



1,3-Bis(carboxymethyl)imidazolium bis(trifluoromethylsulfonyl)imide organic salt: Synthesis, single crystal structure, vibrational spectra, DFT calculations and physical-chemical properties



Ajing Wang^a, Yang Zhao^a, Xiaomeng Liu^a, Liangliang Chang^a, Xiaopeng Xuan^{a,b,*}

^a Henan Key Laboratory of Green Chemical Media and Reactions, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, PR China

^b Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Normal University, Xinxiang, Henan 453007, PR China

ARTICLE INFO

Article history:

Received 23 January 2016

Received in revised form 8 April 2016

Accepted 9 April 2016

Available online 11 April 2016

Keywords:

1,3-Bis(carboxymethyl)imidazolium bis(trifluoromethylsulfonyl)imide

Crystal structure

Vibrational spectrum

Ion pairs

Thermal stability

Solubility

ABSTRACT

The bis(trifluoromethylsulfonyl)imide anion (TFSI) is one of the common anions forming hydrophobic ionic liquids at room temperature. In this work, through an introduction of two carboxyl groups into the imidazolium cation, a hydrophilic 1,3-bis(carboxymethyl)imidazolium bis(trifluoromethylsulfonyl)imide (BCITFSI) organic salt was synthesized and its crystal structure, vibrational spectra, physical-chemical properties such as thermal stability, *pKa* and solubility in water were experimentally determined. Present results are suggesting a possibility to tune the properties of ionic liquids by an appropriate change in cation structure, leading to new “designer solvents”.

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1. Introduction

Functional ionic liquids have been applied in synthesis [1], separation [2], electrochemistry [3] and so on [4,5]. Theoretically possible amount of ionic liquids having a variety of structures and substituents was estimated at as high as 10^{18} , and it provides enormous scope for the scientific innovation [6]. For the purpose of studying and designing of novel functional ionic liquids, the demand for structure–property relationships is increased in recent years. From our literature survey, most of the structural analyses of ionic liquids are dealing with their structures in the liquid state [7,8], few reported on those in crystalline state have appeared [9], although the latter can provide a more direct structural parameters.

Ionic liquid based on bis(trifluoromethanesulfonyl)imide anion (TFSI) is one of the most popular ionic liquids with low melting point, low viscosity and high electrical conductivity and hydrophobicity [10,11], and of considerable interest because of its use in absorption of SO_2 and CO_2 [12], lithium battery electrolytes

[13–15], and separation as an extraction medium [16,17]. Due to the delocalization of negative charge along the S–N–S bond of the TFSI anion and the additional steric effects of the sulfonyl and trifluoromethane groups, this kind of ionic liquid often has a weak anion–cation interaction, and is difficult to crystallize compared with other ionic liquids. 1-Ethyl-2-methyl-3-benzyl-imidazolium is the first organic TFSI salt, whose structure has been determined by single-crystal X-ray diffraction [18]. Its low melting point and high fluidity result from the charge delocalization of anion and the lack of strong hydrogen bonds between cation and anion. Subsequently, a number of alkylimidazolium [19–24], alkylpyridinium [20,25,26] salts with TFSI anion have been reported. For example, Holbrey et al. [22] reported the crystal structures of the most common 1,3-dimethylimidazolium TFSI and 1,2,3-triethylimidazolium TFSI ionic liquids. They found the experimental evidence that TFSI has *trans* and *cis* conformations. This result provided a deep insight into the conformational flexibility of the TFSI anion in the crystalline and liquid state, and into the key structural feature in physicochemical properties.

Generally, ionic liquids are described as designer solvents, which means that their properties can be tailored by the modification in the structure and by tuning the combination of anion and cation [6]. Although the ionic liquids with TFSI anion are

* Corresponding author.

E-mail address: xpxuan@henannu.edu.cn (X. Xuan).

often hydrophobic, this can be possibly changed. For example, the introduction of a hydrophilic COOH group into cation can theoretically alter solubility of ionic liquids in water. An example is 1-carboxymethyl-3-methylimidazolium TFSI [27], which has increasing solubility in water at room temperature and is even fully miscible with water above 64 °C. The increase in solubility is the result of the break in the hydrogen bonds between cation and anion, and the subsequent hydration of ion [27]. Recently, Fei et al. [24,28,29] reported the properties and crystal structures of a series of COOH-functional ionic liquids (COOH-ILs) or organic salts with Cl^- , Br^- , BF_4^- and CF_3SO_3^- anions. Nockemann et al. [27,30–32] synthesized a novel betainium TFSI ionic liquid, and used it to dissolve and separate metal oxide. In our previous works, we also determined the crystal structures of a series of mono-carboxyl-functionalized imidazolium organic salts with different anions including TFSI [33,34], and depicted the rough relation between the characteristic of hydrogen bonds and solubility in water. This paper is a continuation of our structural studies of COOH-ILs. Herein we reported synthesis and crystal structure of the BCITFSI, which has two COOH groups on the cation ring, and discussed the coexistence of strong $\text{O}-\text{H}\cdots\text{O}$ and the weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds in the solid state. BCITFSI has substantially greater solubility in water, different from other commonly ionic liquids with TFSI anion. According to the vibrational spectroscopic investigation and DFT calculation, the reason of the increase in solubility was proposed. Due to the structural similarity of ionic liquid and organic salt with TFSI anion, these results provided a further understanding, at the molecular level, on the structural variation and its impact on their properties.

2. Experimental and theoretical methods

2.1. Materials and synthesis

All materials were commercially available and used without further purification. Freshly prepared 1,3-bis(carboxymethyl)imidazole bromide and LiTFSI (molar ratio = 1:1) were dissolved in water, then the mixture was refluxed for half an hour, giving the white crystals of target compound. Crystals suitable for X-ray analysis were obtained by slow cooling of its solution at room temperature.

2.2. Characterization and quantum chemical calculations

FT-IR and Raman spectra of samples were collected on a Thermo-Nicolet Nexus FT IR/Raman spectrophotometer. Single crystal structure was determined by a Bruker Smart APEX II CCD diffractometer using $\text{Mo-K}\alpha$ ($\lambda=0.71073 \text{ \AA}$) radiation, and was solved by direct method and refined by full matrix least-squares method with the SHELXTL-97 program package [35]. Powder X-ray

diffraction was measured on a Bruker D8 Advance diffractometer with graphite monochromatized $\text{Cu-K}\alpha$ radiation ($\lambda=1.54178 \text{ \AA}$) at room temperature. Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) were carried out with a Netzsch STA 409 PC and DSC 204F1 analyzer at a heating rate of $10^\circ\text{C}/\text{min}$ using a N_2 atmosphere, respectively. pK_a value was determined using a PHSJ-4F pH-meter (Shanghai LeiCi Device Works) in 0.01 mol/L aqueous solution. The determination of solubility was conducted using the previously reported method [36]. Quantum chemical calculations were performed using the Becke-3-Lee-Yang-Parr method (B3LYP) in Gaussian 09 program [37]. The interacting energy (ΔE) is defined by the difference in energy between the complex and species. During the calculations, vibrational analyses were used to verify all of optimized structures as true minima on the potential energy surface. The theoretical frequencies, calculated at B3LYP/6-311++G(d,p) level, below 1700 cm^{-1} were scaled with a factor of 0.983, and frequencies above 1700 cm^{-1} by 0.958 [38], respectively. The more experimental and calculated details can be found in our previous works [33,34,39].

3. Results and discussion

3.1. Crystal structure and hydrogen bond network

The structure of the BCITFSI was shown in Fig. 1a, and the crystallographic and powder X-ray diffraction data were given in Table S1 and Fig. S1, respectively. Crystal file is also deposited in Cambridge Crystallographic Data Centre and can be freely accessed at www.ccdc.cam.ac.uk (CCDC no. 1423990). In the asymmetric unit, the imidazole ring of cation shows a nearly planar structure, and two COOH moieties locate the same side of ring, forming a *cis* conformation. Two carboxyl groups are inclined by different angles of 54.1° and 63.0° , respectively, to the cation ring plane. This conformation differs from others 1,3-bis(carboxymethyl)imidazolium salts with bromide [40–42], chloride [41], fluoride [41], perchlorate [41] and from the long alkyl chain 1,3-bis(carboxypropyl)imidazolium chloride [41]. As for TFSI anion, it mainly adopts the *trans* conformation in the solid phase, while both the *cis* and *trans* conformers coexist in the liquid state or its aqueous solutions [19,22]. In this study, TFSI anion is found to be *trans* conformation with $\text{C}-\text{S}\cdots\text{S}-\text{C}=180^\circ$, which is generally preferred in the organic TFSI salt structures [19,22] since it is more stable than the *cis* conformer by 3.5 kJ mol^{-1} calculated at B3LYP/6-311++G(3df) level [43]. Additionally, this anion displays 1:1 disorder of two differently orientated components with the shared carbon and sulfur atoms. This phenomenon has also been observed in other ionic liquid with TFSI [23].

Two kinds of strong $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds between two COOH groups of the adjacent cations were found for this crystal as

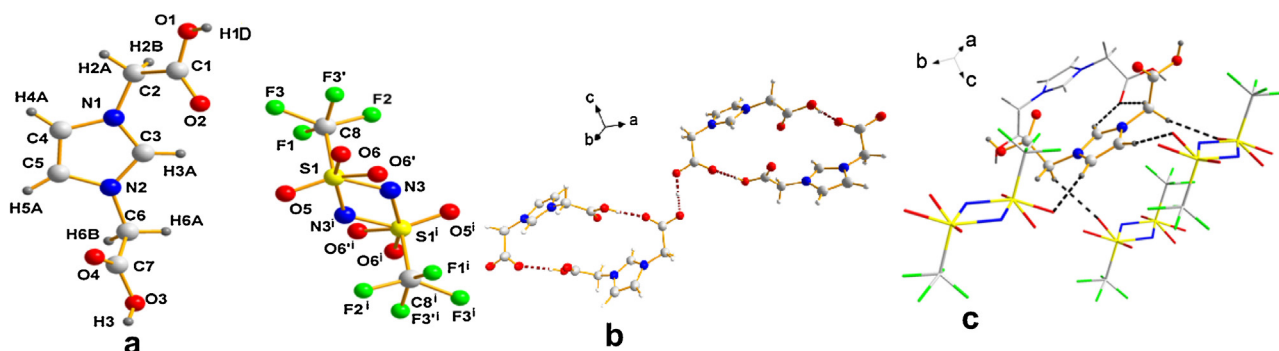


Fig. 1. The atomic numbering scheme [symmetry code, $i: -x, -y, z$] (a), strong $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds (b) and weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding surrounding each cation (c) in the crystal of BCITFSI.

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