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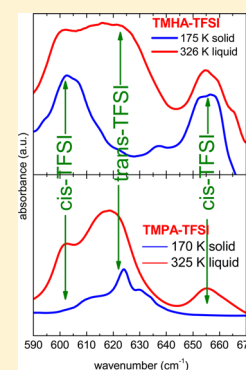
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ABSTRACT: The infrared absorption spectra of two ionic liquids with bis(trifluoromethanesulfonyl)imide (TFSI) as an anion and ammonium with different alkyl chains as cations are reported as a function of temperature. Using the comparison with *ab initio* calculations of the infrared-active intramolecular vibrations, the experimental lines were ascribed to the various ions composing the ionic liquids. In the liquid state of the samples, both conformers of the TFSI ion are present. In the solid state, however, the two conformers survive in *N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)imide (TMPA-TFSI), while only *cis*-TFSI is retained in *N*-trimethyl-*N*-hexylammonium bis(trifluoromethanesulfonyl)imide (TMHA-TFSI). We suggest that the longer alkyl chains of the former compound stabilize the less stable conformer of TFSI by means of stronger interactions between anions and cations.



INTRODUCTION

Ionic liquids (ILs) are salts with melting temperatures below 100 °C. Typically, they are formed by organic cations, like imidazolium, pyrrolidinium, ammonium, or alkyl phosphonium, and organic/inorganic anions, like hexafluorophosphate, tetrafluoroborate, triflate, dicyanamide, tetracyanamethanide, or bis(trifluoromethanesulfonyl)imide (TFSI).^{1–5} The presence of such bulky and asymmetric ions decreases the ion–ion interactions and lowers the melting point with respect to more classical salts.

ILs present peculiar physical and chemical properties: an extremely low vapor pressure, a high ionic conductivity, a high thermal, chemical and electrochemical stability, a high thermal capacity, and a good solvent capacity. Due to these peculiarities, ILs have been proposed for a large variety of applications in chemistry and physics, such as, for example, green solvents, electrolytes for electrochemistry, lubricants, ingredients for pharmaceuticals, and heat exchangers.^{1–11}

There are many classes of ILs, depending on the particular choice of anion or cation. In this paper, we will investigate two ILs of the ammonium family. Ammonium-based IL investigations are scarce compared to other classes of ILs; they exhibit, however, some interesting properties compared to other cations. Indeed, ammonium-based ILs are commercially available and find successful applications as catalysts, solvents, lubricants, gas capture agents, coating materials, or chemical sensors.^{12–16} They have a better thermal and chemical stability in comparison with pyridinium and imidazolium-based ILs.¹⁷

Macroscopic properties of ILs, such as viscosity or ionic conductivity, have been largely investigated. However, a deep comprehension of the connection among these macroscopic features and the microscopic structure of cations and anions is still needed. In some cases, even in the liquid phase, one can observe the formation of nanoaggregates that change the physical properties of the ILs.¹⁸

It should be noted that the anion of the IL here investigated, TFSI, is a flexible molecule that can adopt two different conformations, energetically inequivalent, whose concentration in the liquid or solid phase can affect the physical and chemical properties of ILs. The *transoid* conformer with a *C*₂ symmetry is more stable than the *cisoid* one, which has a *C*₁ symmetry.¹⁹ However, the two conformers are energetically separated by only 2.2 kJ/mol, so that in the liquid state, both conformers are usually present.^{19–23} The *cisoid* and *transoid* forms of TFSI give different Raman and infrared spectra, as confirmed by experimental and computational studies.^{19–23} In particular, Herstedt et al. pointed out that *cis*- and *trans*-TFSI vibrational absorption show the main differences between 260 and 370 cm^{−1} in the Raman spectra and at around 600 cm^{−1} in the infrared spectra. The comparison between calculations and experiments confirmed that the spectral lines observed at 602 and 650 cm^{−1} can be assigned to the *cis* conformer, whereas the line at 628 cm^{−1} can be assigned to *trans*-TFSI.¹⁹ Some Raman

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spectroscopic investigations by means of Raman measurements of the thermal evolution of the two TFSI conformers have been reported in the liquid phase of some ILs^{21,24,25} and for the solid phase of 1-H-3-methylimidazolium TFSI,²⁶ in which the TFSI ion adopts the trans conformation.

In order to expand the knowledge of the microscopic configurations of anions and cations in ILs, we investigated by means of infrared spectroscopy two ammonium-based ILs, *N*-trimethyl-*N*-propylammonium TFSI (TMHA-TFSI) and *N*-trimethyl-*N*-hexylammonium TFSI (TMHA-TFSI). The extension of the ab initio computational study of the intramolecular vibrations to the ammonium ions allowed the attribution of the single absorption lines to specific movements. The experimental study was conducted both in the liquid and in the solid phase in order to ascertain the changes of the intramolecular structure induced by the crystallization/melting process. To the best of our knowledge, the solid phases of ammonium-based ILs have never been investigated, despite the fact that some of these ILs display melting points quite close to room temperature.

EXPERIMENTAL SECTION

TMPA-TFSI, with a declared melting temperature $T_m = 15\text{ }^\circ\text{C}$ (288 K), and TMHA-TFSI with $T_m = 27\text{ }^\circ\text{C}$ (300 K) were purchased from Solvionic. The purity of those samples was higher than 99.9%, and therefore, no further purification was used before measurements.

Differential scanning calorimetry (DSC) measurements were performed by a Mettler-Toledo DSC 821, under an inert nitrogen flux, cooling from 315 K down to 150 K and then heating back to 315 K with a temperature rate of 5 K/min.

Infrared spectroscopy measurements were performed by means of a Bruker Vertex 125 HV spectrometer at the AILES beamline of the SOLEIL Synchrotron.^{27,28} For measurements in the region below 670 cm^{-1} , the interferometer was equipped with a $6\text{ }\mu\text{m}$ Mylar beamsplitter, a global source, and a bolometer detector at a spectral resolution of 0.5 cm^{-1} . Above 600 cm^{-1} , a global source, a KBr beamsplitter, and a MCT detector were used, and the resolution of spectra was 0.25 cm^{-1} . Thin layers of ILs were placed between two KBr or polyethylene windows for measurements in the mid- and far-infrared regions, respectively. The transmission was recorded using as a reference the spectrum of the optical windows. Transmission measurements were converted to absorbance data, as usual. The samples were cooled down to 175 K by means of a Cryomac cryopump with a temperature rate of $\sim 5\text{ K/min}$, and data were collected on heating between this minimum temperature and 330 K.

COMPUTATIONAL

The infrared vibrational spectra of the isolated ions were calculated by means of the Firefly package^{29,30} and visualized by means of the wxMacMolPlt software.³¹ We chose to compute the infrared spectra of the single ions composing the ILs because such approximation has been widely used and validated in the previous literature.^{19–23,26,32–35} For the present study, we investigated TMPA and TMHA and the two conformers of TFSI, *trans*- and *cis*-TFSI. The atomic positions in each ion were obtained by means of the energy optimization procedure, adopting the 6-31G** basis set and the density functional theory at the level of B3LYP approximation. Such a combination had already been used to determine the

vibrational modes of the two TFSI conformers and gave good agreement with the experimental data.¹⁹ In the following, we will consider only the all-trans configurations for the TMHA and TMPA ions (both in the liquid and in the solid phases) because this is the minimum-energy state found by ab initio calculations. Moreover, the number of observable infrared absorptions due to the cations is extremely low and can give only a limited contribution in verifying possible structural changes.

RESULTS AND DISCUSSION

DSC curves measured with a temperature rate of 5 K/min cooling from 315 K down to 150 K and then heating back to 315 K are reported in Figure 1. Both ILs exhibit an intense

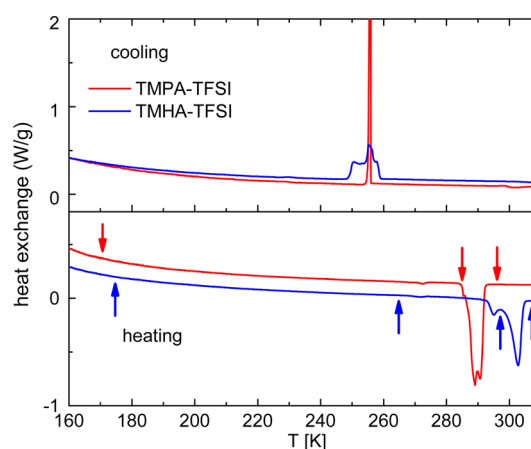


Figure 1. DSC traces of the two ILs measured with a temperature scan rate of 5 K/min upon cooling and upon subsequent heating. The arrows indicate the temperatures at which infrared spectroscopy measurements were performed (upon heating after cooling at 5 K/min).

exothermic peak upon cooling between 260 and 250 K, which can be attributed to the crystallization of the samples. Upon heating, TMPA-TFSI (TMHA-TFSI) shows a complex endothermic peak between 285 and 292 K (293 and 304 K), corresponding to the melting of the solid. It is worth noticing that the IR spectra were acquired at temperature values attained with the same temperature scan rate used for this DSC experiment; therefore, we are certain that both samples are in a crystalline state after cooling down to 170 K and undergo a melting process at around room temperature, without additional phase transitions.

The absorbance spectra of liquid TMPA-TFSI and TMHA-TFSI at around 325 K are reported in Figure 2 in the spectral range between 150 and 670 cm^{-1} . In this liquid state, they display absorption bands centered around the same frequencies, 206, 225, 288, 335, 363, 398, 409, 454, 515, 571, 602, 618, and 646 cm^{-1} in TMPA-TFSI and 207, 225, 287, 325, 363, 397, 408, 513, 571, 602, 622, and 656 cm^{-1} in TMHA-TFSI. In order to have quantitative information, a fit of the experimental data of both liquids at 325 K has been performed by means of Lorentzian peaks. The vibrational frequencies are reported in Table 1.

In order to ascribe the absorption lines to molecular vibrations, we performed ab initio calculations on the single ions composing the ILs, TFSI, TMPA, and TMHA. Indeed, the vibrational properties of only a few ILs have been investigated

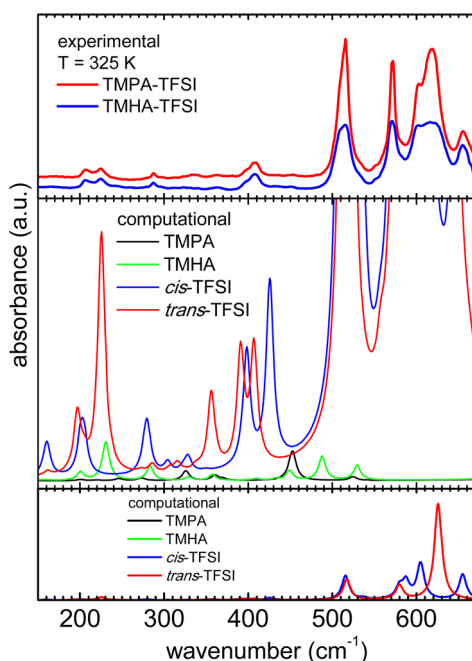


Figure 2. Experimental absorbance spectra of TMPA-TFSI and TMHA-TFSI at 325 K (upper panel) compared with the calculated absorbance spectra of the single ions composing the ILs (the two lower panels report the same data with different vertical scales). For the two TFSI conformers, a frequency scaling factor of 1.04 was used, while no scaling factor was applied for TMPA and TMHA.

computationally and experimentally by means of Raman or infrared spectroscopy, and none of them possess ammonium as the cation. In contrast, the TFSI anion has been widely investigated. It is known both experimentally and computationally that TFSI shows strong absorption bands below 800 cm^{-1} and in the frequency range between 1000 and 1350 cm^{-1} .^{19–24,36}

In the present paper, we reperformed ab initio calculation of the vibrational frequencies and infrared intensities of the two TFSI conformers at the B3LYP/6-31G** level, similarly to ref 19, in order to validate our computational approach. After validation of the method, we extended the calculations to the two cations because, to the best of our knowledge, no calculations on ammonium ions are available. The optimized structure of ions is shown in Figure 3, while the unscaled vibrational frequencies below 700 cm^{-1} and the corresponding infrared intensities are reported in Tables 2 and 3. The lower part of Figure 2 displays the infrared spectrum of the single ions, calculated by summing 10 cm^{-1} width Lorentzian curves centered at each computed IR vibrational frequency. In the TFSI conformers case, a scaling factor of 1.04 gives a good coincidence of the frequencies of the experimental lines with our scaled calculated ones, as already reported in ref 19.

For the ammonium ions, the unscaled frequencies were used to construct the absorption spectrum. Indeed, no other comparison between the calculated and experimental data were available, and therefore, the scaling factors are here determined for the first time. In the following, we compare the most intense absorption lines obtained from experiments with those obtained by the ab initio calculations.

In view of the ab initio calculations, one can attribute some of the absorption lines of the two ILs (see Table 1); the spectral marks of *cis*-TFSI are located at ~ 288 , 340 , 531 , 602 , and 655

Table 1. Vibration Frequencies (in cm^{-1}) Obtained from the Fit of the Experimental Data Reported in Figure 2 for TMPA-TFSI and TMHA-TFSI at Two Temperatures and Assignment to Ions Based on the Ab Initio Calculations

TMPA-TFSI		TMHA-TFSI		assignment
$T = 325\text{ K}$	$T = 175\text{ K}$	$T = 325\text{ K}$	$T = 170\text{ K}$	
206	206	207	206	<i>cis</i> -TFSI
	214		213	TMPA/TMHA
225	230	225		<i>trans</i> -TFSI
		240	243	TMHA
288		287	289	<i>cis</i> -TFSI
	298		308	TFSI
	317			TFSI
335	340	325	333	<i>cis</i> -TFSI + TMHA/ TMPA
363	362	363		<i>trans</i> -TFSI
398	397	397		<i>trans</i> -TFSI
409	408	408	406	<i>cis</i> -TFSI
		438	435	<i>cis</i> -TFSI
454	459			TMPA
			452	TMHA
509	505			TFSI
515	517	513	512	TFSI
			532	<i>cis</i> -TFSI + TMHA
			550	
			559	
571	571	571	572	TFSI
			582	
602		602	604	<i>cis</i> -TFSI
618	613			
	624	622		<i>trans</i> -TFSI
	632		638	
646		656	655	<i>cis</i> -TFSI

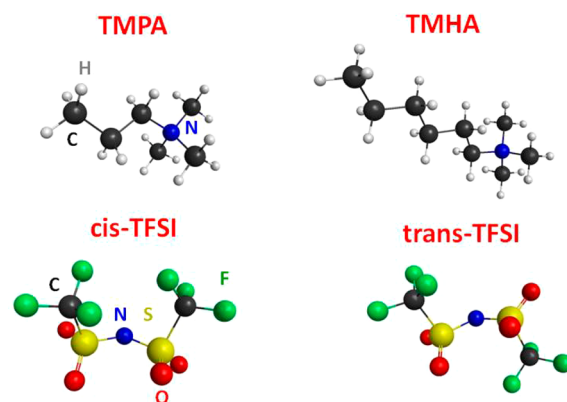


Figure 3. Structural formula of the ions composing the ILs.

cm^{-1} , while those of *trans*-TFSI can be found at ~ 227 , 363 , and 622 cm^{-1} . The most striking difference between the spectra of the two conformers comes from the intense lines between 600 and 650 cm^{-1} ; indeed, as already pointed out in ref 19, *trans*-TFSI displays only one line at around 622 cm^{-1} , while *cis*-TFSI shows two absorptions at around 602 and 655 cm^{-1} . Moreover, the very evident absorption centered at around 227 cm^{-1} is due to the *trans* conformer. Also, the absorption lines between 190 and 210 cm^{-1} and between 390 and 440 cm^{-1} are different in the two conformers. Detailed attributions of the lines in the latter frequency ranges will be presented in the following based on their temperature dependence. Other absorptions at around

Table 2. Unscaled Vibrational Frequencies and IR Intensities Calculated for the Two TFSI Conformers below 700 cm^{-1}

<i>trans</i> -TFSI		<i>cis</i> -TFSI	
frequency (cm^{-1})	intensity (km/mol)	frequency (cm^{-1})	intensity (km/mol)
155	0.2	154	1.5
189	2.5	192	1.1
197	0.5	193	0.1
217	10.2	197	1.6
262	0.2	265	0.3
275	0.4	269	2.2
295	0.2	292	0.5
304	0.4	310	0.1
325	0.2	316	0.7
342	3.3	336	0.1
376	4.9	383	4.9
391	5.0	409	7.7
497	73.7	496	86.2
519	0.0	516	6.1
536	1.5	535	1.1
544	0.3	546	2.0
557	51.3	557	40.1
570	0.0	565	60.6
602	343.5	582	128.9
608	3.1	630	91.0

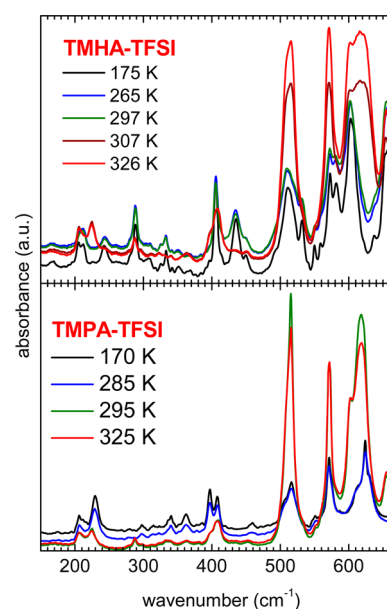
Table 3. Unscaled Vibrational Frequencies and IR Intensities Calculated for TMPA and TMHA below 700 cm^{-1}

TMPA		TMHA	
frequency (cm^{-1})	intensity (km/mol)	frequency (cm^{-1})	intensity (km/mol)
200	0.0	156	0.0
220	0.0	201	0.3
246	0.1	230	0.1
273	0.1	231	1.5
288	0.0	249	0.0
326	0.4	283	0.6
360	0.2	291	0.0
370	0.1	329	0.1
450	0.4	357	0.2
453	0.9	409	0.1
524	0.1	432	0.1
		449	0.4
		488	1.0
		529	0.6

300, 505, 515, and 570 cm^{-1} seem to contain contributions from both conformers of TFSI.

Concerning the cations, the spectra at 325 K suggest that one can observe some of the most intense absorption lines expected from the quantum simulations. For TMPA, experimentally, we find two absorptions at around 333 and 454 cm^{-1} , which can correspond to the computed vibrations centered at 326 and 450 cm^{-1} (scaling factors are 1.02 and 1.01, respectively). For the TMHA cation, at 325 K, we observe two experimental lines at 240 and 325 cm^{-1} , which correspond to the computed vibrations centered at 231 and 329 cm^{-1} (scaling factors are 1.04 and 1.01, respectively). The lines at around 330 cm^{-1} are superimposed on lines due to the TFSI ion. As discussed in the following, additional lines of the cations are found experimentally at low T 's.

As a preliminary attribution of the experimental lines is settled, we investigate in the following the evolution of the infrared spectra of the two samples as a function of temperature (see Figure 4). Most of the spectral lines of the solid phases are

**Figure 4.** Temperature dependence of the absorbance spectra of TMPA-TFSI and TMHA-TFSI.

located at the same frequencies as those observed for the liquid one, as in other molecular solids (see ref 37). However, the two ILs display a very different dependence of the intensities of some spectral lines on T . Indeed, in TMPA-TFSI, the intensities of the lines centered at around 288, 601, and 650 cm^{-1} drastically decrease when lowering the temperature, while new lines at around 298 and 459 cm^{-1} appear. Moreover, the absorptions at around 230, 340, 360, and 397 cm^{-1} become more intense at low T 's. On the contrary, in TMHA-TFSI, the lines at 225, 362, 397, and 622 cm^{-1} disappear at low temperatures, while the absorptions at around 240, 333, 450, and 532 cm^{-1} become well-defined. All of these changes in the infrared spectra occur at the melting temperature. In order to be more quantitative, we fitted the spectra of the two samples measured at the lowest temperature by means of Lorentzian peaks; the best-fit frequencies are reported in Table 1.

In the solid phase of TMPA, the intensity of the absorption lines at 288, 601, and 650 cm^{-1} , attributed by the comparison with the quantum calculations to vibrations of the cisoid conformer of TFSI, drastically decreases. On the contrary, the lines centered at around 230 and 360 cm^{-1} , due to the transoid TFSI conformer, increase their intensity in the low-temperature phase. The vibration at around 624 cm^{-1} due to *trans*-TFSI is still present in the solid. The absorption at 298 cm^{-1} increases its intensity, but it contains contributions from both conformers of TFSI. Also, the intensity of the vibrations of the TMPA ions centered at ~ 340 and 459 cm^{-1} increase their intensity and narrow. These results indicate that the concentration of *cis*-TFSI drastically decreases in the solid phase of TMPA-TFSI. It can be noted that also the intensity of absorption centered at around 395 cm^{-1} increases at low T . In this frequency range, quantum calculations suggest the presence of lines of both TFSI conformers. Here, we propose that the line centered at around 395 cm^{-1} is due to the transoid conformer of TFSI. In

fact, the *ab initio* calculations indicate that among the various lines expected between 380 and 450 cm^{-1} , the absorption located at the lowest frequency comes from *trans*-TFSI; moreover, the temperature dependence of the intensities of the vibrations at around 600 cm^{-1} suggests that the concentration of *trans*-TFSI increases in the solid phase.

In summary, TMPA-TFSI shows the absorption lines of both conformers of TFSI both in the liquid and in the solid states. In fact, although the intensities of the *cis*-TFSI vibrational lines at ~ 600 and 645 cm^{-1} are drastically reduced in the solid state, the modes at ~ 206 and 408 cm^{-1} due to the same conformer are still present at low temperatures. These findings indicate that in the crystalline phase of TMPA-TFSI, both TFSI conformers are present, even though the transoid form becomes strongly predominant.

Concerning TMHA-TFSI, in the solid phase, we observe a strong decrease of the intensity and an almost vanishing of the lines centered at around 225, 362, 397, and 622 cm^{-1} . All of these absorptions have been attributed to vibrations of the *trans*-TFSI conformer; therefore, these results strongly support the fact that in the solid phase of TMHA-TFSI, only the *cis* conformer is present. Consistently, we can observe an increase of the intensity of the lines at around 290, 333, and 532 cm^{-1} , which were attributed to the *cis*-TFSI. The last two lines have contributions also from the TMHA ion. Moreover, at low temperature, one can observe a strong absorption at 450 cm^{-1} , which could be attributed to TMHA. The scaling factors for the TMHA absorptions found experimentally at around 452 and 532 cm^{-1} are 1.006 and 1.005, respectively, considering that they should correspond to the lines found at around 449 and 529 cm^{-1} by means of *ab initio* simulations (see Table 3).

In the low-temperature spectrum of TMHA-TFSI, one observes also lines at 213 and 240 cm^{-1} , attributable to the TMHA ions, which are predicted by computations at 201 and 231 cm^{-1} (scaling factors of 1.06 and 1.04, respectively). The vibrations at 409 and 438 cm^{-1} strongly increase their intensity at low T 's. In view of the fact that other spectral marks indicate that the *trans* conformer is practically absent in the solid form of TMHA-TFSI, we can ascribe to the *cisoid* conformer the vibrations centered at 409 and 438 cm^{-1} , which become more intense in the solid and cannot be attributed to the cation as TMHA should possess only very weak bands in this spectral range. The scaling factor for the two lines is 1.07, slightly larger than that for the other bands.

In summary, also TMHA-TFSI displays the spectral lines of both conformers in the liquid state. However, below the melting point only the absorptions of the *cisoid* conformer (206, 288, 340, 408, 435, 531, 602, 655 cm^{-1}) are retained, while those of the *trans*-TFSI (227, 366, 397, 622 cm^{-1}) are completely suppressed.

Solid phases in which the *cisoid* conformer of TFSI is stabilized are extremely rare. Indeed, thermodynamically, the isolated *trans*-TFSI is the most stable conformer by about 2.2 kJ/mol. 1,3-Dimethylimidazolium TFSI with a melting point of 22°C (299 K) was the first example of IL with the unusual *cis* geometry;³⁸ previously, also the alkali metal salts of TFSI were reported to stabilize the *cisoid* conformer,³⁹ even though in those crystals, a variety of solvent inclusion was observed. Another structural characterization of pure, anhydrous $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ indicates that the anion is found in the *trans* conformation.⁴⁰ In solid $\text{Li}_2(\text{EMIm})(\text{N}(\text{SO}_2\text{CF}_3)_2)_3$, two of the three anions present in the unit cell have a *cis* conformation, while the third anion shows a *trans* configuration.⁴¹ Moreover,

Choudhury et al.⁴² reported that 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide adopts the *cisoid* conformation of the TFSI anion in the solid. On the basis of a Raman spectroscopy investigation, it was determined that 1-ethyl-3-methylimidazolium TFSI stabilizes in the solid phase the *cis*-TFSI isomer after slow cooling ($\sim 1 \text{ K/min}$), whereas fast cooling ($\sim 20 \text{ K/min}$) quenches the anion in the *transoid* conformation with only a small amount of the *cisoid* one.⁴³ Henderson et al. reported that the *cis*-TFSI conformer is kinetically favored by fast cooling, whereas the more stable *trans* conformer is stabilized by slow cooling.⁴⁴

In trying to interpret those experimental findings, it was observed in the series of the alkali metal salts³⁹ that the *transoid* form is favored when there are only weak cation–anion interactions but that the *cisoid* form is often found when the anion is chelated to a metal center. Concerning 1,3-dimethylimidazolium TFSI, Holbrey et al.³⁸ suggested that the stabilization of the *cis* conformer is due to the formation of an extended hydrogen-bonding network generated by the interaction between the O atom of the anion and C–H group of the cation. Usually,³⁸ the TFSI anion adopts the lower energy *trans* conformation, consisting of $p_\pi \rightarrow d_\pi$ charge delocalization within the S–N–S moiety.^{45,46} The *trans* configuration allows the charge-bearing region of anion (S–N–S) to remain close to the cation and enables the $-\text{CF}_3$ groups of adjacent anions to interact, forming alternating cation and anion sheets.^{38,47} Indeed, the charge delocalization within the TFSI ion is shielded by the oxygens and the $-\text{CF}_3$ groups from Coulombic interactions with neighboring cations, thus increasing the ion mobility and reducing the lattice energy in the crystalline state.⁴⁷

In view of these observations, the results of the infrared spectroscopy reported in this work seem to indicate that the TMHA ion interacts more strongly than the TMPA anion with the TFSI cations. This hypothesis is supported also by the observation in the spectra of TMHA-TFSI of evident overtones or combination bands in the mid-infrared range between 1600 and 2600 cm^{-1} , which are extremely weak in the experimental absorption spectrum of TMPA-TFSI (results not shown in the present paper).

CONCLUSIONS

The liquid phases of *N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)imide (TMPA-TFSI) and *N*-trimethyl-*N*-hexylammonium TFSI (TMHA-TFSI) are characterized by the presence of both *cis*- and *trans*-TFSI cations, as already reported for some ILs containing TFSI. However, different behaviors are exhibited by the two compounds when cooled in the solid state; in TMPA-TFSI, the relative concentration of the conformers is strongly shifted toward a predominance of the *transoid* conformer; on the contrary, TMHA-TFSI retains only *cis*-TFSI, which is the less thermodynamically stable rotamer. We suggest that the stabilization of the *cisoid* conformer can be induced by the stronger anion–cation interaction occurring in TMHA-TFSI.

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Notes

The authors declare no competing financial interest.

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