

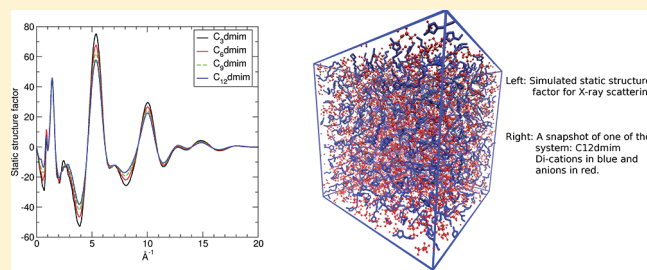
Structure of Geminal Imidazolium Bis(trifluoromethylsulfonyl)imide Dicationic Ionic Liquids: A Theoretical Study of the Liquid Phase

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ABSTRACT: In this work, we report molecular dynamics simulations of the bulk liquid phase of geminal di-imidazolium bis(trifluoromethylsulfonyl)imide ionic liquids. We characterize a few interesting features of the local structure in the liquid phase, and we make a comparison both with gas phase structures and with the monoimidazolic counterparts. We analyze in detail the diffraction properties of these fluids by simulating X-ray and neutron scattering factors and we report on the long-range structural order that seems to also arise in one of these compounds.



INTRODUCTION

Among the most exciting and successful materials developed and studied in the last twenty years, ionic liquids^{1–4} are part of those that can certainly claim one of the most rich field of applications in industry and in applied technologies. Their long story, that has its roots in the molten salts research field, dates back to 1914 with the synthesis of ethyl-ammonium nitrate by Paul Walden and, in more recent times, has seen an extraordinary parallel development between academic research and industrial applications.⁵ Indeed, even today, ionic liquids remain a growing research area in academia because of their unconventional properties that defy a simple description under many points of view.^{6–8} The large variety of applications includes their use as a replacement of organic solvents,^{9,10} lubricants,¹¹ ingredients for pharmaceuticals,¹² reaction media in organic chemistry,^{13,14} extraction media in analytical chemistry,¹⁵ and transport media in electrochemistry.¹⁶ These substances contain an organic cation (which can, for example, be an asymmetric derivative of the 1-alkylpyridinium, tetraalkylphosphonium, 1,3-dialkylimidazolium, or tetraalkylammonium ions) and an anion that can be as simple as chloride or a more complex structure such as bis{(trifluoromethyl)sulfonyl}imide ([Tf₂N][−]). Their versatility depends on the fact that their properties can be tuned by varying the molecular structure of the cation and of the anion.

Recently, the development of atomistic simulation techniques and the parallel growth of computational power¹⁷ have reached the point in which it is possible to reliably provide a nanoscopic interpretation of the bulk properties of these materials.^{18,19} Theoretical modeling plays a crucial role in the ionic liquid research field because it offers the possibility of a rationalization of the experimental observations and because it is becoming a valuable tool in designing new ionic liquid systems with properties optimized for specific technological applications. Since their introduction to the scientific community,²⁰ the force fields for

molecular dynamics (MD) simulations of ionic liquids have been refined, expanded,^{21,22} and reparametrized several times^{23,24} and have now reached a point in which molecular dynamics simulations are able to make reliable predictions of many liquid properties. In 2004, Canongia-Lopes and Pádua^{25,26} proposed an Optimized Potential for Liquid Simulations (OPLS-AA) derived force field for the description of imidazolium and bistriflylimide based liquids that has proven to provide a good rendition of various observables. For example, we have recently used such force fields in order to provide an interpretation of the local structure of 1-alkyl-3-methylimidazolium based liquids ([C_nmim]⁺[Tf₂N][−], *n* = 2,4,6,8).²⁷

A special class of ILs has recently been obtained using geminal imidazolium dications.^{28–32} They represent a very interesting variation of the cationic partner with various advantages over the traditional monocationic ionic liquids when used as lubricants,^{33–35} catalyst,³⁶ solvents,^{37–39} and as separation media.^{28,40,41} While experimental determinations are extensive,^{28,32} only very few previous theoretical studies of geminal dicationic imidazolium-based ionic liquids have been performed: Bhargava and co-workers have studied the aqueous solutions of 1,3-bis(3-decylimidazolium-1-yl) propane,⁴² and Vitorino et al. focused on the determination of the gas phase molecules after evaporations of the liquid.⁴³ The bis{(trifluoromethyl)sulfonyl}imide anion was already known in 1996 as a basis for hydrophobic electrolytes for electrochemical studies.⁴⁴ Its stability (both in air and in water) added to its relatively poor reactivity have made it an interesting ion for experimental and theoretical studies, therefore inducing the IUPAC committee to select 1-hexyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide ([C₆mim]⁺[Tf₂N][−]) as a

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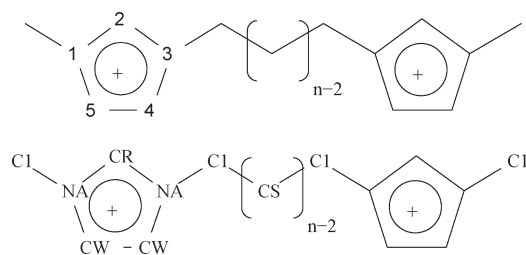


Figure 1. Schematic structure of the molecules studied in the present work: the total number of linkage carbon atoms n can be 3, 6, 9, or 12.

standard for comparing the variability of experimental measurements carried out by different research groups.^{45,46}

A schematic view of the molecular structures, which we denote C_n dmim or simply C_n , that we shall examine in the present work is reported in Figure 1: we have a linkage chain (whose length can be 3, 6, 9, or 12 for the compounds analyzed in the present work) that connects two imidazolium rings with a net positive charge on them and that are substituted with a methyl group. Various ILs have been obtained by mixing these dications with Br^- , Tf_2N^- , BF_4^- , and PF_6^- . These ILs have thermal stabilities larger than their monocationic counterpart, their densities decrease when increasing the linkage chain length,²⁸ while the viscosities increase. Except for those with the Tf_2N anions, many of these dicationic ILs (especially those with short linkage chains) are solid at room temperature and melt at temperatures higher than 100 °C.²⁸ Increasing the linkage chain length decreases the melting temperature, and the C_{12} is a liquid at RT with all anion counterparts.

We have recently analyzed the behavior of such compounds by calculating the structures of the gas phase complexes:⁴⁷ we have evaluated the dissociation energy of each of these dicationic structures into three separate ions that turned out to be around 200 kcal/mol, and we have proved that the linkage chain assumes an entangled structure through which the two cationic heads interact with the two anions. Structures with an elongated linkage chains are 40 kcal/mol higher in energy. We have estimated the energy necessary to create these entangled chains to be around 20 kcal/mol for the C_3 , C_6 , and C_9 and 100 kcal/mol for the C_{12} . The relatively low conformational mobility of the bent chains and the compactness of the resulting geometries in the gas-phase led us to surmise that the local structure of these ionic liquids might be completely different from the monocationic imidazolium ones. As we shall see in the following, owing to the results of the present simulations, this is not the case: these compounds share many common features with their monoimidazolic counterparts.

We have adopted the imidazolium/ Tf_2N force field of Canongia-Lopes et al.^{21,26} without any further adaptations. We have run the molecular dynamics protocol using the DLPOLY⁴⁸ package and various in-house software to analyze the results. The partial atomic charges are those reported by Canongia-Lopes et al. even if, as we have discussed in our previous work,⁴⁷ a certain degree of polarization is present in these compounds because the partial atomic charges of the cation are different for different arrangements of the linkage chain. In particular, in ref 47, we have shown by means of ab initio calculations that, for the isolated geminal dication cation (that is characterized by an extended linkage chain), there is a qualitatively similar trend between our computed charges and those of the Canongia-Lopes force field. A more marked difference (especially in the linkage chain charge distribution) was noticed when comparing the charges of the

Table 1. Calculated Quantities for the 4 Compounds Compared to the Experimental Ones

link. chain	exptl ^a	exptl ^b	theory (present)
Density (g/cm ³)			
3	1.61		1.67
6	1.52	1.546	1.57
9	1.47	1.479	1.51
12	1.40	1.428	1.43
Glass Trans. Temp. (K)			
3	269		219
6	259–269	209.9	225
9	259	210.8	235
12	247	212.0	220

^a From ref 28. ^b From ref 32.

Canongia-Lopes force field with those calculated in the ionic complex. Anyway, it seemed to us improper to adopt the latter charges because they were determined assuming a well-defined geometry of the isolated ionic complex which, as we shall show below, is unlikely to survive in the liquid phase.

RESULTS AND DISCUSSION

The MD protocol used is fairly standard: we have generated very low density random samples made by 300 ionic complexes (containing 300 dications and 600 anions). These cells were left to evolve in a NPT (Nosé–Hoover barostat) for 100 ps subjected to a very high pressure (10 kbar). The dense samples obtained in this way were subjected to a 2 ns dynamics with the NPT ensemble at 1 atm with the electrostatic interactions turned off. In this way we have obtained dense and mixed starting configurations. A first equilibration run was then performed for ~1 ns until an almost constant density was achieved. The production runs were performed for 0.5 ns at a constant density using the NVT ensemble. The side of the cubic box during the NVT simulations was between ~61 and ~67 Å depending on the compound. The time-step was held fixed at 1 fs, and the electrostatic forces were calculated using PME with an accuracy of 1 ppm. The van der Waals cutoff was set to 10 Å and the electrostatic one to 20 Å. For the C_3 and C_6 compounds, we have performed additional 10 ns, but the calculated structure factors did not present any substantial change. Furthermore, an additional set of calculations performed with large cells of about 100 Å of box side length and containing 1200 cations for the C_6 and C_3 compounds did not show significant differences in the calculated quantities. The resulting calculated densities are in very good agreement with the measured ones reported in refs 28 and 32 and are reported in Table 1. In order to further validate our choice, we have calculated the glass transitions temperatures by performing short NPT equilibration runs (50 ps) at different temperatures on our systems. We have chosen temperature sufficiently far from the supposed transition point, but it is to be noted that the two existing experimental determinations of the glass transition temperature differs by about 40–50 K.^{28,32} However, other measurements^{29,35} on similar compounds lead us to believe that the temperatures around 200–210 K are the correct ones. The glass state at low temperature was clearly identified by the dumped oscillatory response of the density to the temperature change and by evaluation of the atomic MSD, which turned

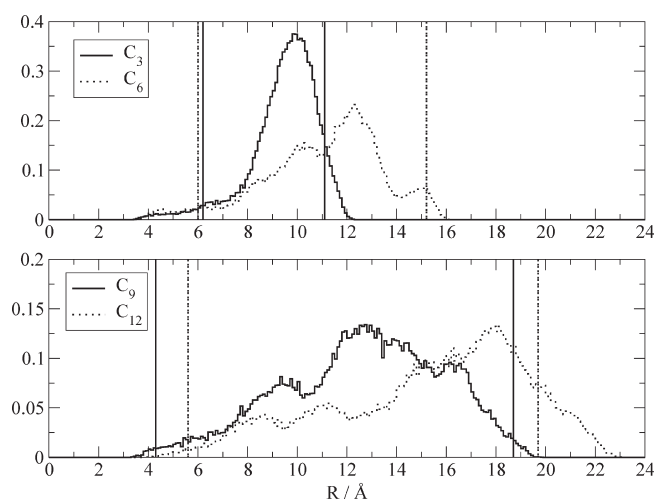


Figure 2. External C1 carbon atom radial distribution function. The vertical lines are the distances that we have found in the ab initio modeling of the gas phase ionic complexes (short distances) and of the isolated dication (long distances).

out very low and almost independent of temperature. We have used a linear interpolation of the density variation upon temperature for the glass and the liquid, and we have determined approximately the transition region. In any case, the temperature we have found falls about 10 to 20 K above the lowest ones identified by the experiments. It is well-known that the adopted force field overestimates the molecular interactions giving rise to a more strongly bound system, which probably explains the values of the transition temperatures. This, as well as other issues such as the underestimation of diffusion coefficients, could be solved by adopting a scaled charge scheme or a polarizable force field (see refs 49 and 50 for a discussion). Despite these shortcomings, we have shown in analogous molecular systems²⁷ that the adopted force field is accurately reproducing available static structural experimental data such as diffraction patterns, and therefore, we believe that the local geometrical structures of the liquid is reasonably well described by this choice.

One of the first interesting questions about the local liquid structure of such compounds is the shape of the linkage chain. As we have already addressed in our previous paper,⁴⁷ there are two limiting cases that occur in the gas phase: when the cation is isolated, the chain is extended (though not completely for $n = 12$), and the distance between the two imidazolium rings is maximum (consistent with the electrostatic repulsion between them); when the cation interacts with two anions, we have a much more compact structures, and the two imidazolium rings are very close to each other. Moreover, we have also registered only two possible mutual orientations of the two rings in the ab initio gas phase structures: either parallel or nearly perpendicular (with an angle of about 60 degrees).

The first analysis that we present is represented by the radial distribution function (RDF) between the two external C1 atom types inside the same cation. The intramolecular radial distribution is presented in Figure 2 where we report also the maximum and minimum distances that we have found in our gas-phase calculations:⁴⁷ one is short and is the one we have found in the ionic complex; the other is much larger and represent the C1–C1 distance in the isolate dication. As can be seen from Figure 2, the linkage chain is found to be much more elongated

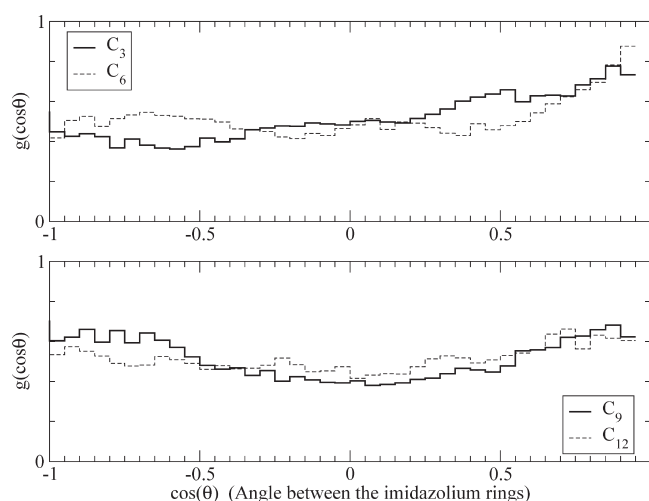


Figure 3. Angle distribution between the two interconnected imidazolium rings.

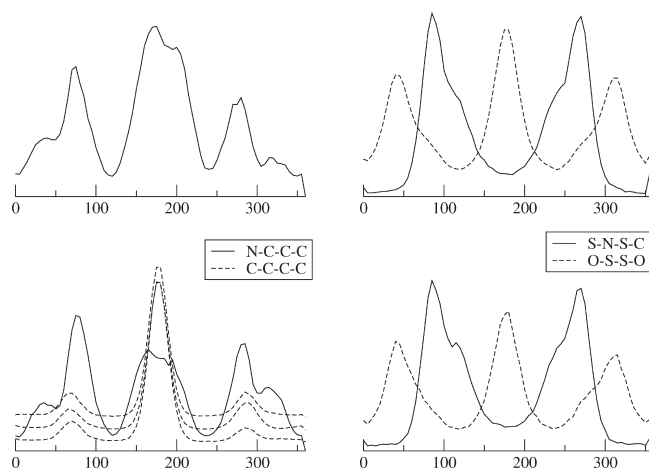


Figure 4. Dihedral angle distributions for C_3 (upper panels) and C_{12} (lower panels): the left panels report the linkage chain angles, the right ones two representative angles in the Tf_2N anion.

than it appears in the gas-phase structures we had found for the ionic complexes. The radial distributions present only a very small fraction of the population with short C1–C1 distance in all four compounds. For any length of the chain, except C_{12} , the C1–C1 distance distribution is within the limit imposed by the elongated chain length in the free cation, while for C_{12} we see a certain number of configurations with longer distances. This is obviously due to the fact that the isolated C_{12} cation has a slightly bent linkage chain.

Another interesting aspect of the chain conformation is the relative positioning of the two imidazolium rings in the same molecule. We have calculated the distribution of the cosine of the angle between the two planes of the imidazolium rings and we have reported it in Figure 3. We can see that the two imidazolium rings of the same molecule do not show any particular orientational preference and give rise to rather broad distributions. In the C_3 and C_6 compounds the two imidazolium rings show a weak preference for a parallel configuration while for the other compounds we notice that this preference is less and less visible as the linkage chain length grows.

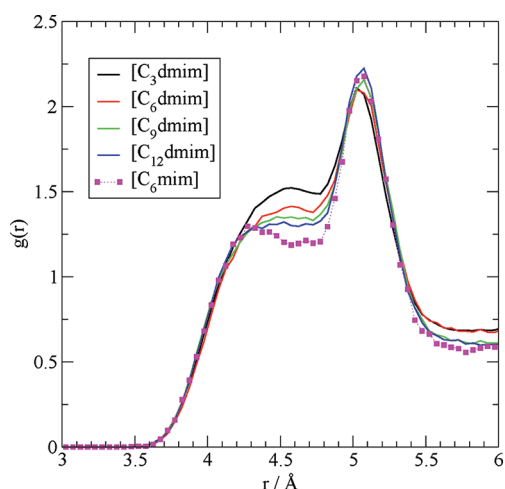


Figure 5. Carbon–carbon RDFs in the $[\text{Tf}_2\text{N}]^-$ anion for the four ionic liquids analyzed here and a monocationic variant taken for our work in ref 27.

The structure of the linkage chain has been further analyzed by calculating the torsional distribution along the chain starting with the N–C–C–C dihedral angle and continuing to the C–C–C–C ones. The computation is reported in Figure 4 for the C_3 (upper panels) and the C_{12} (lower panels) species. The longer chains show a profile that is very typical of other C_n -imidazolium systems in connection with Tf_2N anions such as those reported in our previous work.²⁷ The C–C–C–C angles in the C_{12} compound (dashed lines in the lower-left panel) are seen to prefer an anti conformation of the atoms. The N–C–C–C angle, however, shows a more complex profile with respect to monoimidazolium compounds (see, for example, ref 27): there is a strong preference for an anti and two distorted (70 degrees) gauche configurations, but there is a significant population of angles others than these that is probably due the greater strain to which the chain is subjected in these compounds.

Also, the local structure of the Tf_2N anion can be characterized by an analysis of its torsional angles.^{51,52} The probability distribution of the dihedral angles for two representative choices of the atoms in the chain: the S–N–S–C angle and the O–S···S–O angle are shown in Figure 4. The former distribution is in agreement with that shown in ref 51 and clearly denotes the existence of two conformers: one, more abundant, with dihedral angles around 90 and 270 degrees (trans form) and another with the angles around 120 and 240 degrees (cis form). The O–S···S–O angles shows instead that the highly polarized oxygen atoms in the anion clearly prefer an anti conformation. It is notable that the structure of the anion depends very little on the size of the linkage alkyl chain of the cation. By comparing these findings with those that we have already found in monoimidazolic analogue compounds,²⁷ we can see that the dihedral angle distributions are almost identical (for example, by directly comparing the data for the C_{12}dmim and the C_6mim compounds). Therefore, we conclude that the conformation of the anion seems not only to be greatly insensitive to the length of the chain but also to the different nature of the cation.

The relative conformation of the anion has been shown to be predominantly of trans type,²⁷ at least at room temperature. It is very simple to provide a further confirmation of this aspect of the local structure by looking at the carbon–carbon RDFs of the

anion that is reported in Figure 5. It can be seen that the second peak (corresponding to the larger C–C distance) is always dominant in our simulations. While we can say that in these compounds the trans form of the anion is clearly dominant, if we compare the present C–C RDF with that of a mono imidazolic cation such as the $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$,²⁷ we see that in the present dicationic forms, we find the cis form slightly more abundant. The shortest linkage chain compound $[\text{C}_3\text{dmim}]$, in particular, shows such an effect in a more pronounced form, and we believe that is probably due to an energetic preference of the cis conformations because of the possibility offered by the presence of two cationic heads of coordinating two hydrogens of the imidazolium rings at the same time with the same anion. This is an effect that we had noticed in the gas phase geometric optimizations reported in ref 47 where the cis structure was favored by a double coordination of the oxygens with the imidazolium rings.

Another important indicator of the short-range structure of the liquid is the structure factor. The calculation of a structure factor involves a sum over the cosine-transforms of the radial distribution functions. In the case of X-ray structure factors, each component of the sum is multiplied by a wave vector dependent scattering factor⁵³ that depends on the kind of atoms involved. The radial distribution function between particle type i and j is defined as

$$g_{ij}(r) = \frac{n_{ij}(r)}{4\pi r^2 dr \rho_j} \quad (1)$$

where ρ_j is the number density of particles j , and $n_{ij}(r)$ is the number of particles of type j between distance r and $r + dr$ from a particle of type i . Given c_j , the molar fraction of particles j , $\rho_j = c_j \cdot \rho_0$ where ρ_0 is the total number density of the sample. The total scattering for X-ray can be then written as

$$S(Q) = \rho_0 \sum_{i,j} c_i c_j f_{ij}(Q) \int_0^\infty 4\pi r^2 [g_{ij}(r) - 1] \frac{\sin(Qr)}{Qr} dr \quad (2)$$

where Q is the scattering wave-vector modulus, and f_i are the atomic Q -dependent X-ray scattering factors⁵³ and where

$$f_{ij}(Q) = \frac{f_i(Q)f_j(Q)}{[\sum_{i=1}^n c_i f_i(Q)]^2} \quad (3)$$

Since $S(Q)$ is going to zero rapidly for an unstructured liquid, sometimes, it is preferred not to include the normalization factor in eq 3 and multiply $S(Q)$ by an enhancing factor given by

$$M(Q) = \left(\frac{f_N(0)}{f_N(Q)} \right)^2 \exp[-0.01Q^2] \quad (4)$$

where we use the nitrogen atomic scattering factor. Calculating the neutron scattering structure factors is easier because the scattering factors are Q -independent and equal to the coherent scattering lengths. Neutron scattering factors are obtained using eq 2 by fixing at the appropriate value the scattering factors f_i .

The static X-ray structure factors for the four compounds are reported in Figure 6 where we show it in units of number density as a function of the wave vector. The structure factors have been multiplied by the enhancing factor obtained from nitrogen in order to make their structure more apparent. The four compounds evidently share a common structure at short-range (large Q region, between 4 and 20 \AA^{-1}) that is due to the

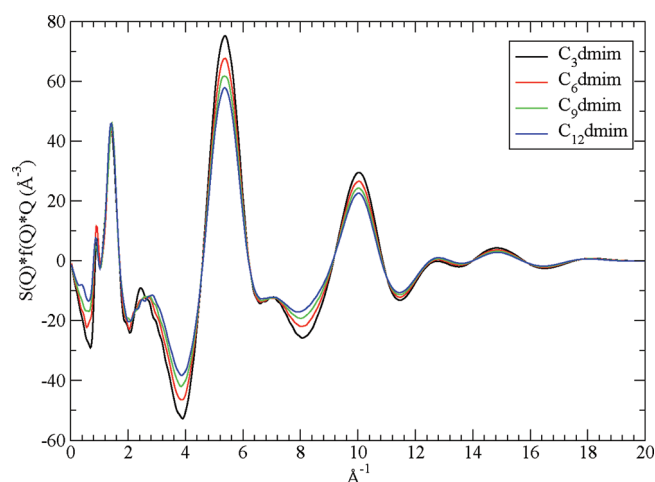


Figure 6. Total X-ray structure factor as calculated by our simulations.

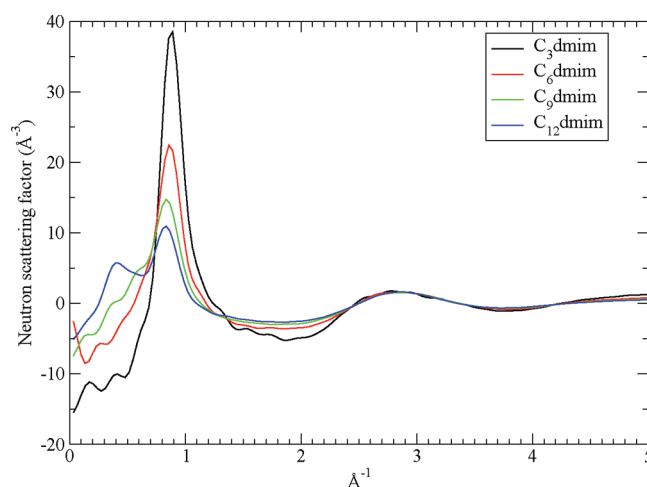


Figure 8. Total neutron scattering structure factor for $[C_n\text{dmim}][\text{Tf}_2\text{N}]$ with $n = 3, 6, 9$, and 12 .

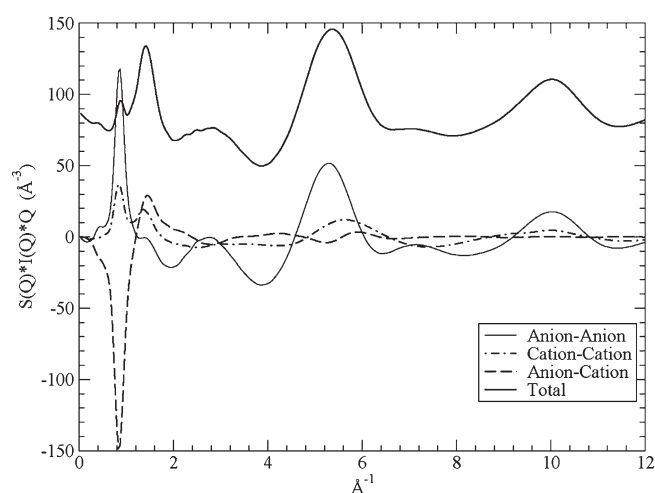


Figure 7. Total X-ray structure factor for $[C_{12}\text{dmim}][\text{Tf}_2\text{N}]$ and its decomposition in cation and anion contributions. The total structure factor has been shifted upward to make the figure clear.

intramolecular atomic arrangements. The dominant contribution here is that of the anion (see also Figure 7) so that the structure factor is very similar for all 4 compounds. At low Q , the structure factors show the typical^{27,54} long-range double peak clearly located at $0.8\text{--}2\text{ Å}^{-1}$. The following interpretation of these peaks has been suggested by Santos et al.:⁵⁴ the first peak at 0.8 Å^{-1} is mainly due to anion–anion and cation–cation self-correlation, i.e., to real space ordering along scale lengths at which the closest ion of the same charge occurs in the liquid ($7.5\text{--}7.3\text{ Å}$); the second peak, instead, arises from intermolecular contributions among atoms on adjacent ions or, to a smaller extent, on alternating anions ($4.6\text{--}4.7\text{ Å}$). We report the different contributions to $S(Q)$ arising from the anion–anion, cation–cation, and mixed correlations in Figure 7 for the $[C_{12}\text{dmim}][\text{Tf}_2\text{N}]$ compound. We can say that, in these compounds, the second peak, as suggested, is mainly determined by cation–anion and, to a smaller extent, by cation–cation interactions, while the first peak is due, instead, to cation–cation and anion–anion self-correlation since the mixed one gives a negative contribution.

Another interesting feature of the reported structure factors is the absence (with the exception of the C_{12} compound) of a low- q prepeak^{55,56} at $Q < 0.8$, which instead appears in the structure factor of the long chain monoimidazolic counterpart²⁷ and other ionic liquids with long side chains such as imidazolium bromides and chlorides.⁵⁷ These prepeaks at low- Q have been interpreted as the result of alkyl chain segregation that is due to the competition between the electrostatic interactions between the imidazolium rings and the anions and the van der Waals forces between the apolar alkyl chains that induce the formation of apolar domains.^{52,58} More recently, Hardacre and co-workers⁵⁹ have pointed out that the existence of such peaks might not be an indicator of nanosegregation phenomena, but they may arise because of the anisotropic effect due to the asymmetric solvation around the cation. Such low- Q peaks have already been characterized by MD simulations in other systems even though the agreement with experimental values was only qualitative, and generally, both their intensity and the associated correlation lengths were underestimated.⁵⁹ Nevertheless, it seems to us very reasonable that the MD simulations are describing, at least qualitatively, the true physics beyond the experimental prepeaks. For example, coarse grained models have been applied by Bhargava et al.^{60,61} to the study of 1,3-didecyl-imidazolium hexafluorophosphate in order to provide long enough simulation times to analyze the complex long-range structures that arise in such liquid. They found the formation of lamellar structures reminiscent of lipid bilayers.

In the present case, we notice a suppression of the low- Q peak if compared to the situation of the monoimidazolium compounds that show a prepeak even for 5-member alkyl chains. The reason for this is not entirely clear: on the one hand, the presence of the dication could be the cause of a decrease in the degree of alkyl chain segregation because the chains are less free to interact with each other, but on the other hand, the presence of a symmetric cation would also inhibit the anisotropy effect suggested by Hardacre or at least make the long-range correlation length larger. The typical spatial correlation length due to the prepeak, for the C_{12} compound, is in the $15\text{--}16\text{ Å}$ range, which turns out to be slightly less than the size of the cation in the liquid (see Figure 2). By looking at the correlation diagram of the real space correlation distances with alkyl chain lengths in

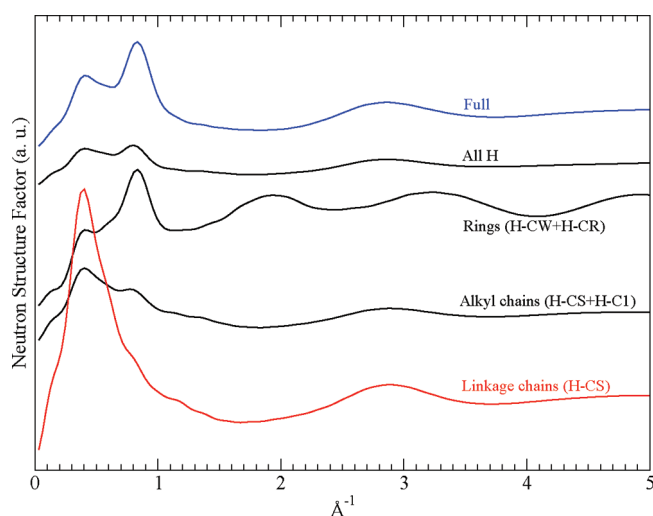


Figure 9. Neutron scattering structure factor for $[C_{12}dmim][Tf_2N]$: total, due only to all H atoms, to those on the alkyl chains, to those on the linkage chains, and to those on the imidazolium rings.

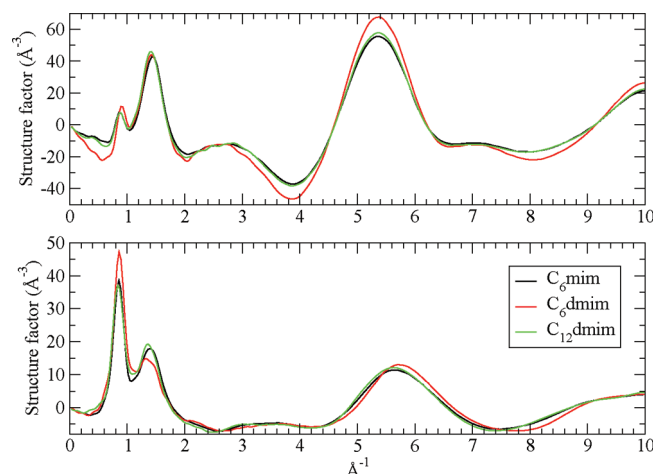


Figure 10. Total X-ray structure factor for $[C_{12}dmim]$, $[C_6dmim]$, $[C_6mim]$, and their respective cation–cation contribution as calculated by our simulations.

monocationic imidazolium based ionic liquid (Figure 4 in ref 59), we see that our compound has an extrapolated behavior as if it were a monoimidazolium cation with an alkyl chain length of 6.

The calculated isotopic averaged neutron scattering factors are reported in Figure 8. In this case, the prepeak for the C_{12} compound is clearly visible. It is also easy to see that the peak arises from a contribution due to the hydrogen atoms on the side chains. We have plotted in Figure 9 the total neutron scattering factor for the C_{12} compound along with the contribution arising from four selected subsets of H atoms: all the H atoms, those on the alkyl chains (including C1), those on the imidazolium rings, and those on the linkage chains (excluding C1). The prepeak is clearly originated by the H atoms on the chain, while the contribution coming from the methyl (C1) hydrogens tends to decrease such a peak.

In order to establish a comparison with the monoimidazolic counterparts, we have reported in Figure 10 (along with the cation–cation contribution) the $S(Q)$ calculated for the dications with a linkage chain of 12 and 6 atoms with that obtained by

us for the C_6 methyl-imidazolium cation that we had shown to be in excellent agreement with the experimental one.²⁷ The static structure functions are very similar to each other, and while the anion contribution (not shown) is clearly very much the same, we notice that even the cation–cation contribution presents only very marginal differences in moving from a geminal dication to a monocation. This result is not too surprising because the force field employed here is the same as that used for the C_6 compound.

CONCLUSIONS

In this work, we have analyzed by means of theoretical MD simulation the liquid structure of four ionic liquids composed by the Tf_2N anion and a geminal methyl-imidazolium dication. The length of the linkage chain has been varied between 3 and 12 carbon atoms. The MD simulations have been performed by using a well-tested force field for imidazolium based liquids in conjunction with Tf_2N anions. We have calculated the equilibrium room temperature densities, which are in very good agreement with the experimentally determined ones. We have then computed various indicators that should be able to describe the local structure of the liquid state of these compounds and we have concluded the following:

- (1) Contrary to what we have found in the gas phase, the linkage chain in the liquid is elongated, especially in the long chain compounds (9 and 12 atoms). The two imidazolium rings of the same molecule do not interact with each other and do not show any particular orientational preference.
- (2) The torsional angles of the linkage chain are very similar to those of a free alkyl chain, and the torsional angles in the anions are identical to those of monoimidazolium compounds.
- (3) The anion is found to exist for the most part in the trans form. The structure of the anion seems to be insensitive to both the linkage chain length and to the fact that in the present case we have a geminal imidazolium cation.
- (4) The calculated X-ray scattering structure factors are very similar in the four compounds (this is due to the similarities in the anion shape) and to the analogous case of a monoimidazolium compound with a side chain length equal to half the linkage chain length.
- (5) For the C_{12} compound, we have noticed the insurgence of a prepeak at 0.4 \AA^{-1} , which we showed to be mainly due to chain–chain correlation by using the calculated neutron scattering factors where it appears more prominently than in the X-ray ones.

In general, it is difficult to say whether all the above enumerated features would then be seen on the real liquid phases of these compounds; however, we are confident that these simulations are carried out with a force field that has been shown several times to provide a good rendition of the structural physical properties of a broad class of ionic liquids and therefore we believe that the present calculations may point to several of the true features of the title compounds.

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