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# Investigation of a family of structurally-related guanidinium ionic liquids through XPS and thermal analysis



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## ABSTRACT

A family of structurally-related guanidinium bistriflimide ionic liquids has been prepared and characterized. TGA analyses showed a high thermal stability for all the proposed ionic liquids while DSC and XPS analyses divided them into distinct subsets depending on whether one or more constraining cycles were present. The results obtained highlighted the influence of the cation structure on some of the physico-chemical properties and thus the possibility to tune them by selecting proper substituents. The solvatochromic parameters of a selected guanidinium IL have also been studied.

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# 1. Introduction

Ionic liquids (ILs) are salts which are, by definition, liquid at a temperature lower than 100 °C. They are composed by an organic cation and an organic or inorganic anion. During the last 20 years they attracted a great deal of interest as neoteric solvents characterized by remarkable and sometimes unique physico-chemical properties [1]. In particular, the high thermal stability, negligible vapor pressure, low flammability and wide electrochemical window suggested from the beginning their potential use as alternatives to traditional volatile organic solvents (VOCs). During the years, the idea of ILs as intrinsically green species has been mitigated by investigating their toxicity [2,3] and degradation [4], and looking at the synthetic strategies to prepare them in more detail [5]. Recently, natural (e.g. amino acids, terpenes, fatty acids) [6,7] or biobased ions [8] have been employed in the development of new ILs as a way to reduce the use of fossil derived materials and enhance their biodegradability. Nowadays, ILs are employed as solvents or additives in a wide and disparate range of applications which span for instance from organic synthesis [9], to biopolymers dissolution and modification [10,11], from innovative separation techniques [12] to biosensor development [13].

Another aspect of ILs which is often praised is the almost limitless number of structures that can be prepared from known ions. This means that their properties can be finely tuned to address a specific problem, hence their reputation as designer solvents. Although this is true, a recent work by Bara et al [14], focused on the frequency of use

\* Corresponding author. E-mail address: lorenzo.guazzelli@unipi.it (L. Guazzelli). of selected ILs deriving from the combination of the most studied 1,3 dialkyl imidazolium cation and 16 anions, demonstrated that only 5% of the possible total structures under consideration are actually present in the literature, even for this simple cation.

Guanidinium ILs have been far less investigated than the imidazolium one, although they showed interesting potential applications as well. In fact, they were used as electrolytes for lithium batteries [15,16], and as possible media for CO<sub>2</sub> capture [17], organic reactions [18,19], cellulose dissolution [20], and electrochemical deposition of elemental titanium [21]. Furthermore, a series of tetramethyl guanidinium ILs resulted as biodegradable and non-toxic for normal HEK 293 and cancerous DLD-1 cell cultures [22].

A peculiar trait of guanidinium ILs is the charge delocalization of the cation core where the positive charge is spread over three nitrogen atoms. Instead, in pyrrolidinium and imidazolium ILs the positive charge is localized on the sole nitrogen atom present in the first case or distributed across the  $\pi$ -ring system in the latter case. As a consequence of the different positive charge density, the interaction between the guanidinium cation and its anion is weaker when compared to pyrrolidinium and imidazolium ILs, as shown by X-ray photoelectron spectroscopy (XPS) analysis [23]. XPS is a surface-sensitive spectroscopic technique which works under high vacuum and is particularly suitable for studying ILs thanks to their negligible vapor pressure [24]. Several features of ILs have been investigated by means of XPS. For instance, anion-cation interactions [25], in situ reaction monitoring [26], surface composition [27], and even the different orientations of chiral enantiopure ionic liquids at the IL/vacuum interface [28].

To gain further insight into the guanidinium ILs family, and in particular into the correlation between cation structure and physico-chemical properties, as well as bulk-surface composition, six structurally-related guanidinium bistriflimide ILs, including also practically not yet explored bicyclic systems, have been prepared. The obtained ILs have been characterized by means of NMR, DFT calculations, TGA, DSC and resolved angle XPS.

### 2. Experimental

#### 2.1. Material and methods

#### 2.1.1. Material

Oxalyl chloride ( $\geq$ 99%), tetramethylurea (99%), 1,3 Dimethyl 2 imidazolidinone ( $\geq$ 99%), and *N* ethylbutylamine ( $\geq$ 98%) were purchased from Sigma-Aldrich. Azepane ( $\geq$ 99%), Piperidine (99%), and *N* butylmethylamine (98%) were obtained from Acros. Lithium bis(trifluoromethylsulfonyl)imide (99%), was purchased from io-li-tech. Rigorously dried organic solvents were used. All amines were dried with KOH pellets and stored under an argon atmosphere.

#### 2.1.2. Characterizations

NMR spectra were recorded at room temperature and 70 °C using a Bruker Instrument at 250 MHz (<sup>1</sup>H) and 62.9 MHz (<sup>13</sup>C) using deuterated chloroform and dimethyl sulfoxide as solvent. Purity of the guanidinium Tf<sub>2</sub>N ILs (**1–6**) was ascertained by <sup>13</sup>C NMR on neat compounds.

Infrared spectra were registered using an ATR-FTIR Agilent 660 (Agilent Technologies, Santa Clara, CA, USA).

The thermal stability of the synthesized ILs was investigated by thermal gravimetric analysis (TGA), conducted in a TA Instruments Q500 TGA. IL (10–20 mg) was heated in a platinum crucible. First, the heating mode was set to isothermal at 60 °C in N<sub>2</sub> (100 mL/min) for 15 min. Then, IL was heated from 45 to 700 °C with a heating rate of 5 °C/ min under nitrogen (100 mL/min) and maintained at 700 °C for 5 min. Mass change was recorded as a function of temperature and time. TGA experiments were carried out in triplicate.

The thermal behavior of the ionic liquids was analyzed by a differential scanning calorimeter (TA DSC, Q250, USA). About 3–5 mg of sample was loaded in hermetic aluminium crucibles and the phase behavior was explored under nitrogen atmosphere in the temperature range of 90–130 °C. DSC experiments were carried out in duplicate.

2.1.2.1. Determination of Kamlet-Taft parameters. UV–vis absorption spectra of the three solvatochromic dyes (Reichardt's betaine dye, *N*,*N* diethyl 4 nitroaniline, and 4 nitroaniline) dissolved in **2** were registered using a quartz cell with a light path length of 1 mm on a Cary 300 UV–Vis spectrophotometer (250–800 nm). To remove water and volatile impurities, before measurements, ILs were dried by heating ( $\approx$ 80 °C), with constant stirring, and at high vacuum ( $\approx$ 10<sup>-4</sup> Pa) for at least 48 h. Proper amounts of Reichardt's betaine dye (ET<sub>30</sub>), *N*,*N* diethyl 4 nitroaniline and 4 nitroaniline were added to **2** (2 mL) in order to have absorptions in the range of 1–1.5 at the respective  $\lambda_{max}$ .

The solvent dipolarity/polarizability,  $\pi^*$  was determined on the basis of the wavelength maximum of the lowest energy band of *N*, *N* diethyl 4 nitroaniline (probe 1), a nonhydrogen bond donor solute, using Eq. (1).

$$\pi^* = 8.649 - 0.314 \nu_1 \tag{1}$$

where  $v_1$  is the frequency of probe 1 at the absorption maximum, expressed as wavenumber in kK.

The hydrogen bond donating (HBD) acidity,  $\alpha$ , is calculated using ET  $_{(30)}$  and  $\pi^*$  values as follows:

$$\alpha = 0.0649E_T(30) - 2.03 - 0.72\pi^* \tag{2}$$

Finally, the hydrogen bond accepting (HBA) basicity,  $\beta$ , is determined on the basis of the absorption of 4 nitroaniline (probe 2) and *N*, *N* diethyl 4 nitroaniline by using Eq. (3):

$$\beta = \frac{1.035\nu(2)_{\text{max}} - \nu(1)_{\text{max}} + 2.64}{2.80} \tag{3}$$

The  $\text{ET}_{(30)}$  value was determined on the basis of the absorption maximum of the Reichardt's dye 30, with the polarity scale ET(30) being defined as reported in following equation:

$$E_T(30) = \frac{28591}{\lambda_{\max}(in \text{ nm})}$$

*2.1.2.2. DFT calculations.* Calculations have been performed on a Linux Workstation (Xeon E5-1660 (six cores), 32 Gb RAM) using Gaussian 16 rev. B.01 [29].

2.1.2.3. X-ray photoelectron spectroscopy. Ionic liquids were drop-casted on a gold plate to form a thin layer. The gold plate with the ionic liquid was then transferred into the XPS ultra-high vacuum (UHV) chamber. In the UHV chamber is located a manipulator that permits to tilt, to rotate, to warm up and to cool down samples. The XPS instrumentation makes use of a non-monochromatic X-ray source (VSW Scientific Instrument Limited model TA10, Mg K $\alpha$  radiation, 1253.6 eV), operating in this case at 120 W (12 kV and 10 mA), and of a hemispherical analyser (VSW Scientific Instrument Limited model HA100). The analyser was equipped with a 16-channel detector and dedicated differential pumping system that permits to work during the acquisition with pressure in the main chamber up to  $10^{-8}$  Torr range. The pass energy was set to 22 eV. The obtained spectra were analyzed using CasaXPS dedicated software. The inelastic background was subtracted using Shirley's method [30] and a mixed Gaussian and Lorentzian contributions were used for each component. The calibration of spectra was obtained shifting to 284.8 eV the lowest component relative to the 1 s transition of carbon for adventitious carbon [31].

Measurements were made at two temperatures: 40 °C (ionic liquids at liquid state) and -140 °C (ionic liquids at solid state). The conformation of the bulk and the surface of the ionic liquids were determined by means of angle resolved X-ray photoelectron spectroscopy (AR-XPS). The measurements were performed at 4 take-off angles from 0° (normal emission) to 80° (grazing angle).

# 2.2. General procedure for the preparation of hexaalkyl guanidinium chloride

A solution of urea (50 mmol) in dry  $CH_2Cl_2$  (10 mL) was added dropwise at 0 °C under an Argon atmosphere to a solution of freshly distilled oxalyl chloride (55 mmoL) in dry  $CH_2Cl_2$  (25 ml). The reaction mixture was allowed to reach rt. and was stirred at rt 6h. The solvent was then evaporated under reduced pressure to afford a brown solid which was washed with dry  $Et_2O$  (4 × 20 mL) to give a white solid.

The white solid was dissolved in dry acetonitrile (40 mL) and then added dropwise to a mixture of secondary amine (50 mmol) and triethylamine (50 mmol) at 0 °C. The resulting solution was stirred at rt. overnight with formation of a white solid. The obtained suspension was filtered, and the resulting solution was concentrated under vacuum. A 0,1 M NaOH solution was added to the resulting oil until the pH was slightly alkaline. The aqueous solution was washed with diethyl

ether (3  $\times$  50 mL) and then concentrated under reduced pressure to give the final product.

#### 2.2.1. N,N,N',N' tetramethyl N",N" butylmethylguanidinium chloride (1a)

White solid 9,83 g, yield 89%; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.15 (t, *J* = 7.6 Hz, 2H), 3.07 (s, 3H), 3.00 (s, 6H), 2.97 (s, 6H), 1.50 (m, 2H), 1.34–1.07 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  163.4, 52.5, 40.8, 40.46, 38.3, 29.6, 19.9, 13.7 ppm. IR (ATR):  $\nu$  = 2956 (m), 2931 (m), 2872 (m), 1576 (i), 1468 (b), 1403 (i), 1254 (b) cm<sup>-1</sup>.

#### 2.2.2. N,N,N',N' tetramethyl N",N" butylethylguanidinium chloride (2a)

White solid 9,43 g, yield 80%; <sup>1</sup>H NMR (DMSO)  $\delta$  2.86–2.65 (m, 4H), 2.53 (s, 12H), 1.10 (bs, 2H), 0.94–0.76 (m, 2H), 0.71 (t, *J* = 7.1 Hz, 3H), 0.48 (t, *J* = 7.2 Hz, 3H) ppm. <sup>13</sup>C NMR (DMSO)  $\delta$  162.0, 47.7, 43.6, 38.7, 28.0, 18.9, 12.5, 10.9 ppm.

2.2.3. N,N,N',N' tetramethyl N",N" pentamethyleneguanidinium chloride (3a)

White solid 8,27 g, yield 75%; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.18 (m, 4H), 2.83 (s, 6H), 2.81 (s, 6H), 1.57 (bs, 6H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  162.8, 50.1, 41.0, 40.8, 25.3, 22.5 ppm. IR (ATR):  $\nu$  = 2930 (m), 2856 (m), 1564 (i), 1435 (m), 1407 (i), 1277 (b), 1253 (b) cm<sup>-1</sup>.

# 2.2.4. N,N,N',N' tetramethyl N",N" esamethyleneguanidinium chloride (4a) White solid 8,97 g, yield 77%; <sup>1</sup>H NMR (CDCl<sub>3</sub>) $\delta$ 3.28 (bs, 4H), 2.94 (s, 6H), 2.89 (s, 6H), 1.44 (bm, 8H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) $\delta$ 163.1, 52.0, 40.6, 29.1, 26.5 ppm. IR (ATR): $\nu$ = 2912 (m), 2852 (m), 1579 (i), 1479 (b), 1449 (b), 1408 (i), 1299 (b), 1233 (b) cm<sup>-1</sup>.

#### 2.2.5. 1 (1,3 Dimethylimidazolidin 2 yliden) piperidinium chloride (5a)

Amber clear oil 5,27 g, yield 48%; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.64 (s, 4H), 3.18 (bs, 4H), 2.86 (s, 3H), 2.86 (s, 3H), 1.45 (bs, 6H) ppm. <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>)  $\delta$  162.7, 49.5, 49.4, 36.4, 25.5, 22.8 ppm. IR (ATR):  $\nu$  = 2937 (m), 2857 (m), 1615 (i), 1557 (i), 1447 (b), 1414 (b), 1303 (i) cm<sup>-1</sup>.

# 2.2.6. 1 (1,3 Dimethylimidazolidin 2 ylidene) azepanium chloride (6a)

Amber clear oil 5,01 g, yield 43%; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.73 (bs, 4H), 3.46–3.40 (m, 4H), 2.99 (s, 6H), 1.72–1.60 (s, 4H), 1.58–1.53 (m, 4H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  164.4, 52.3, 50.1, 37.2, 28.4, 27.9 ppm. IR (ATR):  $\nu$  = 2925 (m), 2856 (m), 1602 (i), 1556 (i), 1452 (b), 1413 (b), 1305 (m), 1299 (b), 1233 (b) cm<sup>-1</sup>.

# 2.3. General procedure for the preparation of hexaalkyl guanidinium bistriflimide

A solution of lithium bis(trifuoromethylsulfonyl)imide (0,59 g, 2 mmol) in water (5 mL) was added dropwise to a solution of hexaalkylguanidinium chloride (2 mmol) in water (6 mL). The resulting solution was stirred at room temperature for 3 h and then 30 mL of dichloromethane were added. The organic phase was separated and washed with several portions of deionised water until chloride could not be detected (AgNO<sub>3</sub> test). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure. The obtained product was analyzed by NMR and FTIR.

2.3.1. N,N,N',N' tetramethyl N",N" butylmethylguanidinium bis (trifluoromethylsulfonyl) imide (1)

Light yellow clear liquid 0,903 g, yield 95%; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.12 (t, J = 7.6 Hz, 2H), 2.91 (s, 12H), 2.88 (s, 3H), 1.55 (bs, 2H), 1.38–1.19 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  163.4, 128.1–112.4, 52.5, 40.1, 37.7, 29.5, 19.8, 13.5 ppm. IR (ATR):  $\nu = 2963$  (b), 2878 (b), 1578 (i), 1409 (m), 1348 (i), 1176 (i), 1134 (i), 1053 (i) cm<sup>-1</sup>.

2.3.2. N,N,N',N' tetramethyl N",N" butylethylguanidinium bis (trifluoromethylsulfonyl) imide (2)

Clear liquid 0,916 g, yield 95%; <sup>1</sup>H NMR (DMSO)  $\delta$  3.41–3.07 (m, 4H), 2.94–2.91 (d, 12H), 1.67–1.37 (m, 2H), 1.36–1.20 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H) ppm. <sup>13</sup>C NMR (DMSO)  $\delta$  162.3, 126.7–111.3, 47.8, 43.4, 39.3, 39.2, 28.5, 19.0, 12.6, 12.0 ppm. IR (ATR):  $\nu$  = 2963 (b), 2938 (b), 2879 (b), 2816 (m), 1565 (i), 1411 (m), 1348 (i), 1177 (i), 1135 (i), 1054 (i) cm<sup>-1</sup>.

2.3.3. N,N,N',N' tetramethyl N",N" pentamethyleneguanidinium bis (trifluoromethylsulfonyl) imide (3)

Clear liquid 0,910 g, yield 96%; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.22 (bm, 4H), 2.94–2.92 (d, 12H), 1.67 (s, 6H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  162.8, 127.7–111.6, 49.9, 40.2, 40.2, 25.1, 23.4 ppm. IR (ATR):  $\nu$  = 2944 (b), 2864 (b), 1619 (i), 1563 (i), 1416 (b), 1348 (i), 1175 (i), 1134 (i), 1052 (i) cm<sup>-1</sup>.

2.3.4. N,N,N',N' tetramethyl N",N" esamethyleneguanidinium bis (trifluoromethylsulfonyl) imide (4)

Light yellow clear liquid 0,930 g, yield 95%; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.32 (s, 4H), 2.89 (s, 12H), 1.66 (bm, 8H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  163.3, 128.1–117.8, 52.1, 40.3, 40.1, 29.5, 26.4 ppm. IR (ATR):  $\nu$  = 2936 (b), 2863 (b), 1588 (m), 1562 (i), 1410 (m), 1347 (i), 1175 (i), 1134 (i), 1053 (i) cm<sup>-1</sup>.

2.3.5. 1 (1,3 Dimethylimidazolidin 2 yliden) piperidinium bis (trifluoromethylsulfonyl) imide (5)

Yellow clear liquid 0,907 g, yield 96%; <sup>1</sup>H NMR (DMSO)  $\delta$  3.14 (bs, 4H), 2.82 (bs, 4H), 2.43 (bs, 6H), 1.13 (bs, 6H) ppm. <sup>13</sup>C NMR (DMSO)  $\delta$  162.1, 126.6–111.3, 48.3, 48.1, 34.6, 24.5, 22.0 ppm. IR (ATR): v = 2947 (b), 2864 (b), 1619 (i), 1563 (i), 1416 (b), 1348 (i), 1175 (i), 1134 (i), 1052 (i) cm<sup>-1</sup>.

2.3.6. 1 (1,3 Dimethylimidazolidin 2 yliden) azepanium bis (trifluoromethylsulfonyl) imide (6)

Light yellow clear liquid 0,897 g, yield 92%; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.64 (bs, 4H), 3.45–3.33 (m, 4H), 2.91 (s, 6H), 1.68 (sm, 4H), 1.65–1.52 (sm, 4H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  164.2, 127.4, 122.3, 117.2, 112.0, 52.0, 49.4, 36.4, 28.4, 27.4 ppm. IR (ATR):  $\nu$  = 2938 (b), 2863 (b), 1604 (i), 1562 (m), 1416 (b), 1348 (i), 1174 (i), 1134 (i), 1052 (i) cm<sup>-1</sup>.

#### 3. Results and discussion

# 3.1. Synthesis and conformational analysis

A well-known procedure has been followed to prepare the six guanidinium ILs (Fig. 1, top) [16]. Briefly, a commercial urea (either tetramethyl urea or N,N' dimethylethylene urea) was reacted with oxalyl chloride to afford the corresponding chloroformamidinium chloride which was then treated with a secondary amine. The obtained guanidinium chloride IL was converted into the corresponding bistriflimide IL through a metathesis reaction with LiTf<sub>2</sub>N. The structures of the ILs **1–6** are summarized in Fig. 1 (bottom). It is worth mentioning that a drop in yield was observed in the first step for the cyclic urea, from 75–80% (**1–4**) to 43–48% (**5,6**).

The identity of the obtained compounds has been ascertained by means of NMR and IR analyses. IR spectra displayed the distinctive absorption band for the  $CN_3^+$  at around 1561–1578 cm<sup>-1</sup>.

As reported before for other guanidinium ILs [32], a split for the methyl signals of compound **1–4** was observed in the <sup>13</sup>C NMR spectra. These were performed in co-axial tubes with DMSO  $d_6$  in the internal capillary as a lock and chemical shift reference. The observed phenomenon arises from the C-NR<sub>2</sub> partial double bond character which hinders the free rotation and thus renders the otherwise magnetically equivalent symmetrical substituents on the nitrogen atoms magnetically non-equivalent. By heating at 70 °C, the rotation barriers were overcome,



Fig. 1. General synthetic procedure to prepare guanidinium Tf<sub>2</sub>N ILs (top); structures of the six guanidinium Tf<sub>2</sub>N ILs studied (bottom).

and coalescence of the signals was observed. Fig. 2 shows this behavior for compound **3** (please refer to the supporting information file for compounds **1**, **4–6**).

This behavior of hexaalkyl guanidinium salts is attributed to a peculiar non-planar propeller-like shape which is favored over a planar sterically crowded structure. Substituted guanidinium cations are indeed sterically hindered species. Except when almost all substituents are hydrogens, the steric repulsion between sidechains placed on different nitrogen atoms lead to a deviation from planarity and to hindering the rotation of the carbon atoms that are in the  $\alpha$  position with respect to the nitrogen ones. Substituted guanidinium cations deviate from the ideal planar trigonal



Fig. 2. Enlargement of the <sup>13</sup>C NMR spectrum of 3 at 20 °C (top) and at 70 °C (bottom).

form where the central carbon, the three nitrogen atoms and the six atoms in  $\alpha$  position with respect the nitrogen atoms lie on the same plane to assume a propeller-like shape.

We have performed some DFT calculations to evaluate the interplay between sterical hindering, delocalization of the  $\pi$  electrons, etc. The cations considered are, among those examined in this work, those reported in Fig. 3.

Energetic and geometrical results are reported in Table 1. All calculations have been performed at the B3LYP/6–311++G(d,p) level of theory using the Gaussian 16 package [29].

We have neglected cations **2** and **6** that are very similar to cations **1** and **4**, respectively.

To evaluate the extent of the sterical hindering effect we have first optimized the structures of these ions and then optimized analogues where the central moiety is planar, like the simple guanidinium ion.

The difference in energy between the free optimized cation and the flattered one can be defined as sterical deformation energy. All the flattered structures are not local minima since they present three imaginary frequencies each related to the rotation of one of the R-N-R' groups. Cations **1**, **3**, **4** present a flattering energy of about 250 J/mol (slightly lower in the case of **4** where the seven membered ring permits a certain degree of relaxation) while, in the case of **5** it is about a quarter (58.50 kJ/mol). This last one is the only cation where a cycle includes the central carbon and the nitrogen atoms of the guanidinic group. The resulting five-membered ring (that contains 3 sp<sup>2</sup> atoms) is almost flat. Furthermore, the three carbon-nitrogen bonds are shorter than in the other substituted cations. The rotation of the R-N-R' groups can be evaluated by using torsional angles. In the case of guanidine, the torsion between any of the N-C-N-R groups is 0.0° when the R group is in a cislike position with respect to the first nitrogen, 180° when it is in trans-



Fig. 3. Guanidinium ions considered in the text. They can be structurally related by metareactions.

#### Table 1

Energetic and geometric quantities related to cations. All calculations have been performed at the B3LYP/6–311++G(d,p) level of theory. N1 is the nitrogen enclosed in the 6 or 7 membered rings (**4**, **5**) or bounded to a methyl and a butyl group (**1**). Orbitals energies are relative to the HOMO-2 absolute value.

System	Guanidinium	1	3	4	5
$\Delta E/(kJ/mol)$	0.00	246.70	242.29	210.07	58.50
$R(C-N_1)/Å$	1.335	1.351	1.349	1.352	1.343
$R(C-N_2)/Å$	1.335	1.352	1.353	1.352	1.349
$R(C-N_3)/Å$	1.335	1.351	1.352	1.353	1.349
N1-C1-N2-X/°	0.0	-37.2	-33.7	-32.9	-18.8
	180.0	143.5	145.2	144.9	174.6
Sum	180.0	180.7	178.9	177.8	193.4
N1-C1-N3-/°	0.0	-33.5	-36.9	-36.4	-23.3
	180.0	145.2	143.6	143.8	172.1
Sum	180.0	178.7	180.5	180.2	195.4
N2-C1-N3-X/°	0.0	-35.4	-35.6	-36.0	-6.8
	180.0	145.8	143.8	143.7	157.7
Sum	180.0	181.2	179.4	179.7	164.5
LUMO (A2')/Ha	0.46320	0.28886	0.28888	0.27548	0.30142
HOMO (E")/Ha	0.15899	0.05856	0.06012	0.04934	0.06562
	0.15899	0.05328	0.05362	0.04138	0.06113
HOMO-2 (A2")/Ha	0.00000	0.00000	0.00000	0.00000	0.00000
Absolute energy/Ha	-0.65134	-0.45528	-0.45393	-0.44045	-0.45488

like position. A rigid rotation must lead to different torsion but the sum of the two angles must be conserved. The data reported in Table 1 show that acyclic or monocyclic cations have a torsion of about 35° and the torsion is almost rigid. The bicyclic one presents deformations and lower torsion angles. It is the most similar structure to the simple guanidinium one.

It is interesting to note the effect of this deviation from planarity on the orbitals of the  $\pi$  conjugated system. The orbitals of the guanidinium cation and of **3** are reported in Fig. **4**. Full size orbital figures are reported in the supporting information file. In the case of **3**, the no longer parallel p orbitals superimpose with orbitals of nearby atoms with compatible symmetry, like  $\sigma$  bonding orbitals of C—H bonds. This effect is larger in the HOMO-2 full symmetric orbital. Relative orbital energies show a similar trend to bond distances: those of **5** are larger and more like guanidinium than the other ones.

Finally, we studied the conformational barrier of rotation of one of the  $CH_3$ -N- $CH_3$  group in **3**. The geometry of the top of barrier structure, that presents a notable degree of pyramidalization on the nitrogen atom, is reported in Fig. 5. The conformation barrier is of 67.30 kJ/mol (in the case of ethane is of 11.31 kJ/mol at the same level of theory). This further confirms that we are in presence of a highly hindered system.

A paper by Butschies et al. [33] presents some similar DFT calculation on not too different guanidinium cations. Their calculations have been performed at the B3LYP/6-31G(d,p) level. The cations studied have, generally, an aromatic substituent. Given the similarities between the structures and the level of calculation (the functional is the same, our is a triple-zeta basis set with diffuse functions vs double-zeta without diffuse functions, but both belong to the Pople's family) is possible to qualitatively compare the results. The magnitude of torsional angles is about 30° in both studies. They do not consider flattering energies, but the torsional barriers calculated for similar systems lie in the range of 60-70 kJ/mol where our calculated value is of 67.30 kJ/mol.

#### 3.2. Thermal analysis of prepared guanidinium ILs

TGA analysis were performed using the following experimental conditions: mass at 15–18 mg, N<sub>2</sub> atmosphere with flowing rate 100 mL/min, platinum pans, and a 5 °C/min heating rate.  $T_{onset}$  and  $T_{peak}$  values are reported in Table 2 and are the average values of three temperatureramped TGA experiments.

The six guanidinium ILs display similar high thermal stability, ILs **1** and **5** as the lower and upper limits of the series, with a single degradation

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Fig. 4. Orbitals of the π conjugated system. Left: guanidinium cation. Right: IL 3. Symmetry symbols are related to the D<sub>3h</sub> guanidinium cation. Degeneration is removed in sterical hindered compounds, but the energies of the related orbitals are still close.



**Fig. 5.** Structure of **3** at minimum (left) and at the top of the barrier structure for torsion of the CH<sub>3</sub>-N-CH<sub>3</sub> group (right) with respect the guanidinium moiety. The torsion angle of the minimum is  $-33.7^{\circ}$  while the top of barrier structure is of  $-54.9^{\circ}$ . The difference in energy is of 67.30 KJ/mol. It is evident the pyramidalization of the nitrogen atom.

event (Fig. 6). Cao and Mu [34] classified 66 ILs into five different levels on the basis of their  $T_{onest}$ : least stable (200 °C <  $T_{onest}$  < 250 °C), less stable (250 °C <  $T_{onest}$  < 300 °C), moderate (300 °C <  $T_{onest}$  < 350 °C), more stable (350 °C <  $T_{onest}$  < 400 °C), most stable (400 °C <  $T_{onest}$  < 450 °C). All the guanidinium Tf<sub>2</sub>N belong to the most stable level of this classification, which is essential for some applications as for instance for their use as electrolytes in batteries.

ILs **3,5** and **4,6** can also be seen as guanidinium-piperidinium and guanidinium-azepanium mixed structures, respectively. Previous works on piperidinium  $Tf_2N$  ILs reported thermal stabilities both lower [35] and higher [36] than the one obtained here for **3** and **5**, thus further studies are required to properly understand the contribution of the guanidinium frame to the decomposition events. Instead, considering the lower thermal stability of the azepanium ILs reported in the literature to date [37], it seems that the guanidinium structure prevails over the azepanium one in determining the thermal stability for **4** and **6**.

While TGA analysis didn't show any discernible trend throughout the six guanidinium  $Tf_2N$ , DSC curves allowed for their division into distinct groups. DSC study was performed at 10 °C/min in nitrogen flow, according to the following protocol:

Table 2
Tonset and Tpeak value for guanidinium Tf <sub>2</sub> N ILs 1-6 measured under a nitrogen atmosphere
and with a heating rate of 5 °C/min.

ILs	1	2	3	4	5	6
T <sub>onset</sub> (°C)	413	415	422	425	434	419
T <sub>peak</sub> (°C)	451	449	449	461	473	459

- cooling from 40 °C to -90 °C at 20 °C/min;
- heating from -90 °C to +130 °C at 20 °C/min;
- cooling from 120 °C to -90 °C at 10 °C/min;
- heating from -90 °C to +100 °C at 10 °C/min;
- cooling from 100 °C to -90 °C at 5 °C/min;
- heating from -90 °C to +100 °C at 5 °C/min

As reported by Domínguez et al. [38], three thermal behaviors are generally expected for ILs: structures without a true phase transition that show only the formation of an amorphous glass (type I), ILs which present a freezing transition, forming crystals upon cooling and a melting transition upon heating (type II), and finally ILs that don't show a crystallization upon cooling, but exhibit a cold crystallization event upon heating (type III).

ILs **1** and **2** well fit into the first type of ILs as reversible glass transitions are reproducibly observed at -78.9 °C and -81.7 °C, respectively, in the form of an endothermic small peak in all heating half cycles.

ILs **3** and **4**, which present the piperidinium and the azepanium cycles respectively, display a cold crystallization transition just before the melting transition (third type of thermal behavior). Both transitions appear as the overlapping of two different events.

IL **5** instead behaves as a low melting salt, thus belonging to the second type of ILs, and is characterized by a sharp endothermic melting peak at about 25 °C in the heating half cycle (reproducible temperatures for I and II cycles). In the cooling half cycle, a comparable freezing peak is found at about -20 °C. The recorded shift is probably due to a significant supercooling effect.

Finally, the thermal behavior of IL **6** is a variation of the third type of thermal behavior and presents two subsequent distinct transitions after



Fig. 6. Temperature-ramped TGA thermographs for guanidinium Tf<sub>2</sub>N ILs 1,3,5 with heating rate of 5 °C/min.

the crystallization during the isothermal step: a solid/solid transition at -20 °C and a melting transition at 32 °C. These transitions were assigned by changing the heating rate from 5 °C/min to 10 °C/min; the first peak moved which is typical for solid/solid transitions. The latter transition is again the result of two overlapping events.

The picture obtained here divides the guanidinium  $Tf_2N$  ILs on the basis of the number of cycles present in their structures (at least for the couples 1,2 and 3,4) and is in good agreement with previous findings [39]. It is worth noting that in general the bistriflimide anion plays a dual role on the thermal properties of ILs. In fact, because of its low nucleophilicity and basicity, it increases the thermal stability of the ILs in comparison at least to halide anions [40–42]. On the other hand, it decreases the melting points widening the liquid range, as reported before for other guanidinium salts [43].

#### 3.3. X-ray photoelectron spectroscopy

The six guanidinium ILs were analyzed by angle resolved XPS (AR-XPS) in order to elucidate the composition of the outmost regions of the IL/air interface.

Two sets of experiments were carried out either at -140 °C or at 40 °C to assess the surface composition in different conditions: glass and liquid status. In the first case we can consider the surface "frozen" while in liquid state we can consider the surface in a dynamic equilibrium with the bulk. For each sample the spectra were recorded at different angles between the normal (0°) and the grazing (80°) take-off angle in order to change the probing depth.

High resolution spectra were recorded for the individual elements (C1s, F1s, and N1s).

The F1s electron emission spectrum is well resolved and since fluorine is only present in the anion, this signal's relative intensity was used to monitor the enrichment or depletion of anion at the surface (Fig. 7a). The two ILs containing the piperidinium ring (**3** and **5**) display fluorine content higher respect to the others ILs and, in some cases, it results superior to the stoichiometric amount. This trend can be reasonably explained by anion surface enrichment. For all the samples the amount of fluorine decreases as function of take-off angle; i.e. the outermost portion of the surface results fluorine depleted respect to aliphatic carbon. Accordingly, this trend is also displayed by the C-F signal shown in Fig. 7b which confirms these observations. Two different phenomena can account for this trend: 1) the absorption of tiny amount of aliphatic contaminants which remain segregates in the outermost portion of the IL and 2) the arrangements of the aliphatic chains which orientate themselves to pointing towards vacuum. Data collected on the other XPS signals support the second hypothesis. It is worth noting that at 40 °C this trend is less evident, probably due to dynamic equilibrium.

Fitting of the C1s peak resulted quite difficult due to overlapping of the different types of carbon atoms. Anyway, it was possible to distinguish the aliphatic carbons (those not directly linked to the nitrogen atom) and the C-F carbon already discussed.

It is evident that there is an enrichment of the aliphatic carbon as by moving from the bulk to the surface for all the ILs both, at -140 °C and at 40 °C (Fig. 8).

A similar behavior, namely the tendency of aliphatic carbons to move towards the surface is not unusual and has been reported before for imidazolium ILs [24].

Again, the structural differences among the six guanidinium ILs influence this trend. In fact, ILs **1** and **2**, exhibit at 40 °C the most pronounced aliphatic enrichment of the surface followed by azepanium ILs **4** and **6**, and by the piperidinium ILs **3** and **5**. At low temperature, instead, **4**,**6** gave the most prominent effect followed by **1**,**2** and then **3**,**5**.

The N1s components, both from the anion and the cation (Fig. 9), and the C-F component support the above conclusions for the surface aliphatic carbon component enrichment and inner positioning of the anion, although caution is required when analyzing these components which are characterized by weak peaks, just above the detection limit of the technique.

# 3.4. Polarity

The solvatochromic parameters for IL **2** were also measured. Polarity is indeed a fundamental property for a liquid to ascertain its potential as



Fig. 7. Total fluorine content (a) and carbon (C-F) (b) in the samples as a function of the temperature and the take-off angle.

a solvent, since it affects not only the dissolution ability but also dramatically the kinetic and stereochemical behavior of the reactions occurring inside. Thus, IL **2** was selected taking into account several aspects as for instance the high synthetic yields, its stability and liquid state over a wide range of temperatures, and the aliphatic carbon component surface enrichment as obtained by XPS analysis. In particular, the solvatochromic Kamlet Taft parameters, which have been largely employed to define ILs polarity, were determined at 25 °C, on a previously accurately dried sample of **2**.

As expected, **2** shows a high dipolarity/polarizability ( $\pi^* = 0.943$ ), which fits perfectly into the relatively limited range characterizing ILs (0.8–1.20) associated to a quite low hydrogen bond basicity ( $\beta = 0.296$ ). This latter parameter depends indeed principally from the IL anion and bistriflimide salts are normally characterized by values lower than 0.3. Furthermore, IL **2** is characterized by a hydrogen bond



Fig. 8. Total carbon content in the samples as a function of the temperature and the takeoff angle.

acidity ( $\alpha = 0.552$ ) comparable to bistriflimide based pyridinium salts [44]. Since this property is principally determined by the IL cation, although a strong hydrogen bonding acceptor anion can decrease the donor ability of the related cation, the obtained  $\alpha$  value suggests a not negligible acidity of some of the protons of **2**, probably of those on carbons adjacent to the positively charged sp<sup>2</sup> nitrogen atoms.

# 4. Conclusions

Six hexaalkyl guanidinium Tf<sub>2</sub>N ILs, characterized by a close structural relationship, have been prepared and studied to find differences and similarities among them. On the basis of their structures, these ILs may be divided into different subsets, as for instance two groups with the same total number of carbon atoms (10 carbon atoms for odd numbered ILs, 11 carbon atoms for even numbered ILs) but a diminished degree of freedom due to the presence of 1 or 2 cycles, or three groups considering the number of cycles in the structure (**1,2** no cycles; **3,4** one cycle; **5,6** two cycles) or the type of cycles (**1,2** no cycles; **3,5** piperidinium cycle; **4,6** azepanium cycle).

NMR analysis and DFT calculations confirmed the propeller-like shape for all the ILs, which is however less marked for the bicyclic ILs. Regarding the thermal stability, TGA analysis showed again a similar behavior for all ILs which resulted highly stable ( $T_{onset} > 400$  °C) with a single degradation event. Conversely, DSC analysis allowed to highlight structural related thermal behaviors: only glass transitions were found for **1** and **2**, while **3** and **4** displayed a cold crystallization followed by a melting transition in the heating half cycle. The two bicyclic ILs **5** and **6** displayed a different peculiar thermal behavior. Finally, XPS analysis showed an inner positioning of the anion and a surface carbon component enrichment for all ILs, which decreases with the following order: **1**,**2** > **4**,**6** > **3**,**5** at 40 °C, and **4**,**6** > **1**,**2** > **3**,**5** at -140 °C. Solvatochromic parameters for IL **2** were also measured.

# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2018.12.083.



**Fig. 9.** Content of cationic (a) and anionic (b) nitrogen in the samples as a function of the temperature and the take-off angle.

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