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Hydrogen Bonds in Imidazolium Ionic Liquids

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It is critically important to understand the structural properties of ionic liquids. In this work, the structures of cations, anions, and cation−anion ion-pairs of 1,3-dialkylimidazolium based ionic liquids were optimized systematically at the B3LYP/6-31+G* level of DFT theory, and their most stable geometries were obtained. It was found that there exist only one-hydrogen-bonded ion-pairs in single-atomic anion ionic liquids such as [emim]Cl and [emim]Br, while one- and two-hydrogen-bonded ion-pairs in multiple atomic anion ionic liquids such as [emim]BF_4 and [emim]PF_6 exist. Further studies showed that the cations and anions connect each other to form a hydrogen-bonded network in 1,3-dialkylimidazolium halides, which has been proven by experimental measurement. Furthermore, the correlation of melting points and the interaction energies was discussed for both the single atomic anion and multiple atomic anion ionic liquids.

1. Introduction

Ionic liquids are a class of novel compounds composed exclusively of organic cations and inorganic anions. They possess appealing features such as low melting points, negligible vapor pressure, nonvolatile, nonflammable, wide electrochemical windows, and so on.[1−5] Their physical properties could be tailored by adjusting the structures and species of cations and/or anions for a given end use, therefore ionic liquids have been referred to as “designed solvents”.[6] Such tunable properties have led to wide applications in many fields, for example, organic synthesis and catalytic reaction,[7] electrochemistry,[8,9] biochemistry,[10−12] and material engineering.[13]

In fact, the possible combination number of cations and anions is uncountable.[14,15] To select or design reasonable ionic liquids for a variety of applications, it is essential to understand their microstructures and interactions in various ionic liquid systems. It is, however, time-consuming and cost-intensive to study the physical properties of ionic liquids by experiments, therefore computer simulations have become an efficient and indispensable approach.[15]

The structural,[16,17] thermodynamic,[18−20] and dynamic properties[17,21−25] of both pure ionic liquids and their mixtures with other compounds have been studied extensively by computer simulations. Because the structural properties are the bases for understanding the thermodynamic, dynamic, and other properties of ionic liquids, increasing interest has been aroused in recent years, especially in hydrogen bonds of ionic liquids. Dieter et al.[26] reported the forming of hydrogen bonds in C2−H···Cl, C4−H···Cl, and C5−H···Cl fragments of [emim]Cl by the semiempirical AM1 method. Recently, Meng et al.[27] demonstrated the existence of the hydrogen bonds of C−H···F and N−H···F in [bmim]PF_6 by using the ab initio method. The existence of hydrogen bonds in a series of 1-alkyl-3-methylimidazolium hexafluorophosphates ([rmim]PF_6) has also been found by calculating Raman and IR spectra at the B3LYP/6-311+G(2d,p) level of DFT theory.[28]

TABLE 1: Bond Distances (Å), Bond Angles (deg), and Dihedral Angles (*D*, deg) of Four Imidazolium Cations

	$[mmim]^+$	$[emim]^+$	$[pmim]^+$	$[bmim]^+$	exptl(av)[31−33]
N1−C2	1.339	1.338	1.339	1.338	1.315
C2−N3	1.339	1.340	1.340	1.340	1.300
N3−C4	1.384	1.383	1.383	1.383	1.390
C4−C5	1.365	1.365	1.365	1.365	1.374
C5−N1	1.384	1.383	1.383	1.383	1.410
C2−H6	1.080	1.080	1.080	1.080	
C4−H7	1.080	1.080	1.080	1.080	
C5−H8	1.080	1.080	1.080	1.080	
N1−C9	1.472	1.484	1.483	1.484	1.550
N3−C10	1.472	1.471	1.471	1.470	1.480
∠N1−C2−N3	108.95	109.06	109.08	109.08	110.0
∠N3−C4−C5	107.14	107.10	107.83	107.09	104.0
$D_{N1-C2-N3-C4}$	−0.005	0.023	0.039	0.042	
$D_{C2-N3-C4-C5}$	0.007	0.041	0.055	0.063	

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. It is difficult to find some general rules of hydrogen bonds with the variation of cations and/or anions according to the reported simulation results.

To understand the hydrogen bonds in the imidazolium ionic liquids, a series of ionic liquids composed of cations such as $[mmim]^+$, $[emim]^+$, $[pmim]^+$, and $[bmim]^+$ and the anions such as Cl^-, Br^-, BF_4^-, and PF_6^- have been systematically studied by ab initio and DFT in this work. The structures of not only the single ions and single ion-pairs but also of multiple ion-pairs have been investigated.

2. Calculation Methods

Calculations were performed with Gaussian03. To compare the energy profile and determine the most stable geometry the conformational analysis of the cations was carried out at the HF/6-31+G*, MP2/6-31+G*, and B3LYP/6-31+G* levels. The

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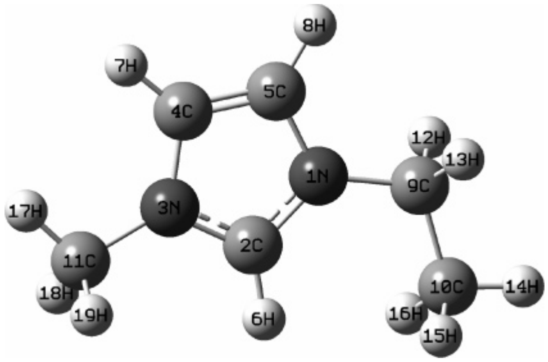


Figure 1. The initial geometry of the [emim]$^+$ cation.

TABLE 2: Bond Distances (Å), Bond Angles (deg), Dihedral Angles (*D*, deg), and Interaction Energies (*E*, kJ/mol) of Three [emim]Cl Ion-Pairs[a]

	[emim]Cl(1)	[emim]Cl(2)	[emim]Cl(3)
N1−C2	1.339	1.342	1.337
C2−N3	1.342	1.338	1.343
N3−C4	1.388	1.384	1.387
C4−C5	1.364	1.367	1.367
C5−N1	1.385	1.387	1.385
C2−H6	1.124	1.079	1.079
C4−H7	1.079	1.105	1.078
C5−H8	1.078	1.078	1.105
N1−C9	1.481	1.472	1.486
N3−C10	1.464	1.477	1.461
∠N1−C2−N3	107.94	108.76	108.77
∠N3−C4−C5	106.71	106.35	107.64
$D_{\mathrm{N1-C2-N3-C4}}$	0.068	0.014	0.010
$D_{\mathrm{C2-N3-C4-C5}}$	0.102	0.075	0.012
H···Cl	2.000	2.156	2.161
∠Cl···H−C*	159.64	152.29	150.52
$D_{\mathrm{Cl\cdots H-C^*-N^*}}$	3.28	2.13	11.94
E	−378.03	−344.69	−346.01

[a] C* and N* represent carbon atoms and nitrogen atoms in ion-pairs of the hydrogen bond.

geometries of different ion-pairs were optimized at the B3LYP/6-31+G* level so that the electronic correlation between cation and anion was taken into account.[29,30] The local structures were calculated at the B3LYP/3-21+G* level with PBC. The vibrational analyses on all structures revealed a lack of imaginary frequencies, ensuring the presence of a true minimum.

All the calculations were carried out on the SHENTENG 6800 supercomputer and DAW-NING 4000 computers running the Linux operation system. Each node of the SHENTENG 6800 supercomputer contains four Intel Itanium 1.3 GHz processors and each node of DAWNING 4000 contains two Intel Xeon 2.4 GHz processors.

3. Results and Discussions

3.1. The Structures of Single Ions. The simplest 1,3-dimethylimidazolium cation ([mmim]$^+$) was optimized directly at the B3LYP/6-31+G* level. The most stable geometry was obtained, and showed a planar structure with the dihedral angles $D_{\mathrm{N1-C2-N3-C4}}$ and $D_{\mathrm{C2-N3-C4-C5}}$ of −0.005° and 0.007° respectively (Table 1).

To find the most stable geometry of the 1-ethyl-3-methylimidazolium cation ([emim]$^+$), the simulations were conducted by the following two steps. First, all the degrees of freedom were relaxed except that the dihedral angle of $D_{\mathrm{C2-N1-C9-C10}}$ increased with a step of 10° at a range of 0−170° (Figure 1). Three profiles of torsion energy were obtained at the HF/6-31+G*, MP2/6-31+G*, and B3LYP/6-31+G* levels, which were presented in Figure 2, parts A, B, and C, respectively. It can be found that there is a global minimum at 110° and a local minimum at 10° for all three levels. Such a phenomenon may be due to the interactions between the H atoms on the ring and the terminal H atoms on the alkyl side chains. The interactions between the H atoms on the methyl side chain and the H atom of C2−H on the ring is dominant at 0−10°, while the interactions between the H atoms on the ethyl side chain and the H atom of C2−H on the ring become main factors at 10−170°. Second, the initial value of the dihedral angle of $D_{\mathrm{C2-N1-C9-C10}}$ was set as 110° and all the degrees of freedom were relaxed; the geometry was fully optimized at B3LYP/6-31+G* level. The most stable geometry of [emim]$^+$ was obtained at $D_{\mathrm{C2-N1-C9-C10}} = 105.04°$ (Table 1).

For 1-propyl-3-methylimidazolium cation ([pmim]$^+$), each of the three terminal H atoms on the ethyl fragment of [emim]$^+$ were replaced by a methyl fragment ($-\mathrm{CH_3}$) respectively as initial geometries of [pmim]$^+$, which were fully optimized directly at the B3LYP/6-31+G* level. The most stable geometry is obtained with the minimum value of energy (for the structrural sizes see Table 1). Similarly, the most stable geometry of the 1-butyl-3-methylimidium cation ([bmim]$^+$) was also obtained (for the structrure sizes see Table 1).

By comparing the calculated values and experimental data[31−33] for the most stable geometries of [mmim]$^+$, [emim]$^+$, [pmim]$^+$, and [bmim]$^+$ cations, it was found that they are in good agreement (Table 1). For all four cations, the imidazolium rings show a planar structural property, while the two dihedral angles of $D_{\mathrm{N1-C2-N3-C4}}$ and $D_{\mathrm{C2-N3-C4-C5}}$ are significantly different. The distortions become larger with the *n*-alkyl side chains increasing although the largest variation is less than 0.1°. The above results indicate that the effects of *n*-alkyl side chains on the structures of the imidazolium ring of cations are negligible.

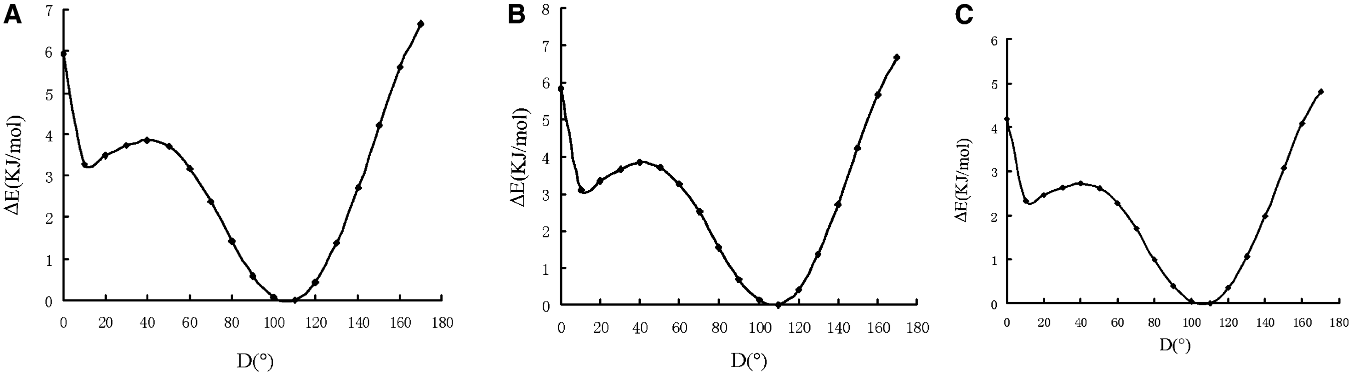


Figure 2. The differences in energy between the most stable and less stable structures of [emim]Cl: (A) the HF/6-31+G* level, (B) the MP2/6-31+G* level, and (C) the B3LYP/6-31+G* level.

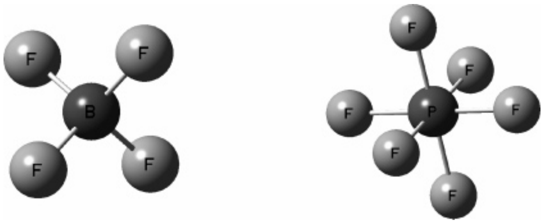


Figure 3. The geometries of the BF_4^- anion (T_d) and the PF_6^- anion (O_h). The four distances of B−F are 1.397 Å in BF_4^-; the six distances of P−F are 1.648 Å in PF_6^-.

For anions such as BF_4^- and PF_6^-, the most stable geometries were obtained at the B3LYP/6-31+G* level. The symmetry of the BF_4^- anion is T_d with B−F bonds of 1.397 Å, and that of the PF_6^- anion is O_h with P−F bonds of 1.648 Å (Figure 3). The calculated values also are in good agreement with the experimental data.[33]

3.2. Hydrogen Bonds of a Single Ion-Pair. For the single atomic anion ionic liquids, dialkylimidazolium halides are typical. For the ion-pair of [emim]Cl, the Cl^- anion may couple with the $[emim]^+$ cation near C2−H, C4−H, or C5−H fragments,[20] therefore three initial geometries could be obtained by considering Cl^- near C2−H, C4−H, or C5−H of the $[emim]^+$ cation, respectively, and the distance of Cl···H was set as 2.000 Å. The three initial geometries were optimized fully at the B3LYP/6-31+G* level. Three most stable geometries for the ion-pairs of [emim]Cl, named [emim]Cl(1), [emim]Cl(2), and [emim]Cl(3), were obtained as shown in Figure 4, and the main structural sizes and interaction energies are presented in Table 2. The dihedral angles $D_{Cl\cdots H-C^*-N^*}$ are 3.18°, 2.13°, and 11.94° for the ion-pairs of [emim]Cl(1), [emim]Cl(2), and [emim]Cl(3), respectively. The values of the dihedral angles $D_{Cl\cdots H-C^*-N^*}$ indicate that the Cl^- anions are nearly coplanar with the imidazolium rings. The distances of Cl···H in [emim]Cl(1), [emim]Cl(2), and [emim]Cl(3) are 2.000, 2.156, and 2.161 Å, respectively, which are much longer than the covalent bond distance of H−Cl (1.31 Å) and shorter than the van der Waals distance of Cl···H (2.95 Å).[34] These values are within the accepted criteria of the C−H···Cl hydrogen bond, which implies that the Cl^- anions form hydrogen bonds with N*−C*−H fragments of the $[emim]^+$ cation.

From Table 2, it can be found that the structures of the imidazolium ring in [emim]Cl show very little change except for the distances of C2−H, C4−H, and C5−H, for example, the distance of C2−H changes from 1.080 Å to 1.124 Å, which indicates that the H atoms of N*−C*−H fragments are attracted by the Cl^- anions due to the larger positive charge distribution on the N*−C*−H fragments of the cations. The C*−H fragments and Cl^- anions are not on a line but form certain angles of 159.64°, 152.29°, and 150.52° for Cl···C2−H, Cl···C4−H, and Cl···C5−H, respectively (Table 2), which indicates that the *N*-alkyl side chains have certain influences on the formation of hydrogen bonds with Cl^- anions.

TABLE 3: Bond Distances (Å), Bond Angles (deg), and Interaction Energies (*E*, kJ/mol) of Four Dialkylimidazolium Chloride Ion-Pairs

	[mmim]Cl	[emim]Cl	[pmim]Cl	[bmim]Cl
C_2-H_6	1.137	1.124	1.188	1.089
$H_6\cdots Cl$	1.924	1.997	2.030	2.129
$\angle C_2-H_6\cdots Cl$	178.19	159.67	159.13	160.63
E(kJ/mol)	−392.95	−378.07	−373.35	−370.14
C_4-H7	1.106	1.105	1.103	1.098
$H_7\cdots Cl$	2.149	2.156	2.185	2.210
$\angle C_4-H_7\cdots Cl$	152.27	152.21	152.06	151.37
E(kJ/mol)	−380.65	−344.69	−339.48	−340.72
C_5-H_8	1.160	1.105	1.102	1.097
$H_8\cdots Cl$	2.149	2.161	2.199	2.228
$\angle C_5-H_8\cdots Cl$	152.32	150.52	150.36	149.94
E	−382.11	−346.01	−342.89	−328.50

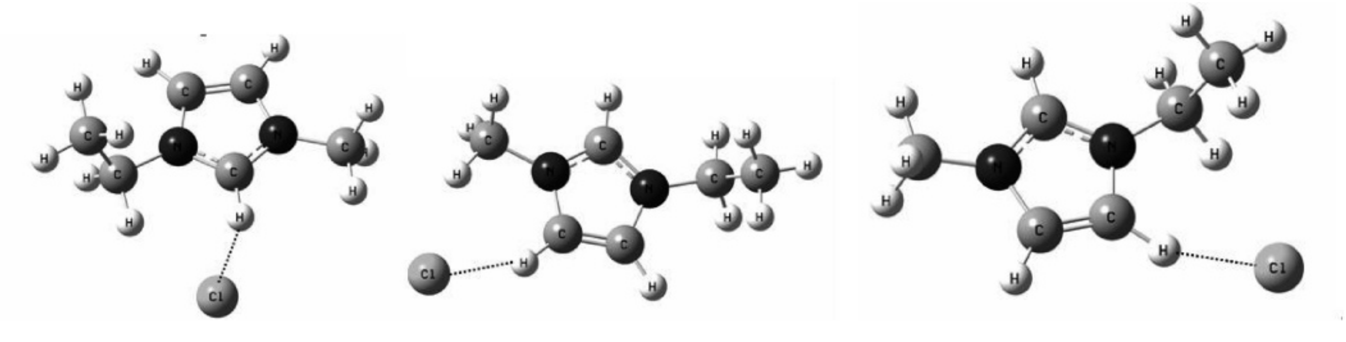
The interaction energies of ion-pairs are defined as follows:

$$E(\mathrm{kJ\cdot mol^{-1}}) = 2625.5[E_{AX}(\mathrm{au}) - (E_+(\mathrm{au}) + E_-(\mathrm{au}))] \tag{1}$$

where E_{AX} is the energy of the ionic system, and E_+ and E_- are the energy of cation and anion, respectively. For the ion-pair of [emim]Cl, the absolute value of the interaction energies is much larger than the normal hydrogen bond energies (50 $kJ\cdot mol^{-1}$), which indicate that there exist strong electrostatic attractions between the imidazolium cations and Cl^- anions.

Similar results were also obtained for [mmim]Cl, [pmim]Cl, and [bmim]Cl ionic liquids (Table 3). It can be found that when the size of the *N*-alkyl side chains increases, the distances of H···Cl increase, while the distances of C*−H, the bond angles of Cl···H−C*, and the interaction energies between Cl^- anions and imidazolium cations decrease, for example, when the *N*-alkyl side chains change from methyl to ethyl, propyl, and butyl, the distances of C2−H change from 1.137 Å to 1.124, 1.188, and 1.089 Å, the distances of Cl···H change from 1.924 Å to 1.997, 2.030, and 2.129Å, the angles of Cl···H−C* change from 178.19° to 159.67°, 159.13°, and 160.63°, and the interaction energies change from −392.95 $kJ\cdot mol^{-1}$ to −378.07, −373.35, and −370.14 $kJ\cdot mol^{-1}$. The above results show that the longer the *N*-alkyl side chains are, the weaker the hydrogen bonds of the ion-pairs would be.

Bromide anionic ionic liquids have similar structural properties to the chloride anionic ionic liquids (Table 4). Taking the ion-pair of [emim]Br as an example, the distances of Br···H in



[emim]Cl(1) [emim]Cl(2) [emim]Cl(3)

Figure 4. The most stable geometries of three ion-pairs of [emim]Cl.

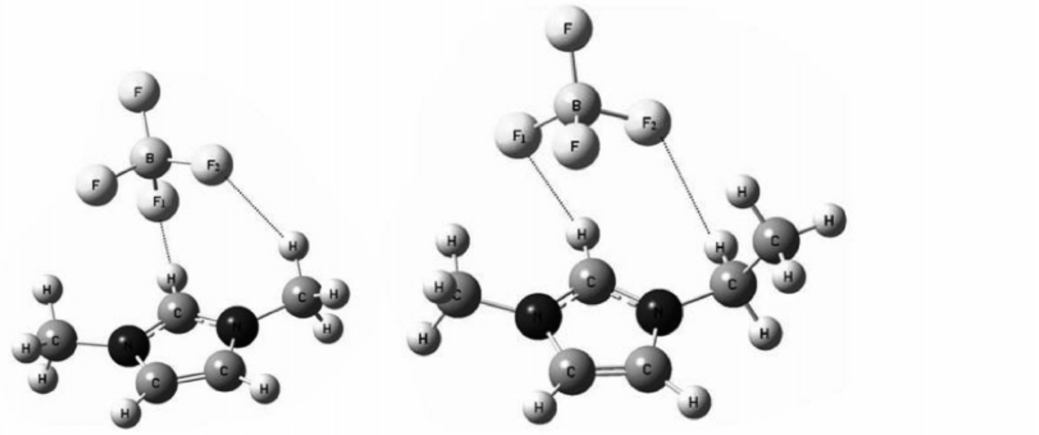
TABLE 4: Bond Distances (Å), Bond Angles (deg), and Interaction Energies (*E*, kJ/mol) of Dialkylimidazolium Bromide Ion-Pairs

	[mmim]Br	[emim]Br	[pmim]Br	[bmim]Br
C2−H	1.112	1.110	1.109	1.108
H···Br	2.195	2.218	2.233	2.239
∠C2−H···Br	157.06	155.18	155.20	153.91
E	−378.07	−372.82	−372.82	−343.94
C4−H	1.100	1.100	1.109	1.100
H···Br	2.313	2.313	2.193	2.316
∠C4−H···Br	152.83	152.95	172.14	152.71
E	−346.57	−341.32	−341.32	−312.43
C5−H	1.101	1.098	1.098	1.098
H···Br	2.313	2.347	2.344	2.368
∠C5−H···Br	152.83	150.25	150.06	149.98
E	−346.57	−346.57	−341.32	−317.68

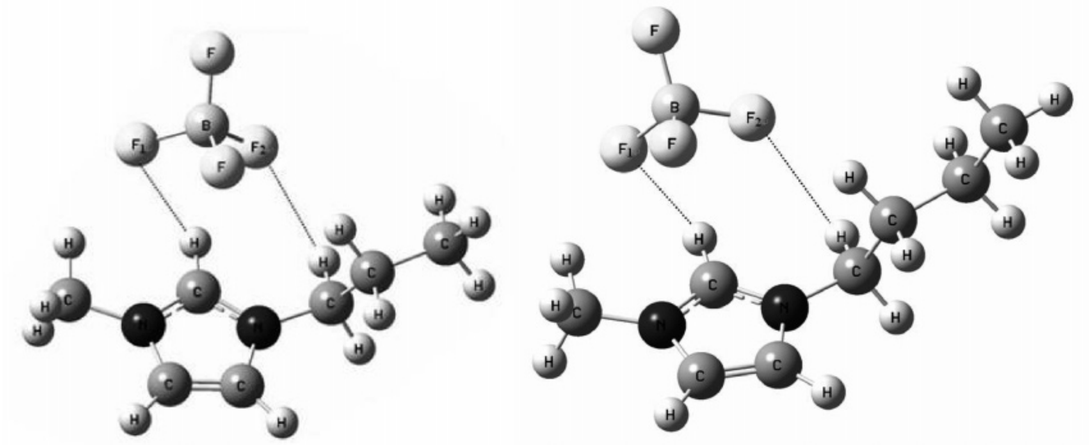
three stable geometries are 2.218, 2.313, and 2.347 Å, respectively, which are also much longer than the covalent bond distance of H−Br (1.46 Å), and shorter than the van der Waals distance of Br···H (3.05 Å).[29] The results suggest that the Br^- anion also forms a hydrogen bond with the C*−H fragment of the imidazolium cation. With the increase in size of *N*-alkyl side chains, the distances of H···Br, the angles of C−H···Br, and the absolute values of the interaction energies increase, while the distances of C*−H decrease.

Dialkylimidazolium tetrafluoroborate and hexafluorophosphate are two kinds of typical multiple atomic anion ionic liquids. Ab initio calculations[35] indicated that fluoride anion (F^-) could snatch up one H atom from cations to form hydrofluoride (HF) so that the C2 atom of the cation would change into the carbene carbon, which could explain the difficulties in synthesizing dialkylimidazolium fluoride salts from 1-methylimidazole and an alkyl fluoride. However, when the F^- anion was replaced by the tetrafluoroborate anion (BF_4^-), the charge was dispersed so that the electrostatic force between the cation and the anion was weakened and finally led to a stable liquid at room temperature.

To obtain the most stable structures of [mmim]BF_4, [emim]BF_4, [pmim]BF_4, and [bmim]BF_4 ion-pairs, the BF_4^- anion was located at different positions on the verge of the imidazolium ring: one of the F atoms of the BF_4^- anion was near the C2−H, C4−H, and C5−H fragments and the distances were set at 2.50 Å,[33] respectively. These initial geometries were fully optimized at the B3LYP/6-31+G* level. The most stable geometries were showed in Figure 5. It is found that the BF_4^- anions are favorable to move near the C2−H fragment above the imidazolium rings. Taking the [emim]BF_4 ion-pair as an example, it can be found that there are two shortest distances of H···F between the $[emim]^+$ cation and the BF_4^- anion, one is formed between the F atom labeled F1 and the C2−H fragment on the imidazolium ring, another between the F atom labeled F2 and the C−H fragment on the ethyl side chain. The two distances between F1···H and F2···H atoms are 2.083 and 2.642 Å, respectively (Table 5), which are longer than the covalent bond distance of H−F (1.07 Å) and shorter than the



[mmim]BF_4 [emim]BF_4



[pmim]BF_4 [bmim]BF_4

Figure 5. Optimized geometries of the ion-pairs of dialkylimidazolium tetrofluoroborate.

TABLE 5: Bond Distances (Å), Bond Angles (deg), and Interaction Energies (*E*, kJ/mol) of Dialkylimidazolium Tetrofluoroborate Ion-Pairs[a]

	[mmim]BF_4	[emim]BF_4	[pmim]BF_4	[bmim]BF_4
F1···H	1.862	2.083	2.220	2.045
H−C2	1.087	1.081	1.080	1.081
∠C2−H···F1	163.07	134.15	125.91	136.60
F2···H	2.282	2.642	2.517	2.655
H−C*(alkyl)	1.092	1.091	1.092	1.092
∠C*(alkyl)-H···F2	137.80	113.32	124.83	113.21
E	−347.88	−345.80	−342.28	−342.89

[a] C*(alkyl) denotes the carbon atom on the alkyl chain connected with the F2 atom by a hydrogen bond.

TABLE 6: Bond Distances (Å), Bond Angles (deg), and Interaction Energies (*E*, kJ/mol) of Dialkylimidazolium Hexafluorophosphate Ion-Pairs[a]

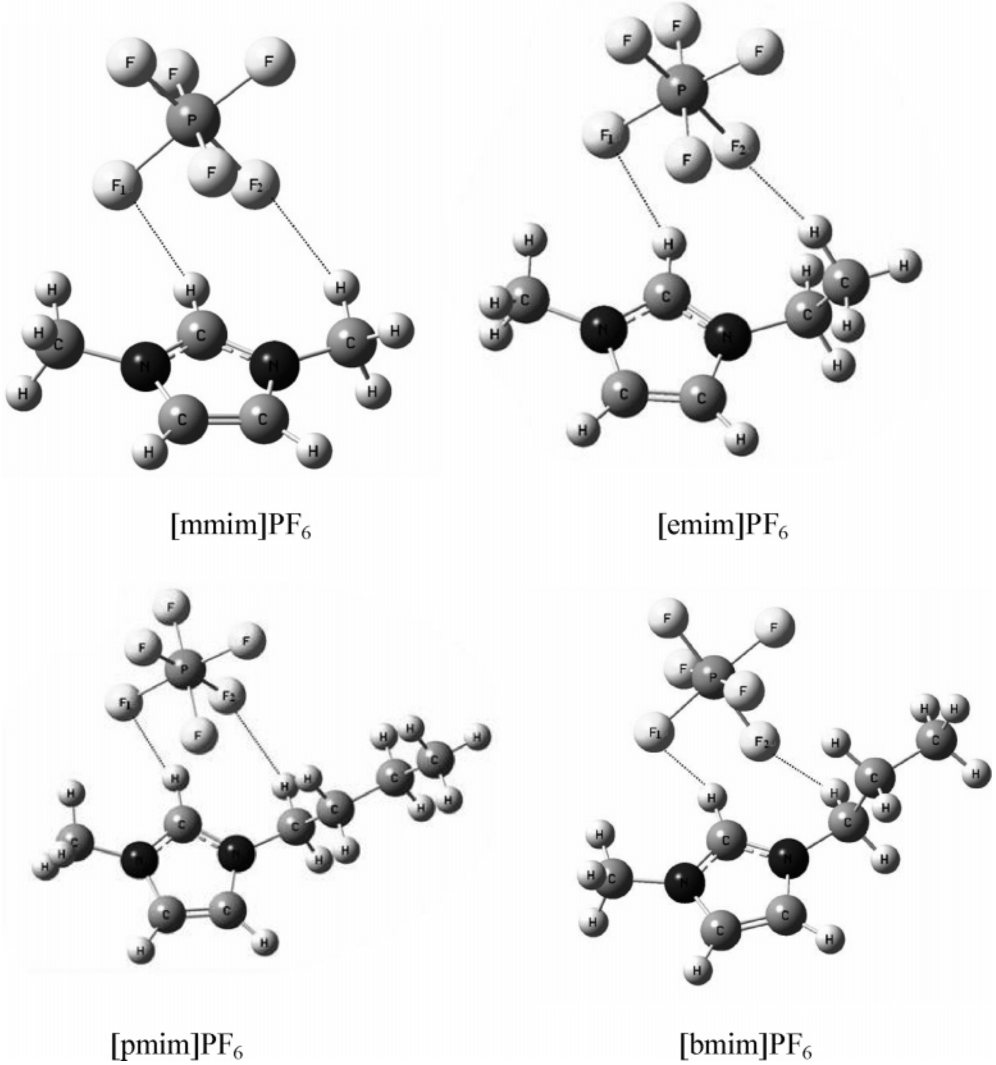
	[mmim]PF_6	[emim]PF_6	[pmim]PF_6	[bmim]PF_6
F1···H*	2.123	2.210	1.968	2.289
H−C2	1.080	1.081	1.082	1.080
∠C2−H···F1	134.00	130.26	158.88	131.02
F2···H*	2.285	2.303	2.272	2.527
H−C*(alkyl)	1.091	1.091	1.092	1.092
∠C*(alkyl)-H···F1	146.83	129.27	151.99	123.40
E	−358.91	−364.68	−317.69	−319.61

[a] C*(alkyl) denotes the carbon atom on the alkyl chain connected with the F2 atom by a hydrogen bond.

van der Waals distance of H···F (2.670 Å).[34] Correspondingly, the two angles of C−H···F1 and C−H···F2 are also largest with the values of 134.15° and 113.32°, respectively. Therefore it can be regarded that the two most stable hydrogen bonds of N*−C*−H···F were formed for the [emim]BF_4 ion-pair, while the other weaker hydrogen bonds were not taken into account in this work. The two most stable hydrogen bonds for [mmim]BF_4, [pmim]BF_4, and [bmim]BF_4 ion-pairs are also reported in Figure 5 and Table 5.

On the basis of the data in Table 5, it is found that with an increase in the size of the *N*-alkyl side chains, the distances of both H···F1 and H···F2 increase, while the angles of both C2−H···F1 and C*(alkyl)−H···F2 and the total interaction energies between the anion and the cation decrease. In general, it can be concluded that with the size of the *N*-alkyl side chains increasing, the BF_4^- anion moves toward the methyl side chain and the hydrogen bonds of ion-pairs become weaker.

Following a similar procedure to that described above, the most stable geometries of [mmim]PF_6, [emim]PF_6, [pmim]PF_6, and [bmim]PF_6 were obtained as shown in Figure 6. It is found that the PF_6^- anion is favorable to move near the C2−H fragment above the imidazolium ring. Taking [emim]PF_6 as an example, it can be found that the two shortest distances of F···H bonds are 2.210 and 2.503 Å (Table 6): one is formed between the F atom labeled F1 and the C2−H fragment on the imidazolium ring and another between the F atom labeled F2



[mmim]PF_6

[emim]PF_6

[pmim]PF_6

[bmim]PF_6

Figure 6. Optimized geometries of the ion-pairs of dialkylimidazolium hexafluorophosphate.

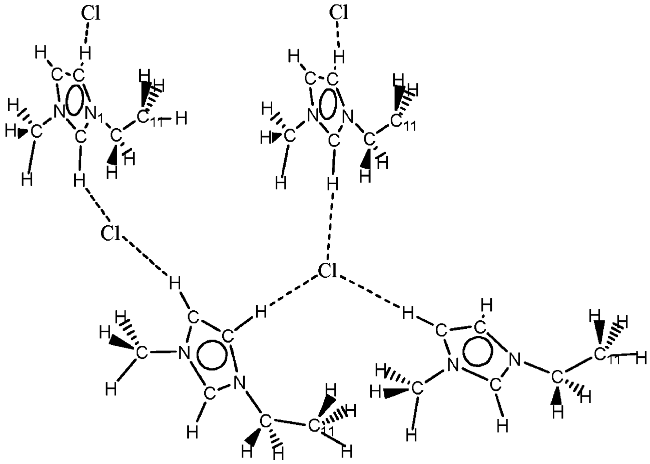


Figure 7. Optimized geometry of four ion-pairs of [emim]Cl with PBC.

and the C−H fragment on the ethyl side chain. The distances are longer than the covalent bond distance of H−Cl (1.07 Å) and shorter than the van der Waals H···F distance (2.670 Å).[34] Correspondingly, The two angles of C−H···F1 and C−H···F2 also are largest, with values of 130.26° and 129.27° respectively. Therefore it can regarded that the two most stable hydrogen bonds of N*−C*−H···F are formed in the [emim]PF$_6$ ion-pairs. The existence of the hydrogen bond ion-pairs in [emim]PF$_6$ ionic liquid has been confirmed by Fuller.[36] Similar cases occur in [mmim]PF$_6$, [pmim]PF$_6$, and [bmim] PF$_6$ ion-pairs (Figure 6 and Table 6).

From Table 6 and Figure 6, it can be found that with the increase in size of the *N*-alkyl side chains, the distances of H···F1 and H···F2 increase and the angles of C*−H···F1 and C*−H···F2 decrease, although there is a slightly unusual change for the ion-pair of [pmim]PF$_6$. The interaction energies do not show an obvious trend and there is a large gap from [emim]PF$_6$ to [pmim]PF$_6$, for example, −364.68 kJ/mol for [emim]PF$_6$ and −317.69 kJ/mol for [pmim]PF$_6$.

3.3. The Structures of Multiple Ions. For the single atomic anion ionic liquid, [mmim]Cl, [emim]Cl, [pmim]Cl, and [bmim]Cl are typical. Taking [emim]Cl as the example, the four ion-pairs were assigned in a cubic box of 10 Å^3,[17,31] and were optimized at the B3LYP/3-21+G* level. During optimization, the periodic boundary conditions (PBC) were used in order to model bulk behavior with a limited number of molecules in two-dimension space. The optimized results are shown in Figure 7 and local structures are given in Figure 8. From Figure 8, it can be seen that there are also three [emim]$^+$ cations around the Cl$^-$ anion, and the distances of C*−H fragments and the Cl$^-$ anion are within the range of a hydrogen bond (1.867, 2.055, and 2.032 Å, respectively). Similarly there are three Cl$^-$ anions around the [emim]$^+$ cation. Therefore the structural properties of the hydrogen bond are reserved for the system composed of multiple ions of [emim]Cl.

The IR spectra were simulated at the B3LYP/3-21+G* level for the structures shown in Figure 8. Both the calculated peak frequencies and experimental data[34] are presented in Table 7. It can be found that the calculated peak frequencies are slightly higher than the experimental values for the same vibration modes. The strongest absorption band was assigned to the C−H stretch vibrations on the imidazolium ring, the frequencies are between 3238.09 and 3056.90 cm^{-1} by calculation, while they are between 3147.00 and 2965.00 cm^{-1} by experiment, which are smaller than the aromatic C−H stretch vibrations between 3200 and 3100 cm^{-1}. The second strong absorption band was assigned to the C−H stretch vibrations on the *N*-alkyl side chain and the frequencies are between 3048.30 and 3038.80 cm^{-1} by calculation, while they are between 2960.00 and 2900.00 cm^{-1} by experiment, which correspond to the normal alkyl C−H stretch vibrations, and imply that the Cl$^-$ anion does not have a strong influence on the *N*-alkyl side chains of the cations. The above results give strong evidence that the structure described in Figure 8 reflects the basic structural properties of the [emim]Cl ionic liquid.

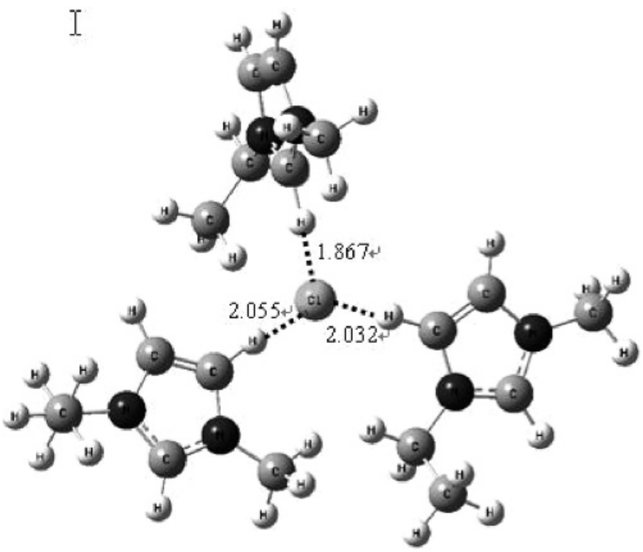


Figure 8. The local structures of hydrogen bonds of [emim]Cl.

TABLE 7: Vibrational Assignment (cm^{-1}) of Local Structures of [emim]Cl

band assign.	peak freq (calcd)	peak freq (exptl)[34]
ring C−H asym str	3238.09	3147.00
ring C−H sym str	3056.90	2965.00
methyl C−H sym str	3038.80	2960.00
ethyl C−H asym str	3048.30	2900.00

In fact, the local structures in Figure 8 can be periodically extended in the *X* direction and the *Y* direction, and an extended structure is shown in Figure 9. The cations and anions are arranged alternately at different rows and the cations share a plane. The rows in the plane represent a cross-section of the layers formed by the staggered stacks of cations running parallel to the plane of the drawing. The alternating rows running perpendicular to the plane represent a similar cross-section. The structure mentioned above is repeated in the next layer except that the orientation of the ring plane is rotated 90° approximately. The two-dimensional structure depicted in Figure 9 is extended to three-dimensional space (*Z* direction) so that a periodic hydrogen-bonded network is formed. That hydrogen-bonded networks exist in both solid and liquid phases has been confirmed by experiment.[35] A similar hydrogen-bonded network was also found to exist in other dialkylimidazolium chlorides such as [mmim]Cl, [pmim]Cl, and [bmim]Cl ionic liquids and dialkylimidazolium bromides such as [mmim]Br, [emim]Br, [pmim]Br, and [bmim]Br by using the DFT method.

For multiple atomic anion ionic liquids such as [emim]BF$_4^-$ and [emim]PF$_6^-$, the computations have proven to be very complicated and quite "time" expensive compared to that for the single atomic anion ionic liquids. We are endeavoring to optimize the hydrogen-bonded network including several cations and anions of the multiple atomic anion ionic liquids.

3.4. The Correlation of Melting Points and Interaction Energies. Melting point is one of the most important properties of ionic liquids and reflects the molecular packing and the

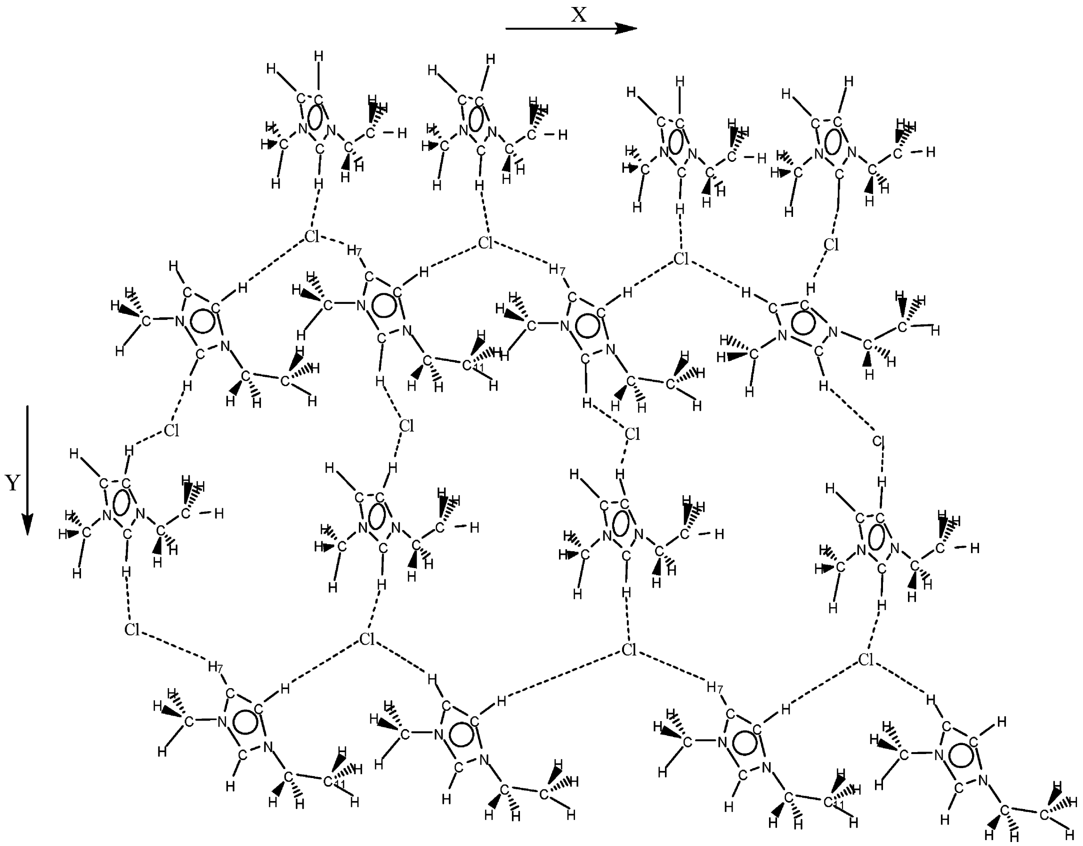


Figure 9. The hydrogen-bond network in [emim]Cl.

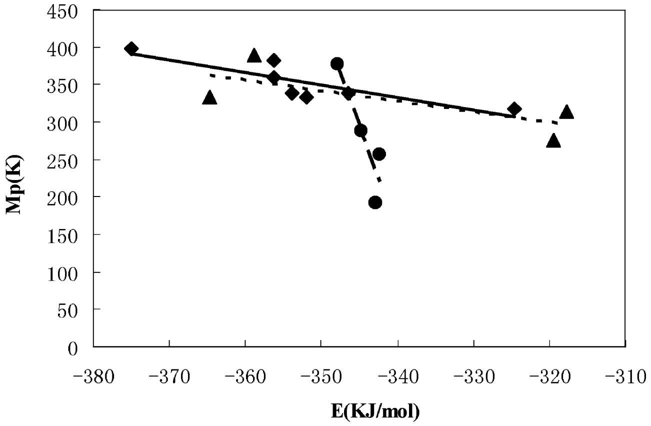


Figure 10. The correlation of melting points and interaction energies for dialkylimidazolium ionic liquids: (▲) Cl^- and Br^- series;(●)BF_4^- series; and (◆) PF_6^- series.

interactions of cations and anions. The plot of the correlation of melting points (mp, K) and interaction energies (*E*, kJ/mol) for dialkylimidazolium chloride, bromide, dialkylimidazolium tetrafluoroborate, and dialkylimidazolium hexafluorophosphate ionic liquids is shown in Figure 10. The linear relationship was taken on for these ionic liquids and the melting points decrease when the size of the *N*-alkyl side chains increases.

Seven species of the Cl^- and Br^- series, except for [pmim]-Br, were correlated and the linear relationship is very pronounced. The melting points are a range from 300 to 400 K while the interaction energies are between −375 and −320 kJ/mol. A similar trend was observed for four species of the PF_6^- series, but the linear relationship is very gross. For four species of BF_4^-, the linear relationship between melting points and interaction energies is also pronounced, but the difference between successive melting points is much greater than the difference between successive energies: the melting points are in a range from 400 to 200 K while the interaction energies are between −350 and −340 kJ/mol. So it is indicated that the more atoms the anions include, the more complicated the interactions between cations and anions are.

4. Conclusion

In this work, the most stable geometries of cations, anions, and ion-pairs of dialkylimidazolium halide (chloride and bromide), dialkylimidazolium tetrafluoroborate, and hexafluorophosphate were obtained by using ab initio and DFT methods. It was found that there exist only one-hydrogen-bonded ion-pairs in the single atomic anion ionic liquids such as [emim]Cl and [emim]Br; however, not only one-hydrogen-bonded ion-pairs but also two-hydrogen-bonded ion-pairs in the multiple atomic anion ionic liquids such as [emim]BF_4 and [emim]PF_6 exist. Further studies showed that the hydrogen-bonded network existed in the dialkylimidazolium halide by the DFT calculations with PBC, which has been proven by experimental measurements. Linear relationships have been found between the melting points and the interaction energies for most of the dialkylimidazolium based ionic liquids. Further work is now in progress for understanding the hydrogen-bonded network and the influence on both the single atomic anion and multiple atomic anion ionic liquids.

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