Density functional theory study on the ionic liquid pyridinium hydrogen sulfate

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A R T I C L E I N F O

A B S T R A C T

The geometry, electronic structure and chemical reactivity of a pyridinium-based ionic liquid, pyridinium hydrogen sulfate ([H−Pyr]$^+$[HSO$_4$]$^−$), have been discussed on the basis of quantum chemical density functional theory calculations using B3LYP/6-311+G(d,p) and B3LYP/6-311++G(2d,2p) approaches. The calculations indicated that [H−Pyr]$^+$[HSO$_4$]$^−$ exists in the form of an ion pair. A large electropositive potential was found on the pyridinium ring, while the regions of a negative electrostatic potential is linked with the lone pair of electronegative oxygen atoms in hydrogen sulfate anion ([HSO$_4$]$^−$). Electron transfer both within the anion, and between the anion and cation of an ion pair were described using natural bond orbital theory. The energy values of −7.1375 and −2.8801 eV were related to HOMO and LUMO orbitals, respectively.

1. Introduction

Ionic liquids (ILs) provide a new class of compounds where molecules are composed of ions. At normal temperatures, ionic liquids have essentially zero vapor pressure and are thermally stable over a wide range of temperature [1,2]. Since some of the ILs properties (melting point, polarity) can be changed by modifying the structure of cation and/or anion, ionic liquids have been regarded as "designer solvents" [3−5]. In addition, numerous publications have discussed application of ionic liquids as environmentally friendly alternatives to the classical organic solvents [6,7], as catalysts [8,9] or as extracting agents for organic or ionic solutes [10,11].

Pyridinium-based salts are an object of a large number of studies. The majority of published works have focused on their synthesis [12,13] macroscopic properties [10,11] and applications [14,15]. For example, Fareghi-Alamdari et al. [16] synthesized 1-allyl-pyridinium bromide, 1-allyl-pyridinium dicyanamide and 1-(1-pyidinium-l-ethyl)-3-methylimidazolium dichloride and reported that the obtained ionic liquids are thermally stable up to 200 °C. In the area of organic synthesis, pyridinium-based ionic liquids are widely used as catalysts [3,17]. Anvar and co-workers [17] established that butylpyridinium tetrachloroindate-(III) possesses high catalytic activity in synthesis of 2,3-disubstituted quinolines via a one-pot three-component reaction of arylamines, arylaldehydes and aliphatic aldehydes. Aupoix et al. [18] have found that N-alkyl-pyridinium trifluoromethanesulfonate (alkyl = C$_4$H$_9$, C$_8$H$_{17}$, C$_{10}$H$_{21}$, C$_{12}$H$_{23}$, C$_{16}$H$_{33}$) catalyzes efficiently the benzoin condensation giving good yields within short reaction time using solvent-free microwave activation conditions.

In order predict the ionic liquids properties and choose a more suitable one for a specific application, i.e. to design more effective pyridinium-based ionic liquids, theoretical studies at the molecular level are required. A great number of molecular theories related to study of geometry, electronic states and chemical reactivity of the chemical compounds were reported [19]. Among these, an important contribution to promotion of theoretical calculations dives the density functional theory (DFT). In the field of DFT, the electronic state of the chemical compounds is expressed by electron density functionals, which are modified by many types of approaches for improving computation accuracy [20]. In this work, a theoretical study on the geometry, electronic structure and chemical reactivity of the ionic liquid pyridinium hydrogen sulfate by density functional theory (DFT) calculations using B3LYP/6-311+G(d,p) and B3LYP/6-311++G(2d,2p) methods was carried out.

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2. Experimental and computational section

2.1. Synthesis of pyridinium hydrogen sulfate ($[H-Pyr]^+[HSO_4]^-$)

Preparation procedure of the ionic liquid $[H-Pyr]^+[HSO_4]^-$ is presented in Fig. 1. It was as follows: 51.06 g (0.6455 mol) pyridine (99 wt%, Merck) and 34.86 g (1.9365 mol) ultra clean water was charged into a 0.250 L three-necked flat bottom reactor, equipped with a magnetic stirring, reflux condenser and thermometer.

The aqueous solution of pyridine was then stirred at room temperature for 0.5 h, where after the temperature was reduced to 275−281 K. Then 63.31 g (0.6455 mol) sulphuric acid (98 wt%, Merck) was added dropwise over a period of 1.5 h under vigorous stirring. The reaction mixture was stirred at reflux for an additional period of 5 h at 353 K.

For solvent removing, the aqueous solution of pyridinium hydrogen sulfate was distilled at 333 K and reduced pressure (0.050 MPa) and the product was dried under the same conditions for 8 h until the weight of the residue remained constant. After cooling, the resulting colourless solid ($[H-Pyr]^+[HSO_4]^-$) was washed with diethyl ether (0.100 L) for three times and dried in vacuum (0.050 MPa) at 353 K for 12 h.

FT-IR spectroscopy was used for identification of $[H-Pyr]^+[HSO_4]^-$. The infrared spectrum was recorded in the frequency region of 4000−400 cm^{-1} by means of a Nicolet iS 50 Thermo Scientific FT-IR spectrophotometer equipped with DTGS KBr detector (4 cm^{-1}) at scan's numbers of 32. Before IR analysis the sample was mixed with nujol.

Thermal stability of the investigated ionic liquid was studied using NETZSCH STA 449 F3 instrument. The sample was heated from 298 to 973 K at 10 K/min under nitrogen atmosphere (0.020 L/min).

Characterization results: colorless crystals; melting point: 366 K; crystallization point: 344 K; thermal decomposition point: 579 K. FT-IR (Nujol, ν cm^{-1}): 3397, 3253, 3070, 2951, 2912, 2848, 1639, 1528, 1493, 1290, 1179, 1052, 1004, 885, 845, 750, 673, 575, 456.

2.2. Calculation details

Calculations were performed using DFT method subjected to the gradient-corrected hybrid density functional B3LYP method. The latter is a combination of the three parameters potential of Becke with the hybrid correlation functional of Lee-Yang-Parr (B3LYP) [21,22]. For each structure, a geometry optimization was performed by means of 6-311+G(d,p) and 6-311++G(2d,2p) basis sets [23]. All calculations were converged to 10^{-8} a.u. The optimized structural parameters were used in the vibrational frequency calculations at the DFT level to characterize the stationary point as minima. The absence of imaginary frequencies in the calculated vibrational spectrum confirms that the structure corresponds to minimum energy. Geometry was visualized using GaussView 5 software package [24].

For studying the intermolecular bonding and interaction among bonds, the natural bond orbital (NBO) analysis is widely used. Moreover, it also enables a convenient basis for investigating charge transfer or conjugative interaction in molecular systems
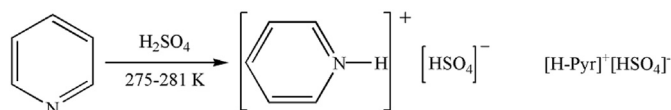
[25]. Since the traditional bonding concepts (local bonding, orbital hybridization) can be easily connect with the results of the NBO, the electronic properties of the ionic liquid $[H-Pyr]^+[HSO_4]^-$ were discussed based on the natural bond orbital theory [26] and the frontier molecular orbital (FMO) theory [27]. All calculations were performed in Gaussian 03 program package [28].

3. Results and discussion

3.1. Geometry description

The optimized geometrical parameters (bond lengths, valence angles and selected dihedral angles) were computed by B3LYP method with 6-311+G(d,p) and 6-311++G(2d,2p) levels are summarized in Table 1. For comparison, experimental X-ray crystal data obtained by Rogers and Bauer [29] are also presented. The molecular geometry of pyridinium hydrogen sulfate with atom numbering obtained by B3LYP/6-311+G(d,p) and B3LYP/6-311++G(2d,2p) methods is shown in Fig. 2.

X-ray crystal data showed that the longest distance of 1.527 Å is registered for S^1-O^2 bond in the hydrogen sulfate anion (Table 1). The O atom in position two (O^2) is covalently bonded to a hydrogen atom (H^6). The S^1-O^5 bond separation exhibits the shortest distance of 1.399 Å, while S^1-O^4 one is next − 1.417 Å. It was observed that the hydrogen atom (H^7) connected with the pyridinium ring in

Table 1

Experimentally determined structural parameters of pyridinium hydrogen sulfate [29] and theoretically calculated using B3LYP/6-311+G(d,p) and B3LYP/6-311++G(2d,2p) levels.

Structural parameters	B3LYP		
	6-311+G(d,p)	6-311++G(2d,2p)	X-ray data
Bond length (angstrom)			
S^1-O^2	1.658	1.640	1.527
S^1-O^3	1.524	1.510	1.433
S^1-O^4	1.467	1.455	1.417
S^1-O^5	1.456	1.445	1.399
O^2-H^6	0.967	0.965	1.00
$O^3 \cdots H^7$	1.378	1.357	1.79
H^7-N^{13}	1.140	1.150	1.17
$O^4 \cdots H^{18}$	2.188	2.219	−
$N^{13}-C^8$	1.341	1.338	1.36
C^8-C^9	1.385	1.382	1.33
C^9-C^{10}	1.395	1.392	1.32
$C^{10}-C^{11}$	1.392	1.390	1.36
$C^{11}-C^{12}$	1.388	1.385	1.32
$C^{12}-N^{13}$	1.342	1.339	1.26
Valence angle (degree)			
$O^2-S^1-O^3$	103.8	103.8	108.9
$O^2-S^1-O^4$	103.2	103.6	107.2
$O^2-S^1-O^5$	106.3	105.9	103.7
$O^3-S^1-O^4$	110.3	110.4	109.0
$O^3-S^1-O^5$	112.4	112.2	112.7
$O^4-S^1-O^5$	119.2	119.2	114.9
$S^1-O^2-H^6$	107.4	106.3	−
$S^1-O^3-H^7$	114.5	112.4	−
$O^3 \cdots H^7-N^{13}$	178.9	176.5	160.5
$H^7-N^{13}-C^8$	119.5	118.8	−
$N^{13}-C^8-C^9$	120.6	120.8	119.4
$C^8-C^9-C^{10}$	118.6	118.6	119.2
$C^9-C^{10}-C^{11}$	119.7	119.6	119.8
$C^{10}-C^{11}-C^{12}$	119.0	119.0	119.5
$C^{11}-C^{12}-N^{13}$	120.1	120.3	121.0
$C^{12}-N^{13}-C^8$	121.9	121.7	121.2
$O^4 \cdots H^{18}-C^{12}$	135.8	132.7	−
Dihedral angle (degree)			
$S^1-O^3-H^7-N^{13}$	−175.1	−170.0	−
$S^1-O^3-N^{13}-C^{12}$	−4.3	−6.1	−
$S^1-O^4-H^{18}-C^{12}$	4.5	−1.1	−
$O^3-S^1-O^2-H^6$	−85.6	−94.1	−

Fig. 1. Scheme for synthesis of pyridinium hydrogen sulfate.