Research Article

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Electronic structural properties of amino/hydroxyl functionalized imidazolium-based bromide ionic liquids

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Abstract: Electronic structural properties of the three different imidazolium-based ionic liquids, namely, 1-butyl-3-methyl imidazolium bromide (C_4mimBr), 1-(4-hydroxybutyl)-3-methylimidazolium bromide ($C_4OHmimBr$), and 1-(4-aminobutyl)-3-methylimidazolium bromide (C_4NH_2mimBr), were investigated with density functional theory at the B3LYP/6-311++G(d,p) level. The conformations of the mentioned cations were fully studied first using CONFLEX 8.A program. The quantum theory of atoms in molecules was used to investigate the nature of intramolecular interactions. The counterpoise-corrected ion pairs binding energies were obtained at the same level of theory. Natural bond orbital analyses show that the largest intra-molecular interaction comes from the orbital overlap between $n(N1)$ and $\pi^*(N4-C5)$ in the mentioned compounds. The energy levels of frontier molecular orbitals (FMOs) are displayed. The global quantum chemical descriptors are also calculated based on the energy values of FMOs.

Keywords: ionic liquids, conformations, frontier molecular orbitals, intramolecular interactions

1 Introduction

Ionic liquids (ILs) are usually defined as salts with a melting point below 100°C, commonly having a large

organic cation and a small inorganic or organic anion [1–3]. ILs have unique physicochemical properties including high thermal stability, negligible vapor pressure, non-flammability, and good solvating ability to inorganic and organic substances [4]. Therefore, ILs are considered as suitable alternatives in numerous applications, especially as green solvents in chemical processes such as synthesis, catalysis, biocatalysis, and separation [5–10]. However, due to the possible combinations of cation and anion, it was estimated that the number of ILs could be up to 10^{18} from the statistical point of view [11]. It is a good way to design the novel task-specific ILs by using a quantum calculation. More interests have been focused on the relationship between the structure and properties [12–14]. Currently, the most widely used imidazolium-based ILs have been studied both experimentally and theoretically [15–17]. The introduction of the amino/hydroxyl group into the alkyl side chain of cation can lead to some interesting modifications to the behavior of the conventional imidazolium-based ILs. For example, Sun et al. [18] found that hydroxyl-functional ILs showed high catalytic activity in the coupling reaction of carbon dioxide and epoxide. Yue et al. [19] used dual amino-functionalized ILs as a catalyst for the synthesis of carbonate. It is of practical importance to develop a molecule-level understanding of the properties of ILs to design or utilize them for future applications. Furthermore, the results of ab initio calculations could be used to develop suitable force fields and models for molecular dynamics simulations that would allow accurate theoretical predictions of ILs [20,21]. In the present work, the molecular structure and electronic properties of three different imidazolium-based ILs, namely, 1-butyl-3-methyl imidazolium bromide (C_4mimBr), 1-(4-hydroxybutyl)-3-methylimidazolium bromide ($C_4OHmimBr$), and 1-(4-aminobutyl)-3-methylimidazolium bromide (C_4NH_2mimBr), were studied with density functional theory (Figure 1).

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$R_1 = \text{CH}_3$, $R_2 = (\text{CH}_2)_3\text{CH}_3$, $-(\text{CH}_2)_4\text{OH}$, $-(\text{CH}_2)_4\text{NH}_2$, $X = \text{Br}$

Figure 1: Scheme of three different imidazolium-based ILs.

2 Computational section

To predict the possible conformations of the cations, the CONFLEX conformational search method [22–24] using strategies designed to exhaustively search the conformational space of the target molecule as implemented in the CONFLEX 8.A [25] program was used. The energy of the predicted conformations was estimated using the MMFF94s force field [26]. To get more accurate geometry and energy order of the predicted conformations, further ab initio computations were performed by Gaussian 16 software package [27]. The predicted conformations were geometry optimized at the B3LYP [28,29] level using the 6-311++G(d,p) basis set. The level of B3LYP/6-311++G(d,p) used to predict the geometry and electronic properties of ILs had been successful during the past few years [30–32]. The MP2 energy was calculated at the B3LYP optimized geometry using the same basis set. Vibration analyses were proceeded to confirm the optimized structure corresponding to the minimum on the potential energy surface by verifying the absence of imaginary frequency and to obtain the zero-point vibrational energy. The basis sets superposition error (BSSE) is calculated with the counterpoise (CP) correction method [33]. Natural population analyses [34] were also carried out at the same level of theory. The analysis of the noncovalent interactions involved in the molecules was performed with Bader's quantum theory of atoms in molecules (QTAIM [35]) as implemented in Multiwfn 3.6 [36]. The topological graphs were drew using VMD 1.9.3 [37].

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

3.1 Conformation and geometry analysis of cations

As a constituent of IL, cation in ILs is usually organic asymmetric ion. Due to the high flexibility of the alkyl

side chains, the conformers of cations are complexed. To obtain the most stable conformer of the cation, the conformational search was first carried out within 10 kcal/mol energy cutoff using CONFLEX 8.A software. After the first conformation searching, 9, 44, and 73 conformations were predicted for C_4mim^+ , C_4OHmim^+ , and $\text{C}_4\text{NH}_2\text{mim}^+$, respectively. The ls4 file, one of the output files after searching, contains a list of conformers in order of free energy. If there is F indicated in the INIT row, it means that some conformational isomers derived from this structure still have not been obtained. Higher energy cutoff value was again set to 20 kcal/mol for C_4OHmim^+ and $\text{C}_4\text{NH}_2\text{mim}^+$. Their ls4 files were included in the Supporting information. Finally, there are 9, 46, and 74 conformations for C_4mim^+ , C_4OHmim^+ , and $\text{C}_4\text{NH}_2\text{mim}^+$, respectively. Among the generated conformations, 6, 2, and 9 conformations were selected, the sum of their distribution was above 90%, for C_4mim^+ , C_4OHmim^+ , and $\text{C}_4\text{NH}_2\text{mim}^+$, respectively. The ab initio calculations were used to get more accurate geometry and energy order of the selected conformations at the B3LYP and MP2 levels in the gas phase. The relative energies based on the molecular mechanics and ab initio calculations are listed in Table 1.

Note that in Table 1, the dihedral angles are also displayed and provided some information on the molecular structure. The number of conformations of $\text{C}_4\text{NH}_2\text{mim}^+$ was reduced to 6 after geometry optimization because the geometry of No. 2 and 3, No. 7 and 8, and No. 1 and 4 is the same. Although the energy order at the B3LYP and MP2 levels is little different from that at the MMFF94s level, the biggest energy gap between the conformations of the mentioned cations is less than 3 kcal/mol. Taking $\text{C}_4\text{NH}_2\text{mim}$ as an example at the MP2 level, the conformation 7/8, the fifth-lowest energy, is higher in energy than the conformation 1 by 2.59 kcal/mol.

3.2 Geometry and QTAIM analysis of ion pairs

The previous work showed that the anion could locate on different places around the cation [38]. When the Br anion is located near the hydrogen atom attached to the C5 atom in the planar imidazolium ring, the most stable structure on the potential energy surface is confirmed. Figure 2 displays the molecular topological graphs based on their gas-phase optimized geometries at the B3LYP/6-311++G(d, p) level.

Table 1: Relative energies of the selected conformations of cations ^{a,b,c,d}

Items	No.	MMFF94s (kcal/mol)	B3LYP (kcal/mol)	MP2 (kcal/mol)	Dihedral angles (°)		
					<i>D</i> (3,4,7,8)	<i>D</i> (4,7,8,9)	<i>D</i> (7,8,9,10)
C ₄ mim ⁺	1	0.00	0.26	0.00	−70.9	−60.4	−177.3
	2	0.05	0.66	0.44	95.7	−64.6	−176.8
	3	0.36	0.00	0.90	74.6	179.9	179.9
	4	0.64	1.10	0.23	−70.8	−64.3	−65.5
	5	0.70	1.47	0.67	95.5	−64.9	−65.1
	6	1.11	0.81	1.37	−75.9	−178.7	−66.3
C ₄ OHmim ⁺	1	0.00	0.00	0.00	−89.01	−62.48	−63.01
	2	0.00	0.00	0.00	−89.02	−62.48	−62.99
C ₄ NH ₂ mim ⁺	1	0.00	0.00	0.00	−85.69	−68.02	−57.78
	2	1.18	0.87	1.29	−150.53	−105.85	63.33
	3	1.19	0.87	1.29	−150.54	−105.85	63.37
	4	1.23	0.00	0.00	−85.73	−68.05	−57.76
	5	1.31	0.96	2.35	71.09	177.14	−76.07
	6	1.39	1.81	1.29	−85.45	−174.37	53.67
	7	1.47	1.57	2.59	99.27	113.99	−77.88
	8	1.48	1.57	2.59	99.25	113.99	−77.87
	9	1.54	1.19	2.57	−82.88	177.82	−75.55

^aNo., B3LYP, and MP2 stand for conformational number, B3LYP/6-311++G(d, p), and MP2/6-311++G(d, p). ^bEnergy of conformation 1 of C₄mim⁺ at the MMFF94s, B3LYP, and MP2 is 26.19 kcal/mol, −423.062830 a.u., and −421.773144 a.u., respectively; energy of conformation 1 of C₄OHmim⁺ at the MMFF94s, B3LYP, and MP2 is 18.10 kcal/mol, −498.304494 a.u., and −496.851973 a.u., respectively; energy of conformation 1 of C₄NH₂mim⁺ at the MMFF94s, B3LYP, and MP2 is 15.82 kcal/mol, −478.415974 a.u., and −476.984135 a.u., respectively. ^cQualitative description of the dihedral angles is based on the B3LYP/6-311++G(d, p) geometry. ^dDihedral angles are for optimized conformers at the B3LYP/6-311++G(d,p) level, and atom numbering is shown in Figure 2.

Figure 2: Topological graphs of (a) C₄mimBr, (b) C₄NH₂mimBr, and (c) C₄OHmimBr. H atoms are in white, C atoms are in cyan, N atoms are in blue, O atoms are in red, and Br atoms are in ochre.

We further employed a QTAIM study on the ion pairs to show X⋯H interactions which were identified as bond paths (shown in Figure 2 as an orange line) between atoms (atom critical points) and bond critical points (BCPs, shown in Figure 2 as an orange point). Topological parameters, such as the electron density and the Laplacian of electron density at the BCP, have been computed and listed in Table 2.

$G(r)$ is the kinetic energy density at the BCP (always positive), and $V(r)$ is the potential energy density at the

BCP (always negative). Generally, the value of $\rho(r)$ greater than 0.20 a.u. is for covalent bonding interactions and less than 0.10 a.u. is for closed-shell interactions [39]. The parameters (ρ and $\nabla^2\rho$) can also be used to distinguish between covalent and ionic bonding, hydrogen bonding, and van der Waals interactions. A negative value of $\nabla^2\rho$ stands for a concentration of electron density. For BCP, positive $\nabla^2\rho$ indicates noncovalent bonding. E_{int} is determined by $0.5 V(r)$ and used to estimate weak interatomic interaction energies,

Table 2: Topological parameters of the QTAIM in C₄mimBr, C₄NH₂mimBr, and C₄OHmimBr

Ion pairs	Intramolecular interactions	$\rho(r)$	$\nabla^2\rho(r)$	$G(r)$	$V(r)$	$-G(r)/V(r)$	E_{int} (kcal/mol)
C ₄ mimBr	H13...Br26	0.034	0.063	0.019	-0.022	0.864	6.903
	H15...Br26	0.011	0.028	0.006	-0.005	1.200	1.569
C ₄ NH ₂ mimBr	H14...Br28	0.026	0.058	0.014	-0.014	1.004	4.520
	H25...Br28	0.013	0.033	0.007	-0.006	1.232	1.767
	H27...Br28	0.015	0.039	0.009	-0.007	1.182	2.267
	H20...Br28	0.003	0.008	0.002	-0.001	1.310	0.405
	H15...N11	0.017	0.049	0.011	-0.009	1.167	2.910
C ₄ OHmimBr	H14...Br28	0.015	0.088	0.019	-0.015	1.221	4.768
	H24...Br28	0.010	0.039	0.008	-0.002	5.161	0.501
	H25...Br28	0.015	0.091	0.020	-0.016	1.195	5.123
	H14...O11	0.005	0.021	0.005	-0.004	1.191	1.205
	H15...O11	0.015	0.064	0.014	-0.012	1.140	3.919

particularly for hydrogen bonds [40]. It is obvious from Table 2 that all $\nabla^2\rho$ values are positive and the $\rho(r)$ values are all less than 0.10 a.u. The interaction energies listed in Table 2 can be classified as weak (0–4 kcal/mol) or medium (4–14 kcal/mol) according to Jeffrey's classification of hydrogen bonds [41]. It is noted that more hydrogen bonds are formed when amino or hydroxyl functional groups are introduced. Compared with C₄mim⁺, the introduction of the amino/hydroxyl functional group has a great effect on the spatial distribution of the alkyl side chain.

3.3 Ion-pair binding energy

The binding energy of the ion pairs is defined as the difference between the total energy of the ion pair and the sum of the energies of the isolated ions:

$$\Delta E(AB) = E^{AB} - [E^A + E^B]$$

where E^A or E^B is the energy of isolated cation or anion and E^{AB} is the energy of the ion pair. Each of the energies has been corrected with the zero-point energy. The binding energy is further corrected with the BSSE with the CP correction method. The CP corrected ion-pair binding energies are calculated using the following equation:

$$\Delta E^{\text{CP}}(AB) = \Delta E(AB) + \delta_{AB}^{\text{BSSE}}.$$

The results are listed in Table 3.

The values of binding energy in Table 3 show that the introduction of the amino/hydroxyl group has a little effect on the increase of the binding energy compared with C₄mimBr.

Table 3: Ion-pair binding energies, BSSEs, and CP-corrected binding energies (kcal/mol), calculated at the B3LYP/6-311+G(d,p) level

Entry	Ion-pair binding energy	BSSE	CP-corrected binding energy
C ₄ mimBr	-85.63	0.17	-85.46
C ₄ OHmimBr	-87.50	0.23	-87.27
C ₄ NH ₂ mimBr	-85.94	0.20	-85.74

3.4 NBO analysis

Natural bond orbital (NBO) analysis provides a convenient method for interpreting intra- and intermolecular bonding and interactions among bonds in the molecule. For a better understanding of the orbital interactions, the stabilization energy $E(2)$ is calculated according to the second-order perturbation theory [42]. For each donor NBO(i) and acceptor NBO(j), the stabilization energy associated with delocalization i, j orbitals is estimated as

$$E(2) = q_i \frac{(F_{i,j})^2}{E_i - E_j}$$

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. Some major donor-acceptor NBO interactions and the second-order perturbation stabilization energies are listed in Table 4. In NBO analysis, the larger the $E(2)$ value, the more intensive the interaction between electron donors and electron acceptors and the greater the extent of conjugation of the whole system.

Due to the structural similarity of the three imidazolium-based compounds, a similar trend of interaction is observed. Taking C₄NH₂mimBr as an example, the

Table 4: The major interactions and the stabilization energies at the B3LYP/6-311++G(d, p) level

Donor NBO(<i>i</i>)	Bond type	Occupancy	Acceptor NBO(<i>j</i>)	Bond type	Occupancy	<i>E</i> (2) kcal/mol	<i>E</i> _(<i>j</i>) – <i>E</i> _(<i>i</i>) a.u	<i>F</i> _(<i>i,j</i>) a.u
C₄mimBr								
LP (4)Br	n	1.8578	BD*(2) N4–C5	π*	0.5542	18.61	0.14	0.050
LP (1)N1	n	1.5264	BD*(2) C2–C3	π*	0.2571	31.51	0.28	0.089
LP (1)N1	n	1.5264	BD*(2) N4–C5	π*	0.5542	75.50	0.22	0.118
BD(2)N4–C5	π	1.8913	BD*(2)C2–C3	π*	0.2571	17.40	0.37	0.074
BD*(2)N4–C5	π*	0.5542	BD*(2)C2–C3	π*	0.2571	19.12	0.06	0.047
C₄OHmimBr								
LP(4)Br	n	1.8598	BD*(2) N4–C5	π*	0.5540	18.17	0.14	0.050
LP(1)N1	n	1.5246	BD*(2) C2–C3	π*	0.2573	31.62	0.28	0.089
LP(1)N1	n	1.5246	BD*(2) N4–C5	π*	0.5540	75.91	0.22	0.118
LP(2)O11	n	1.9657	BD*(1)C10–H24	σ*	0.0224	4.46	0.74	0.051
LP(2)O11	n	1.9657	BD*(1)C10–H25	σ*	0.0260	6.59	0.72	0.062
BD(2)N4–C5	π	1.8914	BD*(2)C2–C3	π*	0.2573	17.38	0.37	0.074
BD*(2)N4–C5	π*	0.5540	BD*(2)C2–C3	π*	0.2573	19.11	0.06	0.047
C₄NH₂mimBr								
LP(4)Br	n	1.8595	BD*(2) N4–C5	π*	0.5534	18.33	0.14	0.050
LP(1)N1	n	1.5258	BD*(2)C2–C3	π*	0.2572	31.52	0.28	0.089
LP(1)N1	n	1.5258	BD*(2) N4–C5	π*	0.5534	75.69	0.22	0.118
LP(1)N11	n	1.9650	BD*(1)C10–H25	σ*	0.0264	6.52	0.74	0.062
BD(2)N4–C5	π	1.8913	BD*(2)C2–C3	π*	0.2572	17.40	0.37	0.074
BD*(2)N4–C5	π*	0.5534	BD*(2)C2–C3	π*	0.2572	19.16	0.06	0.047

most strongest intra-molecular hyper conjugative interaction is formed by the orbital overlap between n(N1) and π*(N4–C5). The interaction of n(N1) and π*(N4–C5) results in the increases of electron density (0.5534e) in π*(N4–C5) that weakens the respective bonds leading to stabilization of about 75.69 kcal/mol. Another intra-molecular hyper conjugative interaction between n(N1) and π*(C2–C3) ca. uses the increases of electron density (0.2572e) in π*(C2–C3) and leads to stabilization of about 31.52 kcal/mol. The interaction of n(4)Br and π*(N4–C5) contributes to the stabilization with the value of 18.33 kcal/mol. These major interactions are also observed for C₄mimBr and C₄OHmimBr. The NBO analysis also shows the natural hybrids on atoms in the molecule. The hybridization of n(N1) has considerable p-character (99.88%) with a low occupation number (1.5258e). The hybridization of n(4)Br has a high p-character (96.60%) with a high occupation number (1.8595e). The π(N4–C5) bond is formed from sp^{4.16} on nitrogen with a mixture of 0.17% s, 99.78% p, and 0.04% d atomic orbitals. The information about the hybridization on the atom and the bonding configuration shows the strong delocalization and hyperconjugative interactions in the molecule. As for C₄OHmimBr, the stabilization energy caused by the interaction of n(2)O and σ*(C10–H25) is 6.59 kcal/mol. As for C₄NH₂mimBr; it is similar that the interaction between n(1)N11 and σ*(C10–H25) resulted in the decreasing energy with a value of 6.52 kcal/mol.

To understand the distribution of electron density and the electron transfer between cation and anion, the natural population atom charges of ion pairs were also computed. Most of the negative charge is located on the Br atom. They are –0.856e, –0.850e, and –0.866e for C₄mimBr, C₄OHmimBr, and C₄NH₂mimBr, respectively. The electron transfer from the Br anion to cation is 0.144e, 0.150e, and 0.134e for C₄mimBr, C₄OHmimBr, and C₄NH₂mimBr, respectively.

3.5 Frontier molecular orbitals

The frontier molecular orbitals (FMOs) are mainly at the “frontier” of electron occupation, especially the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO). The 3D plots of FMOs are drawn at 0.05 a.u. by using the program Multiwfn [36] and VMD1.9.3 [37]. FMOs of ion pairs are displayed in Figure 3.

The blue color reflects a positive phase, whereas the red color refers to a negative phase. It is observed that the HOMO in C₄mimBr, C₄OHmimBr, and C₄NH₂mimBr is the non-bonding orbital (lone pair of Br anion). The energy values of HOMO for them are –4.96, –5.42, and –5.16 eV, respectively. LUMO is anti-bonding in nature π*(N4–C5) in the ring. The energy values of LUMO are –3.65, –3.07, and –3.88 eV, respectively. The energy levels

Figure 3: HOMO (lower) and LUMO (upper) orbital plots at the B3LYP/6-311++G (d, p) level: (a) $C_4\text{mimBr}$, (b) $C_4\text{OHmimBr}$, and (c) $C_4\text{NH}_2\text{mimBr}$

Table 5: Chemical reactivity descriptors (unit: eV)

Entries	$C_4\text{mim}^+$	$C_4\text{mimBr}$	$C_4\text{OHmim}^+$	$C_4\text{OHmimBr}$	$C_4\text{NH}_2\text{mim}^+$	$C_4\text{NH}_2\text{mimBr}$
Hardness (η)	3.33	1.83	3.24	1.54	2.84	1.94
Softness (σ)	0.15	0.27	0.15	0.33	0.18	0.26
Electrophilicity (ω)	10.75	2.57	9.85	4.27	10.04	2.63
Chemical potential (μ)	-8.46	-3.14	-7.99	-3.89	-7.55	-3.22
Electronegativity (χ)	8.46	3.14	7.99	3.89	7.55	3.22
Ionization potential (I)	11.79	4.96	11.23	5.42	10.39	5.16
	(13.67)	(7.59)	(13.17)	(7.81)	(12.58)	(7.50)
Electron affinity (A)	5.13	1.31	4.75	2.35	4.71	1.28
	(3.23)	(0.11)	(2.93)	(0.13)	(2.92)	(0.06)

of HOMO and LUMO give information on electronic properties. The energy gap between LUMO and HOMO is also an important parameter for chemical reactivity and stability.

According to Koopmans' theorem, the ionization potential (IP) and electron affinity (EA) can be estimated from the HOMO and LUMO energy values. The global reactivity descriptors such as hardness, softness, electrophilicity, and chemical potential, electronegativity are related to the energy values of HOMO and LUMO. They were also calculated using HOMO and LUMO energy values and listed in Table 5. The values of IP and EA in parentheses were also calculated according to the difference between the total energies of the $N - 1$ electron and N electron states, while EA is the difference between the total energies of the N electron and $N + 1$ electron states [43].

The hardness of a given species shows the extent of its electron cloud distortion in the electric field. The hardness order is shown below. The softness order was opposite to the hardness order.

Cations are harder than ion pairs. Cations implied higher stability and opposing charge transfer. Ion pairs are more reactive than cations.

4 Conclusions

According to our results, the following conclusions could be drawn. The conformations of $C_4\text{mim}^+$, $C_4\text{OHmim}^+$, and $C_4\text{NH}_2\text{mim}^+$ were fully searched by using the

CONFLEX method. The introduction of the amino/hydroxyl group changes the special distributions of the alkyl chain. The Br anion is flexible around the cation. When Br is in the planar place with the ring, the geometry has the most stable structure. QTAIM analysis shows the nature of intramolecular interactions, particularly for hydrogen bonds. The computed values of ion-pair bonding energy show that the introduction of the amino/hydroxyl group attached to the butyl side chain in the cation has a little effect on the value of the binding energy. The NBO analysis displays the strong electron delocalization on the imidazolium ring. The largest intramolecular interaction comes from the orbital overlap between $n(N1)$ and $\pi^*(N4-C5)$ as for the studied compounds. The second-largest interaction comes from the orbital overlap between $n(N1)$ and $\pi^*(C2-C3)$. It is worth noting that the interaction of $n(2)O$ and $\sigma^*(C10-H25)$, $n(1)N11$ and $\sigma^*(C10-H25)$ is 6.59 and 6.52 kcal/mol, respectively. The energy values of FMOs are related to the molecular global quantum descriptors. To design the task-specific ILs, the introduction of the functional group such as amino/hydroxyl is a good way at the starting point.

Conflict of interest: The authors declare no conflict of interest.

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