

Molecular interactions in 1,3-dimethylimidazolium-bis(trifluoromethanesulfonyl)imide ionic liquid

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Abstract

Molecular interactions in 1,3-dimethylimidazolium-bis(trifluoromethanesulfonyl)imide ionic liquids are studied by employing the ab initio Hartree–Fock and density functional methods. Different conformers are simulated with respect to molecular interactions between cation and anion. Manifestation of these molecular interactions in the vibrational spectra is discussed. Direction of frequency shifts of the normal vibrations relative to those in free anion and cations are explained by calculating difference electron density coupled with molecular electron density topography.

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1. Introduction

In recent years ionic liquids have gained wide popularity because of their unique properties and wide range of applications. These ionic liquids have features including low melting points, negligible vapor pressure, non-volatility, non-flammability and good thermal and chemical stability, particularly in the presence of air and moisture [1–6]. Due to these unique properties ionic liquids have shown use in many industrially important reactions as viable substitutes for organic solvents, in synthesizing electrolytes for electronic devices such as batteries and photo-electrochemical cells and in catalytic and engineering applications [8]. Many applications of ionic liquids have been possible because of their high viscosity relative to organic solvents. Ionic liquids offer high ionic conductivity and are especially resistant to oxidation, which explains the extensive electrochemical studies focused on them [9]. Recently the use of ionic liquids to replace organic solvents in biocatalytic processes has also received much attention [10]. For instance, Cull et al. [10] have shown that ionic liquids have

potential as alternatives to organic solvents for multiphase biotransformations. Other research has also shown that enzymes maintain higher stability in ionic liquids relative to those in organic solvents.

Molecular interactions are important in determining transport properties, such as conductivity and diffusivity, of the conformational states. In the investigation of novel ionic liquids, interactions between the anion and cation play an important role. These interactions yield the low melting points and hence have the greatest potential to produce ionic compounds that are liquid at room temperature [11,3,12]. Molecular interactions is one of the important factor in the ionic liquids should be understood well. Raman and infrared spectroscopy coupled with ab initio molecular orbital calculations are widely used to study the molecular interactions in ionic liquids [13–16]. Thus the electronic structure and molecular interactions in ionic liquids can be studied at the molecular level by employing different molecular orbital methods.

Ionic liquids exclusively include molecular interactions between organic cations and inorganic anions [17]. It is necessary to make a link between the fundamental properties of the system such as electronic structure and molecular interactions. The thermodynamic, dynamic and other

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properties of ionic liquids especially regarding the hydrogen-bonded interactions can be understood from the structural properties of the ionic liquids [18]. Further these physical properties of the ionic liquids can be adjusted by the structure and species of the cations and anions and thus make their applications in different areas of science [7]. In order to design ionic liquids or even choose one ionic liquid suitable for a specific reaction, the physical properties and molecular interactions should be understood well. Thus the molecular orbital methods can be useful to study the electronic structure and molecular interactions of the ionic liquids.

Ionic liquids containing inorganic perfluorinated sulfonylimide anions are of great interest because of their use in making hydrolytically stable, 'hydrophobic' ionic liquids with low viscosity and high electrical conductivity. Bis(trifluoromethanesulfonyl)imide (TF₂N), is one of the most widely studied anion, due to its unique properties such as charge-diffusion and weak cation coordination. In TF₂N delocalization of negative charge along S–N–S core of the anion reduces the strength of cation–anion interactions. Further this also enables the formation of low melting, fluid ionic liquids with a wide range of cations such as ammonium, pyridinium, imidazolium and pyrrolidinium cations [19,20]. In this respect it is important to understand the hydrogen-bonding environments in the ionic liquids. These molecular interactions and conformational changes influence lattice energy, melting point and general behavior of the salts. Thus the conformations and interactions provides valuable information about the favorable properties such as low melting points, restricts structural studies, which are useful to design a best ionic liquid. Tsuzuki et al. [21] have studied magnitude and directionality of interactions in ion pairs of ionic liquids. Magnitude and directionality of interaction energies of the ion pair play crucial roles in determining ionic dissociation/association in ionic liquids. Thus molecular interactions are an important factor of ionic liquids that should be well understood.

In the present work we focus on the molecular interactions and conformational analysis of 1,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide ionic liquid. Different conformers are simulated with respect to different molecular interactions between cation and anion. Manifestation of these interactions is discussed in detail. Direction of frequency shifts are explained by calculating the difference electron density coupled with electron density topography.

The computational method used in this work is outlined next.

2. Computational method

Different conformers were simulated on the basis of molecular interactions between 1,3-dimethylimidazolium cation and bis(trifluoromethanesulfonyl)imide anion. Restricted Hartree–Fock (HF) self-consistent molecular orbital calculations were performed on different conform-

ers of 1,3-dimethylimidazolium-bis(trifluoromethanesulfonyl)imide using the GAUSSIAN 03 program [22] with the internally stored 6–31G(d, p) basis set. Subsequently these geometries were also optimized by employing the hybrid density functional theory incorporating Becke's three-parameter exchange with Lee, Yang and Parr's (B3LYP) correlation functional [23,24]. Stationary point geometries obtained were characterized as the saddle points or local minima on the potential energy surface by examining the number of imaginary frequencies and the eigenvalues of the Hessian matrix. Normal vibrations were assigned by visualizing displacements of atoms around their equilibrium (mean) positions using the UNIVIS-2000 code [25]. The molecular electron density (MED) topography and identification of critical points were carried out [22,26]. Four types of nondegenerate critical points (CPs) of rank 3 were identified in the three dimensional space. These include: (3, –3) referred to as maxima (e.g. nuclear position); (3, +3) referred to as minima, generally known as cage critical points (ccp); (3, –1) and (3, +1) the saddle points, which refer to the bond critical point (bcp) and ring critical point (rcp), respectively. The difference electron density ($\Delta\rho$) was calculated by subtracting the sum of electron densities of the cation and the anion from the electron density of the of 1,3-dimethylimidazolium-bis(trifluoromethanesulfonyl)imide complexes. For cations and the anion their geometries as in the lowest energy conformer were used for obtaining the difference electron density maps. Thus difference electron density maps showing contours from ± 0.001 au to ± 0.0009 au, (au is atomic unit), are displayed in Figs. 2a and 2b.

An experimentally obtained single crystal of 1,3-dimethylimidazolium-bis(trifluoromethanesulfonyl)imide adopts *cis* conformation of the anion [19]. In the Hartree–Fock method, the lowest energy conformer possesses *cis* conformation of the anion, whereas *trans* conformation of anion is predicted in B3LYP calculations. A comparison of the experimental geometric parameters of 1,3-dimethylimidazolium-bis(trifluoromethanesulfonyl)imide obtained from a single crystal with those derived from the HF/6-31G(d, p) and B3LYP/6-31(d, p) calculations (cf. Table 1) justifies the use of low level HF/6-31G** calculations. In the present work we present the results derived from the HF/6-31G** method. The atomic numbering scheme used in the present work is displayed in Fig. 1a.

3. Results and discussion

Different conformers are simulated on the basis of different molecular interactions between 1,3-dimethylimidazolium cation and bis(trifluoromethanesulfonyl)imide anion. In C1, C2, C5 and C7 conformers, the TF₂N anion adopted *cis* conformation whereas in C3, C4 and C6 conformers, *trans* conformation was predicted (cf. Figs. 1a and 1b). Bifurcated C–H...O interactions were predicted for C1, C2, C3, C5 conformers through the C₂–H₂₄ bond involvement of the cation. In C1 and C5 conformers the C₂–H₂₄

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