

# Journal of Nano Simulation

journal homepage: jons.du.ac.ir



# Volume 1, Issue 1, Winter 2025, 44-56 DOI: 10.22128/jons.2025.947.1003

# A multiscale study of Hydrogen bonding in Geminal Dicationic Ionic liquids 1,3- bis[3methylimidazolium-1-yl]butane Halides

# Saeid Yeganegi<sup>1,\*</sup>, Azim Soltanabadi<sup>2</sup>

<sup>1</sup> Department of Physical Chemistry, Faculty of Chemistry, University of Mazandaran, Babolsar, Iran
 <sup>2</sup> Department of Physical Chemistry, Faculty of Chemistry, Razi University, Kermanshah, Iran

# HIGHLIGHTS

# G R A P H I C A L A B S T R A C T

- The study reveals that hydrogen bonding in [C4(mim)2][X]2 is strongest with Cl<sup>-</sup> and weakens with larger halide anions.
- The most stable ion pair adopts a Ushaped configuration with bent imidazolium rings.
- Anion diffusion decreases with increasing size, following the trend  $Cl^- > Br^- > l^-. \label{eq:cl}$
- Interaction energies and spectroscopic data confirm stronger bonding with smaller halide ions.



# ARTICLE INFO

Article history: Received: 2025-03-04 Received in revised form: 2025-05-03 Accepted: 2025-05-24

Available online: 2025-06-23

Keywords: Geminal IL molecular dynamic simulation RDF diffusion interaction electronic structure AIM In this study, the properties of the geminal dicationic ionic liquids (DILs) 1,3- bis[3-methylimidazolium-1-yl] butane halides ( $[C_4(mim)_2][X]_2, X^- = CI^-, Br^- and I^-$ ) were studied using the molecular dynamic simulation (MD) and density functional theory (DFT). The liquid structure of  $[C_4(mim)_2][X]_2$  (X=CI, Br, I) was analyzed by radial distribution function(RDF), dihedral angle distribution of n-butyl side chains in the  $[C_4(mim)_2]^{+2}$  cations, distance between two rings in the  $[C_4(mim)_2]^{+2}$ , spatial distribution function (SDF) and combined distribution function (CDF). The calculated RDFs show that anions spend most of their time around the hydrogens attached to the cation rings. The calculated SDFs show that the halide anions show the highest probability densities around the hydrogen atoms of the imidazolium rings. The calculated diffusion coefficients show that the diffusivities of the anions are one order of magnitude higher than that of cations and other hydrogen atoms. The effects of anion type on the diffusion coefficient were also studied. DFT calculations show that the most stable structure of the cation in the DIL is a U-shaped form, where the rings of cation bend towards each other and anions are close to the atoms of both rings. Our results show that hydrogen bonding is crucial in the interaction between the  $[C_4(mim)_2]^{+2}$  cation and anion atoms in the most stable configurations of an ion pair. These hydrogen bonds were analyzed by the atoms in molecules (AIM) and natural bond orbital (NBO) analysis. The ion pair interactions decrease with increasing the halide atomic weight.

<sup>\*</sup> Email: yeganegi@umz.ac.ir

## 1. Introduction

Ionic liquids (ILs) are simply mixtures of large organic cations and anions that do not pack well and remain liquid at low to moderate temperatures. They are attracting increasing attention in many fields including organic chemistry [1,2], electrochemistry [3-6], catalysis [7-9], physical chemistry and engineering [10-14] with their special physical and chemical properties, such as low vapor pressure, low inflammability, high inherent conductivities, thermal stability, liquidity over a wide temperature range, easy recycling, and being a good solvent for a wide variety of chemical compounds. The physicochemical properties of an ionic liquid vary greatly with the molecular structure, e.g., miscibility with water and organic solvents, melting point, and viscosity [15-17]. Besides, ionic liquids are "designable" as structural modifications in both the cation and anion permit the possibility to design task-specific applications when the ionic liquid contain a specific functionality covalently incorporated in either the cation or anion. A special classes of ionic liquids have been obtained using geminal imidazolium dications [18,19], This class of compounds represents an interesting variation of the cationic partner and may present several advantages over the traditional monocationic ionic liquids in their applications as lubricants [20,21] solvents [22-24] and separation media[25].

Geminal dicationic ILs have higher melting point, wider liquid range, and better thermal stability compared to conventional monocationic ILs. They can be used in the high temperature reactions due to large thermal stability ranges [26-30]. However; it is well known that the deeper and broader knowledge of physical and chemical properties of dicationic ILs is necessary to modify their properties. DILs have received very little attention of researchers compared to the monocationic ILs. Qingbin Liu and *et al.*[31] synthesized a new class of DILs,  $([Cn(min)_2][X]_2, n=1, 4, 6, 8, 12 and X=Cl<sup>-</sup>, l<sup>-</sup> and nft<sub>2</sub><sup>-</sup>) and determined their melting points. Their results show that the melting point of DIL with Cl<sup>-</sup> anion is more than others and melting point of ionic liquids decrease with an increase in the carbon chain length.$ 

Many studies of imidazolium based ILs have considered H-bonding; these include experimental [32-35], classical molecular dynamics[36], ab initio molecular dynamics[37], and quantum chemical studies[38-40]. Recent theoretical[41-43] and experimental studies[44-59] have probed H-bonding in ILs; however, the nature of the interaction between hydrogens of the imidazolium ring and anions has been the subject of controversial discussions in recent years[60-63]. Dieter et al.[64] reported the forming of hydrogen bonds in C2-H...Cl, C4-H...Cl, and C5-H...Cl fragments of [emim]Cl (see Figure 2 for numbering of atoms) by the semi empirical AM1 method. Meng et al.[61] proved the existence of the hydrogen bonds of C-H...F and N-H...F in [bmim]PF<sub>6</sub> using ab initio methods. The existence of hydrogen bonds in a series of 1-alkyl-3-methyl imidazolium hexafluorophosphates ([rmim]PF<sub>6</sub>) has also been found by calculating Raman and IR spectra at the B3LYP/6-311+G-(2d,p) level of DFT theory. Kanzaki et al. [62] studied the ion-ion interaction in 1- ethyl-3-methylimidazolium tetraflouroborate by large angle X ray scattering experiment and MD simulations. They concluded that the characteristics of "weak interaction" of the hydrogens of the rings and anions are considerably different from that of the conventional hydrogen bonds. Dong and Zhanga[63] reviewed the hydrogen bonding in ionic liquids and stated that hydrogen bonds exist in many different ILs and have a crucial effect on their properties.

It has been recognized that the hydrogen bonds have a significant influence on the physical properties of imidazolium ionic liquids; however, most of the simulations were limited to single ionic species and/or single ion-pairs of some specific ionic liquids. Up to our knowledge, there are few quantum mechanical studies on DILS. [64-65] Hui Sun et al.[64] studied geometrical and electronic structures of 1,3-bis[3-methylimidazolium-yl]propane bromide. Bode et al.[65] conducted a theoretical study of the gas phase ionic complexes on the structure of geminal imidazolium bis(trifluoromethylsulfonyl)amide ionic liquids.

In most studies, the interactions between the hydrogen attached to  $C_2$  (see Figure 2 for numbering of atoms) are discussed. In this paper we focused on all possible hydrogen bonding in 1,3- bis[3-methylimidazolium-1-yl]butane halides ([C<sub>4</sub>(mim)<sub>2</sub>][X]<sub>2</sub>, X<sup>-</sup>=halides= Cl<sup>-</sup>, Br<sup>-</sup> and l<sup>-</sup>) dicationic ionic liquid by

the molecular dynamics simulation and quantum chemical calculation. The radial distribution function (RDF), spatial distribution function (SDF), coordination numbers, combined distribution function (CDF) and ion diffusivities calculated by molecular dynamic simulation. Whereas, the most stable configurations, interactions between atoms of an anion and a cation are studied by DFT calculations. The natural bond orbital (NBO) and atoms in molecule (AIM) analyses have been applied to understand the nature of the interactions between atoms of ion pairs. In addition, the effects of ion size on local structure, dynamic properties, interaction energies of ion pairs, and IR and Raman spectra of studied DILs are discussed.

# 2. Computational methods

#### 2.1. Simulation details

The force field used in this work for DILs ( $[C_4(mim)_2][X]_2, X^-$ =halides= CI<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>) DILs was adapted from the all-atom force field developed by Canongia-Lopes et al. [66] based on the OPLS framework. Molecular dynamic simulations have been carried out of three DILs ( $[C_4(mim)_2][X]_2, X = CI^-, Br^$ and I<sup>-</sup>) using DL-POLY code. [67] The initial structure of a cation are derived from the crystallographic X-ray (Figure 1 and Figure 2) of solid 3,3'-Dimethyl-1,1'-(butane-1,4-di-yl)diimidazolium bis-(tetrafluoroborate).[68] The starting configurations were generated randomly with PACKMOL package[69] by placing 120 DILs cations [ $C_4(mim)_2$ ]<sup>+2</sup> and 240 anions (CI<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>) in a very large cubic box.

Simulations were performed using the Nosé–Hoover thermostat and barostat algorithm[70-71]. The relaxation times used for the thermostat and barostat are 0.1 and 0.5 ps respectively. Periodic boundary conditions were employed, and equations of motion were integrated using the Verlet leapfrog scheme.[72] All intermolecular interactions between atoms in the simulation box were calculated within a cutoff distance of  $R_{\text{cutoff}} {=} 14.0$  Å for all simulated systems. The electrostatic long-range interactions were calculated using the Ewald summation method[73] with a precision of  $1 \times 10^{-6}$ . Time step for all of the simulations was set 1.0 fs. All of the simulations were done at P=1.0 atm and T=500 K in order to ensure that all compounds are liquid. The simulations were started in NPT ensemble at a much higher temperature, 800 K and low density. The system was equilibrated for 500 ps, then the temperature was lowered to 500 K in 50K steps where simulations was conducted for 500 ps at each temperature. Finally, a 5ns production simulation after 1ns equilibration at 500 K were performed in NVT ensemble to enhance the statistics of the data averages. The radial distribution function calculated by NVT simulations in which the positions of particles were recorded every 0.2 ps. The starting point of each NVT simulation was an equilibrated final configuration of a relevant NPT simulation. By the end of the equilibration, the total energies and volumes were monitored until the corresponding time series were stationary.



di-yl)diimidazolium bis-(tetrafluoroborate)



Figure 2 The structure of cation  $[C_4(mim)_2]^{2*}$  from crystallography, type and atom number are shown on atom. Atoms which occupy similar positions have same atomic indexes.

## 2.2 Quantum calculation details

For obtaining the equilibrium geometry of the DIL molecules, quantum mechanical calculations are used. First the initial structures of all DIL molecules were established by molecular mechanical method, then the obtained structure were used for a first estimation of the equilibrium geometry as input for the restricted Hartree Fock (RHF) method with the 6-31G(d,p) basis set. It is well known that DFT method [73-74] seems to be an excellent compromise between computational cost and accuracy of the computational results. Furthermore, considering the wide existence of hydrogen bonds in ILs, [75-76] it has been established [77] that hybrid functionals are generally accurate enough to describe the complexes involving strongly ionic hydrogen bonds. Next, the optimized structures at the HF level were used as input for full geometry optimization and electronic properties calculations at the Becke's three parameter hybrid method with LYP correlation (B3LYP)[78] level of DFT with 6-311++G(d,p) basis set for all atoms and DGDZVP [79] for I<sup>-</sup> anion, due to the large atomic number of iodine atom. The interaction energies of the cation and anions for each GIL  $\Delta E_{int}$  are defined as follows:

$$\Delta E_{int} = E_{GIL} - (2E_a - E_c) \tag{1}$$

Where  $E_{GIL}$ ,  $E_a$ , and  $E_c$  are the energies of the geminal ionic liquids, anions, and cation. The zero-point vibrational energy corrections (ZPE) have been obtained within the harmonic approximation, and the basis set superposition error (BSSE) were determined using the counterpoise method[80]. The ion-triplets interactions have been calculated for all optimized structures at the same level of theory and basis set. All calculations were carried out using the Gaussian 09 suites of programs.[81] The structures of dication and ion pair were verified as local minima by the absence of imaginary vibrational frequencies.

To better clarify the nature of the intermolecular H-bonding interactions in the DILs, natural bond orbital (NBO) and Bader atoms in molecule theory (AIM) analyses have also been carried out on the optimized structures[82-83]. Both methods have been widely and successfully used to study hydrogen bonding in various systems. For the NBO analyses, the orbital interactions between the proton donor and proton acceptor can be estimated through the second-order perturbation theory,[82]

$$E(2) = \Delta E_{ij} = q(i)(F_{ij})^2 / (E_i - E_j)$$
<sup>(2)</sup>

Where  $q_i$  is the donor orbital occupancy,  $E_i$  and  $E_j$  are diagonal elements (orbital energies), and  $F_{i,j}$  is the off diagonal NBO Fock matrix element. For the AIM analyses [83], the nature of the H-bonding interaction can be predicted from the topological parameters, such as the electron density, the Laplacian of electron density and bond critical point (BCP).

## 3. Results and discussion

## 3.1 Liquid structure

Densities of ionic liquids are one of the most accurate sources of experimental data. Densities of all three studied DILs were calculated by NPT simulations at 500 K and 1 atm and results are shown in Table 1. According to this Table, densities increase by the increasing atomic weight of anion. The order of densities of DILs, in Table 1, for a particular cation approximately follows the decreasing order of the molecular weight of the anions  $I^{-}>Br^{-}>CI^{-}$ , a similar trend has been observed in mono cationic ILs.[84]

Enthalpy of vaporization  $\Delta H_{vap}$ , also known as the heat of vaporization or heat of evaporation, is the energy required to transform a given quantity of a liquid into gas at a given pressure. It is difficult to measure the enthalpy of vaporization of DILs directly from experiment, since all DILs are non-volatile. The enthalpy of vaporization,  $\Delta H_{vap}$ , calculated as follows:

```
\Delta H_{vap} = RT - (U_{int} - U_{ion triplet}) 
(3)
```

Where, R is the gas constant, T is the absolute temperature,  $U_{int}$  is the average of energy per mole of an ion triplet in the liquid, and  $U_{ion triplet}$  represents the average internal energy of a neutral ion triplet in the gas state. The  $U_{ion triplet}$  was calculated by simulations of a dictation and two anions in a large simulation box[85].

Unfortunately, the lack of experimental data for heat of vaporizations does not allow a quantitative comparison. However, the simulation studies allow investigation of the contributions of van der Waals and Coulombic interactions on the heats of vaporization. Table 1 shows the calculated  $\Delta H_{vap}$ for three studied DILs as well as van der Waals and coulombic contributions to the interaction of an ionic triplet in the liquid. Due to the strong interactions in DILs, the calculated  $\Delta H_{vap}$  is generally larger than that of the mono cationic ionic liquids.[86-87] The calculated  $\Delta H_{vap}$  in Table 1 decrease in the order Cl<sup>-</sup> > Br<sup>-</sup> > l<sup>-</sup> reflecting the size of the anions which agrees well with the pervious works.[88]

The liquid structures were studied by calculating partial radial distribution functions (RDFs) and spatial distribution function (SDF) of ions over the 5.0 ns of the trajectories at 500 K and 1 atm. The hydrogen atoms of a DIL cation can be partitioned into three main types based on atomic partial charge (on each H atom) and the computed C–H vibrations [89-90], (see Figure 2).

The first type are "ring" hydrogen atoms (st) attached to the aromatic ring (H<sub>9</sub>, H<sub>10</sub> and H<sub>11</sub>). The second type are denoted "first" hydrogen atoms (nd), those closest to the ring; first in the attached substituent groups, H<sub>12</sub>, H<sub>13</sub>, H<sub>14</sub> (methyl), and H<sub>15</sub>,H<sub>16</sub> (the hydrogens of the methylene groups adjacent to the imidazolium rings ) which are named H<sub>0</sub> and H<sub>1</sub> respectively. The third types are denoted "alkyl"

#### H<sub>10</sub> (or H<sub>11</sub>). The RDF of anions around the second type of hydrogen atoms

Table 1 Calculated densities, heats of vaporization, van der Waals and Coulombic contributions to the heats of vaporization in the liquid state at 500 K and 1 atm

DILs	Density(gr/Lit)	$\Delta H_{vap}(kJ/mol)$	$\Delta U_{Coulomb}(kJ/mol)$	$\Delta U_{vdw}(kJ/mol)$
[C4(mim)]2[Cl]2	1.145	278±3	-174±2	-89±3
[C4(mim)]2[Br]2	1.494	253±1	-171±1	-92±1
[C4(mim)]2[I]2	1.868	201±1	-167±1	-53±1

hydrogen atoms (rd) and include all the remaining alkyl group hydrogen atoms

on the butyl or ethyl chains which are shown as  $\mathsf{H}_2\textbf{.}$ 

The calculated RDFs of anion and all hydrogen atom types (H<sub>0</sub>, H<sub>1</sub>, H<sub>2</sub>, H<sub>9</sub>, H<sub>10</sub> and H<sub>11</sub> in Figure 2) for all of the studied DILs are shown in Figure 3. The calculated RDFs for halide anion - the first type of hydrogen atoms (hydrogen atoms attached to the imidazolium rings H<sub>9</sub>, H<sub>10</sub>, and H<sub>11</sub>) are shown in Figure 3a-c, show a first sharp peak about 2.6-2.9 Å and a second broad peak at 5-6.17 Å. The well-defined first peaks at about 2.68-2.88 Å in Figure 3a-c indicate that there is a strong interaction between a first type of hydrogen and the halide anion. <sup>91</sup> However, the differences in the amplitude of the obtained RDFs, indicate that the H<sub>9</sub> has the strongest interaction among the other ring hydrogens. However, by increasing the size of the anion from Cl to I, the intensity of peaks are decreased and the first and second peaks shift to the longer distances due to the size effect of anions as the order of I > Br > CI. According to Canongia-Lopes force filed, C2-H9 atom pair constitutes the largest amount of positive charge on the cation, so it is not surprising that the anion interacts more strongly with that part of the cation. Similar results were observed and reported for imidazolium mono cationic ILs.92



Figure 3 Radial distribution function of a halide anion around the imidazolium ring(a,b,c),  $H_0,H_1(d,e,f)$ and  $H_2$  (g,I,h) for  $[C_4(mim)_2][X]_2$ ,  $X=Cl^-$ ,  $Br^-$  and  $l^-$  ionic liquid at 500 K and 1 atm.

The second peak for H9 RDF at 6.03-6.28 Å can be attributed to the correlation with second anions shell. However, the second peaks for  $H_{10}$  and  $H_{11}$  in Figure 3a-c are much broader and shifted to the smaller distances with respect to that of  $H_9$ . This can be attributed to the fact that the first shell of anions around  $H_{10}$  (or  $H_{11}$ ) has some contribution from the second shell of anions for

 $H_{12}$ ,  $H_{13}$ ,  $H_{14}$  (H<sub>0</sub>) and  $H_{15}$ ,  $H_{16}$  (H<sub>1</sub>) and third type of hydrogen atoms  $H_{17}$ ,  $H_{18}$  (H<sub>2</sub>) are shown in Figure 3d-f and Figure 3g-i, respectively. Accordingly, these RDFs are shorter and broader than the first type hydrogen atoms. However, by changing the anion type from Cl<sup>-</sup> to Br<sup>-</sup> and l<sup>-</sup>, the intensity of the first peaks decreased and the first and second peaks shift to the longer distances.

In summary, the calculated RDFs reveal that the interactions between the halide anions and the hydrogen atoms of the cation decreases in the order of first type hydrogen > second type hydrogen > tried type hydrogens, (types  $1^{st} > 2^{nd} > 3^{rd}$ ) and size of the halide anions  $CI^- \sim Br^- > I^-$ .

Coordination numbers N(r) of halide ions around the hydrogens were obtained by integrating the corresponding RDFs up to the first minimum.

$$N(r) = 4\pi \int_0^{r(min)} \rho g(r) r^2 dr$$
(4)

where  $\rho$  is the total number density and  $R_{min}$  refers to the first minimum in g(r). The first shell coordination numbers of halide and all hydrogen type are calculated and shown in Table 2.

 Table 2 The calculated first shell coordination numbers of halide around all hydrogen types for
  $[C_4(mim)_2][X]_2, X=CI^-, Br^-$  and  $I^-$  ionic liquid at 500 K and 1 atm.

	Cl	Br	I	
H9	3.05	3.03	2.95	
H <sub>10</sub>	2.56	2.58	2.53	
H <sub>11</sub>	2.54	2.57	2.51	
H0(H <sub>12</sub> ,H <sub>13</sub> ,H <sub>14</sub> )	2.53	2.55	2.48	
H1(H15,H16)	2.14	2.20	2.11	
H2(H <sub>17</sub> ,H <sub>18</sub> )	1.75	1.91	1.73	

According to Table 2, coordination number of halides around the hydrogens are as  $H_9>H_{10}>H_{11}>HO(H_{12}, H_{13}, H_{14})>H1(H_{15}, H_{16})>H2(H_{17}, H_{18})$ . So, RDFs and halide coordination numbers show that the anions tend to spend most of their time around the first type hydrogen atoms (hydrogen attached to imidazolium rings) rather than second type and third type hydrogen atoms.

To further characterize the DILs structures, the calculated probability distribution of dihedral angle C7-C8-C8'-C7' in the  $[C_4(mim)_2][X]_2 X=Cl^-$ , Br<sup>-</sup> and I<sup>-</sup> DILs are shown in Figure 4. One can see that the most probable values for the dihedral angles in liquid phase are 75, 180 and 285 degrees.

Figure 5 shows that the most probability distance N1 and N1' in  $[C_4(mim)_2[X]_2 X=CI^-$ , Br<sup>-</sup> and I<sup>-</sup>. The most probable distance of N1 and N1' is 5.9 Å and changing the anion type have no effect on it.

In order to investigate the effect of halide type on the structure, the space distribution functions (SDFs) were computed, which could stand for the probability of finding an atom in the three- dimensional space around a center

ion/molecule. SDFs visualized by the software package Aten[93] are shown in Figures 6 and 7. The spatial distribution of the anion around cation for  $[C_4(mim)_2][X]_2 X=Cl^-$ , Br<sup>-</sup> and l<sup>-</sup> are shown in Figure 6. As expected, the probability of finding anions around the imidazolium rings is higher than that of the alkyl chain and by increasing the size of the anion, probability of finding

anions decreased.



Figure 4 Probability distribution of dihedral angles dihedral angle C7-C8-C8'-C7' in the  $[C_4(mim)_2][X]_2 X=C1^-$ , Br<sup>-</sup> and I<sup>-</sup>.



Figure 5 The most probability of distance N1 and N1' in [C4(mim)2][X]2 X=CI, Br and I see Figure 2.



Figure 6 Spatial distribution functions (SDFs) of anions around the cation for (a)  $[C_4(mim)_2][Cl]_2$ , (b)  $[C_4(mim)_2][Br]_2$  and (c)  $[C_4(mim)_2][1]_2$  at 500 K. The surface is drawn at five times the average density.

To be more specific, the SDFs of the anion around an imidazolium ring for  $[C_4(mim)_2][X]_2 X=CI^-$ , Br<sup>-</sup> and I<sup>-</sup> calculated and shown in Figures 7. The SDFs for  $[C_4(mim)_2][X]_2 X=CI^-$ , Br<sup>-</sup> and I<sup>-</sup> are similar to our previous paper and has already been discussed [88]. The SDFs obtained show that the anion population above and below the imidazolium plane in the  $[C_4(mim)_2][CI]_2$  is larger than that in the  $[C_4(mim)_2][Br]_2$  and  $[C_4(mim)_2][I]_2$  in dicationic ionic liquids and similar to mono cationic ILS[88].

To obtain further insight into the structural of the  $[C_4(mim)_2][X]_2 X=CI^-, Br^$ and  $I^-$ , Combined Distribution Function, (CDF), distribution of the distance between the  $H_9$  ... X and the distribution of the angle formed by  $C_2-H_9-X$  are



Figure 7 Spatial distribution functions (SDFs) of anions around the imidazolium ring for (a):  $[C_4(mim)_2][Cl]_2$ , (b):  $[C_4(mim)_2][Br]_2$  and (c):  $[C_4(mim)_2][l]_2$ . The surface is drawn at 10 (purple) and 5 (blue) times the average density. The second imidazolium ring and the hydrogens of the alkyl chains are not shown for clarity.

calculated and shown in Figure 8. This CDF correlates the distance between the H<sub>9</sub>–X and distribution of the angle formed by C<sub>2</sub>–H<sub>9</sub>–X. The region of maximum occurrence in the contour plot corresponds to the distance range from 2.5 to 2.9 Å and to the angular interval of 140–160 degrees. The second region of maximum of SDFs for H<sub>9</sub> – X at 6 to 6.5 Å, can be attributed to the correlation with second shell halides.



Figure 8 (a) Definition distance H<sub>9</sub>...X, and angle C2–H<sub>9</sub>...X, (X=Cl,Br,I) for Combined radial/angular distribution analysis; (b), (c) and (d) combined radial/angular distribution functions between  $[C_4(mim)_2]^{2*}$  and Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> respectively.

# 3.2. Diffusion Coefficient

We have also analyzed the dynamic behavior of the ions for the studied dicationic ionic liquid through the predicted self-diffusion coefficients, D, obtained from molecular dynamics simulations using the Einstein's relationship [94]

$$D_{self} = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} < [r_i(t) - r_i(0)]^2 >$$
(5)

Where the quantity in braces is the ensemble-averaged mean square displacement (MSD) of the molecules and  $r_i$  is the vector coordinate of the center of mass of ion i. The trajectories were dumped for 5.0 ns every 200 fs at 500.0 K after 1.0 ns equilibration and the self-diffusion coefficients obtained from the slopes of the line fitted to the MSDs in the range 2.0-5.0ns.

 Table 3 The calculated diffusion coefficient of cations (D<sup>+</sup>), anions (D<sup>-</sup>) and all hydrogens (D<sup>H</sup>) from the slope of MSD plots in Figure 8 for 2-5ns for all dicationic ionic liquids at 500 K and 1.0

DILs	$D^+ (10^{-11}m^2/s)$	D <sup>-</sup> (10 <sup>-11</sup> m <sup>2</sup> /s)	$D^{H} (10^{-11} m^2/s)$
$[C_4(mim)]_2[Cl]_2$	0.061	0.101	0.061
$[C_4(mim)]_2[Br]_2$	0.061	0.098	0.061
$[C_4(mim)]_2[I]_2$	0.058	0.083	0.058

The simulated mean squared displacements (MSD) of center of mass of the cations, all hydrogen types and anions using NVT simulations up to a time of 5.0 ns for all three studied DILs are shown in Figure 8a-c. The effect of the anion size on the MSDs of hydrogen atoms and cations are shown in Figures 9a-c. The initial rapid increase of calculated MSDs in Figure 9 continues until 2 ns, which shows that a sufficiently long simulation is necessary for an accurate evaluation of the self-diffusion coefficients of the ions in the ionic liquid. The asymptotic linear regions (t > 2 ns) were used for the calculation of the diffusion coefficients.



Figure 9 Calculated MSDs anion, cation and all hydrogen type for (a) [C4(mim)2][Cl]2, (b) [C4(mim)2][Br]2 and (c) [C4(mim)2][l]2 at 500 K and 1 atm.

The diffusion constants were obtained from the slope of the a linear part of MSDs from 2.0 to 5.0 ns and the values are listed in Table 3. It is found that the diffusion constants of the ions in DILs are on the order of  $10^{-11}$  m<sup>2</sup> s<sup>-1</sup>, which is 2 orders of magnitude smaller than that of the common small molecules, such as water, and one order of magnitude smaller than that of a mono cationic ILs with a comparable molar mass at room temperature.[93-95]

The higher charge density in dicationic ionic liquids (two times larger than mono cationic ionic liquids) results in the stronger interaction than mono cationic ionic liquids.

Kelkar and Maginn[96] show that times much longer than 1.0 ns are required to observe diffusive dynamics in equilibrium MD simulations, and they recommend the use of nonequilibrium MD simulations to extract transport coefficients for ionic liquids. Due to the stronger interactions between ions in dicationic ionic liquids than mono cationic ILs, the time required to observe diffusive dynamics is longer.

The anion size has two opposite effects in the electrical conductivity. On the one hand, the large anions have a smaller surface electrical charge density and thus higher ionic mobility. On the other hand, the larger size of the anion limits the dynamical movement and decreases the electrical conductivity. From other view point, the smaller anions are better packed in the ionic phase, which may limit their motion. The observed trend for the diffusion coefficients of anions in Table 3 is  $CI^- > Br^- > I^-$ , where the calculated diffusion coefficients of anion are larger than that of cations. The observed

trend for the anion diffusion coefficients can be explained in terms of the size and mass of the anions. The I<sup>-</sup> anion is the largest anions and has the lowest surface charge density, while Cl<sup>-</sup> has the highest surface charge density due to its small size. Also one note that in Table 2 the [C<sub>4</sub>(mim)<sub>2</sub>][Cl]<sub>2</sub> DILs has lower density than the [C<sub>4</sub>(mim)<sub>2</sub>][Br]<sub>2</sub> and [C<sub>4</sub>(mim)<sub>2</sub>][l]<sub>2</sub> DILs.

The calculated MSDs and diffusion coefficients values for all hydrogen types and cations in the  $[C_4(mim)_2][X]_2 X=CI^-$ ,  $Br^-$  and  $I^-$  dicationic ionic liquids are similar.

#### 3.2 Quantum mechanical calculations

## 3.2.1 Cations

In addition, we investigated the interaction between halide anions and a cation by quantum mechanics. The structure of dication  $[C_4(mim)_2]^{2+}$  were taken from the crystallographic X-ray (Figure 1) of solid 3,3'-Dimethyl-1,1'- (butane-1,4-di-yl)diimidazolium bis-(tetrafluoroborate) then optimized at B3LYP/6-311++G(d,p) level of theory. The potential energy surface for the C7-C8-C8'-C7' dihedral angle scanned from 0.0° to 360.0° with a step size of 5.0°. No symmetry and geometry constraints were applied during the geometry optimization and potential surface scan.

The potential energy surface scan for relax rotation around the C7-C8-C8'-C7' dihedral angle in  $[C_4(mim)_2]^{+2}$  are visualized in Figure 10. The optimized structures revealed that each imidazolium ring in DILs is a planar pentagon as expected.[97] Furthermore the optimized structure for  $[C_4(mim)_2]^{+2}$  shows that two imidazolium rings have the maximum distance from each other and the dihedral angle between two imidazolium ring is 180.0°. The significant optimized values of the geometric parameters (bond lengths, bond angles, and dihedral angles) of the studied dication ILs are reported in Table 4.



Figure 10 Potential energy surface for relax rotation around the C7-C8-C8'-C7' dihedral angle in  $[C_4(mim)_2]^{2*}$  calculated at the B3LYP/6-311++G(d,p) level of theory.( for number refer to Figure 2)

Table 4 Some selected bond lengths (Å), bond angles and dihedral angles (deg) of studied DILs [C4(mim)<sub>2</sub>][X]<sub>2</sub>, X=Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> in most stable configuration at gas phase which calculated at DFT/B3LYP level with 6-311++G(d,p) basis set for Cl<sup>-</sup>, Br<sup>-</sup> and DGDZVP basis set for I<sup>-</sup>.

IL	$[C_4(mim)_2]^{+2}$	[C4(mim)2][Cl]2	[C4(mim)2][Br]2	[C4(mim)2][I]2	
Bonds					
N <sub>1</sub> -C <sub>2</sub>	1.341	1.339	1.339	1.343	
C2-H9	1.078	1.086	1.086	1.087	
C4-H10	1.077	1.076	1.076	1.080	
C5-H11	1.077	1.082	1.082	1.085	
С6-Н	1.088	1.093	1.093	1.093	
C7-H	1.091	1.094	1.094	1.094	
C8-H	1.095	1.095	1.095	1.096	
C2-N3	1.335	1.337	1.337	1.341	
N <sub>3</sub> -C <sub>4</sub>	1.382	1.385	1.385	1.386	
C4-C5	1.360	1.361	1.361	1.366	
C5-N1	1.384	1.386	1.386	1.387	
N3-C6	1.475	1.467	1.467	1.468	
Bond Angels					
N1-C2-N3	108.9	108.4	108.4	108.5	
Dihedral Angles					
N1-C2-N3-C4	-0.2	0.6	0.5	0.5	
C2-N3-C4-C5	0.3	-0.5	-0.4	-0.3	
N1-C7-C8-C8'	177.6	-83.1	-84.0	-83.4	
C7-C8-C8'-C7'	180.0	89.5	90.5	92.1	

The value of C7-C8-C8'-C7' dihedral angle in Table 4 reveals that the trans conformation for  $[C_4(mim)_2]^{+2}$  is the most stable conformation. The optimized geometry of DILs, (the most stable structures) show that the butyl groups are in trans–trans configuration for  $[C_4(mim)_2]^{+2}$ , i.e. C7-C8-C8'-C7' dihedral angle is 180°.

# 3.2.2 Ion Pairs

As we are aware, 1-alkyl-3-methylimidazolium fluoride ( $C_4(\min)_2F_2$ ) was not prepared synthetically[98-99]. To obtain the most stable geometry of ion pairs ([ $C_4(\min)_2X$ ]<sup>+</sup>, X=Cl<sup>-</sup>, Br<sup>-</sup> and l<sup>-</sup>), the halide anions were initially put at all possible sites in the vicinity of imidazolium rings and the alkyl chain. Then, the optimization carried out to find the most stable conformers of all ion pairs. The obtained most stable structures are shown in Figure 11.



Figure 11 Optimized structure of ion pairs at B3LYP/6-311++G(d,p) level of theory, for Cl<sup>-</sup>, Br<sup>-</sup> where DGDZVP basis set was used for l<sup>-</sup>. Distances between halide and near hydrogen are shown.

According to Figure 11, for the most stable configuration, rings bend toward each other and making a U-shaped structure, which causes the anions to be closer to the hydrogen atoms of two imidazolium rings. The significant optimized values of the geometric parameters (bond lengths, bond angles, and dihedral angles) of the structures shown in Figure 11 are reported in Table 4, the numbering scheme introduced in Figure 2. Table 4, shows that the values of the optimized N<sub>1</sub>-C<sub>2</sub>-N<sub>3</sub> bond angle does not change significantly (<1 °) across the studied DILs. Also, it is seen that there are significant difference in alkyl dihedral angle of the geometry structures between  $[C_4(mim)_2]^{+2}$  and  $([C_4(mim)_2X_2], X=Cl^-, Br^- and l^-)$ . The dihedral angle in butyl groups (C7-C8-C8'-C7') is 180.0° in  $[C_4(mim)_2]^+$ , while the optimized geometry of  $[C_4(mim)_2X_1^+, X^-=Cl^-, Br^- and l^- DILs$ , show that the dihedral angle in butyl groups (C7-C8-C8'-C7') is about 90°. Furthermore the optimized structures of  $[C_4(mim)_2]^{2+}$  show that two imidazolium rings tend to have the maximum distance from each other. Our results show that the structure of dicationic ionic liquid in gas phase are completely different from the liquid phase and  $[C_4(mim)_2][BF_4]_2$  in crystallography data in solid phase.

The interaction energy ( $\Delta E_{int}$ ), enthalpy ( $\Delta H_{int}$ ) and Gibbs free energy ( $\Delta G_{int}$ ) of the [C<sub>4</sub>(mim)<sub>2</sub>X]<sup>+</sup>, X<sup>-</sup>= Cl<sup>-</sup>, Br<sup>-</sup> and l<sup>-</sup> were calculated at B3LYP level of DFT with 6-311++G(d,p) basis set for Cl<sup>-</sup>, Br<sup>-</sup> and DGDZVP basis set for l<sup>-</sup> and reported in Table 5. For an ion pair the interaction energy between [C<sub>4</sub>(mim)<sub>2</sub>]<sup>+2</sup>, cation and X<sup>-</sup> anions can be estimated as follow:

$$\Delta E_{\rm int} = E_{a-c} - (E_a + E_c) \tag{6}$$

Where,  $\Delta E_{int}$ ,  $E_a$  and  $E_c$  stand for the ion-pair, anionic and cationic species energies, respectively.  $\Delta H_{int}$  and  $\Delta G_{int}$  were calculated in a similar manner. The large values of  $\Delta E_{int}$ ,  $\Delta H_{int}$  and  $\Delta G_{int}$  in Table 5 are results of the strong columbic attractions between the anion and the cation. For the ion pairs, the interaction energies range from -1527 to -1079 kJ/mol. Generally, the Hbonded interaction energies of these ion pairs are more than mono cationic ionic liquids. The interaction energies for [emim]Cl, ion pair are reported to be about -380.66 kJ/mol [100]. The interaction energies of DILs are four times larger than that of the mono cationic ILs. According to Table 5, interaction energy of DILs decreases with the increasing the anion size. The increase of anion size leads to weaker interaction energies and hydrogen bonds in ion pairs. A similar effect has been also expected in mono cationic ionic liquids.

 Table 5 Calculated thermodynamic interaction energy (kJ/mol) of the ion pairs at B3LYP level of DFT

 with 6-311++G(d,p) basis set for  $CI^-$ ,  $Br^-$  and DGDZVP basis set for  $I^-$ 

	[C <sub>4</sub> (mim) <sub>2</sub> Cl] <sup>+</sup>	[C <sub>4</sub> (mim) <sub>2</sub> Br] <sup>+</sup>	[C <sub>4</sub> (mim) <sub>2</sub> I] <sup>+</sup>
$\Delta E_{int}$	-1527.32	-1462.11	-1079.12
$\Delta H$	-1526.98	-1461.22	-1073.9
$\Delta G$	-1475.07	-1409.6	-1024.44

## 3.3.3 H-bonding interaction

Hydrogen bonds play very important roles in the physical properties of imidazolium ionic liquids [101]. A hydrogen bond is formed if the Y-H---X (Y and X = electronegative atoms) distance is smaller than the sum of the van der Waals radius of X and H atoms and the Y–H---X angle is greater than  $90^{\circ}$ [102]. Based on the van der Waals radii of H (1.20 Å), Cl (1.85 Å), Br (1.95 Å) and I (2.15 Å) [102] atoms, the maximum distance for the formation hydrogen bonds could be 3.05 Å, 3.15 Å and 3.45 Å for H---Cl, H---Br and H---I hydrogen bonds, respectively. For each ion pairs, the possible hydrogen bonds are carefully evaluated and the results are shown in Figure 11. The results show that for  $[C_4(mim)_2X]^+$  ion pairs, there are eight hydrogen-bonds that are formed between the H<sub>9</sub>, H<sub>12</sub>, H<sub>15</sub>, and H<sub>11</sub> atoms with X atom. It is noted that these Hydrogen-bond lengths are smaller than those found from the MD simulations in 3.1 section, i.e. the distance of the maximum of RDFs in Figure 3. This is mainly because the interaction between  $[C_4(mim)_2]^{2+}$  cations and halide anions in the bulk liquid can be disturbed by the adjacent ions. The results show that the Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> anions prefer to locate almost within the imidazolium plane, near the C2-H9 which lead to bending the rings towards each other and making a U-shaped structure The calculated hydrogen bond length, bond angle and dihedrals angles are reported in Table 6.

 Table 6
 Optimized bond distance (Å) and angle (deg) for  $C_2$ -H<sub>9</sub>...,X, X = Cl<sup>-</sup>, Br<sup>-</sup> and l<sup>-</sup> of ion pairs at B3LYP

 level of DFT with 6-311++G(d,p) basis set for Cl<sup>-</sup>, Br<sup>-</sup> and DGDZVP basis set for l<sup>-</sup>.

ion pairs	[C4(mim)2Cl]+	[C4(mim)2Br]*	[C4(mim)2I]+
C <sub>2</sub> -H <sub>9</sub> -X	2.334	2.495	2.760
C6-H12-X	2.628	2.779	3.042
C5-H11-X	2.590	2.744	2.960
C7-H15-X'	2.548	2.699	2.998
А с2-н9х	133.1	134.5	133.2
A <sub>C2'-H9'X'</sub>	133.3	134.5	133.2
А сб-н12х	144.9	146.7	146.8
А сб'-н12'х'	144.9	146.7	146.8
А с5'-н15'х	133.2	136.7	143.3
А <sub>с5-н15х'</sub>	133.3	136.7	143.3
А с7'-н15'х	154.2	156.7	157.6
А с7-н15х'	153.6	156.7	157.6

From Table 6, it can be seen that the hydrogen bond length of C<sub>2</sub>–H<sub>9</sub>....X increases gradually from Cl<sup>-</sup>to Br<sup>-</sup> and ,l<sup>-</sup> following the trend of electronegativity of halogen atoms (Cl= 3.0, Br = 2.8 and I = 2.5).<sup>103</sup> Thus, the H-bond interaction strength is as follows: C<sub>2</sub>–H<sub>9</sub>....Cl > C<sub>2</sub>–H<sub>9</sub>....Br> C<sub>2</sub>–H<sub>9</sub>....I. Figure 12a-d shows the calculated IR spectrum for  $[C_4(mim)_2]^{+2}$  and  $[C_4(mim)_2][X]_2$ , X<sup>-</sup> = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>. By comparing IR spectrum for  $[C_4(mim)_2]^{+2}$  and  $[C_4(mim)_2][X]_2$  it can be observed that these C-H bonds all have a red shift after the formation of the hydrogen banding. Also it can be seen from Figure 12a that the C<sub>2</sub>-H<sub>9</sub> stretching peaks shift to right with increasing the size of anions from Cl<sup>-</sup> Br<sup>-</sup> to I<sup>-</sup>. Since the strength of hydrogen bond depends on the type of anion, the shift in C<sub>2</sub>-H<sub>9</sub> stretching frequency is an indicator of the strength of the hydrogen bond that is formed between H<sub>9</sub> atom in C<sub>2</sub>–H<sub>9</sub> and halide (Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>). These data suggest that the hydrogen bonding formation occurred for all anions and these bonds become weaker as follows: Cl<sup>-</sup>> Br<sup>-</sup>> I<sup>-</sup>. The intensity of C<sub>2</sub>-H<sub>9</sub> stretching for Cl<sup>-</sup> that occurred in 3137.36 cm<sup>-1</sup> is high and shown in Figure 13a. The intensity of this peak decreases and shifts to higher frequencies with increasing the size of anions.



Figure 12 Calculated IR spectra (a):  $[C_4(mim)_2][X]_2, X^- = CI^-, Br^-, I^-, (b): [C_4(mim)_2]^{*2}$  at B3LYP level with 6-311++G(d,p) basis set for CI<sup>-</sup>, Br<sup>-</sup> and DGDZVP for I<sup>-</sup>.

The stabilization energy gain due to H-bonding interaction between cation and anion is found to be higher in the case of C<sub>2</sub>–H<sub>9</sub> compared to that of involving C<sub>4</sub>-H<sub>9</sub>, C<sub>5</sub>–H<sub>9</sub>. This can be explained as C<sub>2</sub> is more positive than C<sub>4</sub> and C<sub>5</sub> (due to the electron deficient C=N,  $\Pi$  bond formation). These results are in agreement with reported results for mono cation ILs.<sup>104, 105</sup>

## 3.3.4 Aim analysis

To obtain further insights into the nature of the formed H bonds, AIM theory has been employed. As shown in Table 7, the intermolecular H bonds has been further confirmed by the location of the corresponding bond critical point (BCP) according to the AIM theory. Two main criteria indicate a hydrogen bond: (i) a bond path between two atoms with a bond critical point, BCP, in the middle of the path and (ii) the electronic density at BCP,  $\rho_{BCP}$ , and the Laplacian of that electron density,  $\nabla^2 \rho$ , must be within the 0.002-0.035 and 0.024-0.139 ranges, respectively, both in atomic units[106-107]. The Laplacian  $\nabla^2 \rho$ , at the BCP is the sum of the three curvatures of the density at the critical point, the two perpendicular to the bond path,  $\lambda 1$  and  $\lambda 2$ , being negative (by convention,  $\lambda 1 > \lambda 2$ ) whereas the third,  $\lambda 3$ , lying along the bond path, is

# positive.

The negative curvatures measure the extent to which the density is concentrated along the bond path and the positive curvature measures the extent to which it is depleted in the region of the interatomic surface and concentrated in the individual atomic basins. For covalent bonds, the two negative curvatures are dominant and  $\nabla^2 \rho < 0$ ; in contrast. In the case of closed-shell bonding, for example, ionic, hydrogen bonding, or van der Waals interactions, the interaction is characterized by a depletion of density in region of contact of two atoms and  $\nabla^2 \rho > 0$ . The results of AIM calculations for all DILs are shown in Figure 13 and Table 7.



Figure 13 Properties of the [C4(mim)2][X]2, X<sup>-</sup>=halides=Cl<sup>-</sup>, Br<sup>-</sup> and l<sup>-</sup> ionic pair calculated at B3LYP/6-311++G(d,p) basis set for Cl<sup>-</sup>, Br<sup>-</sup> and DGDZVP basis set for l<sup>-</sup>. The AIM analysis of the pair showing bond critical points (BCP, red circles) and shown only bond paths (pink lines) for the sake of visibility.

According Table 7, the charge density  $\rho$  at the BCP of the intermolecular C<sub>2</sub>-H.... halide bonds is also larger than other similar halide bonds (C<sub>7</sub>-H...halide, C<sub>5</sub>-H...halide and C<sub>7</sub>-H...halide bonds). Thus, the C<sub>2</sub>-H sites in the imidazolium ring are more favorable than those in methyl and ethyl groups. According to the criterion of the H bond ( $\rho$  <sub>BCP</sub>, is in 0.002-0.035 and laplacian  $\nabla^2 \rho$ , is in 0.024-0.139), there are eight possible hydrogen bonds in studied DILs.

# 3.3.5 Natural bond orbital (NBO) analysis

A better understanding of interactions between ion pairs of studied DILs is

NBO (j), the stabilization energy E(2) associated with delocalization  $i \rightarrow j$  is estimated and shown in Table 8. The NBO results show that the

	$\rho(cp)$	$\nabla^2(cp)$
[C4(mim)]2 [Cl]2		
C₂-H <sub>9</sub> -X	0.0215	0.0632
C6-H12-X	0.0120	0.0340
C5-H11-X	0.0129	0.0388
C7-H15-X	0.0140	0.0395
[C4(mim)]2 [Br]2		
C <sub>2</sub> -H <sub>9</sub> -X	0.0191	0.0499
C6-H12-X	0.0111	0.0283
C5-H11-X	0.0117	0.0314

0.0129

0.0155

0.0094

0.0105

0.0102

0.0041

0.0324

0.0389

0.0228

0.0264

0.0241

0.0105

C7-H15-X

 $C_2$ - $H_9$ -X

C6-H12-X

C5-H11-X

C7-H15-X C8-H17-X

[C4(mim)]2 [I]2

 Table 7 The AIM analysis of studied DILs at B3LYP level of DFT with 6-311++G(d,p) basis set for Cl<sup>-</sup>, Br<sup>-</sup> and DGDZVP basis set for l<sup>-</sup>.

.P(halide) $\rightarrow \sigma^*(C_2-H)$ donor acceptor interactions are most important ones.						
The NBO results show that the most important donor acceptor is						
$P(halide) {\rightarrow} \sigma^*(C_2{-}H_9).$ It can be seen that the main stabilization energy						
between the dicationic and halide anion is the electrostatic interaction						
between the hydrogen atom attached to $C_2\text{-}H_9$ and the halide anion. From						
Table 8, it can be seen that the LP(halide) $\rightarrow \sigma^*(C_2-H_9)$ for $[C_4(mim)_2][Cl]_2$ is too						
arge and decreases by increasing the size of the anion. Also, one can see that						
the significant donor-acceptor natural bond orbital interactions for						
$[C_4(mim)_2][X]_2,X^-\!=\!Cl^-,Br^-,l^-$ are between H9 hydrogens connected to two						
midazolium rings and the next alkyl chain as LP(halide) $ ightarrow \sigma^*(C_{2^-}$						
H <sub>9</sub> )>LP(halide)→ $\sigma^*(C_7-H_{15})$ > LP(halide)→ $\sigma^*(C_5-H_{10})$ . The decreases of $E(2)$						

**Table 8** Some significant donor-acceptor natural bond orbital interactions of  $[C_4(\min)_2][X]_2 X = Cl^-$ ,  $Br^-$  and  $I^-$  ion pairs and their second-order perturbation stabilization energies (kj/mol) at B3LYP level of DFT with 6-311++G(d,p) basis set for Cl<sup>-</sup>,  $Br^-$  and DGDZVP basis set for I.

	Donor (i)	Acceptor (j)		E(2) kJ/mol	E(j)-E(i) a.u.	F(i,j) a.u.
[C4(mim)]2[Cl]2						
LP	(4)Cl	BD*(1)	C2-H9	34.39	0.66	0.066
LP	(3)Cl′	BD*(1)	C7-H15	15.15	0.64	0.043
LP	(3)Cl′	BD*(1)	C5-H11	8.20	0.65	0.032
LP	(2)Cl	BD*(1)	C6-H12	6.23	0.61	0.027
[C4(mim)]2[Br]2						
LP	(4)Br	BD*(1)	C2-H9	31.76	0.63	0.062
LP	(3)Br'	BD*(1)	C7-H15	13.89	0.61	0.04
LP	(3)Br'	BD*(1)	C5-H11	9.04	0.63	0.033
LP	(2)Br	BD*(1)	C6-H12	6.11	0.6	0.026
[C4(mim)]2[I]2						
LP	(4)I	BD*(1)	C2-H9	15.31	0.68	0.045
LP	(3)I'	BD*(1)	C7-H15	7.57	0.68	0.031
LP	(3)I'	BD*(1)	C5-H11	7.28	0.7	0.031
LP	(4)I	BD*(2)	C2-N3	6.86	0.14	0.016
LP	(2)I	BD*(1)	C6-H12	4.48	0.67	0.024
LP	(4)I	BD*(1)	C6-H12	4.14	0.69	0.024

provided by NBO analysis. The energetic importance could be estimated by the second-order perturbation theory. For each donor NBO (i) and acceptor can be related to the strong interactions between anions and H9 atoms then and charge transfers to  $C_2$ -H<sub>9</sub> bond. In summary, the results of NBO analysis

shows that the sum of stabilization energies E(2) of  $[C_4(mim)_2][CI]_2$  is much larger than that other DILs and decreases whit the size of anion. Also, the significant donor-acceptor natural bond orbital interactions for  $[C_4(mim)_2][X]_2, X^-=CI^-,Br^-,I^-$  are as LP(halide) $\rightarrow \sigma^*(C_2-H_9) > LP(halide) \rightarrow \sigma^*(C_7-H_{15}) > LP(halide) \rightarrow \sigma^*(C_5-H_{10}).$ 

## 4. Conclusion

In this work we focused on the all-possible hydrogen bonding in 1,3-bis[3-methylimidazolium-1-yl]butane halides ( $[C_4(mim)_2][X]_2$ ,  $X^-= CI^-$ ,  $Br^-$  and  $I^-$ ) dicationic ionic liquid by the molecular dynamics simulations and quantum chemical calculations. The stable configurations, ionic interactions and hydrogen bonds are studied and discussed. The natural bond orbital (NBO) and atoms in molecule (AIM) analyses have also been applied to understand the nature of the interactions between ionic pairs in ionic liquids. In addition, the effects of ion size on the magnitude of interaction energies, the stable geometries of the ion pair, IR spectroscopy of these DILs are calculated and compared with each other.

The result of molecular dynamic simulation show that anions tend to spend most of their time around the hydrogen attached to rings rather than other hydrogen and the interaction between the halide and the hydrogen atom decreases in the order first hydrogen > second hydrogen > third hydrogen also the interaction between the hydrogens and the halide atom decreases in the order  $CI^- > Br^- > I^-$ . The calculated SDFs shows that hydrogen attached imidazolium rings have the highest probability densities among other hydrogens. The calculated diffusion coefficients show that the anion diffusivities are one order of magnitude higher than that of cation and other hydrogens atoms.

The results of quantum mechanics show that there are significant difference in geometrical structure between dication  $[C_4(mim)_2]^{+2}$  and  $[C_4(mim)_2][X]_2$ ,  $(X^=halides= Cl^-, Br^- and l^-)$ . In the most stable configuration of the dication, two imidazolium rings tend to have the maximum distance from each other. However, for the ion pair in the lowest energy configuration, two imidazolium rings bend toward each other and forming a U-shaped structure, which causes the anions to be closer to the atoms of the two rings. Furthermore, the cationic structure in the dicationic ionic liquid depends on the type of anion. Inspection of the optimized structures of the ion pair show that there are eight hydrogen-bond interaction which formed between the H<sub>9</sub> with halide anions. The calculated IR spectrum shows that the intensity of H-bonding stretching frequency peaks change in the order of Cl<sup>-</sup> > Br<sup>-</sup>>l<sup>-</sup>.

Analysis of the possible hydrogen bonds by AIM theory reveal that there are eight hydrogen bonds in DILs. Confirm the results of geometry analysis. The results of NBO analysis show that the sum of stabilization energies (E(2)) for interactions in  $([C_4(mim)_2][CI]_2$  is much larger than that other DILs and decreases whit increasing anion size, which indicates these interactions contribute to the strong interaction between  $[C_4(mim)_2]^{+2}$  cation and the halide anions. Also the significant donor–acceptor natural bond orbital interactions for  $[C_4(mim)_2][X]_2, X^{-}=CI^{-}, Br^{-}, I^{-}$  are follows LP(halide) $\rightarrow \sigma^*(C_2-$ H<sub>9</sub>) > LP(halide) $\rightarrow \sigma^*(C_7-H_{15}) >$  LP(halide) $\rightarrow \sigma^*(C_5-H_{10})$ .

## Acknowledgment:

We acknowledge supports of the University of Mazandaran as research facilities and financial grants.

## References

- Earle, M.J., Seddon, K.R. Ionic liquids. Green solvents for the future. *Pure and applied chemistry*. 2000, 72, 1391-8.
- [2] Holbrey, J.D., Reichert, W.M., Swatloski, R.P., Broker, G.A., Pitner, W.R., Seddon, K.R., et al. Efficient, halide free synthesis of new, low cost ionic liquids: 1, 3-dialkylimidazolium salts containing methyl-and ethyl-sulfate anions. *Green Chemistry*. 2002, 4, 407-13.
- [3] Klingshirn, M.A., Spear, S.K., Subramanian, R., Holbrey, J.D., Huddleston, J.G., Rogers, R.D. Gelation of ionic liquids using a cross-linked poly (ethylene glycol) gel matrix. *Chemistry of materials*. 2004, 16, 3091-7.
- [4] Ikegami, S., Hamamoto, H. Novel recycling system for organic synthesis via designer polymer-gel catalysts. *Chemical reviews*. 2009, 109, 583-93.
- [5] Tu, W., Lei, J., Ju, H. Functionalization of carbon nanotubes with waterinsoluble porphyrin in ionic liquid: direct electrochemistry and highly sensitive amperometric biosensing for trichloroacetic acid. *Chemistry–A European Journal.* 2009, 15, 779-84.
- [6] Xu, H., Xiong, H.-Y., Zeng, Q.-X., Jia, L., Wang, Y., Wang, S.-F. Direct electrochemistry and electrocatalysis of heme proteins immobilized in single-wall carbon nanotubes-surfactant films in room temperature ionic liquids. *Electrochemistry communications*. 2009, 11, 286-9.
- [7] Pârvulescu, V.I., Hardacre, C. Catalysis in ionic liquids. *Chemical Reviews*. 2007, 107, 2615-65.
- [8] Singh, M., Singh, R.S., Banerjee, U.C. Stereoselective synthesis of (R)-1chloro-3 (3, 4-difluorophenoxy)-2-propanol using lipases from Pseudomonas aeruginosa in ionic liquid-containing system. *Journal of Molecular Catalysis B: Enzymatic.* 2009, 56, 294-9.
- [9] Karout, A., Pierre, A.C. Silica gelation catalysis by ionic liquids. *Catalysis Communications*. 2009, 10, 359-61.
- [10] Verevkin, S.P., Kozlova, S.A., Emel'yanenko, V.N., Goodrich, P., Hardacre, C. Thermochemistry of ionic liquid-catalyzed reactions. experimental and theoretical study of chemical equilibria of isomerization and transalkylation of tert-butylbenzenes. *The Journal of Physical Chemistry* A. 2008, 112, 11273-82.
- [11] Lassègues, J.-C., Grondin, J., Aupetit, C., Johansson, P. Spectroscopic identification of the lithium ion transporting species in LiTFSI-doped ionic liquids. *The Journal of Physical Chemistry A*. **2009**, 113, 305-14.
- [12] Chang, T.-M., Dang, L.X. Computational studies of structures and dynamics of 1, 3-dimethylimidazolim salt liquids and their interfaces using polarizable potential models. *The Journal of Physical Chemistry A*. 2009, 113, 2127-35.
- [13] Hayamizu, K., Tsuzuki, S., Seki, S. Molecular motions and ion diffusions of the room-temperature ionic liquid 1, 2-dimethyl-3-propylimidazolium bis

(trifluoromethylsulfonyl) amide (DMPImTFSA) studied by 1H, 13C, and 19F NMR. *The Journal of Physical Chemistry A*. **2008**, 112, 12027-36.

- [14] Oxley, J.D., Prozorov, T., Suslick, K.S. Sonochemistry and sonoluminescence of room-temperature ionic liquids. *Journal of the American Chemical Society*. 2003, 125, 11138-9.
- [15] Sobota, M., Dohnal, V., Vrbka, P. Activity coefficients at infinite dilution of organic solutes in the ionic liquid 1-ethyl-3-methyl-imidazolium nitrate. *The Journal of Physical Chemistry B.* **2009**, 113, 4323-32.
- [16] Tong, J., Liu, Q.-S., Guan, W., Yang, J.-Z. Estimation of physicochemical properties of ionic liquid C6MIGaCl4 using surface tension and density. *The Journal of Physical Chemistry B.* 2007, 111, 3197-200.
- [17] Tong, J., Liu, Q.-S., Xu, W.-G., Fang, D.-W., Yang, J.-Z. Estimation of physicochemical properties of ionic liquids 1-alkyl-3-methylimidazolium chloroaluminate. *The Journal of Physical Chemistry B.* 2008, 112, 4381-6.
- [18] Anderson, J.L., Ding, R., Ellern, A., Armstrong, D.W. Structure and properties of high stability geminal dicationic ionic liquids. *Journal of the American Chemical Society*. 2005, 127, 593-604.
- [19] Payagala, T., Huang, J., Breitbach, Z.S., Sharma, P.S., Armstrong, D.W. Unsymmetrical dicationic ionic liquids: manipulation of physicochemical properties using specific structural architectures. *Chemistry of Materials*. 2007, 19, 5848-50.
- [20] Hough, W.L., Smiglak, M., Rodríguez, H., Swatloski, R.P., Spear, S.K., Daly, D.T., et al. The third evolution of ionic liquids: active pharmaceutical ingredients. *New Journal of Chemistry*. **2007**, 31, 1429-36.
- [21] Jin, C.-M., Ye, C., Phillips, B.S., Zabinski, J.S., Liu, X., Liu, W., et al. Polyethylene glycol functionalized dicationic ionic liquids with alkyl or polyfluoroalkyl substituents as high temperature lubricants. *Journal of Materials Chemistry*. 2006, 16, 1529-35.
- [22] Mizuuchi, H., Jaitely, V., Murdan, S., Florence, A. Room temperature ionic liquids and their mixtures: potential pharmaceutical solvents. *european journal of pharmaceutical sciences*. 2008, 33, 326-31.
- [23] Boon, J.A., Levisky, J.A., Pflug, J.L., Wilkes, J.S. Friedel-Crafts reactions in ambient-temperature molten salts. *The Journal of Organic Chemistry*. 1986, 51, 480-3.
- [24] Han, X., Armstrong, D.W. Using geminal dicationic ionic liquids as solvents for high-temperature organic reactions. *Organic Letters*. 2005, 7, 4205-8.
- [25] Xiao, J.-C., Shreeve, J.n.M. Synthesis of 2, 2 '-biimidazolium-based ionic liquids: Use as a new reaction medium and ligand for palladium-catalyzed suzuki cross-coupling reactions. *The Journal of organic chemistry*. 2005, 70, 3072-8.
- [26] Mohamad, S., Surikumaran, H., Raoov, M., Marimuthu, T., Chandrasekaram, K., Subramaniam, P. Conventional study on novel dicationic ionic liquid inclusion with β-cyclodextrin. *International Journal* of Molecular Sciences. **2011**, 12, 6329-45.
- [27] Zhi, H., Lü, C., Zhang, Q., Luo, J. A new PEG-1000-based dicationic ionic liquid exhibiting temperature-dependent phase behavior with toluene and its application in one-pot synthesis of benzopyrans. *Chemical Communications*. 2009, 2878-80.

- [28] Chang, J.-C., Ho, W.-Y., Sun, I.-W., Tung, Y.-L., Tsui, M.-C., Wu, T.-Y., et al. Synthesis and characterization of dicationic ionic liquids that contain both hydrophilic and hydrophobic anions. *Tetrahedron*. **2010**, 66, 6150-5.
- [29] Fang, D., Yang, J., Ni, C. Dicationic ionic liquids as recyclable catalysts for one-pot solvent-free synthesis of  $\alpha$ -aminophosphonates. *Heteroatom Chemistry.* **2011**, 22, 5-10.
- [30] Perdew, J.P., Wang, Y. Accurate and simple analytic representation of the electron-gas correlation energy. *Physical review B*. **1992**, 45, 13244.
- [31] Becke, A.D. Density-functional thermochemistry. III. The role of exact exchange. *The Journal of chemical physics*. **1993**, 98, 5648-52.
- [32] Chattaraj, P., Poddar, A. Molecular reactivity in the ground and excited electronic states through density-dependent local and global reactivity parameters. *The Journal of Physical Chemistry A.* **1999**, 103, 8691-9.
- [33] Remsing, R.C., Wildin, J.L., Rapp, A.L., Moyna, G. Hydrogen bonds in ionic liquids revisited: 35/37Cl NMR studies of deuterium isotope effects in 1n-butyl-3-methylimidazolium chloride. *The Journal of Physical Chemistry B.* 2007, 111, 11619-21.
- [34] Dieter, K.M., Dymek, C.J., Heimer, N.E., Rovang, J.W., Wilkes, J.S. Ionic structure and interactions in 1-methyl-3-ethylimidazolium chloridealuminum chloride molten salts. *Journal of the American Chemical Society*. **1988**, 110, 2722-6.
- [35] Qiao, B., Krekeler, C., Berger, R., Delle Site, L., Holm, C. Effect of anions on static orientational correlations, hydrogen bonds, and dynamics in ionic liquids: A simulational study. *The Journal of Physical Chemistry B*. 2008, 112, 1743-51.
- [36] 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. *Chemistry–A European Journal*. 2006, 12, 6762-75.
- [37] Dong, K., Zhang, S., Wang, D., Yao, X. Hydrogen bonds in imidazolium ionic liquids. *The Journal of Physical Chemistry A*. **2006**, 110, 9775-82.
- [38] Sun, H., Zhang, D. Density functional theory study on the cycloaddition of carbon dioxide with propylene oxide catalyzed by alkylmethylimidazolium chlorine ionic liquids. *The Journal of Physical Chemistry A.* 2007, 111, 8036-43.
- [39] Kempter, V., Kirchner, B. The role of hydrogen atoms in interactions involving imidazolium-based ionic liquids. *Journal of Molecular Structure*. 2010, 972, 22-34.
- [40] Fumino, K., Wulf, A., Ludwig, R. Strong, localized, and directional hydrogen bonds fluidize ionic liquids. *Angew. Chem., Int. Ed.* 2008, 47, 8731-4.
- [41] Bandres, I., Alcalde, R., Lafuente, C., Atilhan, M., Aparicio, S. On the viscosity of pyridinium based ionic liquids: An experimental and computational study. *The Journal of Physical Chemistry B.* 2011, 115, 12499-513.
- [42] Del Pópolo, M.G., Lynden-Bell, R.M., Kohanoff, J. Ab initio molecular dynamics simulation of a room temperature ionic liquid. *The Journal of Physical Chemistry B.* 2005, 109, 5895-902.
- [43] Yu, G., Zhang, S. Insight into the cation-anion interaction in 1, 1, 3, 3-

tetramethylguanidinium lactate ionic liquid. *Fluid phase equilibria*. **2007**, 255, 86-92.

- [44] Cammarata, L., Kazarian, S., Salter, P., Welton, T. Molecular states of water in room temperature ionic liquids. *Physical Chemistry Chemical Physics*. 2001, 3, 5192-200.
- [45] Saha, S., Hamaguchi, H.-o. Effect of water on the molecular structure and arrangement of nitrile-functionalized ionic liquids. *The Journal of Physical Chemistry B.* 2006, 110, 2777-81.
- [46] Danten, Y., Cabaco, M., Besnard, M. Interaction of water highly diluted in 1-alkyl-3-methyl imidazolium ionic liquids with the PF6– and BF4– anions. *The Journal of Physical Chemistry A.* 2009, 113, 2873-89.
- [47] Berg, R.W., Deetlefs, M., Seddon, K.R., Shim, I., Thompson, J.M. Raman and ab initio studies of simple and binary 1-alkyl-3-methylimidazolium ionic liquids. *The Journal of Physical Chemistry B.* **2005**, 109, 19018-25.
- [48] Abdul-Sada, A.a.K., Elaiwi, A.E., Greenway, A.M., Seddon, K.R. Evidence for the clustering of substituted imidazolium salts via hydrogen bonding under the conditions of fast atom bombardment mass spectrometry. *European Mass Spectrometry*. **1997**, 3, 245-7.
- [49] Avent, A.G., Chaloner, P.A., Day, M.P., Seddon, K.R., Welton, T. Evidence for hydrogen bonding in solutions of 1-ethyl-3-methylimidazolium halides, and its implications for room-temperature halogenoaluminate (III) ionic liquids. *Journal of the Chemical Society, Dalton Transactions*. 1994, 3405-13.
- [50] Katsyuba, S.A., Zvereva, E.E., Vidiš, A., Dyson, P.J. Application of density functional theory and vibrational spectroscopy toward the rational design of ionic liquids. *The Journal of Physical Chemistry A*. **2007**, 111, 352-70.
- [51] Aparicio, S., Alcalde, R., Atilhan, M. Experimental and computational study on the properties of pure and water mixed 1-ethyl-3methylimidazolium L-(+)-lactate ionic liquid. *The Journal of Physical Chemistry B.* 2010, 114, 5795-809.
- [52] Wulf, A., Fumino, K., Ludwig, R. Spectroscopic evidence for an enhanced anion–cation interaction from hydrogen bonding in pure imidazolium ionic liquids. Angewandte Chemie International Edition. 2010, 49, 449-53.
- [53] Shukla, M., Srivastava, N., Saha, S. Theoretical and spectroscopic studies of 1-butyl-3-methylimidazolium iodide room temperature ionic liquid: Its differences with chloride and bromide derivatives. *Journal of Molecular Structure*. 2010, 975, 349-56.
- [54] Chang, H.-C., Jiang, J.-C., Tsai, W.-C., Chen, G.-C., Lin, S.H. Hydrogen Bond Stabilization in 1, 3-Dimethylimidazolium Methyl Sulfate and 1-Butyl-3-Methylimidazolium Hexafluorophosphate Probed by High Pressure: The Role of Charge-Enhanced C- H⊙⊙⊙ O Interactions in the Room-Temperature Ionic Liquid. *The Journal of Physical Chemistry B*. 2006, 110, 3302-7.
- [55] Hardacre, C., Holbrey, J.D., McMath, S.J., Bowron, D.T., Soper, A.K. Structure of molten 1, 3-dimethylimidazolium chloride using neutron diffraction. *The Journal of chemical physics*. 2003, 118, 273-8.
- [56] Dieter, M. CJ Jr.; heimer, NE; Rovang, JW; Wilkes, JS, JA Chem. Soc. 1988, 110, 2722.

- [57] Meng, Z. Dolle;, A.; Carper. J. Mol. Struct. 2002, 585, 119-28.
- [58] Kanzaki, R., Mitsugi, T., Fukuda, S., Fujii, K., Takeuchi, M., Soejima, Y., et al. Ion–ion interaction in room temperature ionic liquid 1-ethyl-3methylimidazolium tetrafluoroborate studied by large angle X-ray scattering experiment and molecular dynamics simulations. *Journal of Molecular Liquids*. 2009, 147, 77-82.
- [59] Dong, K., Zhang, S. Hydrogen bonds: a structural insight into ionic liquids. Chemistry–A European Journal. 2012, 18, 2748-61.
- [60] Sun, H., Qiao, B., Zhang, D., Liu, C. Structure of 1-butylpyridinium tetrafluoroborate ionic liquid: quantum chemistry and molecular dynamic simulation studies. *The Journal of Physical Chemistry A*. **2010**, 114, 3990-6.
- [61] Bodo, E., Caminiti, R. The structure of geminal imidazolium bis (trifluoromethylsulfonyl) amide ionic liquids: a theoretical study of the gas phase ionic complexes. *The Journal of Physical Chemistry A.* 2010, 114, 12506-12.
- [62] Canongia Lopes, J.N., Deschamps, J., Pádua, A.A. Modeling ionic liquids using a systematic all-atom force field. *The journal of physical chemistry B.* 2004, 108, 2038-47.
- [63] Smith, W., Forester, T., Todorov, I., Leslie, M. The DL poly 2 user manual. CCLRC, Daresbury Laboratory, Daresbury, Warrington WA4 4AD, England. 2006, 2.
- [64] Martínez, J.M., Martínez, L. Packing optimization for automated generation of complex system's initial configurations for molecular dynamics and docking. *Journal of computational chemistry*. 2003, 24, 819-25.
- [65] Nosé, S. A unified formulation of the constant temperature molecular dynamics methods. *The Journal of chemical physics*. **1984**, 81, 511-9.
- [66] Hoover, W.G. Canonical dynamics: Equilibrium phase-space distributions. *Physical review A.* **1985**, 31, 1695.
- [67] Allen, M.P., Tildesley, D.J. Computer simulation of liquids. *Clarendon: Oxford.* 1987.
- [68] Perdew, J.P., Burke, K., Wang, Y. Generalized gradient approximation for the exchange-correlation hole of a many-electron system. *Physical review B*. **1996**, 54, 16533.
- [69] Aggarwal, A., Lancaster, N.L., Sethi, A.R., Welton, T. The role of hydrogen bonding in controlling the selectivity of Diels–Alder reactions in roomtemperature ionic liquids. *Green Chemistry*. 2002, 4, 517-20.
- [70] Milet, A., Korona, T., Moszynski, R., Kochanski, E. Anisotropic intermolecular interactions in van der Waals and hydrogen-bonded complexes: What can we get from density functional calculations? *The Journal of chemical physics*. **1999**, 111, 7727-35.
- [71] Lee, C., Yang, W., Parr, R.G. Development of the Colle-Salvetti correlationenergy formula into a functional of the electron density. *Physical review B.* 1988, 37, 785.
- [72] Tsuzuki, S., Katoh, R., Mikami, M. Analysis of interactions between 1butyl-3-methylimidazolium cation and halide anions (Cl-, Br- and I-) by

ab initio calculations: anion size effects on preferential locations of anions. *Molecular Physics*. **2008**, 106, 1621-9.

- [73] Boys, S.F., Bernardi, F. The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. *Molecular physics*. **1970**, 19, 553-66.
- [74] Frisch, M., Trucks, G., Schlegel, H., Scuseria, G., Robb, M., Cheeseman, J., et al. gaussian 03, Gaussian. *Inc., Wallingford, CT.* 2004, 371.
- [75] Reed, A.E., Curtiss, L.A., Weinhold, F. Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint. *Chemical Reviews*. **1988**, 88, 899-926.
- [76] Bader, R. Atoms in moleculars: a quantum theory. Oxford University, Oxford, 1990.
- [77] Morrow, T.I., Maginn, E.J. Molecular dynamics study of the ionic liquid 1n-butyl-3-methylimidazolium hexafluorophosphate. *The Journal of Physical Chemistry B.* 2002, 106, 12807-13.
- [78] Lovelock, K.R., Deyko, A., Corfield, J.A., Gooden, P.N., Licence, P., Jones, R.G. Vaporisation of a dicationic ionic liquid. *ChemPhysChem.* 2009, 10, 337-40.
- [79] Deyko, A., Lovelock, K.R., Corfield, J.-A., Taylor, A.W., Gooden, P.N., Villar-Garcia, I.J., et al. Measuring and predicting Δ vap H 298 values of ionic liquids. *Physical Chemistry Chemical Physics*. 2009, 11, 8544-55.
- [80] Yeganegi, S., Soltanabadi, A., Farmanzadeh, D. Molecular dynamic simulation of dicationic ionic liquids: effects of anions and alkyl chain length on liquid structure and diffusion. *The Journal of Physical Chemistry B.* 2012, 116, 11517-26.
- [81] Köddermann, T., Wertz, C., Heintz, A., Ludwig, R. Ion-pair formation in the ionic liquid 1-ethyl-3-methylimidazolium Bis (triflyl) imide as a function of temperature and concentration. *ChemPhysChem.* 2006, 7, 1944-9.
- [82] Prado, C.E.R., Freitas, L.C.G. Molecular dynamics simulation of the roomtemperature ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate. *Journal of Molecular Structure: THEOCHEM.* 2007, 847, 93-100.
- [83] Youngs, T. Aten—An application for the creation, editing, and visualization of coordinates for glasses, liquids, crystals, and molecules. *Journal of computational chemistry*. 2010, 31, 639-48.
- [84] Frenkel, D., Smit, B. Understanding molecular simulation: from algorithms to applications, Elsevier, 2023.
- [85] Liu, Z., Huang, S., Wang, W. A refined force field for molecular simulation of imidazolium-based ionic liquids. *The Journal of Physical Chemistry B*. 2004, 108, 12978-89.
- [86] Kelkar, M.S., Maginn, E.J. Effect of temperature and water content on the shear viscosity of the ionic liquid 1-ethyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide as studied by atomistic simulations. *The Journal of Physical Chemistry B.* 2007, 111, 4867-76.
- [87] Ozawa, R., Hayashi, S., Saha, S., Kobayashi, A., Hamaguchi, H.-o. Rotational isomerism and structure of the 1-butyl-3-methylimidazolium cation in the ionic liquid state. *Chemistry Letters*. 2003, 32, 948-9.
- [88] Hagiwara, R., Hirashige, T., Tsuda, T., Ito, Y. Acidic 1-ethyl-3-

methylimidazolium fluoride: a new room temperature ionic liquid. *Journal of fluorine chemistry*. **1999**, 99, 1-3.

- [89] Turner, E.A., Pye, C.C., Singer, R.D. Use of ab initio calculations toward the rational design of room temperature ionic liquids. *The Journal of Physical Chemistry A*. 2003, 107, 2277-88.
- [90] Bondi, A.v. van der Waals Volumes and Radii. The Journal of physical chemistry. 1964, 68, 441-51.
- [91] Ebenso, E. Synergistic effect of halide ions on the corrosion inhibition of aluminium in H2SO4 using 2-acetylphenothiazine. *Materials Chemistry* and Physics. 2003, 79, 58-70.
- [92] Tsuzuki, S., Arai, A.A., Nishikawa, K. Conformational analysis of 1-butyl-3methylimidazolium by CCSD (T) level ab initio calculations: Effects of neighboring anions. *The Journal of Physical Chemistry B*. 2008, 112, 7739-47.
- [93] Koch, U., Popelier, P.L. Characterization of CHO hydrogen bonds on the basis of the charge density. *The Journal of Physical Chemistry*. **1995**, 99, 9747-54.
- [94] Popelier, P. Characterization of a dihydrogen bond on the basis of the electron density. *The Journal of Physical Chemistry A.* **1998**, 102, 1873-8.