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# Design and synthesis of new family of ionic liquids based on 2-iminium-1,3-dithiolanes: A combined theoretical and experimental effort



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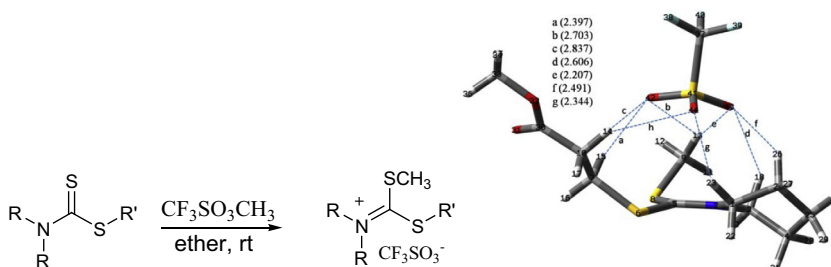
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## HIGHLIGHTS

- 2-Iminium-1,3-dithiolane as a new family of ionic liquids were synthesized.
- Theoretical study on the synthesized ionic liquids was also performed.
- QTAIM analysis show that the hydrogen bonds are closed shell in the nature.
- <sup>1</sup>H and <sup>13</sup>C calculated chemical shifts were obtained for ionic liquids.

## GRAPHICAL ABSTRACT

2-Iminium-1,3-dithiolanes have been synthesized as a new family of ionic liquids theoretical study on the synthesized ionic liquids was also performed by quantum chemistry calculation.



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## ABSTRACT

An efficient method for synthesis of 2-iminium-1,3-dithiolane as a new family of ionic liquids with reaction of dithiocarbamates with methyl trifluoromethanesulfonate was described. Theoretical study on the synthesized ionic liquids was also performed by quantum chemistry calculation. Geometry optimization on the ion pairs was carried out with the B3LYP/6-311++G(d,p) level of theory. The interaction energies were calculated, and corrected by the basis set superposition error (BSSE) calculated by the counterpoise method. The results of natural bond orbital (NBO) and quantum theory of atoms in molecules (QTAIM) analyses indicate that the interactions occur via hydrogen bonding between oxygen atom lone pairs (lp(O)) of trifluoromethanesulfonate anion and antibonding orbitals of  $\sigma^*C-H$  of 2-iminium-1,3-dithiolane cations. Also, the results of QTAIM analysis show that the hydrogen bonds are closed shell (electrostatic) in the nature. Finally, the <sup>1</sup>H and <sup>13</sup>C calculated chemical shifts at the B3LYP/6-311++G\*\* level were in agreement with experimental chemical shifts for synthesized ionic liquids.

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## 1. Introduction

It is well documented that 2-iminium-1,3-dithiolanes are safe agents for crop plants from the action of herbicides without reducing the herbicidal effectiveness against weeds [1]. A variety of methods are available in the literature for the preparation of these biologically active compounds. Unfortunately, difficulties

Abbreviations: DTC, dithiocarbamate; IL, ionic liquid; MeOTf, methyl trifluoromethanesulfonate; NBO, natural bond orbital; BCP, bond critical point.

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are encountered due to the physical nature of the starting materials. The drawbacks of using *vic*-dithiols, the toxicity of cyanogens chloride, the corrosive character of mineral acids, and low yield of products are some limitations of these processes [2].

Ionic liquids (ILs) have found considerable attentions in recent years due to their unique properties. Properties that convert ILs as potential green alternatives to volatile organic solvents are; low flammability, high thermal stability, large electrochemical window, negligible vapor pressure and capacity of dissolution of several organic molecules. It is convenient to change the physical and chemical properties of ILs by controlling the cations and anions [3]. According to the structure of ionic liquids, they have been considered for many applications, including the replacement of organic solvents for organic transformations [4,5], enzyme catalyzed reactions [6], electrochemistry [7], electrolyte for capacitors [8], dye-sensitized solar cells (DSSC) [9], ultra-low-volatility liquid matrices for matrix-assisted laser desorption/ionization mass spectrometry [10], and stationary phases in gas chromatography [11]. Therefore, design and synthesis of novel ILs with the possibility of easy structural tunability is high attractive. For this purpose, here we wish to investigate the synthesis and properties of 2-iminium 1,3-dithiolanes as a novel family of ILs.

## 2. Materials and methods

### 2.1. Quantum mechanical method

The structures of ion pairs and the corresponding monomers were optimized at B3LYP/6-311++G(d,p) level using Spartan 06 software [12]. It is well understood that polarized and diffusive orbitals are needed to account for the H-bonded interactions. Vibrational frequencies were calculated to verify the stationary structure for most of the structures. The interaction energies of the ion pairs are defined as follows:

$$\Delta E_{\text{int}} = E(\text{ion pair}) - E(\text{cation}) - E(\text{anion}) \quad (1)$$

The zero-point vibrational energy corrections (ZPVE) have been obtained within the harmonic approximation, and basis set superposition errors (BSSE) have been determined using the counterpoise method [13]. To examine the nature of interactions between the cations and the anion, natural bond orbital (NBO) analysis of the considered configurations have been performed by B3LYP/6-311++G(d,p) method. The bond characteristics for the relevant configurations were also illustrated based on atoms in molecules (AIM) analysis [14]. The topological properties were performed by using the AIM2000 package [15] with the wave functions generated from the B3LYP/6-311++G(d,p) results.

Chemical shielding calculations were performed using the gauge-including atomic orbital (GIAO) method [16] at B3LYP/6-311++G(d,p) level. The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts,  $\delta_{\text{iso}}$ , were obtained by subtracting the calculated isotropic chemical shielding from the absolute isotropic shielding of TMS calculated by the same approach.

### 2.2. Experimental

#### 2.2.1. General

Dithiocarbamates were synthesized according to our previous works [17]. All reactions were conducted in air without any precaution. NMR spectra's were recorded for solutions in  $\text{CDCl}_3$  with TMS (tetramethyl silane) as internal standard on a Bruker 500 MHz spectrometer. Thermal gravimetric analysis (TGA) has been performed by a Perkin–Elmer Pyris 1 instrument under atmosphere of  $\text{N}_2$  and the sample (ca. 10.9 mg) was scanned between

room temperature and 600 °C at a heating rate of 10 °C/min. Mass spectra were recorded on an Agilent Technology (HP), MS Model: 5973 Network Mass, selective Detector Ion source: Electron Impact (EI) 70 eV, ion source temperature: 230 °C.

#### 2.2.2. General procedure for synthesis of 2-iminium-1,3-dithiolane triflouromethane sulfonate salts

In a test tube equipped with magnet, dithiocarbamate (3 mmol) and diethyl ether (5 mL) was added. To this mixture, methyl triflouromethanesulfonate (3 mmol) was added and the mixture was stirred for 5 h at room temperature. After completion of the reaction as indicated by TLC, the solvent was separated and the residue treated with excess diethyl ether to remove any starting materials. The product was dried in rotary evaporator to remove any solvents and unreacted MeOTf. Quantitative yields were obtained in all the cases except **IL-6** which was achieved in 91% isolated yield. Structure of products was confirmed by  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{13}\text{C}$  NMR and mass spectroscopy.

## 3. Results and discussion

### 3.1. Synthesis and physical properties

In continuation of our interest in the synthesis of novel dithiocarbamates and the use of these compounds as intermediate in organic transformation, we have focused our attention on the synthesis of 2-iminium-1,3-dithiolanes. For this purpose, the dithiocarbamates were prepared with one-pot three component reaction of amines,  $\text{CS}_2$ , and alkyl halides or unsaturated carbonyl compounds. After synthesis of dithiocarbamates, we have tried to convert these molecules to target compounds with a strong methylating agents such as methyl iodide, dimethyl sulfate, and methyl triflouromethanesulfonate. We have found that only MeOTf is an efficient agent for complete conversion of dithiocarbamates to 2-iminium-1,3-dithiolane salts and the reaction was not proceed with methyl iodide and dimethyl sulfate. The reaction was completed with an equimolar of MeOTf in diethyl ether at room temperature. The iminium salts were obtained by simple evaporation of solvent in excellent yields. Next, the reactions of different dithiocarbamates with MeOTf were investigated under optimized conditions and the results are summarized in Table 1. All products were characterized with NMR ( $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$ ) and mass spectroscopy. All products are liquid at room temperature except **IL-1**. By decreasing the temperature to 0 °C, no solidification was happened for the liquid compounds. The **IL-1** was melted at 42–45 °C (see Scheme 1).

The solubility of synthesized iminium salts was screened in different polar and nonpolar solvents. We have found that the synthesized iminium salts are soluble in most of organic solvents such as acetone,  $\text{CH}_3\text{CN}$ , DMF, EtOAc, THF,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , 1,2-dichloroethane, methanol, ethanol, and water (0.1 g of iminium salt in 1 mL of solvent). The products are not soluble in nonpolar solvents such as petroleum ether, diethyl ether, and  $\text{CCl}_4$ . These compounds are stable for more than one year at room temperature when stored in well closed container to prevent contamination with water.

Thermogravimetric analysis (TGA) was conducted to evaluate the physical behavior of **IL-1** as a sample molecule (see Supporting information). The TGA curve shows three weight loses: in the temperature range 210–280 °C (mass loses ~40%) that may be assign for the loses of methyl triflouromethanesulfonate from the structure of the molecule (calculated mass loses 39.90%), 290–325 °C (mass loses ~10%) that may be assigned for the loses of the methoxy or a sulfur group (calculated mass loses 7.78%) and 330–420 °C that may be assigned for the loses of other part of molecule (mass loses 43%, calculated mass loses 44.50%) except a sulfur [remaining

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