

The Interaction Nature of Br⁻ with 1-(4-Butylamino)-3-Methyl Imidazolium

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Abstract: An ionic liquid (IL) interaction system of Br⁻ with 1-(4-butylamino)-3-methyl imidazolium([Bamim]⁺) were investigated using B3LYP and MP2 methods at 6-311++G** level. Three possible stable geometry structures of this IL system were optimized. The energies of these three structures and ion-pair considering zero point energy (ZPE) and basis sets superposition energy (BSSE) correction were calculated. The results show that the interactions between ([Bamim]⁺) and Br⁻ are mainly hydrogen bonds(H-bonds); the interaction energies between ion-pairs are larger than -350KJ/mol, which are far beyond those of H-bonds; the interaction nature of Br⁻ with cation is studied based on natural bond orbital (NBO) calculation and the results show that the electrostatic attraction force plays a very important role in the interaction energy between ion-pair.

Keywords: Ionic liquids, interaction nature, hydrogen bonds, charge redistribution.

1. INTRODUCTION

The worsening environmental problems are receiving increasing attentions, and scientists from all kinds of fields have been trying their best to find out environment-friendly chemical reagents. As one kind of versatile green media, ionic liquids can be used as novel solvents without water and can be recycled, they have been paying more and more attentions [1-4]. And increasing environmentalists attempt to handle environmental matters by using ILs [5-9]. So it is very important to make clearly the properties of different kinds of ILs, due to that ILs are consist of organic cations and organic or inorganic anions, many ion-pairs can form thousands of ILs, thus it needs theoretical efforts to help the experimental technologies [10,11].

Hence in this paper, the ILs of bromide 1-(4-butylamino)-3-methyl imidazolium ([Bamim]⁺) is systematically investigated. The microstructure and the interaction nature between ion-pair were researched through computational quantum chemistry methods.

2. THEORETICAL METHODS

Both B3LYP and MP2 methods were used in this paper. B3LYP method can save much computation cost and offer reliable structure results, MP2 method can offer sound energies when it comes to describing

systems with very weak interactions, therefore the ILs structures are optimized at B3LPY//6-311++G** level, and the energies were calculated at MP2//6-311++G** level. All the calculations were completed by employing gaussian03 [12] and AIM 2000 [13] programs.

3. RESULTS AND DISCUSSIONS

3.1. Geometries of Stable Species

Firstly, we guessed six possible geometries of ILs based on the optimized geometry of [Bamim]⁺, and then optimization works confirmed three stable geometries of ILs, which were represented as ^AIL, ^BIL and ^CIL; The geometries of isolated [Bamim]⁺ and ILs were presented in Figure 1. The real lines demonstrate normal bonds; the dash lines demonstrate hydrogen bonds or weak bonds. The geometry details are shown as follows.

3.1.1. The Geometries of ILs

The three geometries of ILs have three weak bonds and all the weak chemical bonds have been confirmed by using AIM program. There are three hydrogen bonds (H-bonds) between [Abmim]⁺ and Cl⁻ in ^AIL and ^BIL, two H-bonds and a Br28...C2 weak bond appear between [Abmim]⁺ and Br⁻ in ^CIL. The geometry details of these three ILs are discussed as follows.

We shall introduce the geometry of ^AIL firstly. The three H-bonds in ^AIL are Br28...H14-C5 (2.3494Å), Br28...H19-C7 (2.6976Å) and Br28...H21-C8(3.1394Å). It is well known that the shorter of bond length, the stronger of the bond is. Hence, the bond strength order

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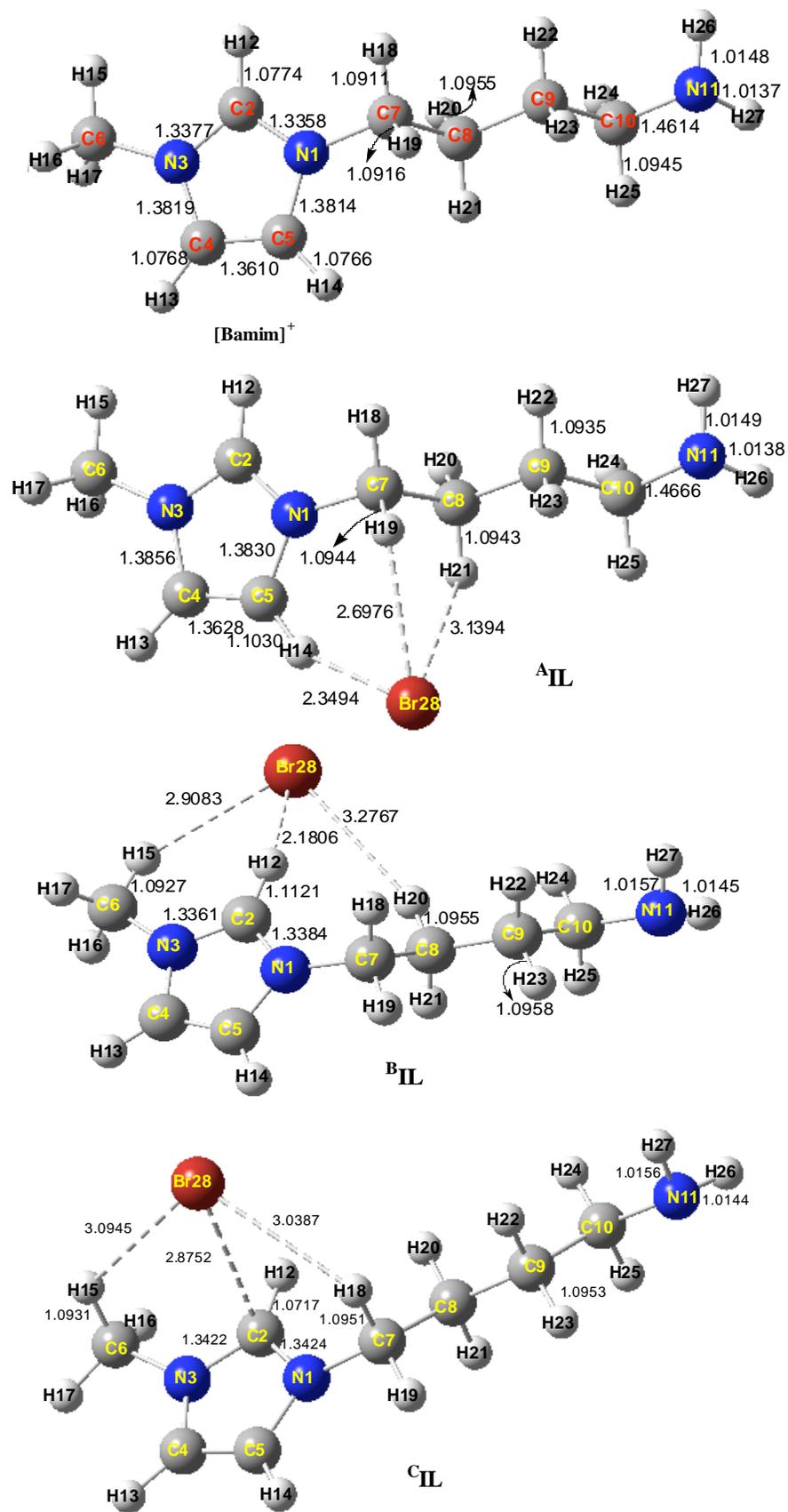


Figure 1: The geometries of the IIs and isolated cation (bond length:Å).

is $\text{Br28}\cdots\text{H14-C5}$, $\text{Br28}\cdots\text{H19-C7}$, $\text{Br28}\cdots\text{H21-C8}$. The H-bonds lengths of $\text{Br28}\cdots\text{H14-C5}$ and $\text{Br28}\cdots\text{H19-C7}$ are shorter than the van der Waals radii of Br and H (3.05Å), which means the formation of the two H-bonds. The bond length of $\text{Br28}\cdots\text{H21-C8}$ is longer than the van der Waals radii of Br and H, which implies that the H-bond can't be formed according to Valence Bond theory, however, a bond critical point (BCP) exists actually between Br28 and H21 according to Atom in Molecular (AIM) calculation. Additionally, when a normal chemical bond participate in forming H-bonds or other weak chemical bonds, some of the bonding electrons are transferred to from the normal chemical C-H bond to form H-bond or weak chemical bond, namely "electron transfer effect", and the normal chemical bond would be weakened, its bond length would be elongated. Such as, C5-H14 and C7-H19 are elongated by 0.0264 Å and 0.0028Å respectively for the "electron transfer effect". C8-H21 participates to form $\text{Br28}\cdots\text{H21-C8}$ H-bond, but its bond length is decreased by 0.0013 Å abnormally.

The three H-bonds in ^BIL are $\text{Br28}\cdots\text{H12-C2}$ (2.1806Å), $\text{Br28}\cdots\text{H15-C6}$ (2.9083Å) and $\text{Br28}\cdots\text{H20-C8}$ (3.2767Å), the bond strength order is $\text{Br28}\cdots\text{H12-C2}$ > $\text{Br28}\cdots\text{H15-C6}$ > $\text{Br28}\cdots\text{H20-C8}$. The bond lengths of $\text{Br28}\cdots\text{H12-C2}$ and $\text{Br28}\cdots\text{H15-C6}$ are shorter than the van der Waals radii of Br and H. But the bond length of $\text{Br28}\cdots\text{H20-C8}$ is longer than the van der Waals radii of Br and H, However, AIM calculation confirmed its existence actually. "Electron transfer effect" leads to the elongation of H12-C2 and H15-C6 bonds. However, the bond length of H20-C8 is shortened instead of being elongated abnormally.

There are two H-bonds of $\text{Br28}\cdots\text{H15-C6}$ (3.0692Å) and $\text{Br28}\cdots\text{H18-C7}$ (3.0387Å) besides a weak chemical bond of $\text{Br28}\cdots\text{C2}$ (2.8752Å) in ^CIL. There are also special phenomenon in ^CIL, for example, $\text{Br28}\cdots\text{H15-C6}$ H-bond is formed despite of its bond length is longer than the van der Waals radii of Br and H; C2-

H12 is shortened by 0.0057 Å abnormally, which involves in forming $\text{Br28}\cdots\text{C2}$ weak chemical bond.

3.2. Energies of all Species

The absolute energies and relative energies of all ILs structures were corrected by ZPE and BSSE correction and were listed in Table 1, in which the energies of the single $[\text{Bamim}]^+$ and Br^- are set as zero for the relative energies of ILs.

The interaction energy between ion-pair is usually evaluated by the energy difference ΔE ($\Delta E = E([\text{Bamim}]^+) + E(\text{Br}^-) - E(\text{IL})$). Table 1 shows that relatively energies between ion-pairs in ^AIL, ^BIL and ^CIL are -350.2kJ/mol, -378.6kJ/mol and -382.0kJ/mol respectively, that is the interaction energies between ion-pair are 350.2kJ/mol, 378.6kJ/mol and 382.0kJ/mol, respectively. The NBO calculation results imply that orbital interaction force between Br28 and $[\text{Bamim}]^+$ are mainly come from the interaction of lone pair electrons with the electron acceptors in $[\text{Bamim}]^+$, the total orbital interactions in ^AIL, ^BIL and ^CIL are about 19kJ/mol, 36kJ/mol and 22kJ/mol, It is obvious that the interaction energies are far beyond those orbital interaction energies of H-bonds and weak chemical bond between ion-pair, and some other interaction force must play a dominant role besides H-bonds and weak chemical bond. In order to find out the interaction nature NBO analysis details are shown as follows.

3.3. NBO Analysis of All Species

NBO calculations carried out for isolated $[\text{Bamim}]^+$ and the three ILs structures at B3LYP/6-311++G(d,p) level, the NBO atomic charges and the net integral charges of groups are obtained and listed in table 2 and table 3. The discussion details are shown in the following paper.

Table 1: The Absolute Energies and Relative Energies Including ZPE and BSSE of all Species

Species	ZPE	BSSE	E_{absolute}	E_{relative}
	a.u/mol	a.u/mol	a.u/mol	kJ/mol
$[\text{Bamim}]^+ + \text{Br}^-$	0.2427	0.00	-3049.5444	0.00
^A IL	0.2422	0.0004	-3049.6778	-350.2
^B IL	0.2422	-0.0001	-3049.6886	-378.6
^C IL	0.2428	0.0004	-3049.6889	-382.0

Table 2: The Net Integral Charges of the Main Groups

Species	The Charge of Fragments			
	imidazole	methyl	butyl amido	Br
[Bamim] ⁺	0.32658	0.32688	0.34654	
^A IL	0.26652	0.29513	0.32749	-0.88915
^B IL	0.22282	0.31087	0.31586	-0.84953
^C IL	0.21403	0.30183	0.31146	-0.8273

Table 3: The NBO Atomic Charge of All Species

Atom	Cation	^A IL	^B IL	^C IL
N1	-0.34372	-0.34355	-0.36729	-0.38071
C2	0.29502	0.26969	0.27692	0.32025
N3	-0.34619	-0.36204	-0.35989	-0.38423
C4	-0.00641	-0.04135	-0.0337	-0.02697
C5	-0.00360	-0.00416	-0.02564	-0.02097
C6	-0.35306	-0.34904	-0.3673	-0.35512
C7	-0.15939	-0.18349	-0.1513	-0.16343
C8	-0.39091	-0.39758	-0.40797	-0.39347
C9	-0.39121	-0.38868	-0.38599	-0.38706
C10	-0.17321	-0.17404	-0.17565	-0.17225
N11	-0.84390	-0.84064	-0.84568	-0.84378
H12	0.23703	0.21991	0.27748	0.2563
H13	0.24704	0.23036	0.22801	0.22484
H14	0.24741	0.29766	0.22693	0.22552
H15	0.22366	0.21246	0.26786	0.24729
H16	0.22829	0.21556	0.20542	0.20613
H17	0.22799	0.21616	0.20489	0.20353
H18	0.21540	0.18892	0.21359	0.2452
H19	0.22204	0.27552	0.20061	0.19654
H20	0.20326	0.17753	0.23885	0.20611
H21	0.20237	0.23657	0.19457	0.1935
H22	0.19300	0.17489	0.19102	0.1973
H23	0.21039	0.22587	0.19645	0.19946
H24	0.15832	0.14472	0.17075	0.15731
H25	0.18433	0.19419	0.17719	0.17661
H26	0.35192	0.35284	0.35338	0.35239
H27	0.36412	0.34087	0.34604	0.34703
Br28		-0.88914	-0.84953	-0.8273

Theoretically, the unit positive charge in isolated [Bamim]⁺ should belong to N3 atom, but it can be found in Table 2 and 3 that the unit positive charge is

dispersed among the whole [Bamim]⁺, for the unit positive charge in [Bamim]⁺, +0.32688 charge is transferred to methyl, +0.34654 charge to butylamino group, and +0.32658 charge is dispersed among the imidazole ring. When the three ILs are formed, the unit negative charge on Br is decreased by -0.11086, -0.15047 and -0.1727 respectively in ^AIL, ^BIL and ^CIL, which should result in the reduction of the positive charges and the decrease of the atomic negative charges in cation. For the sake of simplification, we set ^AIL as example to discuss how the charge population impacts on the interactions between ion-pair.

Table 3 shows that the net charge of Br28 becomes from -1 to -0.88916 when ^AIL is going to form, which implies that -0.11084 negative charge transfer from Br28 to [Bamim]⁺. For the -0.11084 charge, -0.06006, -0.03174 and -0.01905 charge transfer to imidazole ring, methyl and butylamino respectively calculated from Table 2. And if the unit positive charge does not redistribute, the atomic negative should be increased and the atomic positive charge should be decreased when imidazole ring receive -0.06006 negative charges from Br28. Table 3 shows that the some of the atomic charge changes are consistent with the above assumption, such as the positive charge of C2, H12 and H13 are decreased by 0.02533, 0.01712 and 0.01668, the negative charge of N3, C4 and C5 are increased by 0.01585, 0.03494 and 0.00056. However some of the atomic charge changes are against the assumption, such as, the positive charge on H14 is increased by 0.05025; the atomic negative charge on N1 is decreased by 0.00017. These abnormal charge changes indicate that the positive charge of cation redistributes when ^AIL is formed.

The charge dispersion and redistribution result in the atomic charge changes which lead to the reinforcement of electrostatic attraction force between ion-pair. For example, Table 3 shows that the positive H21 is increased after the dispersion of unit positive charge on N3, and then, the positive charge of H21

becomes from 0.20237 to 0.23657 after the redistribution of the unit charge on cation, hence the electrostatic attraction between H21 and Br28 are much reinforced and displays as Br28···H21-C8 H-bond. And this is the reason for the existence of the special H-bond (bond length is longer than the van der Waals radii of the two corresponding atoms). Additionally, another special phenomenon is that the bond length are shortened abnormally after “electron transfer effect”, such as the bond length of C8-H21 in [^]IL is shortened by 0.0013 Å. It maybe because the atomic charge of H21 (0.20237→0.23657) and C8(-0.39091→-0.39758) reinforce the electrostatic attraction between the two atoms caused by the charge dispersion and redistribution, and the reinforcement of is stronger than the “electron transfer effect”, hence the bond length of C8-H21 is shortened.

4. CONCLUSIONS

The results of the studies on the interaction nature in bromide 1-(4-butylamino)-3-methyl-imidazolium ionic liquids are summarized as follows:

- (1) Three stable geometry structures of this ionic liquid system were optimized and the interaction energies between [Bamim]⁺ and Br⁻ are more than 350 kJ/mol.
- (2) The interaction energy between [Bamim]⁺ and Br⁻ almost come from the electrostatic attraction force, the orbital interactions contributed about 20-36 kJ/mol only.
- (3) The NBO studies show that the main interaction force between [Bamim]⁺ and Br⁻ comes from the electrostatic attractions, the charge dispersion and redistribution of [Bamim]⁺ and Br⁻ reinforce the electrostatic force.

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