Krylov A I, Gill P M W and Head-Gordon M 2006 Advances in methods and algorithms in a modern quantum chemistry program package *Phys. Chem. Chem. Phys.* **8** 3172
49. Hehre W J 2003 In *A guide to molecular mechanics and quantum chemical calculations* (Irvine, CA: Wavefunction Inc.)