

Characterizing the properties of the cation and ion pair for the cyclic tetramethylguanidinium nitrate ionic liquid

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ABSTRACT

We have carried out a detailed theoretical study for the geometrical structures and electronic properties of the cation and the ion pair of the cyclic tetramethylguanidinium nitrate ionic liquid. It is found that in the cation, the triazolium ring presents almost a plane and the NMe_2 group is not coplanar with the ring. The central C2 atom carries high positive charge, which is expected to act as the most active site for the electrostatic attacking of an anion. For the ion pair, three most stable configurations have been located, where the anion lies on either side of the triazolium ring or between C5 and C6 in the cation via multiple hydrogen bonds. However, the calculated results show that the electrostatic interaction between cation and anion plays a crucial role for stabilizing the ion pair. Moreover, the charge-localized character of the cation effectively increases the electrostatic interaction between the cation and anion, which is mainly responsible for the high thermal stabilities of the ionic liquids. There is a close correlation between the charge on C2 and the relative stability of the ion pair: the more positive charge on C2, the more stable the ion pair. Natural bond orbital and frontier molecular orbital analyses reveal that the charge transfer from the anion to cation occurs mainly through the $\text{LP}_0 \rightarrow \sigma_{\text{C-H}}^*$, $\text{LP}_0 \rightarrow \pi_{\text{C}_2-\text{N}_3}^*$ or $\text{LP}_0 \rightarrow \pi_{\text{C}_2-\text{N}_1}^*$ interactions.

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1. Introduction

In recent years, ionic liquids have attracted considerable interests due to their many favorable properties, such as high thermal and electrochemical stability, high ionic conductivity, negligible vapor pressure and strong solvent capacity [1–3]. They have been widely used as environmentally friendly alternatives medium for the conventional organic solvents [4–6] or as catalysts [7,8] in many important organic reactions. Moreover, the number of ionic liquids is essentially limitless by combining various anions with numerous cations, and they can be designed with desired properties for specific applications by changing the composition.

Recently, guanidinium-based ionic liquids (GILs), a new kind of ionic liquids have been synthesized [9,10]. They exhibit many excellent advantages such as high nitrogen content and their remarkable thermal and chemical stabilities [11,12]. GILs can be used as a suitable medium [13,14] and catalyst [15–17] in many organic reactions, as energetic materials [18], for dye-sensitized solar cells [19], and for molecular recognition [20]. However, relevant studies on such new ionic liquids are still limited compared to the extensive studies on imidazolium-based ionic liquids. More recently, a few groups [21–23] have been reported the results of

molecular dynamics simulations for several acyclic GILs. Very recently, Yu and Zhang [24] have studied the structure and interionic interaction of 1,1,3,3-tetramethylguanidinium lactate ion pair by performing *ab initio* calculations and discussed the physical property of this GIL. However, the knowledge of the relevant local properties at molecular and electron level, such as geometrical characteristics and electronic properties of the cation and the ion pair in GILs, as well as the interaction between the cation and the anion are still valuable and necessary for understanding the structures and properties of GILs. In this work, we carry out a systematical study on the cation and the ion pair of the cyclic tetramethylguanidinium nitrate ionic liquid, a representative cyclic GIL, by performing density functional theory (DFT) calculations. We focus our attention on the geometrical and electronic structures of the cation and the ion pair. We expect that the present results can deepen our understanding for the structure and property of cyclic GILs.

2. Computational details

In this work, DFT calculations were carried out using Gaussian 03 program package [25]. All geometry optimizations were performed at the B3LYP/6-311++G(d,p) level without symmetry constraints. Vibrational frequencies were calculated at the same level to ensure that each optimized structure is a real minimum.

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Zero-point vibrational energies (ZPEs) have been taken into account for all the cited energies. We have carried out a natural bond orbital (NBO) analysis [26,27] for all optimized structure to gain a further insight into the electronic properties and bonding characteristics of the cation and the ion pair. The orbital interactions between donor orbital and acceptor orbital were estimated through the second-order perturbation theory [27]. The effect of delocalization can be estimated by examining the second-order perturbation stabilization energy, $E(2)$, which is defined as

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

where q_i is the donor orbital occupation, $E(i)$, $E(j)$ are the diagonal elements (orbital energies), and $F(i,j)$ is the off-diagonal NBO Fock matrix element. The lattice energies of ionic liquids were estimated by using a relationship developed by Jenkins and co-workers [28,29],

$$U_L = 2I \left[\frac{\alpha}{\sqrt[3]{V}} + \beta \right]$$

which has been demonstrated in early studies [30,31] to be feasible for ionic liquids. I is the ionic strength ($=1$). V is the molecular volume (in nm^3), which is equal to the sum of the individual cation and anion volumes, and α and β are empirically parameters which take the values of 28.0 and 12.4 kcal mol^{-1} , respectively, for 1:1 salts.

3. Results and discussion

3.1. The cyclic tetramethylguanidinium cation

Fig. 1 shows the most stable geometrical structure of the cyclic tetramethylguanidinium cation with the atomic numbering scheme. Some selected geometric parameters and bond orders (BOs) are presented in Table 1. It is found that all the C–N and N–N bonds in the triazolium ring lie between the single and double bonds (cf., 1.467 Å for a C–N single bond and 1.269 Å for a C=N double bond, 1.480 Å for a N–N single bond and 1.238 Å for a N=N double bond), which is consistent with the calculated BO values ($1 < \text{BO} < 2$). Specially, the N4–C5 distance is calculated to be 1.295 Å, which is close to the normal C=N bond. The dihedral angles, N1–C2–N3–N4 and C2–N3–N4–C5 are nearly equal to 0° , indicating that the triazolium ring presents almost a plane. In addition, the dihedral angle N1–C2–N3–N8 is close to 180° , suggesting that N8 and the triazolium ring are almost on the same plane. This indicates that the lone pair electrons on N8 are conjugated with the triazolium ring, making that the C2–N8 bond is shorter than a normal C–N single bond. However, the dihedral angles N1–C2–N8–C9 and N3–C2–N8–C10 are found to be 140.16° and 135.09° , indicating that the NMe₂ group is not coplanar with the triazolium ring due to the spatial effect resulting from the dimethylation of the ring.

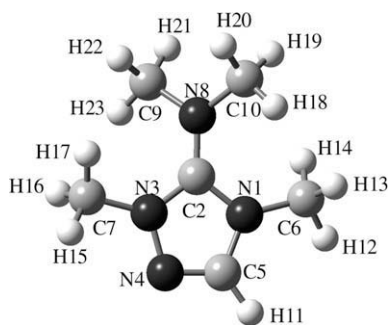


Fig. 1. Optimized geometrical structure for the cation.

Table 1

Calculated geometrical parameters and bond order (BO) values for the cation.^a

	Parameters	BO
N1–C2	1.368	1.19
C2–N3	1.349	1.27
N3–N4	1.369	1.14
N4–C5	1.295	1.66
C5–N1	1.376	1.34
C2–N8	1.346	1.20
N1–C2–N3	105.31	
N1–C2–N8	126.47	
N1–C2–N3–N4	–1.25	
C2–N3–N4–C5	1.73	
N1–C2–N8–N3	178.29	
N1–C2–N8–C9	140.16	
N3–C2–N8–C10	135.09	

^a Bond lengths are in angstrom, and bond angles and dihedral angles are in degree.

Table 2 lists the partial atom charges for the cation from NBO analysis. It is found the positive charges are located on C2 and C5 of triazolium ring and all peripheral H atoms, and the negative charges are located on all N atoms and methyl C atoms. Specially, the central C2 atom carries very high positive charge (approximately 0.667 e) indicating it is almost a carbocation. This situation is unlike the imidazolium-based cation where the position charges are diffused in the imidazolium ring [32]. The high positive charge on C2 can make it as the active site for electrostatic attacking. There are similar charge distributions on C6 (C9) methyl and C7 (C10) methyl, so only that on C6 (C9) methyl is given in Table 2. The positive charges for all peripheral H atoms have essentially tiny difference. On the other hand, there are obvious high negative charges on N1 and N8 than others.

To get further information on electronic structure of the cation, Fig. 2 shows the main natural bond orbitals of the cation. It is found that the orbital occupations of N1 and N8 lone pair orbitals LP_{N1} and LP_{N8} are 1.55 and 1.72 e, respectively, indicating that the large delocalization components are from the LP_{N1} and LP_{N8} . Owing to the donation from the LP_{N1} and LP_{N8} , the $\pi_{\text{N4–C5}}^*$ and the $\pi_{\text{C2–N3}}^*$ are appreciably occupied, as indicated by the occupations 0.55 and 0.26 e, respectively. The $\pi_{\text{N4–C5}}^*$ lies lower in energy than the

Table 2

Selected partial atom charges from NBO analysis for the cation and three stable ion pairs.^a

	Cation	3a	3b	3c
N1	–0.403	–0.399	–0.409	–0.387
C2	0.667	0.714	0.708	0.646
N3	–0.216	–0.230	–0.213	–0.208
N4	–0.235	–0.256	–0.248	–0.272
C5	0.245	0.246	0.245	0.252
C6	–0.360	–0.366	–0.360	–0.382
C7	–0.358	–0.361	–0.364	–0.358
N8	–0.500	–0.506	–0.507	–0.537
C9	–0.352	–0.350	–0.367	–0.345
C10	–0.352	–0.366	–0.350	–0.351
H11	0.234	0.218	0.215	0.292
H12(H15)	0.231	0.207	(0.222)	0.290
H13(H16)	0.221	0.260	(0.256)	0.205
H14(H17)	0.225	0.209	(0.205)	0.197
H18(H21)	0.208	0.254	(0.202)	0.211
H19(H22)	0.207	0.182	(0.181)	0.188
H20(H23)	0.216	0.205	(0.259)	0.204
O1		–0.603	–0.619	–0.575
O2		–0.585	–0.576	–0.581
NO ₃ [–]		–0.935	–0.941	–0.904

^a The values in parentheses are corresponding to the charges on H atoms in parentheses.

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