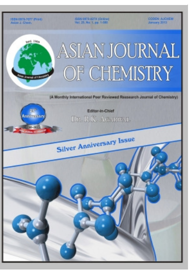
Asian Journal of Chemistry; Vol. 25, No. 6 (2013), 3233-3236

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13600



Structure and Spectral Studies of *N*-Ethyl Pyridinium Bromide Ionic Liquids: DFT and *ab initio* Study

YANSHENG ZHENG[1,2,*], ZHIHAO ZHUO[2], YI HE[2] and QIAN MO[2]

[1]Lushan College of Guangxi University of Technology, Luzhou 545616, Guangxi Province, P.R. China
[2]Department of Biological and Chemical Engineering, Guangxi University of Technology, Liuzhou 545006, Guangxi Province, P.R. China

*Corresponding author: Fax: +86 772 2687033; Tel: +86 772 2685962; E-mail: zhyansh88@163.com

(*Received*: 15 February 2012; *Accepted*: 14 December 2012) AJC-12555

Ionic liquids, due to their unique properties and solvent capabilities, have aroused wide concern and much potential utility value investigation have been carried out. In this article, the constitutive property and spectroscopy have been calculated by density function theory B3LYP, B3PW91 and (*ab initio*) HF at 6-31G+(d,p) and 6-311G+(d,p) level for the ionic liquid *N*-ethyl yridinium bromide ([EPy]Br). The assignment of atomic charge and the IR spectra have been respectively obtained by natural bond orbital analysis and vibration analysis. Compared experimental IR frequency and calculated. And then this paper sumed up and analyzed vibration frequencies. The results show that some charges have transferred between the anion and cation and IR characteristic spectrum of theoretical calculation is consistent with experimental result for the B3PW91 and HF methods using the 6-311G+(d,p).

Key Words: Ionic liquids, *N*-Ethyl pyridinium bromide, *ab initio*, Density function theory.

INTRODUCTION

Within the last two decades, ionic liquids have attracted rising interest with a diversified range of applications. Ionic liquids are salts with a melting point below 373 K and hence are liquid at moderate temperature, defined as liquids composed of organic cations and inorganic anions[1,2]. Owing to their ionic nature, many ionic liquids exhibit characteristics such as non-volatility, non-flammability, high electro-conductivity and good thermal stability[3]. The use of ionic liquids has proved beneficial in numerous areas including those of sensors, fuel cells, batteries, capacitors, thermal analysis, synthesis, catalysis, separation and so on[4]. In order to implement successful in most new applications, a full and detailed understanding of interrelations between the structure and properties of ionic liquids[5] and obtaining of reliable date on the structure and bonding in ionic liquids are obviously very important.

The method of quantum chemical calculation is used to determine interaction energies[6,7], thermodynamic properties[8,9] and also find a correlation between structure and property of ion-pairs. The *ab initio* and density function theory calculations both have been used to investigate structure properties and predict vibrational frequencies[10] of some ionic liquids. Pakiari *et al.*[11] studied 15 aprotic ionic liquids using density function theory and found that the relationship between the structure of counter-ions and inter-ionic interaction in ion-pairs. In this study, we chose *N*-ethyl pyridimium bromide [Epy]Br to determine the structure of the pyridimium cation and to investigate the IR spectra. Bromide ion, as most simple anion, make it possible to focus on conformational analyses of the cation only. The assignment of atomic charge and the IR spectra have been obtained by natural bond orbital analysis and vibration analysis, respectively. Compared experimental IR frequency and calculated and then sumed up and analyzed vibration frequencies.

EXPERIMENTAL

Model build and computational methods: The molecular structure and atomic symbol of *N*-ethyl-pyridine bromide ([EPy] Br) were shown in Fig. 1.The 3D model of [EPy] Br were optimized by Semi-empirical PM3 method, the most stable molecular structure were optimized by density functional theory method at B3LYP/6-31G + (d,p), B3LYP/6-311G + (d, p) and B3PW91/6-311G + (d,p) levels. The structural parameters such as bond length, bond angle, dihedral angle were analyzed. The charge distribution of the atoms were obtained by natural bond orbital analysis. The vibration frequency and intensity of [EPy]Br were obtained by vibration analysis), continuous infrared spectra figure were got by program transformation). Meanwhile, ab initio (ab initio) HF/6-31G + (d, p) and HF/6-311G + (d, p) method were compared. All calculations completed in the PC-Pentium (R) 2.0 G.

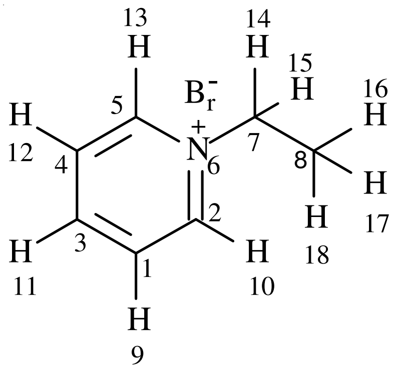


Fig. 1. Structure of [EPy]Br

RESULTS AND DISCUSSION

Molecular structure: The molecular structures of *N*-ethyl-pyridine cation ($[EPy]^+$) and *N*-ethyl-pyridine bromide ([EPy] Br) were determined at the B3LYP/6-311G + (d,p), its molecular structure were obtained (Fig. 2). The structural data such as bond lengths, bond angles, dihedral angle and charge distribution were optimized in each method and basis set (Tables 1-3).

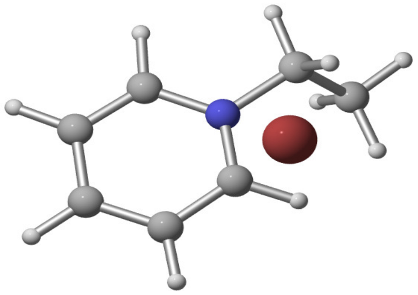


Fig. 2. Optimized structures of [EPy]Br, B3LYP/6-311G + (d,p)

TABLE-1
COMPARED CALCULATION OF BOND LENGTH OF [EPy]Br AT DIFFERENT LEVEL θ (nm)

	B3LYP/6-31+G (d,p)	B3LYP/6-311+G (d,p)	B3PW91/6-311+G (d,p)	HF/6-31+G (d,p)	HF/6-311+G (d,p)
C1-C2	0.1414	0.1404	0.1409	0.1385	0.1384
C1-C3	0.1374	0.1374	0.1369	0.1373	0.1372
C3-C4	0.1417	0.1411	0.1412	0.1397	0.1397
C4-C5	0.1371	0.1369	0.1365	0.1364	0.1362
C2-N6	0.1367	0.1360	0.1360	0.1330	0.1328
C5-N6	0.1365	0.1361	0.1359	0.1342	0.1342
N6-C7	0.1480	0.1481	0.1471	0.1485	0.1487
C7-C8	0.1528	0.1526	0.1520	0.1521	0.1521
C1-H9	0.1083	0.1080	0.1082	0.1071	0.1072
C2-H10	0.1078	0.1075	0.1077	0.1068	0.1068
C3-H11	0.1085	0.1083	0.1084	0.1075	0.1075
C4-H12	0.1083	0.1081	0.1082	0.1072	0.1072
C5-H13	0.1083	0.1081	0.1082	0.1072	0.1072

According to the results of [EPy]Br optimization, bond lengths and bond angles were more consistent with level of each basis set. The C-C bond length of pyridine ring was shorter than the single C-C (0.1540 nm) and longer than the single C=C (0.1340 nm), the C-N bond length was shorter than the single C-N (0.1470 nm) and longer than the single C=N (0.1270 nm), that the single bond and double bond of pyridine ring has the average trend on the bond length. When $[EPy]^+$ and Br^- formed a neutral salt, the calculated dihedral angle of $\theta_{C_2N_6C_5C_4}$ and $\theta_{C_3C1C_2N_6}$ were largely different from which dihedral angle were -10.8° and -11.03° in the B3LYP/6-31G + (d,p) basis sets and in the HF/6-311G + (d,p) level computation were -2.20° and -2.10°. The general trend is that the atoms on the pyridine ring are no longer in the same plane, because of the strong electrostatic interaction between negatively charged Br^- and positively charged $[EPy]^+$, so that the atoms N6, C1, C3 of pyridine ring shift to the atom Br and keep the pyridine ring was a little chair-type structure in the end but the pyridine ring is still a conjugated system.

TABLE-2
COMPARED CALCULATION OF BOND ANGLE AND DIHEDRAL ANGLE OF [EPy]Br AT DIFFERENT LEVEL θ (°)

	B3LYP/6-31+G (d,p)	B3LYP/6-311+G (d,p)	B3PW91/6-311+G (d,p)	HF/6-31+G (d,p)	HF/6-311+G (d,p)
C1-C2-N6	118.7	119.3	118.7	120.9	120.8
C2-N6-C5	120.2	120.6	120.7	120.6	120.8
N6-C5-C4	121.3	121.2	121.3	121.4	121.4
C5-C4-C3	118.8	118.9	118.7	118.5	118.5
C4-C3-C1	119.5	119.5	119.6	119.6	119.6
C3-C1-C2	119.9	119.8	119.9	118.8	118.9
N6-C7-C8	113.0	113.0	113.0	112.1	111.9
C1-C2-N6-C5	15.45	9.72	12.6	5.78	2.95
C2-N6-C5-C4	-10.8	-6.91	-8.49	-4.31	-2.20
C4-C3-C1-C2	1.89	0.55	1.19	1.10	0.52
C3-C1-C2-N6	-11.03	-6.53	-8.95	-4.17	-2.10
C2-C5-N6-C7	-166.2	-169.7	-168.9	-172.5	-175.9

TABLE-3
COMPARED CALCULATION OF ATOMIC CHARGES OF [EPy]Br AT DIFFERENT LEVEL

	B3LYP/6-31+G (d,p)	B3LYP/6-311+G (d,p)	B3PW91/6-311+G (d,p)	HF/6-31+G (d,p)	HF/6-311+G (d,p)
C1	0.121	-0.069	-0.057	0.031	-0.185
C2	-0.542	-0.300	-0.385	-0.260	-0.079
C3	-0.326	-0.233	-0.316	-0.347	-0.211
C4	0.022	-0.132	-0.153	-0.017	-0.214
C5	-0.052	-0.043	-0.086	-0.072	0.048
N6	0.149	0.274	0.404	0.038	0.226
C7	0.050	-0.144	-0.183	0.004	-0.114
C8	-0.421	-0.391	-0.475	-0.354	-0.364
H9	0.156	0.161	0.175	0.214	0.178
H10	0.168	0.216	0.241	0.287	0.239
H15	0.212	0.212	0.224	0.235	0.237

According to the [EPy]Br charge distribution (Table-3), the atoms of pyridine ring were all positive charge and the positive charge of atoms H9, H10, H15 were larger than others. The negative charge of atom C2 on [EPy]Br was larger, because there are strong electrostatic interaction between negatively charged Br^- and the positively charged pyridine ring, so that Br^- shift to N pyridine ring and locates below N pyridine ring. The results showed that the charge of Br^- were -0.542 C, -0.582 C, -0.538C by B3LYP/6-31G + (d,p), B3LYP/6-311G + (d,p) and B3PW91/6-311G + (d,p) levels of computations and the charge of $[EPy]^+$ were +0.542 C, +0.582 C, +0.538 C; the charge of Br^- were -0.828C, -0.802C at the HF/6-31G +

(d,p) and HF/6-311G + (d,p) levels of computations and the charge of [EPy]+ were +0.828 C, +0.802 C. The data above shows [EPy]Br have strong anion-cation interactions (ion-pair effect), owing to some charge from the anion to cation, so the ions remain electric neutrality.

Infrared spectrum: The vibration frequency of each chemical bonds and experimental data were obtained from vibration analysis of optimization. The results of the theoretical and experimental vibrational bands from B3LYP/6-31G+ (d,p) to B3LYP/6-311G + (d,p) (Fig. 3) to B3PW91/6-311G + (d,p) to HF/6-31G + (d,p) to HF/6-311G + (d,p) with the slopes from 0.9982 to 1.0038 to 0.99859 to 0.99859 to 0.9877. The slopes are representative of scale factors of 0.9982 [B3LYP/ 6-31G + (d,p)], 0.9962 [B3LYP/6-311G + (d,p)], 0.9986 [B3PW91/6-311G + (d,p)], 0.9986 [HF/6-31G + (d,p)] and 0.9987 [HF/6-311G + (d,p)] all very close to 1, indicating that the above calculated infrared vibrational frequencies and the experimental dates are consistent in all different calculation methods and basis sets. Comparison of HF/6-31G + (d,p) and HF/6-311G + (d,p) levels of computations showed that the data is very close. In comparison with the experimental results and calculation of two density function theory methods, the B3PW91 methods consistent higher than the B3LYP method but also the corresponding cost of computation is higher too.

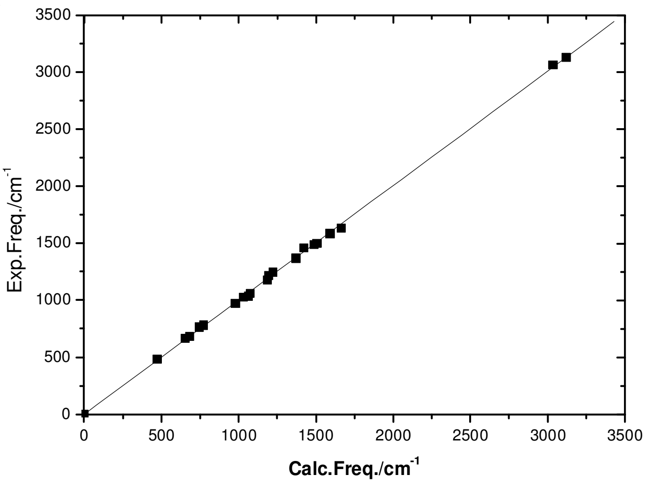


Fig. 3. Experimental frequency (cm^{-1}) *vs*. calculated frequency (cm^{-1}) for [EPy]Br by B3LYP/6-311G + (d,p), slope = 1.0038

The [EPy]Br calculated vibrational Assignments using in HF/6-311G + (d,p) method were shown in Table-4. The frequency of each absorption peak corresponding to the vibration mode were analyzed, the absorption peak at 730 cm^{-1} is symmetric wag of C-H in pyridine ring. The absorption peak at 847cm^{-1} is due to asymmetric wag of C-H in pyridine ring. The absorption peak at 1035 cm^{-1} is asymmetric wag of C-H in ethyl group and pyridine ring. The absorption peak at 1097 cm^{-1} is out of plane bend of pyridine ring and asymmetric wag of C-H in pyridine ring. The absorption peak at 1215 cm^{-1} is in plane scissor of C-H in pyridine ring. The absorption peak at 1289 cm^{-1} is due to stretch of N-CH_2 and asymmetric rock of terminal CH_3 group; the absorption peak of 1331 cm^{-1} is in plane scissor of C-H in pyridine ring and asymmetric rock of terminal CH_3 group; the absorption peak of 1607cm^{-1} is asymmetric rock of terminal CH_3 group. The absorption peak of 1829 cm^{-1} is stretch of C=C in pyridine ring. The absorption peak of 3171 cm^{-1} to 3295 cm^{-1} is stretch of C-H in ethyl, the absorption peaks in 3437-3352 cm^{-1} region is due to stretch of C-H in pyridine ring.

TABLE-4
HF/6-311G + (d,p) VIBRATIONAL
ASSIGNMENTS (cm^{-1}) OF [EPy]Br

Assignment	ν	IR ν_{exp}[12]
Cat-An tors	24	
Cat-An tors	122	
Cat-An bend	161	
Sym wag of C-H in pyridine ring	445	482
Sym wag of CH_2 group and C-H in pyridine ring	515	
Sym wag of C-H in pyridine ring	730	764
Asym wag of C-H in pyridine ring	847	
Sym wag of C-H in pyridine ring	936	973
Asym wag of C-H in ethyl group and pyridine ring	1035	1028
Asym wag of C-H in ethyl group and pyridine ring	1044	1061
Asym wag of C-H in pyridine ring	1090	1091
op bend of pyridine ring and Asym wag of C-H in pyridine ring	1097	1096
Asym wag of C-H in ethyl group and pyridine ring	1163	1176
Asym rock of terminal CH_3 group	1197	
ip scissor of C-H in pyridine ring	1215	1217
ip scissor of C-H in pyridine ring and Asym rock of terminal CH_3 group	1262	1245
Stretch of N-CH_2 and Asym rock of terminal CH_3 group	1289	
ip scissor of C-H in pyridine ring and Asym rock of terminal CH_3 group	1329	1318
ip scissor of C-H in pyridine ring and Asym rock of terminal CH_3 group	1331	1368
Asym wag of C-H in ethyl	1429	1458
Asym wag of C-H in pyridine ring	1505	1500
Asym wag of C-H in pyridine ring and ethyl	1549	
Asym rock of terminal CH_3 group	1607	1583
Asym wag of C-H in pyridine ring and ethyl	1638	1634
Stretch of C-N in pyridine ring	1769	
Stretch of C=C in pyridine ring	1829	
Stretch of C-H in terminal CH_3 group	3171	3130
Stretch of C-H in ethyl	3233	
Stretch of C-H in ethyl	3235	
Stretch of C-H in ethyl	3295	
Stretch of C-H in pyridine ring	3437	3436

Conclusion

The molecular structure of the pre-optimization was built by semi-empirical PM3 method and then the [EPy]Br the optimal configuration were obtained by calculations of respectively the 6-31G + (d,p) and 6-311G + (d,p) basis set using B3LYP, B3PW91 and HF method). The results show that pyridine ring of [EPy]Br is a little chair-type structure, there is charge transfer in the [EPy]Br ions on the formation process that indicating $[EPy]^+$ and Br^- ions have strong electrostatic attraction.

The infrared spectrum bands of [EPy]Br was calculated using the same method and the frequency of calculated and experimental dates was compared, the conclusion shows that the content of consistency of B3PW91/6-311G + (d,p) and HF/6-311G + (d,p) method was the highest and vibration frequencies can be sumed up and analyzed. Therefore, quantum chemical methods can be used to predict the IR spectral data of ionic liquids, such ionic liquids can be provided for the spectrum with the theoretical prediction and structure-properties relationship.

ACKNOWLEDGEMENTS

Financial assistance from Guangxi Department of Education Scientific Research Projects (201012MS123) and Guangxi Graduate Student Scientific Research Innovation Projects (2011105940817M03) are gratefully acknowledged.

REFERENCES

1. T. Welton, *Chem. Rev.*, **99**, 2071 (1999).
2. J.S. Moulthrop, R.P. Swatloski, G. Moyna and R.D. Rogers,, *Chem. Commun.*, 1557 (2005).
3. J. Kiefer and C.C. Pye, *J. Phys. Chem. A.*, **114**, 6713 (2010).
4. H. Olivier-Bourbigou, L. Magna and D. Morvan, *Appl. Catal. A*, **373**, 1 (2010).
5. H. Shirota, J.F. Wishart and E.W. Castner Jr., *J. Phys. Chem. B.*, **111**, 4819 (2007).
6. E.A. Turner, C.C. Pye and R.D. Singer, *J. Phys. Chem. A.*, **107**, 2277 (2003).
7. K. Dong, S. Zhang, D. Wang and X. Yao, *J. Phys. Chem. A.*, **110**, 9775 (2006).
8. Y. Wang, H. Li and S. Han, *J. Phys. Chem. A.*, **110**, 24646 (2006).
9. V.N. Emel'yabebko, S.P. Vervkin and A. Heintz, *J. Am. Chem. Soc.*, **129**, 3930 (2007).
10. E.R. Talaty, S. Raja, V.J. Storhaug, A. Dolle and W.R. Carper, *J. Phys. Chem. B.*, **108**, 13177 (2004).
11. A.H. Pakiari, S. Siahrostami and T. Ziegler, *J. Mol. Struct.: Theochem.*, **955**, 47 (2010).
12. http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi