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# Molecular Dynamics and *ab Initio* Studies of the Effects of Substituent Groups on the Thermodynamic Properties and Structure of Four Selected Imidazolium-Based $[\text{Tf}_2\text{N}^-]$ Ionic Liquids

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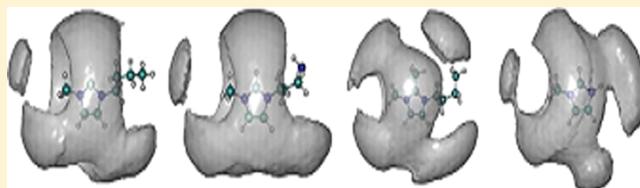
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 Supporting Information

**ABSTRACT:** All-atom molecular dynamics simulations combined with *ab initio* calculations are used to study the thermodynamic properties and microscopic structure of four ionic liquids (ILs) based on the imidazolium cation with different alkyl side branches, ( $[\text{bmim}]^+$ , 1-butyl-2,3-dimethylimidazolium;  $[\text{bmim}]^+$ , 1-butyl-3-methylimidazolium;  $[\text{apmim}]^+$ , 1-(3-aminopropyl)-3-methylimidazolium;  $[\text{mim}]^+$ , 1-methylimidazolium), paired with the  $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ , bis-(trifluoromethanesulfonyl)imide anion, in the temperature range of (298 to 600) K. We observed the highest value of the molar internal energy, enthalpy of vaporization, and cohesive energy density for the amine-functionalized  $[\text{apmim}]^+[\text{Tf}_2\text{N}]^-$  ionic liquid. Structural analysis shows that the amine functionalization of the end of the alkyl side chain of imidazolium cation does not significantly affect the organization of  $[\text{Tf}_2\text{N}]^-$  around  $[\text{apmim}]^+$ , but additional  $\text{NH}_2$  groups lead to short-range cation–cation structural correlations between neighboring  $[\text{apmim}]^+$ . The C2 methylation extensively affects preferential out-of-plane face-to-face locations of  $[\text{Tf}_2\text{N}]^-$  around  $[\text{bmim}]^+$  and also the cation–cation distributions.  $[\text{mim}]^+[\text{Tf}_2\text{N}]^-$  has the highest simulated density and better packing efficiency of liquid phase in comparison with other studied ILs. The strongest first shell probability density region of  $[\text{mim}]^+$  neighbors above and below the imidazolium ring of the reference cation represents better  $\pi$ – $\pi$  stacking in the liquid phase of this ionic liquid. The presented results determine the role of the cation structure on the properties of this family of ILs. Good agreement was achieved between simulation results of the bulk phase and quantum calculations which are performed to determine the optimized structure of isolated ion pairs in chosen configurations and the strength of cation–anion interactions.



## 1. INTRODUCTION

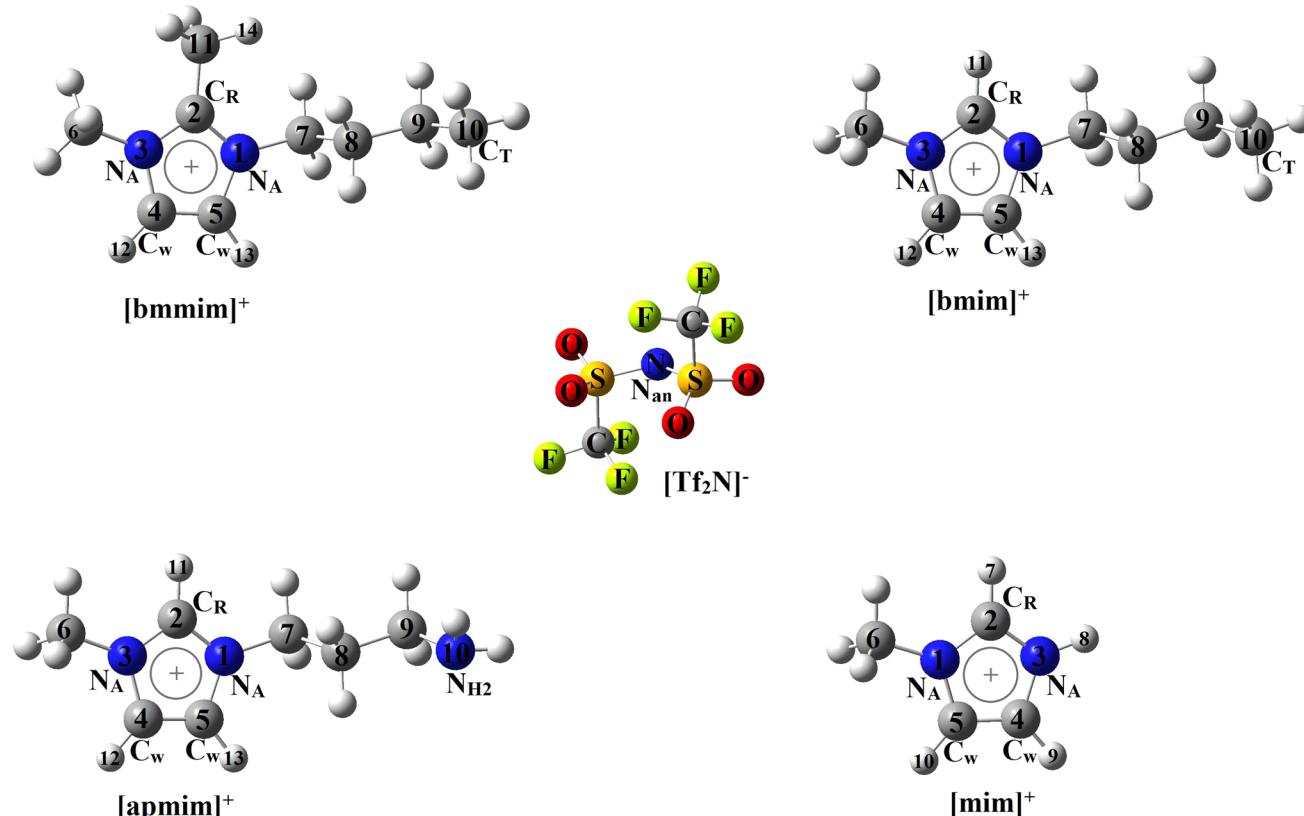
In the past 20 years, marked increases in the use of volatile organic molecular solvents in chemical industries have caused critical environmental problems and become a strong driving force to develop new alternative solvents. Ionic liquids (ILs) have attracted considerable interest as green nonvolatile replacements with a broad range of solution properties and multifarious applications. They have generally negligible vapor pressure, low flammability, good ionic conductivity, and electrochemical and thermal stabilities.<sup>1</sup> ILs can be used for

catalytic,<sup>2</sup> synthetic,<sup>3</sup> separation,<sup>4</sup> and heat transfer purposes.<sup>5</sup> In recent years, several reviews<sup>6–11</sup> and journal special issues<sup>12–15</sup> have highlighted some of the progress previously made and future research directions in the chemical physics and physical chemistry of ionic liquids.

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**Figure 1.** Ball and stick models of four imidazolium cations and the  $[\text{Tf}_2\text{N}]^-$  anion with the main atomic labels and numbering according to the applied force fields in this study.

A huge number of combinations of different anions and cations ( $\sim 10^6$  possible pure ILs and  $10^{18}$  ternary liquid mixtures)<sup>16</sup> or introducing substituent/functional groups to the ions in ILs will open up an infinitely large number of compounds with varied tunable physical and chemical properties which can be tailored for specific applications.<sup>17–21</sup> For the optimum design of new ILs for specific tasks, it is important to understand the correlation between ionic chemical structures and the fundamental properties of ILs.<sup>22</sup> Structural details and thermodynamic and transport properties are particularly important when the ILs are used as solvents, electrolytes, lubricants, and heat transfer fluids. Relatively little data are available on different properties of the vast possible members of these families of ionic liquid compounds.

In general, the ILs based on imidazolium cations and  $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$  (also known as bis-triflimide,  $[\text{Tf}_2\text{N}]^-$ , or  $[\text{TFSI}]^-$ ), which include the target ILs studied in this work, have a relatively low viscosity and melting point, high thermal<sup>23</sup> and electrochemical stability, and favorable solvation properties. They have attracted much attention for the formation of highly tunable and hydrolytically stable molten salts. Hydrophobic  $[\text{Tf}_2\text{N}]^-$  is usually regarded as charge-diffuse and weakly coordinating, and IUPAC has chosen it as a benchmark anion in ILs for extensive analysis. The strong delocalization of the negative charge over a large volume in the bulky  $[\text{Tf}_2\text{N}]^-$  fluoro-containing anion weakens the strength of its interaction with the cation, leading to lower melting point and higher dynamics of ILs with  $[\text{Tf}_2\text{N}]^-$ .<sup>24</sup>

Imidazolium-based  $[\text{Tf}_2\text{N}]^-$  ILs have been widely tested as solvents and electrolytes, e.g., in lithium batteries or capacitors.<sup>25</sup> The reactivity of the acidic proton at the C2

(C<sub>R</sub>) site of the imidazolium ring in Figure 1 and its instability toward Li prevent the use of these ILs in these applications.<sup>26,27</sup> Introducing an alkyl substituent at the imidazolium C2 position improves chemical and electrochemical stability and produces attractive electrolytes for lithium batteries.<sup>28–32</sup> The hydrogen atom with a relatively large positive point charge at the C2 position of the imidazolium ring interacts strongly with anions by hydrogen bonding. The methylation at this position (C2 methylation) destroys this interaction and causes significant changes in the physicochemical properties of imidazolium ILs.<sup>33–42</sup> For instance, C2 methylation commonly enhances the melting point,<sup>43–49</sup> viscosity,<sup>29,42,44,50,51</sup> thermal,<sup>23,29,45,47,49,52</sup> chemical,<sup>29,53</sup> and electrochemical stability,<sup>29,43</sup> and vaporization enthalpy<sup>54</sup> and also decreases the density<sup>23,29,43,49</sup> and conductivity.<sup>29,43,46,47,55</sup> Recent studies focus more on C2 methylation of imidazolium ILs at the molecular level from quantum-chemical<sup>56</sup> and/or molecular dynamics (MD) calculations that were performed with the goal of finding the reason for the unexpected increasing of viscosity and melting point upon C2 methylation of these known salts.<sup>34,35,57–60</sup> Reviewing studies show that not only the “entropy hypothesis” of Hunt<sup>34</sup> but also the “defect hypothesis” of Ludwig et al.<sup>35,57,58</sup> are needed to clarify the changes in the physicochemical properties upon C2 methylation. For more information, we summarized several recent works about C2 methylation in the Supporting Information.

In this work, MD simulations and quantum-chemical calculations are used as predictive complementary tools to study the trends in thermodynamic properties and microscopic structure of ILs with the charge-diffuse  $[\text{Tf}_2\text{N}]^-$  and four imidazolium cations with different alkyl side chains,

**Table 1.** Simulated Density,  $\rho_{MD}$  ( $\text{g}\cdot\text{cm}^{-3}$ ), at Different Temperatures, and Available Experimental Density (with the Error, % $\Delta$ , Values in Parentheses) for Four ILs in This Study

ILs	T/K	$\rho_{MD}$ , our work	$\rho_{exp}$ (% $\Delta$ $\rho$ )	$\rho_{MD}$ , other simulations
[bmim][Tf <sub>2</sub> N]	298	1.483 ± 0.006	1.420 <sup>a</sup> (4.4)	1.403 <sup>b</sup> , 1.411 <sup>c</sup> , 1.439 <sup>d</sup>
	400	1.394 ± 0.008		1.313 <sup>e</sup>
	450	1.353 ± 0.009		1.265 <sup>e</sup>
	500	1.308 ± 0.010		
	600	1.226 ± 0.012		
[apmim][Tf <sub>2</sub> N]	298	1.594 ± 0.006	1.592 <sup>f</sup> (0.12)	1.556 <sup>f</sup>
	350	1.544 ± 0.008		
	400	1.497 ± 0.009		
	450	1.452 ± 0.010		
	500	1.399 ± 0.027		
[bmim][Tf <sub>2</sub> N]	600	1.298 ± 0.084		
	298	1.498 ± 0.007	1.436 <sup>g,h</sup> (4.3), 1.44 <sup>i</sup> (4.0)	1.50 <sup>j</sup> , 1.48 <sup>k</sup> , 1.446 <sup>e</sup>
	400	1.418 ± 0.009		1.345 <sup>e</sup> , 1.40 <sup>j</sup>
	450	1.375 ± 0.011		
	500	1.332 ± 0.011		1.32 <sup>j</sup>
[mim][Tf <sub>2</sub> N]	600	1.240 ± 0.013		
	298	1.757 ± 0.008		
	400	1.659 ± 0.009		
	450	1.609 ± 0.009		
	500	1.568 ± 0.016		
[mim][Tf <sub>2</sub> N]	600	1.480 ± 0.012		

<sup>a</sup>Reference 29. <sup>b</sup>Reference 76, using a nonpolarizable force field. <sup>c</sup>Reference 76, using a polarizable force field. <sup>d</sup>Reference 68. <sup>e</sup>Reference 36. <sup>f</sup>Reference 62. <sup>g</sup>Reference 77. <sup>h</sup>Reference 78. <sup>i</sup>Reference 79. <sup>j</sup>Reference 80. <sup>k</sup>Reference 67.

([bmim]<sup>+</sup>, 1-butyl-2,3-dimethylimidazolium; [bmim]<sup>+</sup>, 1-butyl-3-methylimidazolium; [apmim]<sup>+</sup>, 1-(3-aminopropyl)-3-methylimidazolium; [mim]<sup>+</sup>, 1-methyl-imidazolium); see Figure 1. Between these ILs, [bmim][Tf<sub>2</sub>N] is widely studied in recent experimental and computational work on ILs, and its calculated properties are used as a test for the validity of our current simulations. To our knowledge, this is the first MD study to report the effect of butyl side chain elimination on the properties of the ILs by comparing the results of [mim][Tf<sub>2</sub>N] and [bmim][Tf<sub>2</sub>N]. We also selected an amine-functionalized task-specific imidazolium-based IL, [apmim][Tf<sub>2</sub>N], as one of the target ILs in this study and compare its properties with the isoelectronic [bmim][Tf<sub>2</sub>N] IL. This can clarify the influences of amine addition on the properties of such ILs. Introducing an amine functional group (-NH<sub>2</sub>) to the terminal of alkyl side chain of imidazolium ILs may enhance the CO<sub>2</sub> absorption capabilities. There are only a few MD studies reported for characterization of amine-functionalized ILs in literature.<sup>61–63</sup> Simulations of [apmim][Tf<sub>2</sub>N] were first performed by Gutowski and Maginn,<sup>62</sup> but to our knowledge, this is the first study which compares the structure of the amine-functionalized IL with its alkyl analogue.

We determine the effects of alkyl/functional substituent groups in selected imidazolium cations on a wide range of calculated properties of these ILs. In particular, the current study focuses on detailed descriptions of the effects of C2 methylation or amine functionalization of the end of alkyl side chain of imidazolium cation on the structural details and thermodynamic properties of imidazolium-based [Tf<sub>2</sub>N]<sup>-</sup> ILs. Another purpose of this work is to compare the properties of ILs including the 1-methylimidazolium cation, which are rarely studied, with 1-alkyl-3-methylimidazolium and 1-alkyl-2,3-dimethylimidazolium cations which are more widely used.

This work is organized as follow: In section 2 computational details are defined and represented. In section 3 the

methodology applied to calculate the thermodynamic properties and microscopic structure of four ILs and the results of the MD simulations and quantum calculations are presented and discussed. The work ends with a summary and conclusions in section 4.

## 2. COMPUTATIONAL METHODS

**2.1. Ab Initio Calculations.** For each ionic liquid, ion-pair configurations were generated starting from optimized structures of the cation and anion at the B3LYP/6-311+ +G(d,p) level with the Gaussian 03 suite of programs.<sup>64</sup> This level of theory is widely used to calculate the structure and energy of ion pairs of ILs.<sup>61,65</sup> For each ionic liquid, two possible initial guesses of the ion-pair configurations are considered (see section 3.3), and each optimized structure was also checked to be a stable local minimum by a normal-mode frequency calculation to ascertain no imaginary frequencies were observed.

**2.2. Molecular Dynamics Simulations.** Molecular dynamics simulations of four ionic liquids shown in Figure 1 were done on systems consisting of 125–180 ion pairs. The force field parameters used in MD simulations of this work for [bmim]<sup>+</sup>, [bmim]<sup>+</sup>, [mim]<sup>+</sup>, and [Tf<sub>2</sub>N]<sup>-</sup> ions is from the systematic all-atom force field developed by Canongia Lopes et al.,<sup>66–68</sup> mainly based on the OPLS and AMBER framework. The force field used for [apmim]<sup>+</sup> was developed by Gutowski and Maginn<sup>62</sup> on the basis of CHARMM 27 force field<sup>69</sup> and the work of Cadena et al.<sup>70</sup>

The standard functional form of the force field is given by

$$\begin{aligned}
 V_{\text{tot}} = & \sum_{\text{bonds}} k_b(r - r_{\text{eq}})^2 + \sum_{\text{angles}} k_\theta(\theta - \theta_{\text{eq}})^2 \\
 & + \sum_{\text{dihedrals}} k_\varphi[1 + \cos(n\varphi - \delta)] \\
 & + \sum_{i=1}^{N-1} \sum_{j>1}^N \left\{ 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\} \quad (1)
 \end{aligned}$$

where the right side of eq 1 characterizes the breakdown of the total potential energy into bonds, valence angles, torsional dihedral interactions, the pairwise additive atom–atom 12–6 Lennard-Jones potential, and the electrostatic interactions between point charges centered on the atoms. The values of the force constants and other parameters of eq 1 for four IL systems are given in refs 62 and 66–68. The van der Waals parameters ( $\epsilon$  and  $\sigma$ ) for unlike-atom interactions are obtained from the conventional Lorentz–Berthlot combination rules.

The simulations were performed by the Verlet leapfrog algorithm,<sup>71</sup> with the DL\_POLY program<sup>72</sup> version 2.18. The time step of the simulations was 0.001 ps, periodic boundary conditions were employed, and the intermolecular cutoff distances were set to 16.5 Å for all simulated systems. The electrostatic long-range interactions were calculated using the Ewald summation method<sup>71</sup> with a precision of  $1 \cdot 10^{-6}$ . The initial MD simulations were performed in the *NpT* ensemble of Nosé–Hoover thermostat/barostat<sup>73,74</sup> for  $p = 1$  atm at  $T = (600, 500, 450, 400, 350, \text{ and } 298)$  K, until the total energy and volume of the system converged. The relaxation times used for the thermostat and barostat were 0.2 and 1.0 ps, respectively. Each system was initially equilibrated by starting with replicas of randomly placed anion–cation pairs and annealing with three consecutive runs at (600, 500, and 450) K, each with a total  $1.5 \cdot 10^6$  time steps with 300,000 equilibration steps. Afterward, each system was equilibrated with a set of two runs at 400 K, 1 run at 350 K, and finally following with the couple runs at the lowest temperature (298 K). In this stage, each run consists of a total  $1.5 \cdot 10^6$  time steps with 300,000 equilibration steps. Thus, each ionic liquid totally equilibrated by the *NpT* simulation annealing at different temperatures during (6 and 10.5) ns for target temperatures of (400 and 298) K, respectively. To calculate the radial distribution function (RDF), spatial distribution function (SDF), and various thermodynamic quantities, each of the equilibrated systems was studied with a long *NpT* simulation run for 7.5 ns at each of the target temperatures.

### 3. RESULTS AND DISCUSSION

**3.1. Density and Isobaric Thermal Expansion Coefficient.** The liquid density is one of the simplest properties to compute as a function of temperature from MD simulations and is also one of the most widely available experimental properties, so it provides a good initial test of an applied force field.<sup>75</sup> The computed densities at different temperatures for the four ionic liquids are shown in Table 1. The simulated density and molar volume of the [apmim][Tf<sub>2</sub>N] at 298 K are  $1.594 \text{ g}\cdot\text{cm}^{-3}$  and  $263.59 \text{ cm}^3\cdot\text{mol}^{-1}$ , respectively, which are in excellent agreement with the experimentally determined the density of  $1.592 \text{ g}\cdot\text{cm}^{-3}$  (a difference of 0.12 %), and molar volume of  $264 \text{ cm}^3\cdot\text{mol}^{-1}$ .<sup>62</sup> The trend in the calculated density in this set of ILs is [mim][Tf<sub>2</sub>N] > [apmim][Tf<sub>2</sub>N] > [bmim][Tf<sub>2</sub>N] > [bmmim][Tf<sub>2</sub>N]. [mim][Tf<sub>2</sub>N] has a

significantly lower free volume and the largest density in the liquid phase, and as expected, with increasing alkyl chain length, the densities of the ionic liquids decrease. The lengthening of the alkyl chain causes a dispersion of the charge centers and weakening of the electrostatic attractions between the cations and anions but enhances the total strength of the van der Waals interactions. The lower density may be ascribed to the longer alkyl side chains of [bmmim]<sup>+</sup>, [bmim]<sup>+</sup>, and [apmim]<sup>+</sup> compared to that of [mim]<sup>+</sup> which reduce the packing efficiency of the fluid.<sup>61,81</sup> The higher calculated density ( $1.594 \text{ g}\cdot\text{cm}^{-3}$ ) of [apmim][Tf<sub>2</sub>N] compared to [bmim][Tf<sub>2</sub>N] ( $1.498 \text{ g}\cdot\text{cm}^{-3}$ ) is partially the result of the more compact microstructure caused by amine-associated interaction, as discussed below.<sup>61</sup> Based on recent simulations, replacement of the -CH<sub>3</sub> group with an -NH<sub>2</sub> group can increase the density by nearly 7 % and a lower the molar volume by  $\sim 16.5 \text{ cm}^3\cdot\text{mol}^{-1}$ . The computed density of [bmim][Tf<sub>2</sub>N] is higher than [bmmim][Tf<sub>2</sub>N] in agreement with recent experimental and simulation reports.<sup>36,82</sup>

The computed thermal expansivity is defined as<sup>83,84</sup>

$$\alpha_p = \frac{1}{\langle V \rangle} \left( \frac{\partial \langle V \rangle}{\partial T} \right)_p \quad (2)$$

The isobaric thermal expansion coefficient describes how the volume of a fluid changes with a change in temperature at constant pressure. The molar volumes of four ILs as a function of temperature at 1 atm with their linear correlation functions calculated from equilibrated simulation boxes are given in the Supporting Information. The simulated thermal expansion coefficients at several temperatures for four ionic liquids are shown in Table 2. With increasing temperature, the volume

**Table 2. Computed Thermal Expansion Coefficient,  $\alpha_p$  ( $10^{-4} \text{ K}^{-1}$ ), as a Function of Temperature for Four Studied ILs**

	$\alpha_p/(10^{-4} \text{ K}^{-1})$					
	600 K	500 K	450 K	400 K	350 K	298 K
[bmmim][Tf <sub>2</sub> N]	5.76	6.14	6.35	6.55	—	6.96
[apmim][Tf <sub>2</sub> N]	6.15	6.63	6.88	7.09	7.31	7.55
[bmim][Tf <sub>2</sub> N] <sup>a</sup>	5.59	6.00	6.19	6.39	—	6.75 <sup>b</sup>
[mim][Tf <sub>2</sub> N]	5.20	5.51	5.66	5.83	—	6.17

<sup>a</sup>The irregular computed  $\alpha_p$  values from MD simulations of ref 85 at (298, 348, 398, 448, and 498) K are ( $7.41 \cdot 10^{-4}$ ,  $8.98 \cdot 10^{-4}$ ,  $7.53 \cdot 10^{-4}$ ,  $7.93 \cdot 10^{-4}$ , and  $8.11 \cdot 10^{-4}$ )  $\text{K}^{-1}$ , respectively. <sup>b</sup>The experimental datum for  $\alpha_p$  is  $6.36 \pm 0.06$ <sup>86</sup> at 298 K; its computed value from MD of ref 87 is 7.88.

increases and thermal expansion coefficient decreases (see Table 2). However, this expected trend has not been observed properly in the recent MD simulation reported by Androulaki et al.<sup>85</sup> The calculated  $\alpha_p$  of [bmim][Tf<sub>2</sub>N] at 313 K from our simulation is  $6.69 \cdot 10^{-4} \text{ K}^{-1}$ , in excellent agreement with the recent computational and experimental  $\alpha_p$  values at the same temperature, ( $6.8 \cdot 10^{-4}$  and  $6.6 \cdot 10^{-4}$ )  $\text{K}^{-1}$ , respectively.<sup>78,83</sup> The trend in the  $\alpha_p$  in this set of ILs is [apmim][Tf<sub>2</sub>N] > [bmmim][Tf<sub>2</sub>N] > [bmim][Tf<sub>2</sub>N] > [mim][Tf<sub>2</sub>N]. Except for [apmim][Tf<sub>2</sub>N] which is simulated with a different cation force field source,<sup>82</sup> the relative magnitudes of the calculated  $\alpha_p$  are consistent with the relative magnitudes of simulated molar volume (inverse of calculated density). [bmmim][Tf<sub>2</sub>N] has the largest molar volume (and the lowest density value). This IL shows the greatest changes in molar volume with

**Table 3. Cohesive Energy Density ( $c$ ), Molar Volume ( $V_m$ ), Molar Internal Energy of Vaporization ( $\Delta U_m^{\text{vap}}$ ), and Molar Enthalpy of Vaporization ( $\Delta H_m^{\text{vap}}$ ) at (298 and 400) K for  $p = 1 \text{ atm}$**

ILs	$T$	$\Delta U_m^{\text{vap}}$	$\Delta H_m^{\text{vap}}$	$V_m$	$c$
	K	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{cm}^3\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{cm}^{-3}$
[bmim][Tf <sub>2</sub> N]	298	117.4 ± 2.3	119.9 (152.7 <sup>a</sup> , 128.0 <sup>b</sup> )	292.1 ± 1.3	401.9
	400	114.7 ± 2.7	118.0	310.7 ± 1.9	369.1
[apmim][Tf <sub>2</sub> N]	298	184.9 ± 2.6	187.4	263.6 ± 1.0 (264 <sup>c</sup> , 270.1 <sup>d</sup> )	711.0
	400	172.6 ± 3.0	175.9	280.5 ± 1.6	615.2
[bmim][Tf <sub>2</sub> N]	298	137.6 ± 5.6 (149 <sup>e</sup> )	140.1 (151 <sup>e</sup> )	280.0 ± 1.2 (288.53 <sup>e</sup> )	491.4 (515 <sup>e</sup> )
	400	117.1 ± 8.4	120.4	295.7 ± 1.8	396.0
[mim][Tf <sub>2</sub> N]	298	115.5 ± 2.4	117.9	206.8 ± 0.9	558.5
	400	87.5 ± 8.6	90.8	218.4 ± 1.2	400.5

<sup>a</sup>Reference 76, using a nonpolarizable force field. <sup>b</sup>Reference 76, using a polarizable force field. <sup>c</sup>Reference 62, experimental data. <sup>d</sup>Reference 62, simulation data. <sup>e</sup>Reference 99, using CHARMM-derived force field at 293 K and 1 bar.

temperature  $(\partial V/\partial T)_p$ , among the four ILs. These two factors explain the relatively high value of the thermal expansion coefficient for this IL.

**3.2. Enthalpy of Vaporization and Cohesive Energy Density.** The enthalpy of vaporization ( $\Delta H_{\text{vap}}$ ) is also a useful property of ILs generally calculated by MD simulations as an initial test in validating the proposed force fields.<sup>88,89</sup> The [C<sub>n</sub>mim][Tf<sub>2</sub>N] IL family has good thermal stability up to 600 K, and several experimental  $\Delta H_{\text{vap}}$  data of this group have been reported.<sup>90,91</sup>

In MD simulations at constant pressure,  $\Delta H_{\text{vap}}$  has been computed from the difference between the molar internal energy of the gas and the liquid phases,

$$\Delta H_{m,i}^{\text{vap}}(T) = U_{m,i}(\text{gas}) - U_{m,i}(\text{liq}) + RT = \Delta U_{m,i}^{\text{vap}}(T) + RT \quad (3)$$

where  $R$  represents the universal gas constant and the  $RT$  term is used in place of a  $pV$ -work part in the enthalpy. The  $U_{m,i}(\text{gas})$  is determined from corresponding  $NVT$  simulation for a single ion pair at the same temperature in a large adequate simulation box.<sup>92</sup> The molar intermolecular energy in liquid phase  $U_{m,i}(\text{liq})$ , i.e., the sum of molar van der Waals and Coulombic energies, is calculated from the liquid simulation.

The computed values of  $\Delta H_{\text{vap}}$  from MD simulations of four ILs in this work are reported in Table 3. Good agreement is achieved between our simulation results for [bmim][Tf<sub>2</sub>N] and several sets of previous experimental measurements as well as with reported recent MD simulations of this IL<sup>93–99</sup> (see section 3 of the Supporting Information).

The cohesive energy density, ( $c$ ), is equal to the internal energy of vaporization divided by molar volume (see eq 4). It is an indicator of the relative strength of interaction among ion pairs at the liquid phase of an ionic liquid and roughly related to the internal pressure ( $\pi_{\text{int}} = (\partial U/\partial V)_T$ ). The cohesive energy density is easily accessible from the properties that are either readily measured or calculated, namely,  $\Delta U_{m,i}^{\text{vap}}(T)$  and the molar volume ( $V_m$ ) of the liquid at temperature  $T$ .<sup>61,99,100</sup>

$$c = \frac{U_{m,i}(\text{gas}) - U_{m,i}(\text{liq})}{V_{m,i}(\text{liq})} = \frac{\Delta U_{m,i}^{\text{vap}}(T)}{V_{m,i}(\text{liq})} \quad (4)$$

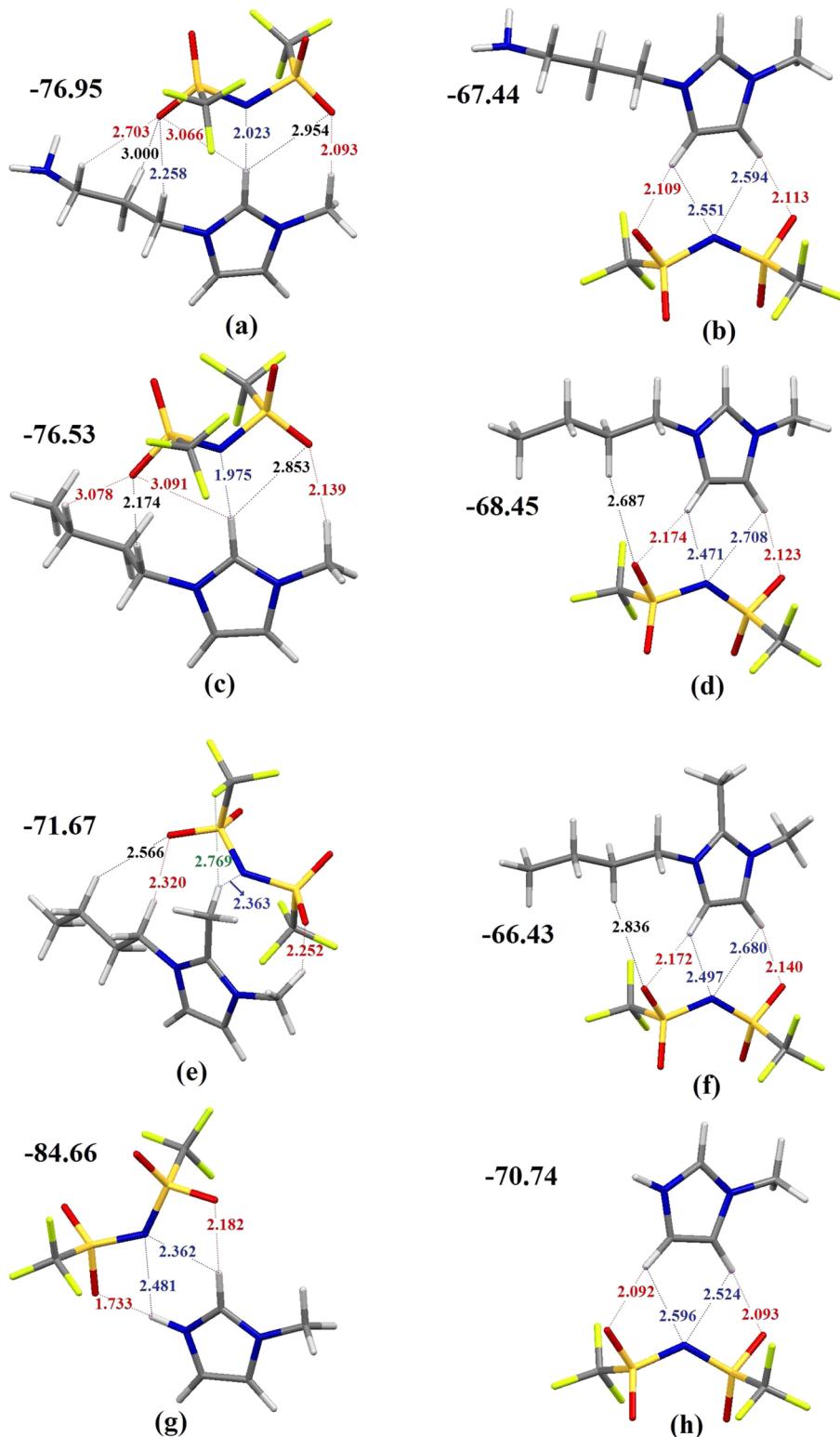
The calculated  $\Delta U_m^{\text{vap}}$ ,  $\Delta H_m^{\text{vap}}$ ,  $V_m$ , and cohesive energy density ( $c$ ) are presented in Table 3. These values are much higher than those of ordinary molecular solvents due to the strong electrostatic ionic interactions in ILs. The highest values of the internal  $\Delta U_m^{\text{vap}}$ ,  $\Delta H_m^{\text{vap}}$ , and cohesive energy density observed for [apmim][Tf<sub>2</sub>N] are consistent with the nature

of negligible vapor pressure and partially related to the strong ionic interaction in amine-functionalized ionic liquids.<sup>61</sup> However, some of the differences between the predicted results of [apmim][Tf<sub>2</sub>N] with the three other studied ILs could be due to the different sources of the applied force field<sup>62</sup> for the cation of this IL. Between three other studied nonfunctionalized ILs, the observed trend in the calculated cohesive energy density which is inversely proportional to the trend of molar volume of the ILs is [mim][Tf<sub>2</sub>N] > [bmim][Tf<sub>2</sub>N] > [bmmim][Tf<sub>2</sub>N], while the trend in the calculated  $\Delta U_m^{\text{vap}}$  and  $\Delta H_m^{\text{vap}}$  is [bmim][Tf<sub>2</sub>N] > [bmmim][Tf<sub>2</sub>N] > [mim][Tf<sub>2</sub>N].

With increasing temperature from (298 to 400) K for each ionic liquid, the  $V_m$  increases, while the  $\Delta U_m^{\text{vap}}$ ,  $\Delta H_m^{\text{vap}}$ , and  $c$  decrease. Increasing volume and thermal expansion of the liquid with increasing temperature lead to a drop in the favorable attractive interactions present in the liquid phase causes a relatively large reduction in the  $\Delta H_m^{\text{vap}}$  and cohesive energy density of the system.<sup>99</sup> Comparison of the computed  $\Delta H_{\text{vap}}$  for [mim][Tf<sub>2</sub>N] with [bmim][Tf<sub>2</sub>N] at 298 K shows that the  $\Delta H_{\text{vap}}$  increases by about 22  $\text{kJ}\cdot\text{mol}^{-1}$  after inserting an *n*-butyl chain in place of hydrogen in the imidazolium ring. This relative prediction is in agreement with recently reported simulation and experimental values. The simulated values of the enthalpy of vaporization by Maginn and Kelkar<sup>99</sup> predict the  $\Delta H_{\text{vap}}$  increases by about 5  $\text{kJ}\cdot\text{mol}^{-1}$  for every additional two carbon units in the alkyl chain. The experiments and simulations of the Santos et al.<sup>95</sup> show larger enthalpy of vaporization increases of about 19 and 14  $\text{kJ}\cdot\text{mol}^{-1}$ , respectively, for every additional two carbon atoms in the chain.

**3.3. Ab Initio Calculation of Ion-Pair Energies and Configurations.** Study of the isolated ion pair of imidazolium ILs by *ab initio* calculations showed that the cation–anion interaction in an ion pair agrees relatively well with that in bulk liquid.<sup>101–107</sup> The quantum chemistry calculations can be employed to investigate the local interactions, such as cation–anion interaction sites, hydrogen bonding, and cation–anion interaction energies, among other properties.<sup>61</sup>

However, full a *ab initio* study of ion-pair energies and configurations is beyond the scope of this work and only two main possible ion-pair configurations of each ionic liquid are studied in detail by quantum calculations to compare with MD results. First initial configurations (named type I) were created through placing [Tf<sub>2</sub>N]<sup>–</sup> in side by side positions and near the top of the C<sub>2</sub> site of the imidazolium cations, and the second possible initial configurations (named type II) were created through placing [Tf<sub>2</sub>N]<sup>–</sup> near the bottom of the C<sub>w</sub> sites (C4



**Figure 2.** Selected distances ( $\text{\AA}$ ) of two optimized geometries of type I (left) and type II (right) for the ion pair of four imidazolium-based  $[\text{Tf}_2\text{N}^-]$  by *ab initio* calculations at the B3LYP/6-311++G(d,p) level.

and C5) of the imidazolium cations. The final stable configurations of both types, I and II, for four ILs obtained at the B3LYP/6-311++G(d,p) level are shown in the left and right parts of Figure 2, respectively.

The final configuration of type I for each ionic liquid is more stable than that of type II, as shown by interaction energies in

Figure 2 and Table 4, which are in good agreement with previous study in this class of ILs.<sup>35</sup> It is clear the alkyl side chains of cations are more affected by cation–anion orientations in the type I optimized structures rather than the type II structures. In all optimized structures of Figure 2,  $[\text{Tf}_2\text{N}]^-$  anions interact effectively with their N and O sites

**Table 4.** Total Energies,  $E_{\text{B3LYP}}$  and  $E_{\text{thermal}}$ , and Interaction Energies,  $E_{\text{interaction}}$ , of Two Optimized Geometries of Types I and II of Ion-Pair Structures of Four ILs, along with the Calculated  $E_{\text{B3LYP}}$  and  $E_{\text{thermal}}$  Energies for the Cations and Anion, The Stabilization Energies,  $E_{\text{form}}$ , and the Deformation Energies,  $E_{\text{def}}$  Obtained from B3LYP/6-311++G(d,p) Calculations

ILs, ions	$E_{\text{B3LYP}}$	$E_{\text{interaction}}$	$E_{\text{thermal}}$	$E_{\text{form}}$	$E_{\text{def}}$
	hartrees	kcal·mol <sup>-1</sup>	hartrees	kcal·mol <sup>-1</sup>	kcal·mol <sup>-1</sup>
[bmimim][Tf <sub>2</sub> N], I	-2290.3484208	-71.67	-2290.012828	-68.97	2.70
[bmimim][Tf <sub>2</sub> N], II	-2290.3400715	-66.43	-2290.004592	-63.80	2.63
[bmim][Tf <sub>2</sub> N], I	-2251.0202342	-76.53	-2250.713975	-74.42	2.11
[bmim][Tf <sub>2</sub> N], II	-2251.0073499	-68.45	-2250.701270	-66.45	2.00
[apmim][Tf <sub>2</sub> N], I	-2267.0602315	-76.95	-2266.764562	-74.77	2.18
[apmim][Tf <sub>2</sub> N], II	-2267.045078	-67.44	-2266.749790	-65.50	1.94
[mim][Tf <sub>2</sub> N], I	-2093.7271817	-84.66	-2093.539768	-82.92	1.74
[mim][Tf <sub>2</sub> N], II	-2093.7049912	-70.74	-2093.517341	-68.84	1.90
[bmim] <sup>+</sup>	-462.6237842		-462.359185		
[apmim] <sup>+</sup>	-439.3271784		-439.101678		
[bmim] <sup>+</sup>	-423.2878485		-423.051648		
[mim] <sup>+</sup>	-265.9818383		-265.863901		
[Tf <sub>2</sub> N] <sup>-</sup>	-1827.6104205		-1827.543730		

**Table 5.** Selected Atomic Partial Charges from the Atomic Polar Tensor (APT) Method of the Four Imidazolium Cations Obtained from B3LYP/6-311++G(d,p) Calculations<sup>a</sup>

site no.	label	[bmimim] <sup>+</sup>	label	[bmim] <sup>+</sup>	label	[apmim] <sup>+</sup>	label	[mim] <sup>+</sup>
1	N <sub>A</sub>	-0.363	N <sub>A</sub>	-0.332	N <sub>A</sub>	-0.320	N <sub>A</sub>	-0.221
2	C <sub>R</sub>	0.415	C <sub>R</sub>	0.257	C <sub>R</sub>	0.257	C <sub>R</sub>	0.231
3	N <sub>A</sub>	-0.335	N <sub>A</sub>	-0.302	N <sub>A</sub>	-0.301	N <sub>A</sub>	-0.293
4	C <sub>W</sub>	-0.004	C <sub>W</sub>	0.008	C <sub>W</sub>	0.009	C <sub>W</sub>	0.045
5	C <sub>W</sub>	0.003	C <sub>W</sub>	0.018	C <sub>W</sub>	0.016	C <sub>W</sub>	0.017
6	C	0.309	C	0.319	C	0.319	C	0.295
7	C	0.375	C	0.395	C	0.388	H <sub>CR</sub>	0.160
8	C	0.042	C	0.041	C	0.427	H <sub>N3</sub> <sup>b</sup>	0.323
9	C	0.136	C	0.138	C	0.012	H <sub>Cw</sub>	0.155
10	C <sub>T</sub>	0.058	C <sub>T</sub>	0.058	N <sub>H2</sub>	-0.506	H <sub>Cw</sub>	0.149
11	C <sub>CR</sub>	-0.014	H <sub>CR</sub> <sup>b</sup>	0.140	H <sub>CR</sub>	0.139		
12	H <sub>Cw</sub>	0.132	H <sub>Cw</sub>	0.138	H <sub>Cw</sub>	0.138		
13	H <sub>Cw</sub>	0.130	H <sub>Cw</sub>	0.136	H <sub>Cw</sub>	0.138		
14	H <sub>C</sub>	0.051			H <sub>N10</sub> <sup>b</sup>	0.155		

<sup>a</sup>The atom numbering is shown in Figure 1. <sup>b</sup>The acidic hydrogen site.

with imidazolium cations, and except for (Figure 2e), the F atoms have no important role in single ion pair interactions. This observation is in agreement with RDF analysis of MD simulations; see the following.

From the left side (type I) configurations of ILs in Figure 2, the strong and localized directional hydrogen bonds between the hydrogen site on C2 (H<sub>CR</sub>) and anionic (N and O) sites are seen for [apmim][Tf<sub>2</sub>N] and [bmim][Tf<sub>2</sub>N], and the nitrogen site of [Tf<sub>2</sub>N]<sup>-</sup> occupies a position in-plane with the cation ring above the H<sub>CR</sub> site (see a and c in Figure 2). In the more stable configuration of [bmimim][Tf<sub>2</sub>N], shown by Figure 2e, the substituted methyl group on the C2 carbon atom causes [Tf<sub>2</sub>N]<sup>-</sup> and [bmimim]<sup>+</sup> to move to a out-of-ring plane. Indeed, C2 methylation blocks a possible hydrogen bond, and the in-plane interactions of the anion with the C2 position of the imidazolium ring in the [bmimim][Tf<sub>2</sub>N] causes the interaction energy of [bmimim][Tf<sub>2</sub>N] (Figure 2e) to be lower than [bmim][Tf<sub>2</sub>N] (Figure 2c; see Table 4). In the absence of n-butyl side chain in the cation of [mim][Tf<sub>2</sub>N] IL (Figure 2g), [mim]<sup>+</sup> and [Tf<sub>2</sub>N]<sup>-</sup> are the closest to each other of the four ILs; therefore there is better packing and stronger interactions in the [mim][Tf<sub>2</sub>N] ionic liquid. As seen in configuration g of [mim][Tf<sub>2</sub>N] in Figure 2, the nitrogen site of [Tf<sub>2</sub>N]<sup>-</sup>

occupied a position in-plane with the cation ring but not exactly above the H<sub>CR</sub> site, but rather above the middle region of H<sub>CR</sub> and H<sub>N3/8</sub>. In this manner, one O···H<sub>N3/8</sub> distance becomes 1.733 Å and a strong hydrogen bond between the O site of [Tf<sub>2</sub>N]<sup>-</sup> and the H<sub>N3/8</sub> site of [mim]<sup>+</sup> is constructed. This observation is in agreement with our RDF and SDF results for [mim][Tf<sub>2</sub>N]; see section 3.4.

It seems that the terminal amine site has not influenced the orientation of the cation–anion pair in both stable configurations (Figure 2a,b) of [apmim][Tf<sub>2</sub>N] IL shown in Figure 2. This observation is also in good agreement with spatial and radial distribution function analysis for this IL (see section 3.4). However, MD simulation results show the presence of strong cation–cation structural correlations between the terminal amine and cationic ring sites/terminal amine groups of side chains of neighboring [apmim]<sup>+</sup> in the liquid phase.

In optimized type II structures of all studied ILs, see right side of Figure 2, similar hydrogen bonds between the hydrogen sites on C<sub>w</sub> (C4/C5) and nitrogen and oxygen sites of [Tf<sub>2</sub>N]<sup>-</sup> can be observed and the nitrogen site of [Tf<sub>2</sub>N]<sup>-</sup> occupies a position in-plane with the cation ring and below of the middle region of C<sub>w</sub> sites. These type II interactions are relatively independent of the type of alkyl side chain of cations and in

agreement with RDF plots of two middle panels of Figure 6; see the text that follows.

The cation–anion interaction energy of ILs,  $E_{\text{interacion}}$ , is defined as the difference between the energy of the ion pair and the sum of the energies of the purely isolated cationic and anionic species (eq 5), which indicates the strength of the cation–anion interaction.<sup>61</sup>

$$E_{\text{interaction}} = E_{\text{tot}}^{\text{ion-pair}} - (E_{\text{cation}} + E_{\text{anion}}) \quad (5)$$

The interaction energy values of two type of configurations for each IL are reported in Table 4.  $[\text{mim}][\text{Tf}_2\text{N}]$  has a stronger cation–anion interaction. The interaction energy for  $[\text{bmim}][\text{Tf}_2\text{N}]$  is more negative than that of  $[\text{bmmim}][\text{Tf}_2\text{N}]$  ionic liquid which is consistent with recently reported simulations by Podgoršek et al.<sup>82</sup> However, reported energies in Table 4 only apply to the selected ion pairs and may differ from average interaction energies of all possible configurations on the liquid state.

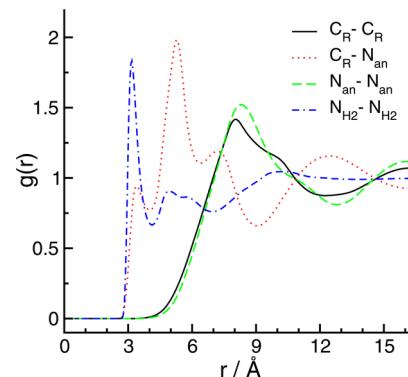
The stabilization energy ( $E_{\text{form}}$ ) for the complex was calculated as the sum of  $E_{\text{interaction}}$  and the deformation energies of ions ( $E_{\text{def}}$ ), which is the sum of the increases of energies for the cation and anion by deformations associated with the complex formation.  $E_{\text{B3LYP}}$  is the total electronic energy and  $E_{\text{thermal}}$  defined as the total electronic energy plus the internal thermal energy which can directly obtained from thermochemistry in the frequency output of the Gaussian 03 suite of programs.<sup>64</sup> The calculated optimized geometry (Figure 2) and the energy results from the quantum chemistry calculations in this work summarized in Table 4 are consistent with the previous works.<sup>35,65,108</sup> Differences in the electronic structure of the isolated different cations may lead to changes in the interactions between cations and  $[\text{Tf}_2\text{N}]^-$ .

We also used atomic polar tensor (APT) method<sup>109</sup> to extract atomic partial charges of imidazolium cations from the same density functional theory (DFT) calculations as reported in Table 5. The main atomic labels are shown in Figure 1. The partial atomic charges help to determine the potential of key atomic sites for strong interactions, such as hydrogen bonding. The positive charge at C2 ( $C_R$ ) is larger in  $[\text{bmmim}]^+$  (+0.41) than in  $[\text{bmim}]^+$  (+0.25). The methyl hydrogen atoms at  $C_{R/11}$  (which is the carbon atom of the methyl group on C2 in  $[\text{bmmim}]^+$ ) are as positive as the imidazolium ring hydrogen atoms (including C2–H of  $[\text{bmim}]^+$ ) and thus, based on a simple Coulombic model, could form hydrogen bonds with the anions. The other atoms of these two ILs have similar the partial charges. The results of partial charge in this work are in good agreement with the previous work by Hunt.<sup>34</sup>

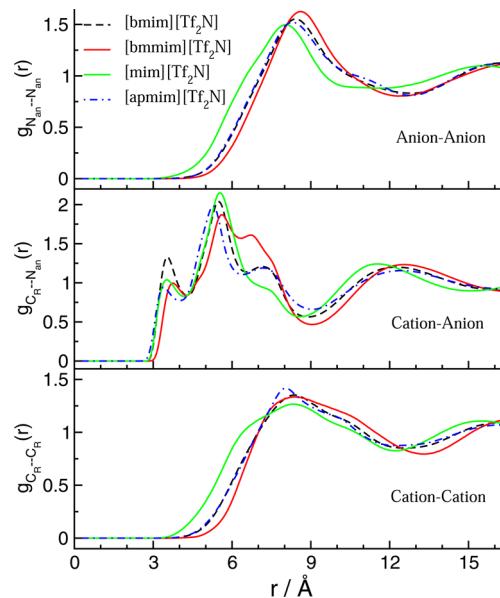
The hydrogen atoms attached to terminal N atom ( $N_{H2}$ –H) in  $[\text{apmim}]^+$  carry as much positive charge (+0.15) as the ring hydrogen atoms (+0.14) and thus, based on a simple Coulombic model, could potentially form hydrogen bonds with the  $[\text{Tf}_2\text{N}]^-$  anion and with  $N_{H2}$  atoms of the other  $[\text{apmim}]^+$  (see Figures 8 and 10). The other atoms of  $[\text{apmim}]^+$  IL have a nearly similar partial charge compared with atomic sites of  $[\text{bmim}]^+$  and  $[\text{bmmim}]^+$ . In the case of  $[\text{mim}]^+$ , the charge at the ring hydrogen atom attached to  $N_{A/3}$  of ring (+0.32) is twice as positive a charge in the other ring hydrogen atoms, and thus, based on a simple Coulombic model, could potentially form strong hydrogen bonds with  $[\text{Tf}_2\text{N}]^-$ , and it is confirmed from our subsequent RDF and SDF results.

**3.4. Structure of the ILs: Radial and Spatial Distribution Functions.** The neighboring liquid structural arrangements between ions of ILs were studied by RDFs,

molecular visualization, and SDF analysis from MD simulations at 400 K as shown in Figures 3–10. The key partial site–site

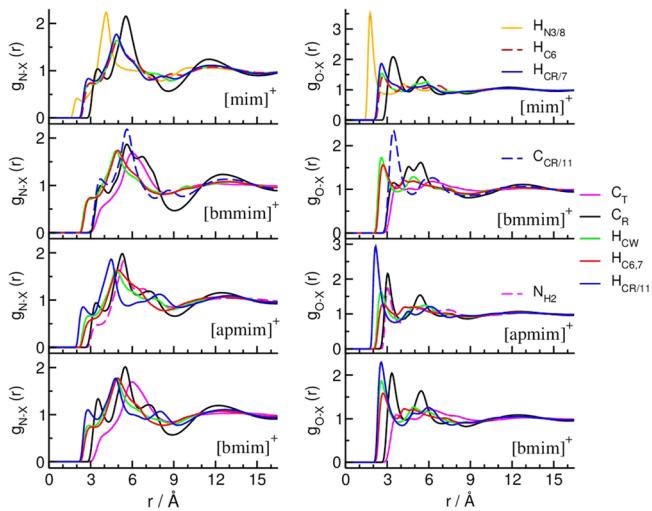


**Figure 3.** Site–site RDFs in the  $[\text{apmim}][\text{Tf}_2\text{N}]$  ionic liquid at 400 K. The RDF between the  $C_R$  carbon atoms of the  $[\text{apmim}]^+$  cations ( $C_R-C_R$ ), that between the nitrogen atoms of  $[\text{Tf}_2\text{N}]^-$  ( $N_{\text{an}}-N_{\text{an}}$ ), that between the  $C_R$  carbon atom of  $[\text{apmim}]^+$  and the nitrogen atom of  $[\text{Tf}_2\text{N}]^-$  ( $C_R-N_{\text{an}}$ ), and that between terminal amine nitrogen sites ( $N_{H2}$ ) of  $[\text{apmim}]^+$  ( $N_{H2}-N_{H2}$ ) are shown.

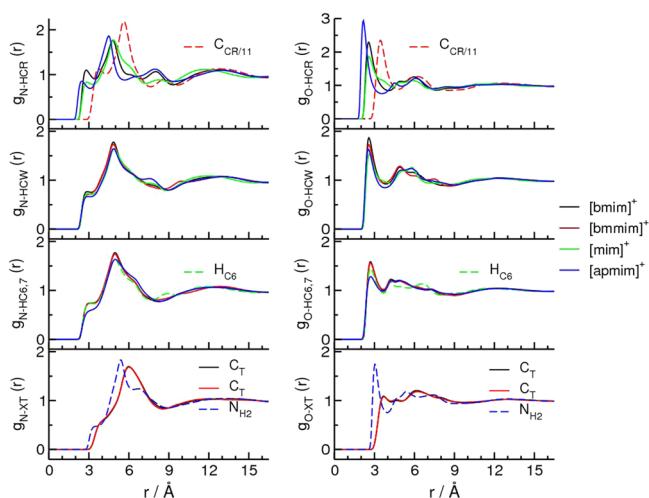


**Figure 4.** Calculated RDFs for the key atomic sites of the anion–anion ( $N_{\text{an}}-N_{\text{an}}$ ), cation–anion ( $C_R-N_{\text{an}}$ ), and the cation–cation ( $C_R-C_R$ ) from the simulations at 400 K for the four ionic liquids.

RDFs for the  $[\text{apmim}][\text{Tf}_2\text{N}]$  ionic liquid are shown in Figure 3. The most central characteristic in these RDFs is the sharp strong first peak of  $g_{(CR-N)}$  with a maximum at  $\sim 5$  Å, indicating highly favored anion–cation structural correlation due to strong electrostatic attraction. Up to 16.5 Å, the second weaker peak of  $g_{(CR-N)}$  is also readily visible in the cation–anion RDFs, which suggests that the second shell structural correlation is broadened. On the other hand, the first peaks of the cation–cation and anion–anion RDFs are much weaker and positioned at larger separations than that of the cation–anion RDF. The first maximum of both broader peaks of cation–cation,  $g_{(CR-CR)}$  related to the location of  $[\text{apmim}]^+$  cations, and anion–anion,  $g_{(N-N)}$  of the neighboring  $[\text{Tf}_2\text{N}]^-$ , are located at about 8 Å as shown in Figure 3. The RDF between the  $C_R$  carbon atom of  $[\text{apmim}]^+$  and the nitrogen atoms of  $[\text{Tf}_2\text{N}]^-$ ,  $g_{(CR-N)}$ , has



**Figure 5.** Anion–cation RDFs between key anionic (N and O) sites of  $[\text{Tf}_2\text{N}]^-$  with several cationic (X) sites of each studied ILs from MD simulations at 400 K.

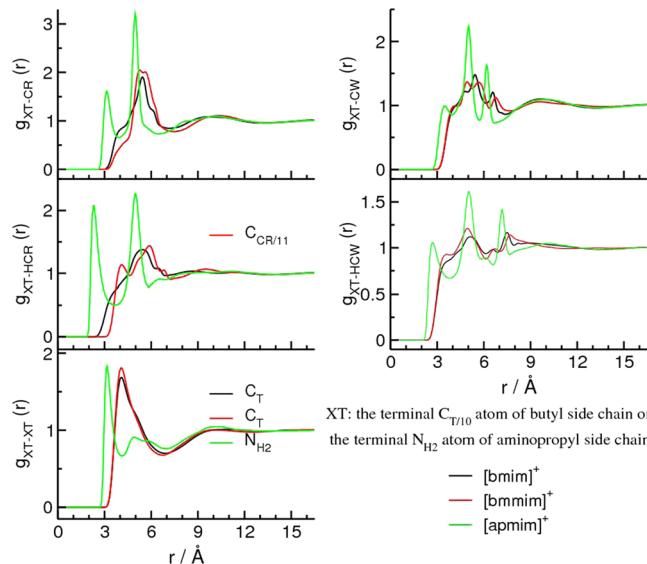


**Figure 6.** Comparison of the anion–cation RDFs between the N or O of  $[\text{Tf}_2\text{N}]^-$  anion and different cationic hydrogen sites or tail  $\text{C}_\text{T}/\text{N}_{\text{H}2}$  atoms of alkyl side chains of cations of the four studied ILs from MD simulations at 400 K.

peaks at shorter distances ((3–7) Å). The  $g_{(\text{CR}-\text{N})}$  has the opposite phase from the  $g_{(\text{N}-\text{N})}$  and  $g_{(\text{CR}-\text{CR})}$ ; the typical charge-ordering structure is recovered.

The first maximum of the sharp RDF of  $\text{N}_{\text{H}2}-\text{N}_{\text{H}2}$  represents the location of the terminal nitrogen ( $-\text{NH}_2$ ) atoms of the 3-aminopropyl side chain of neighboring cations at the relatively short distance of ~3 Å, indicating a strong hydrogen bond interaction between the tail  $\text{N}_{\text{H}2}$  sites; see also the molecular graphical representation of  $\text{N}_{\text{H}2}\cdots\text{N}_{\text{H}2}$  of neighboring  $[\text{apmim}]^+$  in the upper part of Figure 8. This hydrogen bonding is also seen in the SDF of the terminal nitrogen ( $\text{N}_{\text{H}2}$ ) atoms of side chains of neighboring cations around a reference  $[\text{apmim}]^+$  (see following text). This observation is also in agreement with the calculated partial charges on the nitrogen and hydrogen atoms ( $\text{H}_{14}$ ) of the terminal  $-\text{NH}_2$  group reported in Table 5.

The key site–site RDFs at 400 K for the four studied ionic liquids in this work are shown in Figure 4 and the sharp strong first peak of cation–anion ( $\text{C}_\text{R}-\text{N}_{\text{an}}$ ) RDFs at ~5–6 Å support a highly favored cation–anion association. The details of the

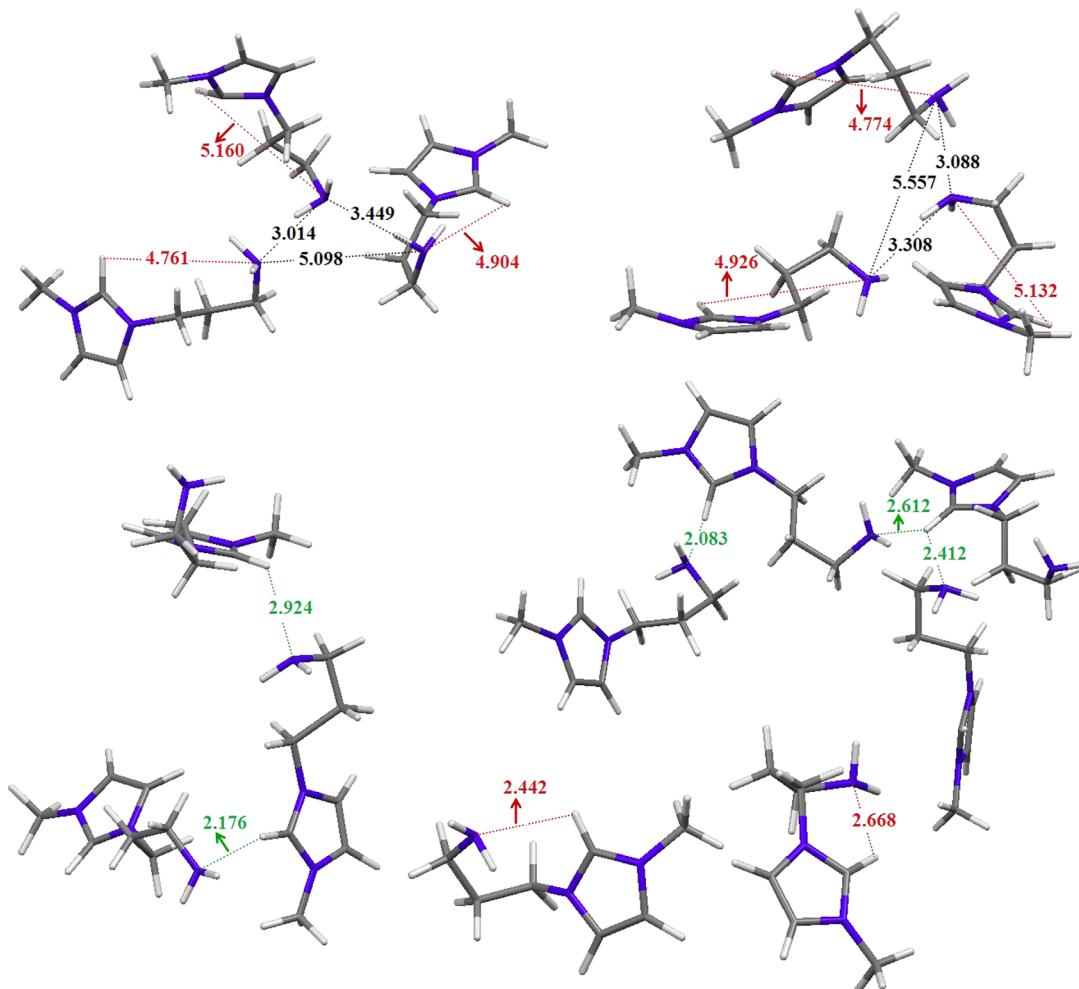


**Figure 7.** Comparison of the cation–cation RDFs between the tail  $\text{C}_\text{T}/\text{N}_{\text{H}2}$  atom of alkyl side chains and the main carbon or hydrogen atoms of imidazolium rings,  $\text{C}_\text{R}$ ,  $\text{C}_\text{w}$ ,  $\text{H}_{\text{CR}}$ , and  $\text{H}_{\text{Cw}}$ , and the atomic tail–tail (XT–XT) RDFs for studied ILs from MD simulations at 400 K.

RDFs depend on the different side chains in the imidazolium cations. In each panel of Figure 4, the RDF sites of imidazolium-based  $[\text{Tf}_2\text{N}]^-$  ILs with  $[\text{bmim}]^+$  and  $[\text{apmim}]^+$  are nearly identical and show clear differences with the corresponding RDFs in  $[\text{mim}][\text{Tf}_2\text{N}]$  and  $[\text{bmmim}][\text{Tf}_2\text{N}]$ . Figure 4 also shows that the charge-ordering structures of  $[\text{mim}][\text{Tf}_2\text{N}]$  and  $[\text{bmmim}][\text{Tf}_2\text{N}]$  ILs are different from each other and the other ILs studied. These interesting points are in agreement with our results from SDFs, see following text, and also from single ion pair optimization.

$[\text{mim}]^+$  has the lowest cation volume and  $[\text{mim}][\text{Tf}_2\text{N}]$  has the highest simulated density in comparison with other ILs in this work. This is the reason the RDF peaks in Figure 4, especially for cation–cation and anion–anion sites, for this IL occur at a shorter distance. The RDFs for  $[\text{bmmim}][\text{Tf}_2\text{N}]$  in Figure 4 occur at the largest distances which is in good agreement with the highest cationic volume of  $[\text{bmmim}]^+$  and the lowest simulated density for  $[\text{bmmim}][\text{Tf}_2\text{N}]$ . Due to the possibility of additional hydrogen bonding in  $[\text{apmim}][\text{Tf}_2\text{N}]$ , the peak of the RDF compared to  $[\text{bmim}][\text{Tf}_2\text{N}]$  occurs at shorter distances.

Figure 5 shows the RDFs between key anionic (N and O) sites of  $[\text{Tf}_2\text{N}]^-$  with several cationic (X) sites of studied ILs. The  $(\text{O}-\text{X})$  RDFs generally show sharper peaks at shorter distances compared to the  $(\text{N}-\text{X})$  RDFs. All studied first shell structural correlations of  $(\text{O}-\text{H})$  sites appear at distances shorter than 3 Å. In Figure 5, the highest RDF intensity is observed for  $g(\text{O}-\text{H}_{\text{N}3/8})$  of  $[\text{mim}][\text{Tf}_2\text{N}]$  which occurs at the smallest distance, with a maximum at ~1.8 Å. This is evidence of the strong anion–cation interaction in this IL in agreement with the  $\text{O}-\text{H}_{\text{N}3/8}$  distance, 1.733 Å, from quantum-optimized structure, case g in Figure 2, and compatible with our SDF results. The second IL of RDF intensity and shorter distance correlation observed for  $g(\text{O}-\text{H}_{\text{CR/11}})$  is  $[\text{apmim}][\text{Tf}_2\text{N}]$ . The trend on RDF intensity of N or O of  $[\text{Tf}_2\text{N}]^-$  with main hydrogen atoms of  $[\text{apmim}]^+$  and  $[\text{bmim}]^+$  is  $\text{H}_{\text{CR/11}} > \text{H}_{\text{Cw}} \sim \text{H}_{\text{C6,7}}$ .



**Figure 8.** Chosen snapshots of several neighbors of  $[\text{apmim}]^+$  cations from the different parts of the simulation box of  $[\text{apmim}][\text{Tf}_2\text{N}]$  at 400 K. The  $\text{N}_{\text{H}_2}\cdots\text{N}_{\text{H}_2}$  and  $\text{N}_{\text{H}_2}\cdots\text{H}_{\text{CR}}$  intermolecular distances in bold black and green, respectively, and the  $\text{N}_{\text{H}_2}\cdots\text{H}_{\text{CR}}$  intramolecular distances in bold red are inserted for more clarification of Figure 7.

For  $[\text{bmimim}][\text{Tf}_2\text{N}]$ , the RDF of  $(\text{N}/\text{O}-\text{H}_{\text{Cw}})$  and  $(\text{N}/\text{O}-\text{H}_{\text{C6,7}})$  appear at relatively shorter distances, but the highest RDF intensity is observed for  $g(\text{N}/\text{O}-\text{C}_{\text{CR}11})$  which is stronger than  $g(\text{N}/\text{O}-\text{C}_\text{R})$  as shown in Figure 5. These observations roughly emphasize specific face-to-face and not in-plane interaction of anion–cation in this IL as illustrated from optimized quantum structure of  $[\text{bmimim}][\text{Tf}_2\text{N}]$  in Figure 2, case e.

The  $(\text{N}/\text{O}-\text{Hx})$  and  $(\text{N}/\text{O}-\text{XT})$  RDFs of the four studied ILs from MD simulations at 400 K are compared in Figure 6. There is clear difference in  $g(\text{N}/\text{O}-\text{H}_{\text{CR}})$  of these ILs in the upper panel, while the location and shape of the peaks of  $g(\text{N}/\text{O}-\text{H}_{\text{Cw}}/\text{H}_{\text{C6,7}})$ , in the two middle panels, for the four ILs are roughly similar. This observation is in good agreement with our finding from types I and II optimized structures in Figure 2. The exchange of the alkyl side chain of imidazolium cations affects the  $g(\text{N}/\text{O}-\text{H}_{\text{CR}})$  which relates the position of the anion near the  $\text{N}_\text{A}-\text{C}_\text{R}-\text{N}_\text{A}$  side of the imidazolium ring of the ILs to a greater extent. The  $g(\text{N}/\text{O}-\text{H}_{\text{Cw}}/\text{H}_{\text{C6,7}})$  which describes the placing of the anion close to the  $\text{C}_\text{w}$  sites of cation imidazole ring is less affected by the alkyl side chains.

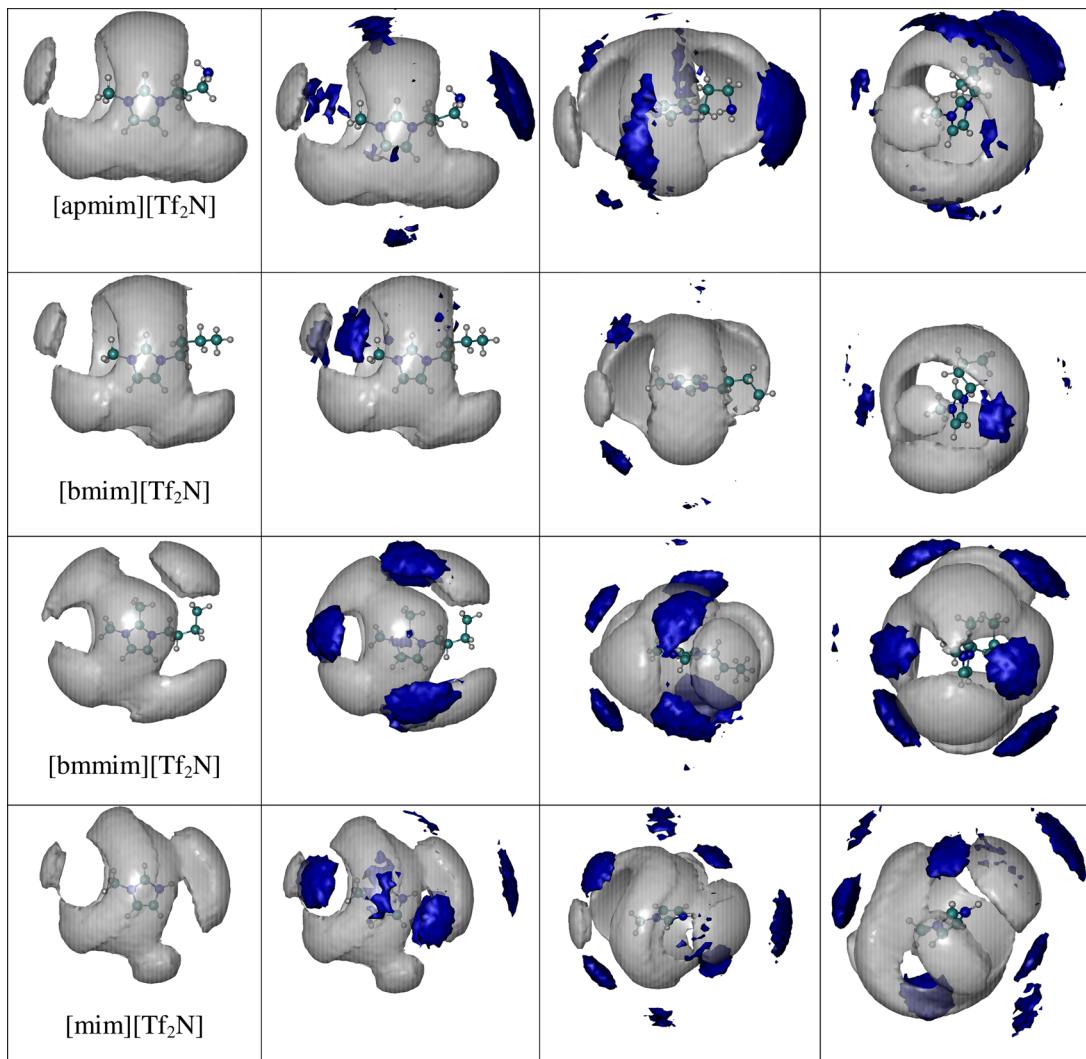
In the lowest panel of Figure 6, the sharper  $(\text{N}/\text{O}-\text{N}_{\text{H}_2})$  RDF at shorter distances for  $[\text{apmim}][\text{Tf}_2\text{N}]$  rather than the corresponding  $(\text{N}/\text{O}-\text{C}_\text{T})$  RDF peaks for  $[\text{bmim}][\text{Tf}_2\text{N}]$  and  $[\text{bmimim}][\text{Tf}_2\text{N}]$  ILs shows specific short-ranged structural

correlations between the tail  $-\text{NH}_2$  of  $[\text{apmim}]^+$  with key anionic ( $\text{N}$  and  $\text{O}$ ) sites of  $[\text{Tf}_2\text{N}]^-$ .

Figure 7 compares the site–site RDFs between the tail  $\text{XT}$  ( $\text{C}_\text{T}/\text{N}_{\text{H}_2}$ ) atom of alkyl side chains and main carbon or hydrogen atoms of imidazolium rings,  $\text{C}_\text{R}$ ,  $\text{C}_\text{w}$ ,  $\text{H}_{\text{CR}}$ , and  $\text{H}_{\text{Cw}}$ . There is also comparison of atomic tail–tail RDF,  $g(\text{XT}-\text{XT})$ , in the lowest panel of Figure 7. It is obvious the different structural correlations between the tail  $\text{N}_{\text{H}_2}$  atom of the aminopropyl side chain with key atomic ring sites of  $[\text{apmim}]^+$  in comparison with the tail  $\text{C}_\text{T}$ -related structural correlations of  $[\text{bmim}]^+$  and  $[\text{bmimim}]^+$ . In all panels of Figure 7, the sharper RDFs at shorter distance observed between the tail  $\text{N}_{\text{H}_2}$  atom with the cationic sites of  $[\text{apmim}]^+$  represents again the specific short-range cation–cation structural correlations associated with amine group in  $[\text{apmim}][\text{Tf}_2\text{N}]$ .

In Figure 8, we carefully focus on the molecular graphical representation of several selected neighboring  $[\text{apmim}]^+$  in the final equilibrated simulation box of  $[\text{apmim}][\text{Tf}_2\text{N}]$  at 400 K to gain more insight and define the types of cation–cation structural correlations related to the tail  $-\text{N}_{\text{H}_2}$  group represented in  $g(r)$  plots of Figure 7.

In the upper part of Figure 8, two sets of three selected  $[\text{apmim}]^+$  are shown with the intermolecular  $\text{N}_{\text{H}_2}\cdots\text{N}_{\text{H}_2}$  distances mainly in  $\sim 3 \text{ \AA}$  (black lines). This typical orientation of neighboring  $[\text{apmim}]^+$  helps to interpret the sharp  $(\text{N}_{\text{H}_2}\cdots$



**Figure 9.** SDFs of the center of masses of  $[\text{Tf}_2\text{N}]^-$  (gray density clouds) and imidazolium cations (dark blue density clouds) around four reference imidazolium cations at 400 K. The first picture in each row only represents anion probability around the reference cation, and the three other pictures in each row show different views of both anion and cation density clouds around the reference cation. The trajectory analysis for computing these SDFs was performed by TRAVIS code<sup>110</sup> and visualized by VMD.<sup>111</sup>

$\text{N}_{\text{H}2}$ ) RDF peak with the maximum  $\sim 3.1 \text{ \AA}$  in the lowest panel of Figure 7.

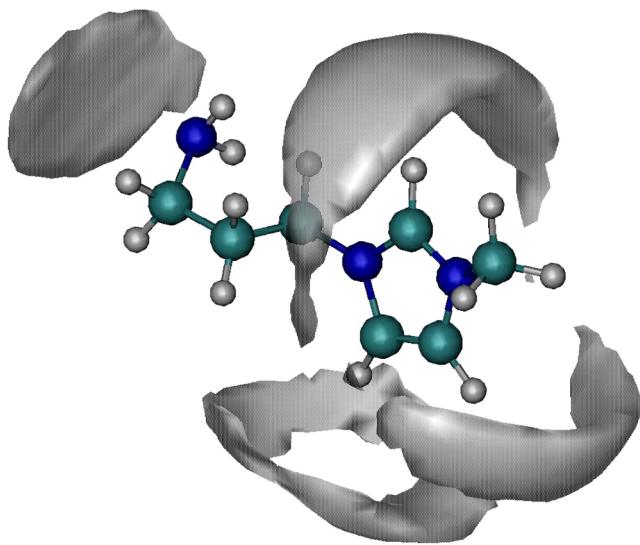
Figure 8 also shows the selected (red lines) intramolecular  $\text{N}_{\text{H}2}\cdots\text{H}_{\text{CR}}$  distances in ( $\sim 2.5$  and  $\sim 5$ )  $\text{\AA}$ , and the bold green intermolecular  $\text{N}_{\text{H}2}\cdots\text{H}_{\text{CR}}$  distances in the range of ( $\sim 2$ – $3$ )  $\text{\AA}$ . Therefore, the first peak of  $g(\text{N}_{\text{H}2}-\text{H}_{\text{CR}})$  with a maximum  $\sim 2.3 \text{ \AA}$  shown in Figure 7 is related to both inter- and intramolecular hydrogen bonding. The main contributions to create the second  $g(r)$  peak with a maximum of  $\sim 5 \text{ \AA}$  or longer are related to the intramolecular structural correlations (e.g., red distances) between tail (- $\text{N}_{\text{H}2}$ ) atoms of side chains of cations with their own key atomic ring sites.

To enhance our intuitive understanding about the liquid structure of ILs, the different view sides of SDFs of the center of masses of  $[\text{Tf}_2\text{N}]^-$  around four imidazolium cations at 400 K are shown by gray density clouds in Figure 9. We also show the cation–cation SDFs (the center of masses of neighboring imidazolium cations around corresponding average configuration of the reference cations) by dark blue density clouds. These SDFs are calculated from analyzing long 7.5 ns

trajectories by the Travis code<sup>110</sup> and visualizing the output using VMD.<sup>111</sup>

The gray probability density cloud representing the spatial distribution of anions around  $[\text{bmim}]^+$  and  $[\text{apmim}]^+$  is roughly similar to the similar observed pattern in the calculated  $\text{C}_{\text{R}}-\text{N}_{\text{an}}$  RDFs in Figure 4. As can be seen in the first column of Figure 9 for  $[\text{apmim}][\text{Tf}_2\text{N}]$  and  $[\text{bmim}][\text{Tf}_2\text{N}]$ , the same main regions with high probability of anion distribution around both of these reference cations at the first shell are the strongly localized gray regions around the  $\text{C}_{\text{R}}$  and  $\text{H}_{\text{CR}}$  atoms in-plane (on top of  $\text{H}_{\text{CR}}$ ) and out-of-plane (both above and below the plane of the ring); the other significant region around the methyl side chain, and finally the region around the  $\text{C}_{\text{W}}$  atoms of the reference cations.

Clear differences for anion spatial distribution around  $[\text{bmmim}]^+$  in comparison with anion distribution around other cations are observed, and C2 methylation extensively affects the preferential locations of anions around  $[\text{bmmim}]^+$ . The clear specific part of the gray density cloud, related to the spatial distribution of anions around the 3-methyl side chain of  $[\text{apmim}]^+$ ,  $[\text{bmim}]^+$ , and to an extent  $[\text{mim}]^+$ , moves to the



**Figure 10.** Calculated spatial distribution function of terminal nitrogen ( $N_{H_2}$ ) atoms of side chains of neighboring cations around a reference  $[apmim]^+$  from MD simulation at 400 K. Specific density clouds of the  $N_{H_2}$  site of neighboring cations near the tail  $N_{H_2}$ ,  $C_R$ ,  $H_{CR}$ , and  $H_{Cw}$  sites of a reference  $[apmim]^+$  are observed.

region between two methyl side chains in  $[bmim]^+$ , and a contradistinctive part of the gray density cloud of anions is observed in the region between the *n*-butyl and 2-methyl side chains of this C2 methylated cation. There are no specific cation–anion interactions. Capping gray density clouds of the anion around C2 and the 2-methyl side chain of  $[bmim]^+$  on top of and in-plane with the imidazolium ring and the capping gray density cloud of anion in-plane with and on top of the C2 sites of  $[apmim]^+$  and  $[bmim]^+$  can be observed. These are better seen in column 3 of Figure 9. Because of exchanging the  $H_{CR}$  atom by a  $CH_3$  group, moving of a  $[Tf_2N]^-$  anion from one face of the  $[bmim]^+$  ring to the other over the top of the ring is difficult,<sup>112</sup> as can be seen no gray density cloud in the top of the 2-methyl side chain of the reference  $[bmim]^+$ .

As seen the gray density cloud for  $[mim][Tf_2N]$  in Figure 9,  $[Tf_2N]^-$  prefer the region around the  $H_{N_{3/8}}$  atom, directly connected to the  $N_A$  site of the imidazolium ring compared to the methyl side chain of the  $[mim]^+$  cation. Similar trends are observed approximately from optimized geometry of single ion pairs from *ab initio* calculations as shown in Figure 2, case g, and it is expected from calculated atomic partial charges for  $[mim]^+$  reported in Table 5 and reflected in the top RDF panel of Figure 5. Distinct gray cloudy regions for each IL in Figure 9 clearly show that both studied ion-pair configurations, types I and II, for each IL in Figure 2 are the main representatives of the possible local minima of cation–anion interactions in the liquid phase of the studied systems.

Comparing of the gray SDFs for  $[apmim][Tf_2N]$  with  $[bmim][Tf_2N]$  in the first column of Figure 9 shows that introducing the amine functional ( $-NH_2$ ) group to the terminal end of the alkyl side chain of imidazolium cation does not significantly affect the organization of  $[Tf_2N]^-$  around  $[apmim]^+$ . This observation is in good agreement with the optimized geometry of single ion pairs and cation–anion ( $C_R-N_{an}$ ) RDFs shown in Figures 2 and 4, respectively.

From another viewpoint, as seen in Figure 10, computing the SDF of terminal nitrogen ( $N_{H_2}$ ) atoms of 3-aminopropyl side chains of neighboring cations around a reference  $[apmim]^+$

shows three main density regions. The clear probability density around the tail  $-N_{H_2}$  site signifies a strong  $N_{H_2}\cdots N_{H_2}$  structural correlation between the tails of 3-aminopropyl side chains of neighboring  $[apmim]^+$  in  $[apmim][Tf_2N]$ . We also show this type of structural correlation in the molecular visualization of selected cations in the upper part of Figure 8. The second probability density semicircular shape region above, in-plane with, and below the central ( $C_R$ ) carbon and  $H_{CR}$ , and the third density cloud around  $C_W$  sites of Figure 10 show similar strong associations of terminal  $N_{H_2}$  sites of neighboring  $[apmim]^+$  with acidic  $H_{CR}$  hydrogen site, the central carbon atom ( $C_R$ ) of the imidazolium ring as well as with  $H_{Cw}$  sites. So there are additional cation–cation  $N_{H_2}$ -based structural correlations (e.g., hydrogen bonding) in  $[apmim][Tf_2N]$  IL compared to unfunctionalized imidazolium ILs. This key point also can be clearly seen in columns 2 and 3 of Figure 9 by focusing on the dark blue density clouds of the center of masses of neighboring cations around the corresponding cation reference for  $[apmim][Tf_2N]$  and  $[bmim][Tf_2N]$ . It is clear that there is a strong dark blue density cloud of  $[apmim]^+$  neighboring cations near the tail of the 3-aminopropyl side chain of reference  $[apmim]^+$ , while no similar density cloud was observed around the tail of butyl side chain of reference  $[bmim]^+$  cation.

Distinct dark blue density clouds of neighboring cations around the reference cation generally are observed at larger radial distances compared to the gray density clouds which show the positions of neighboring anions. There are some low probability regions for the presence of anions (gray density clouds) around each reference cation. These are located near the alkyl chains. Our RDF results showed the first peaks of the cation–cation RDFs are much weaker and positioned at larger separations than that of the anion–cation RDF in Figures 3 and 4. This observation is in agreement with the location of the dark blue cation density cloud compared to the gray anion density cloud around the reference cation. For all studied ILs, two similar dark blue probability density regions can be observed above and below the gray density cloud around the methyl side chain. The strong additional two dark blue density regions above and below the 2-methyl side chain of the reference  $[bmim]^+$  can be observed. However, the strongest dark blue density region above and below the reference imidazolium ring of  $[mim]^+$  represents possibly the best  $\pi\cdots\pi$  stacking for  $[mim][Tf_2N]$ .

#### 4. SUMMARY AND CONCLUSIONS

Molecular dynamics simulations and quantum chemistry calculations of four imidazolium-based  $[Tf_2N]$  ionic liquids under identical computational conditions have been performed to compare the effect of alkyl/functional substituent groups of four imidazolium cations ( $[mim]^+$ ,  $[bmim]^+$ ,  $[bmim]^+$ , and  $[apmim]^+$ ) on the microscopic structure and thermodynamic properties of these ILs. This study focuses on detailed descriptions of the effects of the presence or absence of 1-butyl side chain in methyl-imidazolium cation, C2 methylation, or amine ( $-NH_2$ ) functionalization of the end of the alkyl side chain of imidazolium cation by computational methods.

Analysis of calculated thermodynamic properties from the current simulations shows that replacement of the tail  $-CH_3$  of the butyl group with an  $-NH_2$  in the alkyl side chain of imidazolium cations results in a substantial increase in the density, enthalpy of vaporization, cohesive energy density, and isobaric thermal expansion; however, the different force field used for  $[apmim]^+$  in contrast to the other cations should be

considered when the calculated properties of ILs are compared. The highest thermal expansion coefficient,  $\Delta U_m^{\text{vap}}$ ,  $\Delta H_m^{\text{vap}}$ , and cohesive energy density is observed for [apmim][Tf<sub>2</sub>N] among the four ILs, which is consistent with the nonvolatile nature and more compact structure of amine-functionalized ILs and indicates the strong ionic interaction in the liquid bulk phase of [apmim][Tf<sub>2</sub>N].

We also find that C2 methylation of imidazolium cation results in an increase of the molar volume and thermal expansion coefficient and a decrease of the density and cohesive energy density. Additionally, we simulate [mim][Tf<sub>2</sub>N] for the first time and compare the predicted thermodynamics properties of this IL with [bmim][Tf<sub>2</sub>N]. A significant increasing of the molar volume, enthalpy of vaporization, and thermal expansion coefficient and decreasing of density and cohesive energy density with increasing of alkyl chain length is observed from [mim]<sup>+</sup> to the [bmim]<sup>+</sup>. The lengthening of the alkyl chain causes a dispersion of the charge centers and weakening of the electrostatic attractions between the cations and anions but enhances the total strength of the van der Waals interactions. The ionic liquid [mim][Tf<sub>2</sub>N] has a significantly lower free volume, the highest density and ionic accumulation, the closest cation–anion average distance, the lowest enthalpy of vaporization and isobaric thermal expansion coefficient, and the strongest single ion pair quantum interaction energy between four ionic liquids.

Some structural details of ILs from *ab initio* studies of two main possible ion-pair configurations and MD simulations of the bulk liquid phase are consistent with each other. The *ab initio* studies of type I configurations show that the [Tf<sub>2</sub>N]<sup>-</sup> anions prefer to have close in-plane contact (directional hydrogen bonds) with the C2–H of the imidazolium ring in [apmim][Tf<sub>2</sub>N] and [bmim][Tf<sub>2</sub>N] ILs, and the nitrogen site of [Tf<sub>2</sub>N]<sup>-</sup> occupies positions not only in-plane with the cation ring but also above the H<sub>CR</sub> site. For [mim][Tf<sub>2</sub>N], the nitrogen site of [Tf<sub>2</sub>N]<sup>-</sup> occupies positions in-plane with the cation ring, but not exactly on top of the H<sub>CR</sub> site and on top of the middle region of H<sub>CR</sub> and H<sub>N3/8</sub>. In the absence of the *n*-butyl side chain in the cation, the O···H<sub>N3/8</sub> distance is 1.733 Å, and a strong hydrogen bond between the O site of [Tf<sub>2</sub>N]<sup>-</sup> and the H<sub>N3/8</sub> site of [mim]<sup>+</sup> is formed. The C2 methylation blocks the in-plane anion–cation interaction, and [Tf<sub>2</sub>N]<sup>-</sup> and [bmim]<sup>+</sup> prefer to orient out-of-plane adjacent to each other, as shown in the case e in type I configuration. Although study of the optimized type II configurations of all ILs shows similar hydrogen bonds between the H<sub>CW</sub> sites of cations and nitrogen or oxygen sites of [Tf<sub>2</sub>N]<sup>-</sup> counterions. Indeed, this type II cation–anion orientation is relatively independent of the type of alkyl side chain of the imidazolium cations, in agreement with the corresponding RDF plots.

The *ab initio* calculations of ion pairs and the simulated cation–anion RDF and SDF clearly show that amine functionalization of the end of alkyl side chain of imidazolium cation does not significantly affect the organization of [Tf<sub>2</sub>N]<sup>-</sup> around [apmim]<sup>+</sup>, while C2 methylation extensively affects preferential locations of [Tf<sub>2</sub>N]<sup>-</sup> around [bmim]<sup>+</sup>. Other analyses from the results of computing of atomic partial charges, visualization of chosen neighbor cations from the simulation box, the N<sub>H2</sub>–N<sub>H2</sub> and N<sub>H2</sub>–H<sub>CR</sub> RDFs, and the SDF of terminal N<sub>H2</sub> atoms of 3-aminopropyl side chains of cationic neighbors around a reference [apmim]<sup>+</sup> show the existing effective additional short-ranged cation–cation structural correlations (e.g., hydrogen bonds) between the tail NH<sub>2</sub>

sites of 3-aminopropyl side chains of neighboring cations as well as between tail NH<sub>2</sub> sites with the C<sub>R</sub>, H<sub>CR</sub> or H<sub>CW</sub> sites of the imidazolium ring in the liquid phase of [apmim][Tf<sub>2</sub>N]. The amine functionalization of the tail of butyl side chain results in a slight increase in ionic accumulation and the interaction energy of [apmim][Tf<sub>2</sub>N] compared to [bmim][Tf<sub>2</sub>N] IL.

By intuitive comparison of calculated anion–cation and cation–cation SDFs, the differences in the high probability density regions of first shell neighbor anions or cations around the reference cations of studied ILs are presented. The regions with additional probability density for the location of the [bmim]<sup>+</sup> and [mim]<sup>+</sup> cations around the reference corresponding cations in comparison with two other ILs can be observed.

In future work, we will study the effects of alkyl/functional substituent groups in the cations on the dynamics and transport properties of this family of ionic liquids. In particular, the calculated values of self-diffusion coefficient, ionic conductivity, and viscosity will be presented.

## ■ ASSOCIATED CONTENT

### **S Supporting Information**

Text providing the summary of recent studies on C2 methylation of imidazolium ILs, the molar volume as a function of temperature at 1 atm for four ILs, comparison of the computed value of  $\Delta H_{\text{vap}}$  of [bmim][Tf<sub>2</sub>N] in this simulation study with available literature data, and accompanying references and a figure showing the calculated molar volumes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### **Notes**

The authors declare no competing financial interest.

## ■ REFERENCES

- (1) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, Germany, 2002.
- (2) Zhao, Y. N.; Yang, Z. Z.; Luo, S. H.; He, L. N. *Design of Task-Specific Ionic Liquids for Catalytic Conversion of CO<sub>2</sub> with Aziridines Under Mild Condition*. *Catal. Today* **2013**, *200*, 2–8.
- (3) Welton, T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, *99*, 2071–2084.
- (4) Han, D.; Row, K. H. Recent Applications of Ionic Liquids in Separation Technology. *Molecules* **2010**, *15*, 2405–2426.
- (5) Van Valkenburg, M. E.; Vaughn, R. L.; Williams, M.; Wilkes, J. S. Thermochemistry of Ionic Liquid Heat-Transfer Fluids. *Thermochim. Acta* **2005**, *425*, 181–188.

- (6) Castner, E. W.; Wishart, J. F. Spotlight on Ionic Liquids. *J. Chem. Phys.* **2010**, *132*, 120901–120909.
- (7) Weingärtner, H. Understanding Ionic Liquids at the Molecular Level: Facts, Problems, and Controversies. *Angew. Chem., Int. Ed.* **2008**, *47*, 654–670.
- (8) Hallett, J. P.; Welton, T. Room-Temperature Ionic Liquids: Solvents for Synthesis and Catalysis. *Chem. Rev.* **2011**, *111*, 3508–3576.
- (9) Maginn, E. J. Molecular Simulation of Ionic Liquids: Current Status and Future Opportunities. *J. Phys.: Condens. Matter* **2009**, *21*, No. 373101.
- (10) Maginn, E. J. Atomistic Simulation of Ionic Liquids. In *Reviews in Computational Chemistry*, Vol. 26; Lipkowitz, K. B., Cundari, T. R., Eds.; John Wiley & Sons, Hoboken, NJ, USA, 2009; DOI: 10.1002/9780470399545.ch8.
- (11) Endres, F.; Zein El Abedin, S. *Air and water Stable Ionic Liquids in Physical Chemistry. Phys. Chem. Chem. Phys.* **2006**, *8*, 2101–2116.
- (12) Ludwig, R.; Maginn, E. J.; Balasubramanian, S. Ionic Liquids. *ChemPhysChem* **2012**, *13*, 1601–1963 (Editorial, May 14 Special Issue).
- (13) Rogers, R. D.; Voth, G. A., Guest Eds. Ionic Liquids, *Acc. Chem. Res.* **2007**, *40*, 1077–1236 (November Special Issue).
- (14) Wishart, J. F.; Castner, E. W. Ionic Liquids. *J. Phys. Chem. B* **2007**, *111*, 4639–5029 (Editorial, May 10 Issue).
- (15) Enders, F. Ionic Liquids. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1648–2032 (Editorial, Themed Issue).
- (16) Plechko, N. V.; Seddon, K. R. Applications of Ionic Liquids in the Chemical Industry. *Chem. Soc. Rev.* **2008**, *37*, 123–150.
- (17) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H. CO<sub>2</sub> Capture by a Task-Specific Ionic Liquid. *J. Am. Chem. Soc.* **2002**, *124*, 926–927.
- (18) Zhu, A. L.; Jiang, T.; Han, B. X.; Huang, J.; Zhang, J. C.; Ma, X. M. Study on Guanidine-Based Task-Specific Ionic Liquids as Catalysts for Direct Aldol Reactions Without Solvent. *New J. Chem.* **2006**, *30*, 736–740.
- (19) Lee, S. G. Functionalized Imidazolium Salts for Task-Specific Ionic Liquids and their Applications. *Chem. Commun. (Cambridge, U. K.)* **2006**, 1049–1063.
- (20) Wang, C. M.; Luo, H. M.; Jiang, D. E.; Li, H. R.; Dai, S. Carbon Dioxide Capture by Superbase-Derived Protic Ionic Liquids. *Angew. Chem., Int. Ed.* **2010**, *49*, 5978–5981.
- (21) Giernoth, R. Task-Specific Ionic Liquids. *Angew. Chem., Int. Ed.* **2010**, *49*, 2834–2939.
- (22) Kowsari, M. H.; Alavi, S.; Najafi, B.; Gholizadeh, K.; Dehghanpisheh, E.; Ranjbar, F. Molecular Dynamics Simulations of the Structure and Transport Properties of Tetra-butylphosphonium Amino Acid Ionic Liquids. *Phys. Chem. Chem. Phys.* **2011**, *13*, 8826–8837.
- (23) Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. Thermophysical Properties of Imidazolium-Based Ionic Liquids. *J. Chem. Eng. Data* **2004**, *49*, 954–964.
- (24) Holbrey, J. D.; Reichert, W. M.; Rogers, R. D. Crystal Structures of Imidazolium Bis(trifluoromethanesulfonyl)imide ‘Ionic Liquid’ Salts: the First Organic Salt with a cis-TFSI Anion Conformation. *Dalton Trans.* **2004**, *15*, 2267–2271.
- (25) Ohno, H. *Electrochemical Aspects of Ionic Liquids*; Wiley Interscience, Hoboken, NJ, USA, 2005.
- (26) Andriyko, Y. O.; Reischl, W.; Nauer, G. E. Trialkyl-Substituted Imidazolium-Based Ionic Liquids for Electrochemical Applications: Basic Physicochemical Properties. *J. Chem. Eng. Data* **2009**, *54*, 855–860.
- (27) Fuller, J.; Carlin, R. T.; Osteryoung, R. A. The Room Temperature Ionic Liquid 1-Ethyl-3-methylimidazolium Tetrafluoroborate: Electrochemical Couples and Physical Properties. *J. Electrochem. Soc.* **1997**, *144*, 3881–3886.
- (28) Koch, V. R.; Nanjundiah, C.; Appetecchi, G. B.; Scrosati, B. The Interfacial Stability of Li with Two New Solvent-Free Ionic Liquids: 1,2-Dimethyl-3-propylimidazolium Imide and Methide. *J. Electrochem. Soc.* **1995**, *142*, L116–L118.
- (29) Bazito, F. F.; Kawano, C. Y.; Torresi, R. M. Synthesis and Characterization of Two Ionic Liquids with Emphasis on their Chemical Stability Towards Metallic Lithium. *Electrochim. Acta* **2007**, *52*, 6427–6437.
- (30) Hayashi, K.; Nemoto, Y.; Akuto, K.; Sakurai, Y. Alkylated imidazolium salt electrolyte for lithium cells. *J. Power Sources* **2005**, *146*, 689–692.
- (31) Koch, V. R.; Dominey, L. A.; Nanjundiah, C.; Ondrechen, M. J. The Intrinsic Anodic Stability of Several Anions Comprising Solvent-Free Ionic Liquids. *J. Electrochem. Soc.* **1996**, *143*, 798–803.
- (32) Sutto, T. E. The Electrochemical Behavior of Trialkylimidazolium Imide Based Ionic Liquids and Their Polymer Gel Electrolytes. *J. Electrochem. Soc.* **2007**, *154*, P130–P135.
- (33) Endo, T.; Imanari, M.; Seki, H.; Nishikawa, K. Effects of Methylation at Position 2 of Cation Ring on Rotational Dynamics of Imidazolium-Based Ionic Liquids Investigated by NMR Spectroscopy: [C<sub>4</sub>mim]Br vs [C<sub>4</sub>C<sub>1</sub>mim]Br. *J. Phys. Chem. A* **2011**, *115*, 2999–3005.
- (34) Hunt, P. A. Why Does a Reduction in Hydrogen Bonding Lead to an Increase in Viscosity for the 1-Butyl-2,3-dimethyl-imidazolium-Based Ionic Liquids? *J. Phys. Chem. B* **2007**, *111*, 4844–4853.
- (35) Fumino, K.; Wulf, A.; Ludwig, R. Strong, Localized, and Directional Hydrogen Bonds Fluidize Ionic Liquids. *Angew. Chem., Int. Ed.* **2008**, *47*, 8731–8734.
- (36) Liu, H.; Maginn, E. J.; Visser, A. E.; Bridges, N. J.; Fox, E. B. Thermal and Transport Properties of Six Ionic Liquids: An Experimental and Molecular Dynamics Study. *Ind. Eng. Chem. Res.* **2012**, *51*, 7242–7254.
- (37) Izgorodina, E. I.; Maganti, R.; Armel, V.; Dean, P. M.; Pringle, J. M.; Seddon, K. R.; MacFarlane, D. R. Understanding the Effect of the C2 Proton in Promoting Low Viscosities and High Conductivities in Imidazolium-Based Ionic Liquids: Part I. Weakly Coordinating Anions. *J. Phys. Chem. B* **2011**, *115*, 14688–14697.
- (38) Borodin, O. Polarizable Force Field Development and Molecular Dynamics Simulations of Ionic Liquids. *J. Phys. Chem. B* **2009**, *113*, 11463–11478.
- (39) Mukai, T.; Yoshio, M.; Kato, T.; Ohno, H. Effect of Methyl Groups onto Imidazolium Cation Ring on Liquid Crystallinity and Ionic Conductivity of Amphiphilic Ionic Liquids. *Chem. Lett.* **2004**, *33*, 1630–1631.
- (40) Mele, A.; Romanò, G.; Giannone, M.; Ragg, E.; Fronza, G.; Raos, G.; Marcon, V. he Local Structure of Ionic Liquids: Cation–Cation NOE Interactions and Internuclear Distances in Neat [BMIM][BF<sub>4</sub>] and [BDMIM][BF<sub>4</sub>]. *Angew. Chem., Int. Ed.* **2006**, *45*, 1123–1126.
- (41) Lohse, P. W.; Büsing, R.; Lenzer, T.; Oum, K. Exploring 12'-Apo-β-carotenoic-12'-acid as an Ultrafast Polarity Probe for Ionic Liquids. *J. Phys. Chem. B* **2008**, *112*, 3048–3057.
- (42) Freire, M. G.; Garvalho, P. J.; Fernandes, A. M.; Marrucho, I. M.; Queimada, A. J.; Coutinho, J. A. P. Surface Tensions of Imidazolium Based Ionic Liquids: Anion, Cation, Temperature and Water Effect. *J. Colloid Interface Sci.* **2007**, *314*, 621–630.
- (43) Bonhôte, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts. *Inorg. Chem.* **1996**, *35*, 1168–1178.
- (44) Larsen, A. S.; Holbrey, J. D.; Tham, F. S.; Reed, C. A. Designing Ionic Liquids: Imidazolium Melts with Inert Carborane Anions. *J. Am. Chem. Soc.* **2000**, *122*, 7264–7272.
- (45) Fox, D. M.; Awad, W. H.; Gilman, J. W.; Maupin, P. H.; De Long, H. C.; Trulove, P. C. Flammability, Thermal Stability, and Phase Change Characteristics of Several Trialkylimidazolium Salts. *Green Chem.* **2003**, *5*, 724–727.
- (46) Kölle, P.; Drönkowsky, R. Synthesis, Crystal Structures and Electrical Conductivities of the Ionic Liquid Compounds Butyldimethylimidazolium Tetrafluoroborate, Hexafluorophosphate and Hexafluoroantimonate. *Eur. J. Inorg. Chem.* **2004**, *11*, 2313–2320.
- (47) Yoshida, Y.; Baba, O.; Larriba, C.; Saito, G. Imidazolium-Based Ionic Liquids Formed with Dicyanamide Anion: Influence of Cationic Structure on Ionic Conductivity. *J. Phys. Chem. B* **2007**, *111*, 12204–12210.

- (48) Zhu, J.; Bai, L.; Chen, B.; Fei, W. Thermodynamical Properties of Phase Change Materials Based on Ionic Liquids. *J. Chem. Eng.* **2009**, *147*, 58–62.
- (49) Noack, K.; Schulz, P. S.; Paape, N.; Kiefer, J.; Wasserscheid, P.; Leipertz, A. The Role of the C2 Position in Interionic Interactions of Imidazolium Based Ionic Liquids: a Vibrational and NMR Spectroscopic Study. *Phys. Chem. Chem. Phys.* **2010**, *12*, 14153–14161.
- (50) Strehmel, V.; Laschewsky, A.; Wetzel, H.; Gornitz, E. Free Radical Polymerization of n-Butyl Methacrylate in Ionic Liquids. *Macromolecules* **2006**, *39*, 923–930.
- (51) Malham, I. B.; Turmine, M. Viscosities and Refractive Indices of Binary Mixtures of 1-Butyl-3-methylimidazolium Tetrafluoroborate and 1-Butyl-2,3-dimethylimidazolium Tetrafluoroborate with Water at 298 K. *J. Chem. Thermodyn.* **2008**, *40*, 718–723.
- (52) Awad, W. H.; Gilman, J. W.; Nyden, M.; Harris, R. H., Jr.; Sutto, T. E.; Callahan, J.; Trulove, P. C.; DeLong, H. C.; Fox, D. M. Thermal Degradation Studies of Alkyl-imidazolium Salts and Their Application in Nanocomposites. *Thermochim. Acta* **2004**, *409*, 3–11.
- (53) Handy, S. T.; Okello, M. The 2-Position of Imidazolium Ionic Liquids: Substitution and Exchange. *J. Org. Chem.* **2005**, *70*, 1915–1918.
- (54) Luo, H.; Baker, G. A.; Dai, S. Isothermogravimetric Determination of the Enthalpies of Vaporization of 1-Alkyl-3-methylimidazolium Ionic Liquids. *J. Phys. Chem. B* **2008**, *112*, 10077–10081.
- (55) Monteiro, M. J.; Bazito, F. F. C.; Siqueira, L. J. A.; Ribeiro, M. C. C.; Torresi, R. M. Transport Coefficients, Raman Spectroscopy, and Computer Simulation of Lithium Salt Solutions in an Ionic Liquid. *J. Phys. Chem. B* **2008**, *112*, 2102–2109.
- (56) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785–789.
- (57) Peppel, T.; Roth, C.; Paschek, D.; Köckerling, M.; Ludwig, R. The Influence of Hydrogen-Bond Defects on the Properties of Ionic Liquids. *Angew. Chem., Int. Ed.* **2011**, *50*, 6661–6665.
- (58) Wulf, A.; Fumino, K.; Ludwig, R. Spektroskopischer Nachweis einer verstärkten Anion-KationWechselwirkung durch H-Bräcken in reinen ionischen Flüssigkeiten auf Imidazolumbasis. *Angew. Chem.* **2010**, *122*, 459–463.
- (59) Endo, T.; Kato, T.; Nishikawa, K. Effects of Methylation at the 2 Position of the Cation Ring on Phase Behaviors and Conformational Structures of Imidazolium-Based Ionic Liquids. *J. Phys. Chem. B* **2010**, *114*, 9201–9208.
- (60) Zhang, Y.; Maginn, E. The Effect of C2 Substitution on Melting Point and Liquid Phase Dynamics of Imidazolium Based-Ionic Liquids: Insights from Molecular Dynamics Simulations. *J. Phys. Chem. Chem. Phys.* **2012**, *14*, 12157–12164.
- (61) Zhang, S.; Zhou, G.; Liu, X.; Chen, X. Structure, Interaction and Property of Amino-Functionalized Imidazolium ILs by Molecular Dynamics Simulation and ab Initio Calculation. *AIChE J.* **2007**, *53*, 3210–3221.
- (62) Gutowski, K. E.; Maginn, E. J. Amine-Functionalized Task-Specific Ionic Liquids: A Mechanistic Explanation for the Dramatic Increase in Viscosity Upon Complexation with CO<sub>2</sub> from Molecular Simulation. *J. Am. Chem. Soc.* **2008**, *130*, 14690–14704.
- (63) Liu, X.; Zhou, G.; Zhang, S.; Yao, X. Molecular Dynamics Simulation of Dual Amino-Functionalized Imidazolium-Based Ionic Liquids. *Fluid Phase Equilib.* **2009**, *284*, 44–49.
- (64) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. *GAUSSIAN 03* (Revision C.02); Gaussian: Wallingford, CT, USA2004.
- (65) Tsuzuki, S.; Shinoda, W.; Saito, H.; Mikami, M.; Tokuda, H.; Watanabe, M. Molecular Dynamics Simulations of Ionic Liquids: Cation and Anion Dependence of Self-Diffusion Coefficients of Ions. *J. Phys. Chem. B* **2009**, *113*, 10641–10649.
- (66) Canongia Lopes, J. N.; Deschamps, J.; Pádua, A. A. H. Modeling Ionic Liquids Using a Systematic All-Atom Force Field. *J. Phys. Chem. B* **2004**, *108*, 2038–2047.
- (67) Canongia Lopes, J. N.; Pádua, A. A. H. Molecular Force Field for Ionic Liquids Composed of Triflate or Bistriflylimide Anions. *J. Phys. Chem. B* **2004**, *108*, 16893–16898.
- (68) Canongia Lopes, J. N.; Pádua, A. A. H.; Shimizu, K. Molecular Force Field for Ionic Liquids IV: Trialkylimidazolium and Alkoxycarbonyl-Imidazolium Cations; Alkylsulfonate and Alkylsulfate Anions. *J. Phys. Chem. B* **2008**, *112*, 5039–5046.
- (69) MacKerell, A. D., Jr.; Wiórkiewicz-Kuczera, J.; Karplus, M. An All-Atom Empirical Energy Function for the Simulation of Nucleic Acids. *J. Am. Chem. Soc.* **1995**, *117*, 11946–11975.
- (70) Cadena, C.; Anthony, J. L.; Shah, J. K.; Morrow, T. I.; Brennecke, J. F.; Maginn, E. J. Why Is CO<sub>2</sub> So Soluble in Imidazolium-Based Ionic Liquids? *J. Am. Chem. Soc.* **2004**, *126*, 5300–5308.
- (71) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon: Oxford, U.K., 1987.
- (72) Smith, W.; Forester, T. R.; Todorov, I. T. *The DL\_POLY Molecular Simulation Package*, v. 2.18; Daresbury Laboratory: Daresbury, U.K., 2007.
- (73) Nosé, S. A Unified Formulation of the Constant Temperature Molecular Dynamics Methods. *J. Chem. Phys.* **1984**, *81*, 511–519.
- (74) Hoover, W. G. Canonical Dynamics: Equilibrium Phase-Space Distributions. *Phys. Rev. A* **1985**, *31*, 1695–1697.
- (75) Maginn, E. J. Atomistic Simulation of the Thermodynamic and Transport Properties of Ionic Liquids. *Acc. Chem. Res.* **2007**, *40*, 1200–1207.
- (76) Bedrov, D.; Borodin, O.; Li, Z.; Smith, G. D. Influence of Polarization on Structural, Thermodynamic, and Dynamic Properties of Ionic Liquids Obtained from Molecular Dynamics Simulations. *J. Phys. Chem. B* **2010**, *114*, 4984–4997.
- (77) Dzyuba, S. V.; Bartsch, R. A. Influence of Structural Variations in 1-Alkyl(aralkyl)-3-methylimidazolium Hexafluorophosphates and Bis(trifluoromethylsulfonyl)imides on Physical Properties of the Ionic Liquids. *ChemPhysChem* **2002**, *3*, 161–166.
- (78) Harris, K. R.; Kanakubo, M.; Woolf, L. A. Temperature and Pressure Dependence of the Viscosity of the Ionic Liquids 1-Hexyl-3-methylimidazolium Hexafluorophosphate and 1-Butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide. *J. Chem. Eng. Data* **2007**, *52*, 1080–1085.
- (79) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. Physicochemical Properties and Structures of Room Temperature Ionic Liquids. 1. Variation of Anionic Species. *J. Phys. Chem. B* **2004**, *108*, 16593–16600.
- (80) Andreussi, O.; Marzari, N. Transport Properties of Room Temperature Ionic Liquids from Classical Molecular Dynamics. *J. Chem. Phys.* **2012**, *137*, No. 044508.
- (81) Kowsari, M. H.; Alavi, S.; Ashrafizaadeh, M.; Najafi, B. Molecular Dynamics Simulation of Imidazolium-Based Ionic Liquids. I. Dynamics and Diffusion Coefficient. *J. Chem. Phys.* **2008**, *129*, No. 224508.
- (82) Podgoršek, A.; Salas, G.; Campbell, P. S.; Santini, C. C.; Pádua, A. A. H.; Gomes, M. F. C.; Fenet, B.; Chauvin, Y. Influence of Ionic Association, Transport Properties, and Solvation on the Catalytic Hydrogenation of 1,3-Cyclohexadiene in Ionic Liquids. *J. Phys. Chem. B* **2011**, *115*, 12150–12156.

- (83) Liu, H.; Maginn, E. J. A Molecular Dynamics Investigation of the Structural and Dynamic Properties of the Ionic Liquid 1-n-Butyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide. *J. Chem. Phys.* **2011**, *135*, No. 124507.
- (84) Cadena, C.; Maginn, E. J. Molecular Simulation Study of Some Thermophysical and Transport Properties of Triazolium-Based Ionic Liquids. *J. Phys. Chem. B* **2006**, *110*, 18026–18039.
- (85) Androulaki, E.; Vergadou, N.; Ramos, J.; Economou, I. G. Structure, Thermodynamic and Transport Properties of Imidazolium-Based Bis(trifluoromethylsulfonyl)imide Ionic Liquids from Molecular Dynamics Simulations. *Mol. Phys.* **2012**, *110*, 1139–1152.
- (86) Gomes de Azevedo, R.; Esperanca, J. M. S. S.; Szydlowski, J.; Visak, Z. P.; Pires, P. F. H.; Guedes, J. R.; Rebelo, L. P. N. Thermophysical and Thermodynamic Properties of Ionic Liquids Over an Extended Pressure Range: [bmim][NTf<sub>2</sub>] and [hmim][NTf<sub>2</sub>]. *J. Chem. Thermodyn.* **2005**, *37*, 888–899.
- (87) Logothetis, G. E.; Ramos, J.; Economou, I. G. Molecular Modeling of Imidazolium-Based [Tf<sub>2</sub>N<sup>-</sup>] Ionic Liquids: Microscopic Structure, Thermodynamic and Dynamic Properties, and Segmental Dynamics. *J. Phys. Chem. B* **2009**, *113*, 7211–7224.
- (88) Sambasivarao, S. V.; Acevedo, O. Development of OPLS-AA Force Field Parameters for 68 Unique Ionic Liquids. *J. Chem. Theory Comput.* **2009**, *5*, 1038–1050.
- (89) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. Development and Testing of the OPLS All-Atom Force Field on Conformational Energies and Properties of Organic Liquids. *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236.
- (90) Rebelo, L. P. N.; Canongia Lopes, J. N.; Esperança, J. M. S. S.; Filipe, E. On the Critical Temperature, Normal Boiling Point, and Vapor Pressure of Ionic Liquids. *J. Phys. Chem. B* **2005**, *109*, 6040–6043.
- (91) Zhong, X.; Liu, Z.; Cao, D. Improved Classical United-Atom Force Field for Imidazolium-Based Ionic Liquids: Tetrafluoroborate, Hexafluorophosphate, Methylsulfate, Trifluoromethylsulfonate, Acetate, Trifluoroacetate, and Bis(trifluoromethylsulfonyl)amide. *J. Phys. Chem. B* **2011**, *115*, 10027–10040.
- (92) Liu, Z. P.; Wu, X. P.; Wang, W. C. A Novel United-Atom Force Field for Imidazolium-Based Ionic Liquids. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1096–1104.
- (93) Zaitsau, D. H.; Kabo, G. J.; Strechan, A. A.; Paulechka, Y. U.; Tschersich, A.; Verevkin, S. P.; Heintz, A. Experimental Vapor Pressures of 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imides and a Correlation Scheme for Estimation of Vaporization Enthalpies of Ionic Liquids. *J. Phys. Chem. A* **2006**, *110*, 7303–7306.
- (94) Armstrong, J. P.; Hurst, C.; Jones, R. G.; Licence, P.; Lovelock, K. R. J.; Satterley, C. J.; Villar-Garcia, I. Vapourisation of Ionic Liquids. *Phys. Chem. Chem. Phys.* **2007**, *9*, 982–990.
- (95) Santos, L. M. N. B. F.; Canongia Lopes, J. N.; Coutinho, J. A. P.; Esperança, J. M. S. S. L.; Gomes, R.; Marrucho, I. M.; Rebelo, L. P. N. Ionic Liquids: First Direct Determination of their Cohesive Energy. *J. Am. Chem. Soc.* **2007**, *129*, 284–285.
- (96) Shimizu, K.; Tariq, M.; Costa Gomes, M. F.; Rebelo, L. P. N.; Canongia Lopes, J. N. Assessing the Dispersive and Electrostatic Components of the Cohesive Energy of Ionic Liquids Using Molecular Dynamics Simulations and Molar Refraction Data. *J. Phys. Chem. B* **2010**, *114*, 5831–5834.
- (97) Borodin, O. Relation between Heat of Vaporization, Ion Transport, Molar Volume, and Cation-Anion Binding Energy for Ionic Liquids. *J. Phys. Chem. B* **2009**, *113*, 12353–12357.
- (98) Köddermann, T.; Paschek, D.; Ludwig, R. Molecular Dynamic Simulations of Ionic Liquids: A Reliable Description of Structure, Thermodynamics and Dynamics. *ChemPhysChem* **2007**, *8*, 2464–2470.
- (99) Kelkar, M. S.; Maginn, E. J. Calculating the Enthalpy of Vaporization for Ionic Liquid Clusters. *J. Phys. Chem. B* **2007**, *111*, 9424–9427.
- (100) Alavi, S.; Thompson, D. L. Molecular Dynamics Studies of Melting and Some Liquid-State Properties of 1-Ethyl-3-methylimidazolium Hexafluorophosphate [emim][PF<sub>6</sub>]. *J. Chem. Phys.* **2005**, *122*, No. 154704.
- (101) Meng, Z.; Dolle, A.; Carper, W. Gas Phase Model of an Ionic Liquid: Semi-Empirical and ab Initio Bonding and Molecular Structure. *J. Mol. Struct. (THEOCHEM)* **2002**, *585*, 119–128.
- (102) Turner, E. A.; Pye, C. C.; Singer, R. D. Use of ab Initio Calculations toward the Rational Design of Room Temperature Ionic Liquids. *J. Phys. Chem. A* **2003**, *107*, 2277–2288.
- (103) Hunt, P. A.; Kirchner, B.; Welton, T. Characterising the Electronic Structure of Ionic Liquids: An Examination of the 1-Butyl-3-Methylimidazolium Chloride Ion Pair. *Chem.—Eur. J.* **2006**, *12*, 6762–6775.
- (104) Gong, L.; Guo, W.; Xiong, J.; Li, R.; Wu, X.; Li, W. Structures and Stability of Ionic Liquid Model with Imidazole and Hydrogen Fluorides Chains: Density Functional Theory Study. *Chem. Phys. Lett.* **2006**, *425*, 167–178.
- (105) Hunt, P. A.; Gould, I. R. Structural Characterization of the 1-Butyl-3-methylimidazolium Chloride Ion Pair Using ab Initio Methods. *J. Phys. Chem. A* **2006**, *110*, 2269–2282.
- (106) Dong, K.; Zhang, S.; Wang, D.; Yao, X. Hydrogen Bonds in Imidazolium Ionic Liquids. *J. Phys. Chem. A* **2006**, *110*, 9775–9782.
- (107) Yu, G. R.; Zhang, S. J.; Yao, X. Q.; Zhang, J. M.; Dong, K.; Dai, W. B.; Mori, R. Design of Task-Specific Ionic Liquids for Capturing CO<sub>2</sub>: A Molecular Orbital Study. *Ind. Eng. Chem. Res.* **2006**, *45*, 2875–2880.
- (108) Paulechka, Y. U.; Kabo, G. L.; Emel'yanenko, V. N. Structure, Conformations, Vibrations, and Ideal-Gas Properties of 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide Ionic Pairs and Constituent Ions. *J. Phys. Chem. B* **2008**, *112*, 15708–15717.
- (109) Stephens, P. J.; Jalkanen, K. J.; Kawiecki, R. W. Theory of Vibrational Rotational Strengths: Comparison of a Priori Theory and Approximate Models. *J. Am. Chem. Soc.* **1990**, *112*, 6518–6529.
- (110) Brehm, M.; Kirchner, B. TRAVIS—A Free Analyzer and Visualizer for Monte Carlo and Molecular Dynamics Trajectories. *J. Chem. Inf. Model.* **2011**, *51*, 2007–2023. The TRAVIS page: <http://www.travis-analyzer.de/>, February 2014.
- (111) Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual molecular dynamics. *J. Mol. Graphics* **1996**, *14*, 33–38. The official VMD page: <http://www.ks.uiuc.edu/Research/vmd/>, February 2014.
- (112) Hooper, J. B.; Starovoytov, O. N.; Borodin, O.; Bedrov, D.; Smith, G. D. Molecular Dynamics Simulation Studies of the Influence of Imidazolium Structure on the Properties of Imidazolium /azide Ionic Liquids. *J. Chem. Phys.* **2012**, *136*, No. 194506.