



Theoretical Studies on Task-specific Ionic Liquid of 1-(4-Butylamino)-3-methyl Imidazolium Tetrafluoroborate for Capturing CO₂

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Novel task-specific ionic liquids (ILs) of 1-(4-butylamino)-3-methyl imidazolium [Bamim]⁺ tetrafluoroborate [BF₄]⁻ and its reaction with CO₂ were systematically studied at B3LYP/6-311++G** level. Two stable ionic liquids and two molecular complexes from the reactions of those ionic liquids and CO₂ were optimized with no imaginary frequencies. The energies including zero point energy and basis sets superimposition energy were calculated. The interactions mechanism between the ion-pairs and the reaction characteristics of ionic liquids and CO₂ were analyzed based on natural bond orbital and atom in molecular calculations. The results show that the interactions between ion-pairs are mainly displayed as hydrogen bonds (H-bonds) and they are reinforced by charge dispersion and redistribution of [Bamim]⁺ and [BF₄]⁻. The interaction energies between ion-pairs are greater than -300 kJ/mol and those between ionic liquid and CO₂ are about -10 kJ/mol. The reaction of ionic liquids and CO₂ is physical absorption, the molar absorbing ratio is 1:1 and ionic liquid may have a mild regeneration condition theoretically.

Key Words: Ionic liquid, CO₂ capture, Physical absorption, Charge redistribution.

INTRODUCTION

Ionic liquids are composed of organic cations together with organic or inorganic anions. They are receiving increasing attentions¹⁻⁸ in various fields because of their benign properties, such as the wide liquid temperature range close to room temperature, the high thermal stability, non-volatility and non-flammability. Moreover, ionic liquids can be used as solvents without water and can be recycled, which will not cause secondary pollution. What has made scientists more excited is that functionalized ionic liquids can be synthesized according to our needs by changing their functional groups. So applying ionic liquids to deal with environmental problems is becoming one of the hottest scientific issues. Especially in the background of the worsening greenhouse effect, more and more scientists have been trying to capture CO₂ by applying functional ionic liquids⁹⁻¹⁶, but it is still in a way of "try-and-error", because that the microstructure and interaction mechanism between cations and anions are not very clear due to the limitation of the experimental techniques and expensive cost, which has become the bottleneck of theoretical and experimental research. So it is important to understand the interactions and interaction mechanism between ion-pairs at molecular level and then we can design effective functionalized ionic liquids to satisfy our needs. For this reason, it requires more efforts on the studies of the microstructure and inter-

actions in ionic liquids through computational quantum chemistry methods¹⁷⁻¹⁹.

In this paper, we investigated ionic liquids of 1-(4-butylamino)-3-methyl imidazolium [Bamim]⁺ tetrafluoroborate [BF₄]⁻ and its reactions with CO₂. From the investigation, we have optimized the possible stable geometries of ionic liquids and products from those ionic liquids absorbing CO₂, calculated the natural bond orbital atomic charges and electron density at the bond critical points (BCPs). Besides, the interactions between ion-pairs and interaction mechanism were studied by adopting atom in molecular theory (AIM) and electron density topological theory. Additionally, the reaction characteristics of ionic liquids absorbing CO₂ were also studied through the above mentioned theories and methods.

THEORETICAL METHODS

B3LYP may not be able to offer sound and reliable results when it comes to describing systems with very weak interactions. However, the interaction energy in ionic liquid systems is dominated by electrostatic attractions and the contribution from dispersion forces is not so important. In addition, B3LYP method can save much computation cost, so it has been widely used in the theoretical studies of ionic liquids¹⁻³. So all the calculation works in this paper were performed at B3LYP/6-311++G** level.

All of the possible geometries of ionic liquids and the products from the reactions of ionic liquids and CO₂ were optimized and their stability was confirmed by using vibration frequency analysis. The energies of those stable species including zero point energy (ZPE) and the basis sets superposition energy (BSSE) were calculated. The interaction characteristics and mechanisms were predicted by adopting natural bond orbital and atom in molecular calculations and analysis. All the calculations were completed by employing gaussian03²⁰ and atom in molecular 2000²¹ programs.

RESULTS AND DISCUSSION

In order to find the geometry characteristics of ionic liquids, the geometries of isolated [Bamim]⁺ and [BF₄]⁻ were designed and optimized firstly. A corresponding series of possible geometries for the ion-pairs were designed and two stable conformers were optimized, which were named as ^AIL and ^BIL respectively. Then CO₂ was introduced into ^AIL and ^BIL and the possible corresponding products from those two ionic liquids absorbing CO₂ were optimized, which were represented as ^AIL-CO₂ and ^BIL-CO₂. All the geometry optimization was carried out with all the degrees of freedom relaxed and no symmetry constraints. The geometries of isolate ions and two stable ionic liquids were mapped in Fig. 1, the geometries of ^AIL-CO₂ and ^BIL-CO₂ were mapped in Fig. 2. The real line in Fig. 1 and Fig. 2 demonstrates a normal bond; the dot line demonstrates a hydrogen bond or a weak chemical bond.

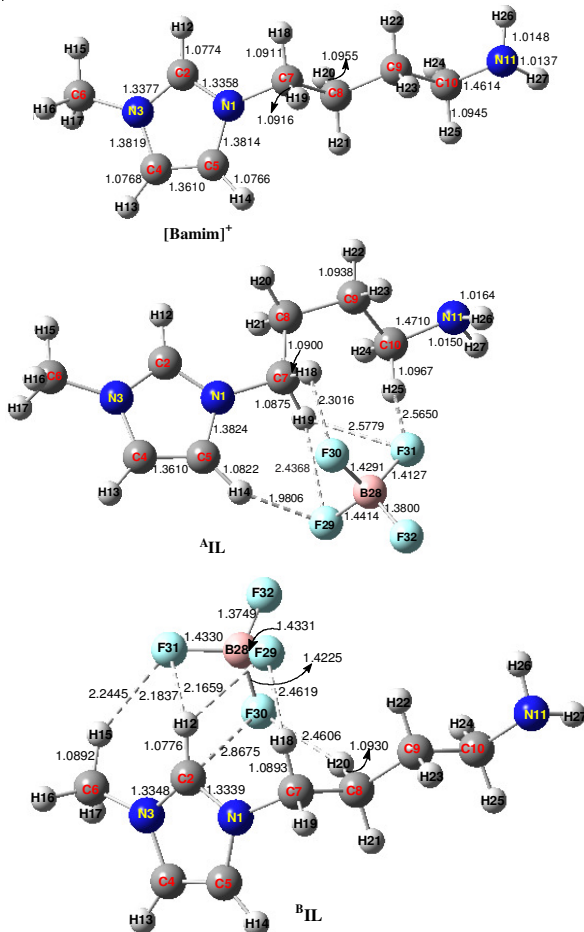


Fig. 1. Geometries of the ionic liquids and isolated cation(bond length:Å)

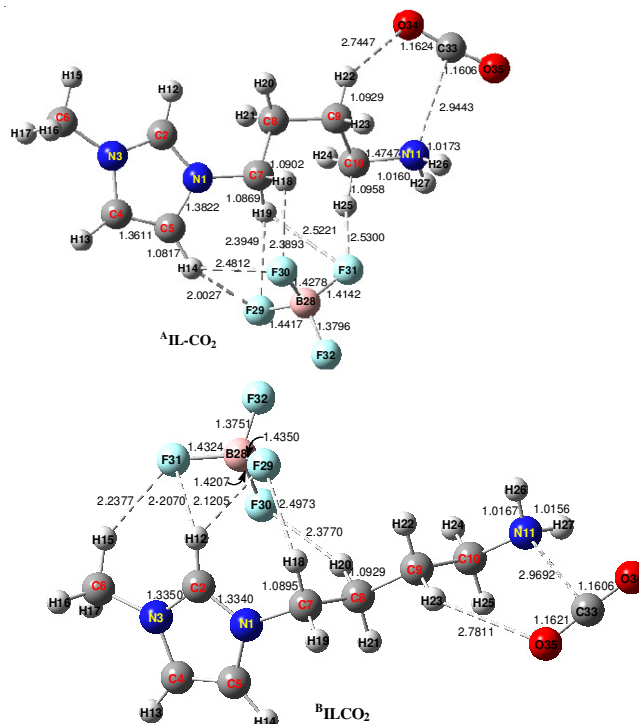


Fig. 2. Geometries of the ILs-CO₂ (bond length : Å)

Geometries of ionic liquids and molecular complexes:

For comparative analysis, the isolated geometries of [Bamim]⁺ are shown in Fig. 1 together with ^AIL and ^BIL. It can be observed that [BF₄]⁻ is closer to imidazole ring and amino-butyl in ^AIL and there are five hydrogen bonds (H-bonds) between [Bamim]⁺ and [BF₄]⁻; [BF₄]⁻ is closer to imidazole and amino-butyl in ^BIL; and there are five H-bonds beside a weak bond between F30 and C2. And further detail studies on the geometries are shown as follows.

The geometry of ^AIL should be discussed firstly, the five H-bonds in ^AIL are F29...H14-C5 (1.9806Å), F29...H19-C7 (2.4368Å), F30...H18-C7 (2.3016Å), F31...H19-C7 (2.4579Å), F31...H25-C10 (2.5650Å) as shown in Fig. 1. As it is known that bond length can be a simple criterion for the formation of a H-bond when the classic H-bonds are investigated and the shorter of bond length, the stronger the bond is. The H-bond lengths of F29...H14-C5, F29...H19-C7 and F30...H18-C7 are shorter than the van der Waals radii of F and H (2.45 Å), which proved the formation of the three H-bonds. The H-bond lengths of F31...H19-C7 and F31...H25-C10 are longer than the van der Waals radii of F and H, which means that the two H-bonds can not be formed according to the valence bond theory. However, bond critical points (BCPs) of the two H-bonds were found through atom in molecular calculation, which prove that the two H-bonds exist theoretically. And the bond strength order of the five H-bonds is F29...H14-C5 > F30...H18-C7 > F29...H19-C7 > F31...H19-C7 > F31...H25-C10 according to the bond length. The bond lengths of C5-H14 and C10-H25 are lengthened by 0.0056 Å and 0.0022 Å respectively, because some of the electrons in H atom are transferred to form H-bond, namely electron transfer effect, thus the two bonds are weakened and the two bonds are lengthened. But the bond lengths of C7-H19 and C7-H18 are shortened by 0.0041 Å and 0.0011Å, which deviate from

"electron transfer effect". Additionally, another special phenomenon is that H19 participates in forming two H-bonds of F29...H19-C7 and F31...H19-C7 simultaneously in spite of the saturation characteristic of H-bond.

The geometry details in ^BIL are similar with those in ^AIL; For the sake of simplification, only some important details are discussed here. A weak chemical bond of F30...C2 (2.8675 Å) is shorter than the van der Waals radii of F and C atoms; and the lengths of the other five H-bonds (F29...H12-C2, F29...H18-C7, F30...H20-C8, F31...H12-C2 and F31...H15-C6) are shorter than the van der Waals radii of F and H. H12 participates in forming two H-bonds of F29...H12-C2 and F31...H12-C2 simultaneously too, the bond length changes of C7-H18 and C8-H20 are also deviate from electron transfer effect.

The reason for abnormal phenomenon and bond changes in ^AIL and ^BIL will be discussed and explained in the following natural bond orbital and atom in molecular studies.

As shown in Fig. 2, when CO₂ is absorbed by ^AIL and ^BIL, two products of ^AIL-CO₂ and ^BIL-CO₂ are produced respectively. And the molar absorption ratio is 1:1. The absorbing interactions between ^AIL and CO₂ is similar to that of between ^BIL and CO₂ and let us take ^AIL-CO₂ for example to illustrate the structure changes and interaction characteristics. The main absorption interactions between ^AIL and CO₂ are two weak bonds of C33...N11 (2.9443 Å) and O34...H22-C9 (2.7447 Å). The bond length of C33...N11 is shorter than van der Waals radii of C and N (3.22 Å); the bond length of O34...H22-C9 is longer than the van der Waals radii of O and H, but atom in molecular calculation proved its existence, which violates Valence bond theory. N11-H26 and N11-H27 take part in forming weak C33...N11 and are elongated by the "electron transfer effect"; however, C9-H22 is shortened abnormally, which is involved in weak chemical bonds. These special phenomenon must associate with the interactions between ^AIL and CO₂. Moreover F30...H14-C5 (2.4812 Å) H-bond is formed when CO₂ is introduced in and the H-bond length between ion-pairs are shortened except for those of C5-H14...F29 and C7-H18...F30. On the other hand, the B-F bonds change slightly when ^AIL-CO₂ is formed. So it can be predicted that the intermolecular interactions affect the interactions between [Bamim]⁺ and [BF₄]⁻. Further studies are carried out to predict and explain the above abnormal phenomenon and changes.

Energies of stable species: The total and relative energies of all species were calculated at B3LYP/6-311++G(d,p) level based on the optimized geometries and corrected by zero point energy and basis sets superposition energy correction, the energy data were listed in Table-1. The energy changes (ΔE) of the cation and anion, is always used to estimate the interaction energy between ion-pairs. Here we define the interaction energy between [Bamim]⁺ and [BF₄]⁻ as $\Delta E(\text{IL}) = E(\text{IL}) - E([\text{Bamim}]^+) - E([\text{BF}_4]^-)$, $E(\text{IL})$ is the energy of IL, $E([\text{Bamim}]^+)$ and $E([\text{BF}_4]^-)$ are the energies of isolated [Bamim]⁺ and [BF₄]⁻. The $\Delta E(^{\text{A}}\text{IL})$ and $\Delta E(^{\text{B}}\text{IL})$ are -300.61 kJ/mol and -341.05 kJ/mol respectively, the interaction energies between [Bamim]⁺ and [BF₄]⁻ are much larger than that of the normal H-bonds, which indicates that the electrostatic attraction play a dominant role in the ionic liquid system. It can be observed that ^BIL has one additional F30...C2 weak chemical bond compared to ^AIL,

so the interaction energy between ion-pairs in ^BIL is -40.44 kJ/mol greater than that in ^AIL, which implies that the bond energy of F30...C2 is about -40 kJ/mol and the bond energy of the other five H-bonds is about -300.0 kJ/mol. On balance, the electrostatic attractions forces are far beyond that of H-bonds. Thus electrostatic attractions must be taken into consideration when we attempt to change the physical and chemical properties of ionic liquids and much more further studies on the relationship between the electrostatic attractions and the physical need be carried in our future studies on ionic liquids.

TABLE-1
ABSOLUTE ENERGIES AND RELATIVE ENERGIES
INCLUDING ZERO POINT ENERGY (ZPE) AND BASIS
SETS SUPERIMPOSITION ENERGY (BSSE) OF ALL SPECIES

Species	ZPE (a.u./mol)	BSSE (a.u./mol)	E _{total} (a.u./mol)	E _{relative} (a.u./mol)
[Bamim] ⁺ + [BF ₄] ⁻	0.2564	0.0	-903.0755	0.00
^A IL	0.2581	0.0023	-903.1900	-300.61
^B IL	0.2581	0.0023	-903.2054	-341.05
^A IL + CO ₂	0.2698	0.0023	-1091.8249	0.00
^A IL - CO ₂	0.2706	0.0003	-1091.8295	-12.08
^B IL + CO ₂	0.2698	0.0023	-1091.8406	-41.22
^B IL - CO ₂	0.2707	0.0005	-1091.8449	-52.51

$\Delta E(\text{IL-CO}_2)$ is the energy change of IL-CO₂ and the isolated molecules of ionic liquid and CO₂ and $\Delta E(\text{IL-CO}_2) = E(\text{IL-CO}_2) - E(\text{IL}) - E(\text{CO}_2)$, which is used to estimate the interaction energy between CO₂ and ionic liquid. $\Delta E(^{\text{A}}\text{IL-CO}_2)$ and $\Delta E(^{\text{B}}\text{IL-CO}_2)$ are -12.08 kJ/mol and -11.29 kJ/mol respectively, which implies that the interaction between ionic liquid and CO₂ belongs to intermolecular interaction, in other words, the reaction of ionic liquid and CO₂ is physical absorption and ionic liquids-CO₂ are molecular complexes. Thus we can speculate that ionic liquids may have a mild regeneration conditions for the interactions between ionic liquid and CO₂ belongs to stronger intermolecular interactions.

Natural bond orbital analysis: In order to reveal how the unit charge redistribution affects the interactions between ion-pairs, as well as between ionic liquids and CO₂, natural bond orbital atomic charges were calculated and analyzed in this part. The natural bond orbital net integral charges of atoms and group fragments were displayed in Tables 2 and 3.

Theoretically, the unit charge of isolated [Bamim]⁺ should belong to N3 atom, but the results in Table-3 suggest that some of the positive charge disperses among the whole cation, with +0.32688 charge transferring to methyl and +0.34654 charge transferring to butyl amine group and the remaining +0.32658 charge disperse among the imidazole ring. In comparison with the atomic charge in BF₃, the positive charges of B atom in isolated [BF₄]⁻ become less and the net negative charges of F atoms become more, which means that the unit negative charge also disperses among the whole [BF₄]⁻ and the total amount of charge transfer is beneficial to forming H-bonds.

It can be observed in Table-2 that the negative charge of [BF₄]⁻ group becomes to -0.96608 when ^AIL is formed and it means that 0.03392 electrons transfer from [BF₄]⁻ group to [Bamim]⁺ caused by the interactions between ion-pairs. In other words, the unit negative charge of [BF₄]⁻ disperses among

TABLE-2
NET INTEGRAL CHARGES OF THE MAIN GROUPS

Species	Charge of fragments					[BF ₄]	CO ₂
	Imidazole	Methyl	Butyl	Amido			
[BF ₄] ⁻						-1.0	
CO ₂							0.0
[Bamim] ⁺	0.32658	0.32688	0.47439	-0.12785			
^A IL	0.31674	0.29736	0.49513	-0.14315		-0.96608	
^B IL	0.31155	0.31727	0.47882	-0.14730		-0.96040	
^A IL-CO ₂	0.31911	0.29811	0.50601	-0.14581		-0.96662	-0.0108
^B IL-CO ₂	0.31229	0.31721	0.49078	-0.14891		-0.96167	-0.00968

TABLE-3
NATURAL BOND ORBITAL NET INTEGRAL ATOMIC CHARGES IN ALL STABLE SPECIES

Atoms	Cation	^A IL	^A IL-CO ₂	^B IL	^B IL-CO ₂	BF ₃	
N1	-0.34372	-0.32969	-0.32839	-0.35622	-0.35506	B	1.40862
C2	0.29502	0.27083	0.27013	0.32851	0.32648	F	-0.46954
N3	-0.34619	-0.36277	-0.36227	-0.35736	-0.35475	F	-0.46954
C4	-0.00641	-0.03830	-0.03674	-0.02292	-0.02325	F	-0.46954
C5	-0.00360	0.01995	0.02321	-0.02083	-0.02018		
C6	-0.35306	-0.34910	-0.34705	-0.36244	-0.35941	B28	1.33358
C7	-0.15939	-0.18939	-0.18821	-0.15968	-0.15762	F29	-0.58342
C8	-0.39091	-0.39902	-0.39419	-0.40160	-0.40117	F30	-0.58339
C9	-0.39121	-0.38182	-0.38681	-0.38856	-0.39329	F31	-0.58338
C10	-0.17321	-0.19077	-0.18971	-0.17158	-0.17134	F32	-0.58339
N11	-0.84390	-0.84574	-0.85812	-0.84861	-0.85724		
H12	0.23703	0.22688	0.22614	0.28086	0.28089	C33	0.99077
H13	0.24704	0.23166	0.23100	0.22890	0.22809	O34	-0.49539
H14	0.24741	0.29818	0.29603	0.23061	0.23007	O35	-0.49539
H15	0.22366	0.21393	0.21349	0.26418	0.26337		
H16	0.22829	0.21702	0.21687	0.20384	0.20292		
H17	0.22799	0.21551	0.2148	0.21169	0.21033		
H18	0.21540	0.25731	0.25066	0.23962	0.23725		
H19	0.22204	0.24866	0.25218	0.19846	0.19938		
H20	0.20326	0.19057	0.18838	0.24394	0.24651		
H21	0.20237	0.19299	0.1952	0.18383	0.18414		
H22	0.19300	0.20751	0.21513	0.20043	0.19932		
H23	0.21039	0.19953	0.19694	0.19469	0.20231		
H24	0.15832	0.16895	0.17102	0.16549	0.16979		
H25	0.18433	0.19061	0.19542	0.17378	0.17550		
H26	0.35192	0.35033	0.35479	0.34855	0.35210		
H27	0.36412	0.35226	0.35752	0.35279	0.35623		
B28		1.33204	1.33240	1.33184	1.33105		
F29		-0.59007	-0.59053	-0.58794	-0.57814		
F30		-0.58740	-0.58693	-0.57897	-0.58848		
F31		-0.57601	-0.57719	-0.58677	-0.58679		
F32		-0.54464	-0.54437	-0.53852	-0.53931		
C33			1.00959		1.00821		
O34			-0.51807		-0.50628		
O35			-0.50232		-0.51161		

the whole ionic liquid during the process of its forming and result in the decrement of the positive charges or the increment of the negative charges of groups in ionic liquid. Such as, the positive charge of imidazole ring and methyl decreases by 0.00984 and 0.02952 respectively, the negative charge of amido increases by -0.01529. However the positive charge of butyl increases by 0.02074 abnormally, which implies that the unit positive charge of [Bamim]⁺ redistributes among the ion-pairs with the unit negative charge dispersion. And the total amount of positive charge transfer to butyl is beneficial to forming H-bonds between butyl and [BF₄]⁻. Let's carry out detail analysis on the atomic charges listed in Table-3. If the unit positive charge of [Bamim]⁺ does not redistribute among the ion-pairs,

then the positive and negative atomic charges in [Bamim]⁺ must be decreased and increased respectively after receiving the electrons coming from [BF₄]⁻. The natural bond orbital atomic charges in Table-3 show that most of the atomic charge changes compared with the isolated [Bamim]⁺ agree with the theoretical prediction, but the positive atomic charges of H14, H18, H19, H22, H14 and H25 are increased abnormally; and the negative atomic charge of N1, C6 and C9 is decreased abnormally. So both the abnormal charge changes of these atoms prove that the unit positive charge of [Bamim]⁺ must redistribute among the whole ion-pairs when ionic liquid going to form. In the following paper, ^AIL will be taken as an instance to reveal how the charge distribution affect the

structures of ionic liquid and the interactions between [Bamim]⁺ and [BF₄]⁻.

Firstly, we should analyze the reason for the existence of the abnormal H-bonds of F31...H19-C7 and F31...H25-C10 (their bond lengths are longer than the van der Waals radii of the F and H atoms). It can be observed from Table 3 that the negative charge of F31 in ^AIL is increased by -0.11384 (-0.46954 → -0.57601) compared with neutral BF₃; and both the atomic positive charge of H19 (0.22204 → 0.24866) and H25 (0.18433 → 0.19061) are increased with positive charge redistribution and the electrostatic attractions between F31 and H19/ H25 are much reinforced and the strengthened electrostatic attractions display as F31...H19-C7 and F31...H25-C10 H-bonds. Both the atomic positive charges on H18 and H14 have increments, so the normal H-bonds of F29...H14-C5 and F30...H18-C7 are reinforced by the electrostatic attractions between F and H14/H18. Above all, these features indicate that the charge dispersion and redistribution strengthen the interactions between [Bamim]⁺ and [BF₄]⁻ and contributes to the stability of the ion-pair system.

Secondly, we should analyze why C7-H19 and C7-H18 are shortened abnormally with the influence of "electron transfer effect". Table-3 shows that the increment of atomic negative charge on C7 is -0.03000 (from -0.15939 to -0.18939) and the increment of atomic positive charges on H18 and H19 are 0.04191 (from 0.21540 to 0.25731) and 0.02662 (from 0.22204 to 0.24866) respectively, so the electrostatic attractions between C7 and H18/H19 are greatly strengthened. Moreover, the strengthening effect is stronger than the weakening effect of the "electron transfer effect", thus the comprehensive result leads to the decrements of the bond lengths of C7-H19 and C7-H18.

The other bonds that involve in the formation of the H bonds also have atomic charge changes during the combination of [Bamim]⁺ and [BF₄]⁻. Such as the atomic charge on C5 change from negative to positive (from -0.00360 to 0.01995), so the electrostatic attractions between C5 and H14 becomes to electrostatic repulsion, furthermore the net positive charge on H14 also has an increment of 0.05077 (from 0.24741 to 0.29818), so the total result together with "electron transfer effect" is that the bond length of C5-H14 is greatly elongated. Both the atomic positive charge on C10 (from -0.17321 to -0.19077) and the negative charge on H25 (0.18433 to 0.19061) have a little increments and the electrostatic attractions between C10 and H25 are somewhat reinforced, but the reinforcement effect is weaker than the "electron transfer effect", so the comprehensive result is that the C5-H14 bond is elongated. The electron distribution features of ^AIL are also shared in ^BIL and for the sake of simplification, the natural bond orbital charge analysis on ^BIL is not repeated here.

In this part, we also take ^AIL-CO₂ for example to discuss the charge distributions changes and the effects on the absorption reaction when ^AIL combines with CO₂. Table-2 shows that -0.01080 electrons transfer from ^AIL to CO₂ when ^AIL-CO₂ going to form and -0.00054 electrons transfer from [Bamim]⁺ to [BF₄]⁻, so the positive and negative charges of groups in [Bamim]⁺ should be increased and decreased theoretically. The net positive charges of imidazole ring, methyl and butyl are increased by 0.00237 (changing from 0.31674 to

0.31911), 0.00075 (changing from 0.29736 to 0.29811) and 0.01088 (changing from 0.49513 to 0.50601) respectively which agree with the theoretical prediction. But the negative charge of amino is increased by -0.00266 (changing from -0.14315 to -0.14581) instead of being decreased; hence the abnormal charge change of amino can only results from the secondary charge redistribution of [Bamim]⁺ during the process of ^AIL absorbing CO₂. And the secondary charge redistribution reinforced the absorption interactions. For example, the atomic positive charges of C33 changes from 0.99077 to 1.00959 and the atomic negative charge of N11 changes from -0.84574 to -0.85812 when going to form ^AIL-CO₂, which indicates that the electrostatic attraction between N11 and C33 is strengthened. The atomic positive charge of H22 is increased by 0.00762 (changing from 0.20751 to 0.21513) and the atomic negative charge of O34 increases by -0.02268 (changing from -0.49539 to -0.51807) and the electrostatic attraction between H22 and C33 is strengthened also and it is the reason for the existence of O34...H22-C9 H-bond although its bond length is longer than the van der Waals radii of O and H. Above all, final conclusion is that the secondary charge redistribution is beneficial to the reaction of ^AIL absorbing CO₂.

Electronic density topological analyses: According to Bader's theory of atoms in molecules (AIM)^{21,22}, if there is a bond critical point (BCP) between two atoms in the molecule, there must form a chemical bond. $\rho(r_c)$ value (the electron density at the BCP) is used to characterize the strength of a bond, the larger the $\rho(r_c)$ value, the stronger the bond. $\nabla^2\rho(r_c)$ value (laplacian value of electron density) is used to describe the nature of a bond, the $\nabla^2\rho(r_c)$ value less than zero means a covalent bond, the smaller the $\nabla^2\rho(r_c)$ value, the stronger of the covalence of the bond; the $\nabla^2\rho(r_c)$ value larger than zero means a ionic bond, the larger the $\nabla^2\rho(r_c)$ value, the stronger of the ionic nature of the bond; the $\nabla^2\rho(r_c)$ value close to zero means a weak bond. ϵ value (the ellipticity value of a bond) is used to characterize the σ or π nature of a bond, the greater the ϵ value, the more obvious π characters of the bond, conversely, the σ characters of the bond is stronger. In the following paper, atom in molecular theory was employed to further analyze the interaction characteristics between ion-pairs and between ionic liquids and CO₂, which based on the topological analysis of electron density $\rho(r_c)$ and its laplacian of electron density $\Delta^2\rho(r_c)$ at bond critical points.

The atom in molecular molecular graphs of ionic liquids and ionic liquids-CO₂ are drawn by atom in molecular program package and were shown in Figs. 3 and 4 respectively, the little red dots between two atoms represent bond critical points, the bond parameters at bond critical points were obtained and listed in the parentheses beside the little red dots and they are ρ values, $\nabla^2\rho(r_c)$ values and ϵ values respectively from top to bottom. We applied electron density topological theory in discussing and predicting the interaction characteristics in ionic liquids, as well as the absorption characteristics between ionic liquids and CO₂. The results shows that the H-bonds nature and characteristics in ^AIL are similar to that in ^BIL and the absorption interactions between ionic liquid and CO₂ in the two IL-CO₂ complexes are resemble, so we set ^AIL and ^AIL-CO₂ as examples for simplification.

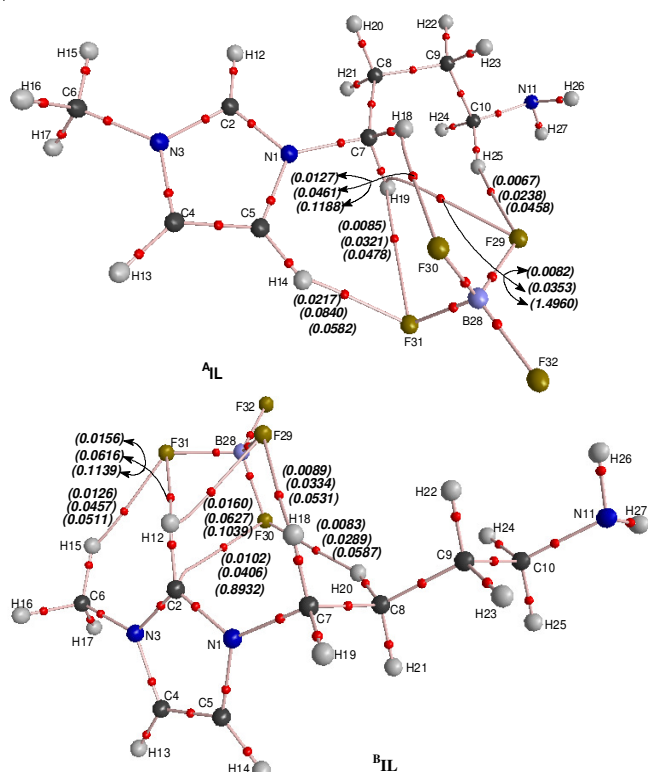
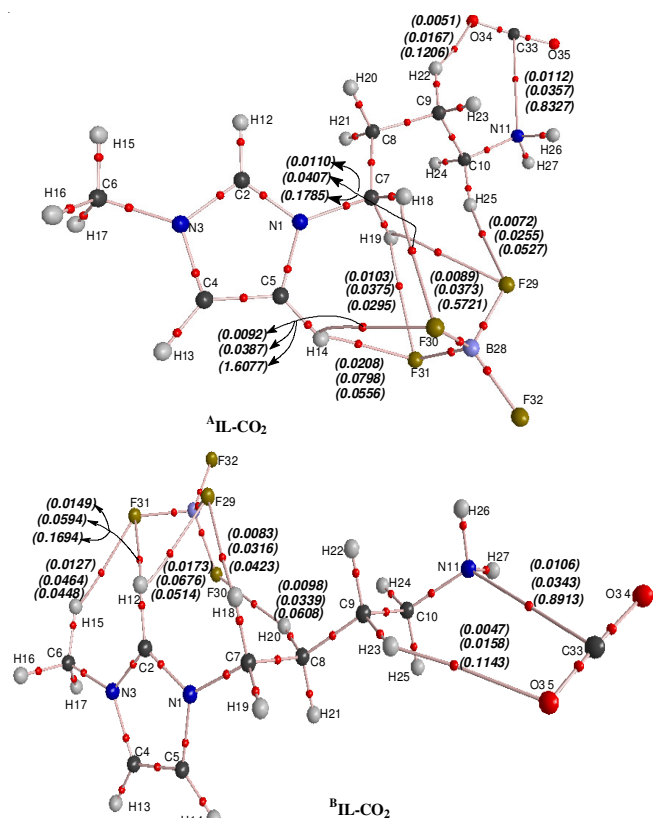


Fig. 3. Electron density topological geometries of ILs (little red ball:BCP)

Fig. 4. Electron density topological geometries of ILs-CO₂ (little red ball:BCP)

It can be seen from the atom in molecular map of ^AIL that there are five bond critical points between [Bamim]⁺ and [BF₄]⁻ which prove the formation of the five H-bonds in its geometry.

And the bond strength is F29...H14-C5 > F30...H18-C7 > F29...H19-C7 > F31...H19-C7 > F31...H25-C10 according to their $\rho(r_c)$ values, which agrees with the order according to the bond lengths. The $\rho(r_c)$ value of F29...H14-C5 is greater than that of a normal H-bond (about 0.01), so it is a stronger H-bond; the $\rho(r_c)$ value of F30...H18-C7 implies that it is a normal H-bond; and the other three are weaker than a normal H-bonds because of their smaller $\rho(r_c)$ values. All the $\nabla^2\rho$ values of the five H-bonds at their bond critical points are close to zero, which indicates that they are weak chemical bonds. The ϵ value at BCP of F31...H19-C7 is 1.4800, so it is of great π characteristics, which maybe result from the strong electrostatic attractions; the other four H-bonds are typical σ -bonds because of their small ϵ values.

The new bond critical point between O34 and H22, as well as between C33 and N11 in ^AIL-CO₂ confirmed the formation of O34...H22-C9 and C33...N11 bonds. The $\nabla^2\rho$ values of the two bonds are close to zero, which means that they are two weak chemical bonds. The $\rho(r_c)$ value and ϵ value of O34...H22-C9 H-bond are respectively 0.0051 and 0.1206, it means that O34...H22-C9 is a weaker H-bond with σ characteristics. The $\rho(r_c)$ value of C33...N11 is 0.0112, which indicates that the bond strength of C33...N11 is equal to that of a normal H-bond. The ϵ value of C33...N11 is 0.8327, so it is of greater π characteristics. So the conclusion can be obtained based on the above analysis-there is no normal chemical bond between ^AIL and CO₂ and the interactions belong to molecular interactions. That is to say, the reaction of ^AIL and CO₂ is physical absorption and ^AIL-CO₂ is a molecular complex. And ionic liquids may have a mild regeneration condition when they were desorbed from ionic liquids-CO₂.

In addition, the intermolecular interactions between ^AIL and CO₂ lead to the formation of the new H-bond of F30...H14-C5 between [Bamim]⁺ and [BF₄]⁻ and result in a little changes in bond strength of the other five H-bonds. The $\rho(r_c)$ values of F29...H14-C5 and F30...H18-C7 are somewhat decreased and the two bonds are weakened. The $\rho(r_c)$ values of F29...H19-C8, F31...H19-C8 and F31...H25-C10 bonds are somewhat increased and the three H-bonds are strengthened. These changes may be caused by the secondary charge redistribution effect or the influence of its geometry changes when ^AIL-CO₂ going to form. And these changes seem to have no strong relationship with the absorbing interaction when compare the H-bond strength changes in ^AIL and ^BIL.

Conclusion

In this paper, 1-(4-amino-butyl)3-methyl-imidazolium tetrafluoroborate and its reaction with CO₂ have been systematically investigated at molecular level and the main conclusions are displayed as follows: 1) Two stable geometries of ionic liquid (^AIL and ^BIL) were optimized and their stabilization energies are more than -300 kJ/mol; 2) The reaction of IL and CO₂ is physical absorption and the molar absorbing ratio is 1:1. And two molecular complexes (^AIL-CO₂ and ^BIL-CO₂) were optimized; their stabilization energies are about -11 kJ/mol, so ionic liquid may have a mild regeneration condition theoretically; 3) The natural bond orbital investigations indicate that the charge dispersion and redistribution of [Bamim]⁺ and [BF₄]⁻ reinforces the interactions between the ion-pairs and is

beneficial to the absorbing interactions; the secondary charge redistribution strengthen the absorption interactions when IL-CO₂ going to form; 4) Electron density topological studies show that the H-bonds between [Bamim]⁺ and [BF₄]⁻, as well as the interactions between CO₂ and ionic liquids are of some ionic bond characteristics. And the main absorption mechanism of C33...N11 is the interactions of π electrons on C33 and N11.

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