Synthesis, characterization, and DFT studies of a new chiral ionic liquid from (S)-1- phenylethylamine

Shuya Cui, Tao Wang, xiaoli Hu

PII: S1386-1425(14)00945-7
DOI: http://dx.doi.org/10.1016/j.saa.2014.06.057
Reference: SAA 12316

To appear in: *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*

Received Date: 7 January 2014
Revised Date: 15 April 2014
Accepted Date: 8 June 2014

Please cite this article as: S. Cui, T. Wang, x. Hu, Synthesis, characterization, and DFT studies of a new chiral ionic liquid from (S)-1- phenylethylamine, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2014), doi: http://dx.doi.org/10.1016/j.saa.2014.06.057

Synthesis, characterization, and DFT studies of a new chiral ionic liquid from (S)-1- phenylethylamine

Shuya Cui [a,*], Tao Wang[b], xiaoli Hu[a]

[a]*College of Chemistry and Chemical Engineering, Mianyang Normal University, Mianyang621000, China*

[b]*Department of Chemistry and Chemical Engineering, Heze University, Heze274015, China*

Abstract

A new chiral ionic liquid was synthesized from (S)-1- phenylethylamine and it was studied by IR, Raman, polarimetry, NMR and X-ray crystal diffraction. Its vibrational spectral bands are precisely ascribed to the studied structure with the aid of DFT theoretical calculations. The optimized geometries and calculated vibrational frequencies are evaluated via comparison with experimental values. The vibrational spectral data obtained from IR and Raman spectra are assigned based on the results of the theoretical calculations by the DFT-B3LYP method at 6-311G(d,p) level. The computed vibrational frequencies were scaled by scale factors to yield a good agreement with observed experimental vibrational frequencies. The vibrational modes assignments were performed by using the animation option of GaussView5.0 graphical interface for Gaussian program.

Keywords: Chiral ionic liquid; Synthesis; Vibrational spectra; DFT

Introduction

Ionic liquids are green media for various chemical synthesis, enzymatic catalysis,

---

*Corresponding author . Tel: +86 816 2200064; Fax: +86 816 2200064.

Email address:huxlcsy@hotmail.com (S. Cui).

and engineering processes. They are based on organic cations (e.g. imidazolium, pyridinium, ammonium, phosphonium and triazolium derivatives) and anions whose choice allows the physicochemical properties of the ionic liquids to be tuned. Because they are designable, ionic liquids are "task-specific" or “tailor-making” materials [1-3]. Many more novel functional ionic liquids have been synthesized. These functional ionic liquids have multiple bonding sites. Chiral ionic liquids are a kind of "task-specific" materials , a renewal for the chemistry of chiral solvents which were designed, synthesized and applied for chiral recognition and asymmetric synthesis So far reported examples are designed either from the chiral pool (aminoacids, hydroxyacids, amines, aminoalcohols, terpenes and alkaloids) or by asymmetric synthesis; they can bear central, axial or planar chirality. Modern applications were focus on asymmetric synthesis, enzymatic chemistry, chiral chromatography, NMR liquid crystals and stereoselective polymerization [4-6].

Considering the chiral ionic liquid is highly effective for asymmetric synthesis and chiral chromatography, we synthesized a novel chiral ionic liquid, (S)-2-(3-methyl-imidazolium)-N-(1-phenylethyl)acetamide tetrafluoroborate, which has the potential application for separating racemates in capillary chromatography. In this work, we reported the synthesis of the chiral ionic liquid and presented the joint theoretical study and experimental spectral characterization of the ionic liquid by density functional theory (DFT). Infrared spectroscopy (IR) and Raman spectroscopy (Raman) are both powerful techniques to elucidate chemical structure Reliable assignments of the IR and Raman spectra of investigated molecules are very essential to understand the relationship between the observed spectral features and molecular structure/reactivity [7-9]. So the application of theoretically computed vibrational frequencies to link experimental data was developed since calculations provide additional interpretation of the vibrational spectroscopic data.

Materials and methods

Synthesis

(S)-1-phenylethanamine and 2-chloroacetyl chloride were purchased from Aladdin reagent company, China. Other reagents were purchased from Chengdu kelong reagent company, China. Reactions were monitored by thin layer chromatography (TLC). Melting points (m.p.) were determined by XT-4 melting point apparatus. Optical rotation was determined by WZZ-2A automatic polarimeter. ^{1}HNMR and ^{13}C NMR spectra were recorded on a Bruker Avance 600 spectrophotometer operating at 600 MHz and 150 MHz respectively, using tetramethylsilane as the internal standard. The following abbreviations were used for the multiplicity of signals in ^{1}H NMR: (s) singlet, (d) doublet, (t) triplet, (q) quartet, (m) multiplet.

Along the synthesis route towards the title ionic liquid, (S)-2-chloro-N-(1-phenylethyl) acetamide was firstly synthesized by Friedel-crafts reaction between (S)-1-phenylethanamine and 2-chloroacetyl chloride. Then obtained acetamide reacted with 1-methylimidazole, and the chloride salt was synthesized. Finally, tetrafluoroborate was added to exchange the anion, the aim product S-shaped imidazolium tetrafluoroborate ionic liquid was prepared. The preparation of acetamide requires anhydrous conditions in order to avoid hydrolysis of 2-chloroacetyl chloride. The reaction path is shown in Scheme 1.

*(S)-2-chloro-N-(1-phenylethyl) acetamide(**1**)*

(S)-1-phenylethanamine (6.06 g, 0.05 mol) and anhydrous potassium carbonate (10 g, 0.065 mol) were added to 150 mL dried THF in three neck flask under stirring at room temperature, then a 20 mL THF solution of 2-chloroacetyl chloride 6.22 g （0.055 mol）was dropwise added to above flask from constant pressure funnel equipped with the flask. The droping time should be longer than 30 min. After finishing the droping, the reaction continued for 4 hours. Above reaction was controlled at 20°C and monitered by TLC. After the reaction finished, the solid was filtered off, washed with THF. Filtrate was concentrated by evaporation to remove THF under vacuum, and then 10-20 mL water added to the residue. The solution was stored in refrigerator at 4°C. and white needle crystal (9.5 g) precipitated. The yield of **1** was 96%. M.p.98–101°C; $[\alpha]_D$ (c=0.6, -77.8 in acetone); IR（KBr） cm^{-1}：1495、1601（Ar）, 3029 cm^{-1} （Ar-H)，1650 cm^{-1} (C=O), 1500~1600 cm^{-1} , 697 cm^{-1}, 750 cm^{-1}(Ar), 1106 cm^{-1}(C-N) . ^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.27-7.37 (m, 5H, Ar), 6.82 (s, 1H, NH), 5.13 (m, 1H, CH), 4.04 (q, 2H, CH_2Cl), 1.53(d, 3H, CH_3) ; ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 165.1 (C=O), 142.5, 129.0, 129.0, 127.8, 126.3.0, 126.3(Ar-C), 49.4(CH), 42.8 (CH_2), 21.8(CH_3).

(S)-2-(3-methyl-imidazolium)-N-(1-phenylethyl)acetamide tetrafluoroborate

(S)-2-chloro-N-(1-phenylethyl)acetamide (8.0 g, 0.05 mol) and methylimidazole (2.38mL, 0.065 mol) were added to 25 mL ethanol in flask under stirring at 90°C, and the reaction continued for five days. Until the reaction finished, the solvent was removed under vacuum. Then water was added to the residue, dichloromethane was used to extract the mixture twice. The obtained aqueous phase was evaporated to dryness under vacuum to give the solid. 3.8g sodium tetrafluoroborate was added to 25 mL methanol solution of above solid under stirring at room temperature for thirty minutes and the solution was evaporated to dryness under vacuum. The residue was extracted with 20 mL acetone three times. Organic extract was dried over anhydrous Na_2SO_4, filtered and the solvent removed under vacuum to give the product as a colorless crystal (0.03mol, 9.8 g). M.p.155–157°C; $[\alpha]_D$(c=0.53, -86.2, in acetone), ^1H NMR (600 MHz, DMSO-d6, δ, ppm): 9.04(s, 1H, H-1 of imidazolium) [10], 8.86 (s, 1H, NH), 7.67(s, 2H, H-2,3 of imidazolium), 7.24-7.35 (m, 5H, Ar), 5.01 (s, 2H, CH_2Cl), 4.94 (t, 1H, CH), 1.40(d, 3H, CH_3) ; ^{13}C NMR (150 MHz, DMSO-d6, δ, ppm): 163.9 (C=O), 143.7, 128.3, 128.3, 126.9, 126.0, 126.0 (Ar-C), 137.7 (C-1), 123.8,122.9 (C-2,3), 50.4 (CH_2), 48.5(CH), 22.3 (CH_3).

Infrared, Raman spectra and Single-crystal X-ray diffraction analysis

IR spectra of the samples were recorded using a FT-IR 8400 spectrophotometer. Raman spectrum was recorded with Renishaw inVia micro- Raman spectrometer. Colorless pillar crystals of the chiral ionic liquid were grown by slow evaporation (at 20°C) of dissolutions of the sample in acetone. A suitable crystal was selected and X-ray diffraction data were collected on an Xcalibur, Eos diffractometer. The crystal was kept at 293.15 K during data collection. Using Olex2 [11], the structure was solved with the Super flip [12] structure solution program using Charge Flipping and refined with the ShelXL-2012 [13] refinement package using Least Squares minimisation. A summary of data collection and refinement conditions for the crystal structure: formula $C_{14}H_{18}BF_4N_3O$, Fw = 331.12, orthorhombic, a =8.1430(4), b = 10.7435(3), c = 18.6436(8) Å, α, β, γ = 90°, V= 1631.02(12) Å3, T = 293.15 K, space group $P2_12_12_1$, Z = 4, μ(Mo–Ka) = 0.71073 mm^{-1}, Reflection collected 4642, Independent/observed reflections 3181 [R_{int} = 0.0154, R_{sigma} = 0.0393], R_1 = 0.0850, wR_2 = 0.2212(I>=2σ (I)), R_1 = 0.1143, wR_2 = 0.2526(all data).

Computational details

In this work, to fit the requirements of accuracy and economy, the theoretical method and basis set should be considered firstly. The density functional theory (DFT) has been proved to be extremely useful in treating electron relativities, and the basis set of 6-311G (d, p) has been used as a very effective and economical level for many molecules [14]. Based on the points, the density functional Becke3–Lee–Yang–Parr (DFT/B3LYP) method with standard 6-311G (d, p) basis set was adopted to compute the properties of the studied compound in the present work. All the calculations were performed using Gaussian09 program package [15] with the default convergence criteria. As the first step of our calculation, the initial geometrical configuration was generated from its X-ray diffraction crystallographic data, and the optimized geometry corresponding to the minimum on the potential energy surface was obtained by solving self-consistent field equation iteratively without any constraints. By combining the results of the GAUSSVIEW 5.0 program, the vibrational wavenumbers of IR and Raman spectra in experiment were accurately elucidated.

Results and discussion

Molecule structure

The results of X-ray crystal diffraction proves that the molecular structure and its packing mode of the ionic liquid are very close to the previous report [16]. In the present case, the strong intra- and intermolecular N-H---F, C-H---F and C-H---O interactions (Table 1) have effect on the packing structure as the values reported previously [16,17]. In order to compare with experimental data better, the optimized parameters gained at B3LYP/6-311G (d, p) level are listed in Table 2. The displacement ellipsoid plots with atomic renumbering are shown in Fig. 1 to be used for stating better in this work. Fig.2 depicted obtained crystal packing and hydrogen bonding interactions in crystal structure.

Seen from the crystal structure, the bond lengths of C- C and C-N in imidazolium ring are 0.1316-0.1389 nm, shorter than normal C-C (0.1540 nm) and C-N (0.1470 nm), longer than normal C=C (0.1340) and C=N (0.1270). This phenomenon demonstrates the bond lengths in imidazolium ring have average trend of single and double bond. The dihedral angles (N2C3C2N1, C3N2C1N1, C1N2C3C2, C1N1C2C3, C2N1C1N2) are -1.5°, -1.5°, 1.8°, 0.6°, and 0.6°, respectively. It indicates that there is a planar structure where all sp2 hybrids in imidazolium ring and the imidazolium ring has aromaticity. The charge disperses in whole imidazolium ring, so imidazolium cation is very stable [16-19]. From Fig.2A and B, it is found that the C1-H fragment on the imidazolium ring interact with a neighboring carbonyl O1=C6 of an adjacent molecule by hydrogen bond. Four imidazolium rings parallel as a basic unit. And the BF_4 anions are near the C1-H fragment above the imidazolium rings because of C1-H…F hydrogen bonds and electrostatic forces between anion and cation. The stable hydrogen bonds in ion-pairs are also reported in Fig.2B and Table 1.

As seen from Table 2, it can be observed that the experimental and theoretical geometric parameters are not agreed with each other completely. It is owing to the following two facts. The first fact is that an isolated molecule considered in theoretical calculation in gas phase is contrary to the packing molecules with intermolecular interactions recorded in condensed phase in experimental measurement [18], and the second one is that a theory derived from reality is generally imperfect with a case. In the crystal structure, cations and anions alternated in the crystal structure and the BF4 anions are positioned closer to the imidazolium rings than that of the gas phase. The carbonyl group is closed to hydrogen atom of C8 of adjacent molecule but not in the gas phase where the distance is very far between the molecular and adjacent molecular [16].

In the studied case, the largest deviations of bond lengths and bond angles between the optimized values and experimental ones are of 0.05 A and 2.7°, respectively. Despite the optimized parameters are slightly different from the crystallographical data for the studied compound, the optimized structure depend upon the method and the basis set used in the calculations are accepted as a base to calculate other properties or to evaluate some characteristics for the studied compound.

Vibrational assignments

Theoretical wavenumbers have been scaled using the scale factors recommended for harmonic vibrational frequencies computed at the B3LYP/6-311G (d,p) level. In the present study, vibrational wavenumbers calculated at B3LYP/6-311G (d,p) level have been scaled by 0.9613 [20, 21]. Comparison of experimental and calculated (scaled) vibrational spectra was shown in Fig.3 (IR) and Fig.4 (Raman). It was found that good correlations among the scaled values of the computed harmonic frequencies and the observed. The assignment of the functional groups in the ionic liquid has been listed in the Table 3. The absorption peak of N-H is calculated to be 3326cm^{-1} and observed at 3195 cm^{-1} in the IR spectrum. The shifting of the mode is due to intra-molecular hydrogen bonding N-H---F. Seen from Table 2, we know the bond length of N-H is longer than normal bond length of N-H in crystal. Based the principle of vibration equations in infrared spectra [22], the bond length became longer, and as a result that the force constant K of chemical bonding became smaller, so the vibrational frequency decreased. The large deviation is because that the calculated value is the result of the gas, and the intramolecular hydrogen bonding due to crystal packing wasn't considered in calculation.

Asymmetric stretching vibration peak of unsaturated C-H occurs at 3141, 3107, 3045cm^{-1}, and it matches with the calculated value (3153, 3112, 3048cm^{-1}). A peak at 2993cm^{-1} gives rise to asymmetric stretching vibration of CH3(C-8). Its deformation vibration appeared at 1375cm^{-1} and is in good agreement with the calculated value

(1360 cm^{-1}). Generally, C=O stretching vibration shows stronger and stronger absorption peak at range of 1810–1710 cm^{-1}. Due to conjugation effects higher than induction effects in amide group, its peak occurs at 1683 cm^{-1} in experimental spectrum but the calculated value is 1683cm^{-1}. Stretching vibration peak of B-F appeared at 520 cm^{-1} with the calculated value (492cm^{-1}).

The middle bands at 1603, 1567cm^{-1} in Raman spectrum are assigned to the aromatic phenyl C=C stretching vibrations, which are good coherence with theoretically calculated data at 1582, 1564 cm^{-1}. Corresponding bands in IR were observed at 1579, 1492, 1427 cm^{-1} with the theoretical data at 1582, 1470, 1430 cm^{-1}. In general, most of these modes are accompanied with the combination of the C-H in-plane bending vibrations. The bands observed at 1348, 563, and 542cm^{-1} in IR spectrum are assigned to C-C-C deformation vibrations of the phenyl ring. The deformation vibrations appear at 1028, 999, 765 and 618cm^{-1} in Raman spectrum. The theoretically computed C-C-C deformation vibrations have been found to show good agreement with recorded spectral date region.

The unsaturated C-H stretching vibrations bands of the aromatic imidazolium ring appear at 3141, 3107, 3045cm^{-1} in IR, and deformation vibrations of the C-H in imidazolium ring at 1253, 623 cm^{-1}. Because of multiple hydrogen bonds between C1-H and O1 or F, the C1-H stretching vibration (3045cm^{-1}) became stronger and the frequency decreased [23].

Conclusions

In this present work, determinations have been made for the molecular structure and spectral assignments of the new chiral ionic liquid synthesized from (S)-1-phenylethylamine from single crystal XRD, FT-IR and FT-Raman spectra with the aid of the theoretical calculations at B3LYP/6-311G(d, p) level. The experimental and theoretical results support well each other. Theoretical–experimental analysis of the molecular structure of the ionic liquid would help achieve a better understanding of the mechanisms of stabilization of its functionality, and which could be related to it potential chemistry role.

Acknowledgements

The authors very much appreciated the support of this work by the Scientific Research Fund of Mianyang normal university (2012A12) and Administration Department of Education, Sichuan Province (14ZA0254, 14ZA0256).

References

[1] A. G. Faddev, M. M. Meagher, Chem. Commun. 3(2001)295-296.

[2] R. Liu, J. F. Liu, Y. G. Yin. Anal. Bioanal. Chem. 393(2009) 871-883.

[3] K. S. Kin, D. Demberelnyamba, H. Lee, Langmuir. 20(2004)556-560.

[4] G. H. Tao, L. He, N. Sun, Y. Kou, Chem Commun. 28(2005) 3562-3564.

[5] J. Levillain, G. Dubant, I. Abrunhosa, M. Guleaa, A.C. Gaumont, Chem. Commun. (2003) 2914-2915.

[6] C. Baudequin, D. Brégeon, J. Levillain, F.Guillen, J.C. Plaquevent, A.C. Gaumont, Tetrahedron: Asymmetry 16(2005) 3921-3945.

[7] V. Balachandran, A. Nataraj, T. Karthick, Spectrochim. Acta A 104 (2013) 114-129.

[8] K. W. Wiitala, C. J. Cramer, T. R. Hoye, Magn. Reson. Chem. 45 (2007) 819-829.

[9] G. Barone, L. Gomez-Paloma, D. Duca, A. Silvestri, R. Riccio, G. Bifulco, Chem.Eur. J. 8 (2002) 3233-3239.

[10] J. D. Holbrey, A. E. Visser, S. K. Spear, W. M. Reichert, R. P. Swatloski, G.A. Broker, R. D. Rogers, Green Chem.5(2003) 129-135.

[11] O. V. Dolomanov, L. J. Bourhis, R.J. Gildea, J. A. K. Howard, H. J. Puschmann,

Appl. Cryst. 42(2009) 339-341.

[12] L. Palatinus, S. J. Prathapa, S. V. Smaalen, J. Appl. Cryst. 45(2012) 575-580.

[13] G. M. Sheldrick, Acta Cryst. A 64 (2008) 112-122.

[14] H. Arslan, O. Algul, T. Onkol, Spectrochim. Acta A 70 (2008) 606–614.

[15] M. J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida; T. Nakajima; Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark; J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi; M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslows Cioslowski, D.J. Fox, Gaussian 09, Revision B.01, Gaussian Inc., Wallingford, CT, 2009.

[16] K. Matsumoto，R. Hagiwara, J. Fluorine Chem. 128 (2007) 317-331.

[17] K. Dong, S. J. Zhang, D.X. Wang, X.Q. Yao, J. Phys. Chem. A 110 (2006) 9775-9782.

[18] Y.X Sun, Y. F. Wang, Z.W. Liu, C.L Huang, C. Yu, Spectrochim. Acta A 96 (2012) 42-50

[19] E. R. Talaty, S. Raja, V. J. Storhaug, A. Dölle, W. R. Carper, J. Phys. Chem. B 108 (2004) 13177-13184.

[20] J. P. Merrick, D. Moran, L. Radom, J. Phys. Chem. A 111 (2007) 11683-11700.

[21] A.P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502-16513.

[22] H. Q. Fang, J.S. Yu, J. Shi, Instrumental analysis, Science press, Beijing, pp330-335.

[23] Y. Jeon , J. Sung , C. Seo , H. Lim , H. Cheong , M. Kang , B. Moon , Y. Ouchi , D. Kim, J. Phys. Chem. B, 112 (2008) 4735-4740.

Figure Captions

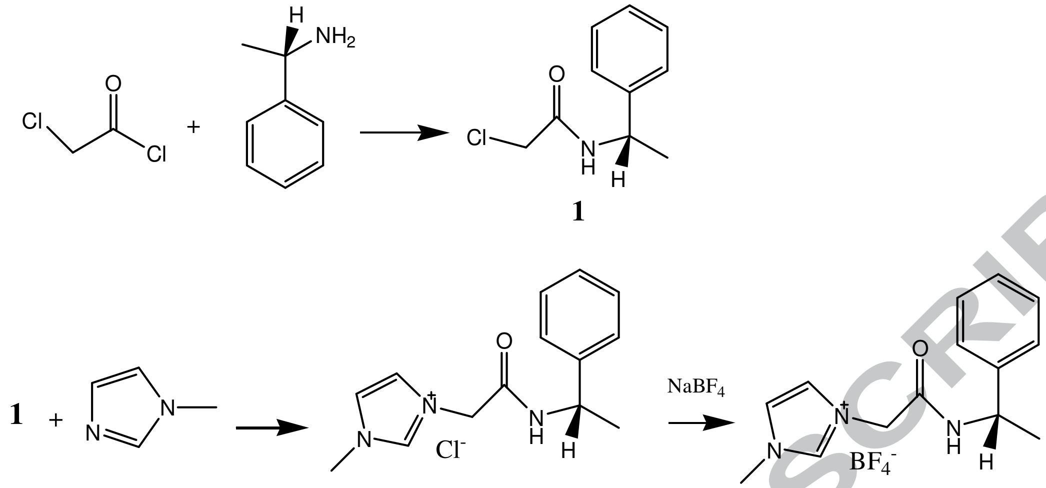
Scheme 1. Synthetic route of the chiral ionic liquid.

Fig. 1. The displacement ellipsoid plots with atomic numbering for the chiral ionic liquid.

Fig. 2. Obtained crystal packing (A), and hydrogen bonding interactions in crystal structure (B)

Fig. 3. Simulated IR spectrum and FT-IR spectrum

Fig. 4. Simulated Raman spectrum and Raman spectrum



Scheme 1.

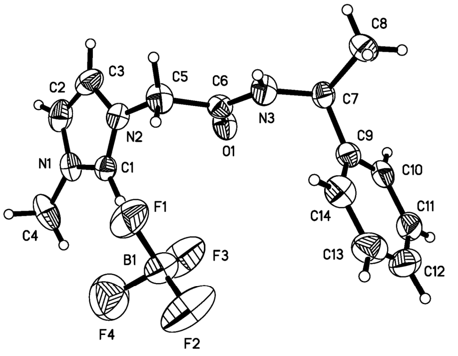
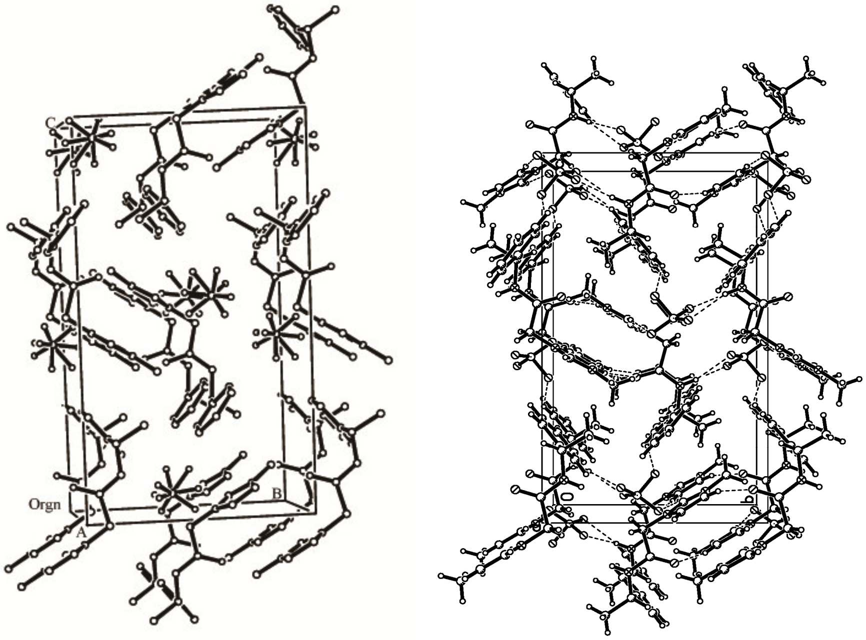

C8
C3
C2
C5
C6
N3
C7
N2
O1
C9
C10
N1
C1
F1
C14
C11
C4
B1
F3
C13
C12
F4
F2

Fig. 1



(A) (B)

Fig. 2

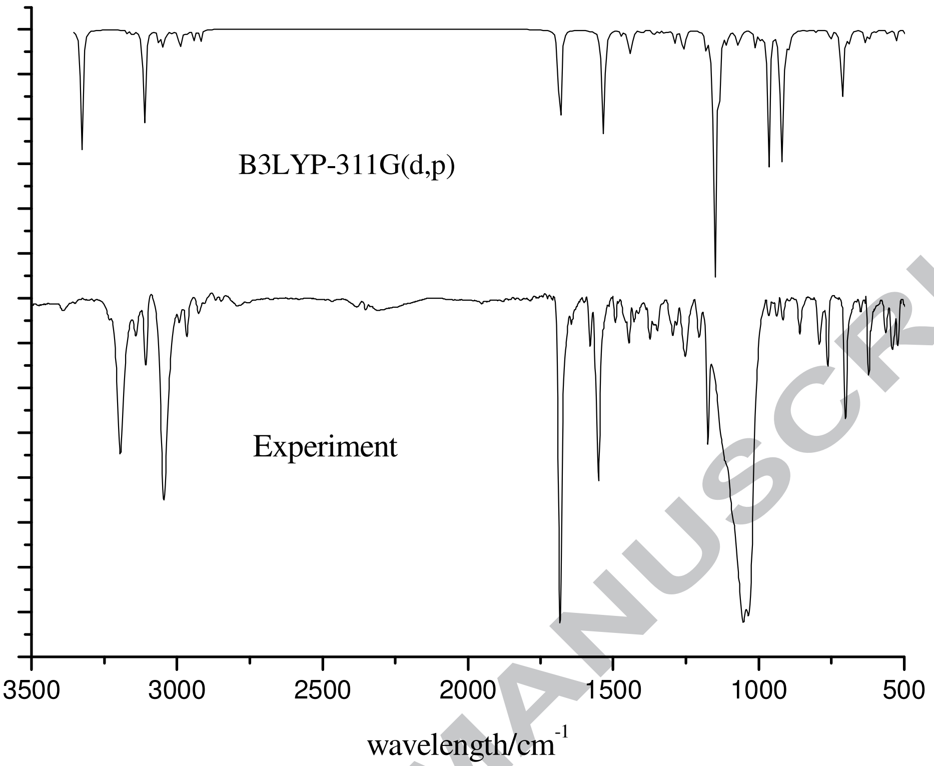

B3LYP-311G(d,p)
Experiment
3500
3000
2500
2000
1500
1000
500
wavelength/cm^{-1}

Fig. 3

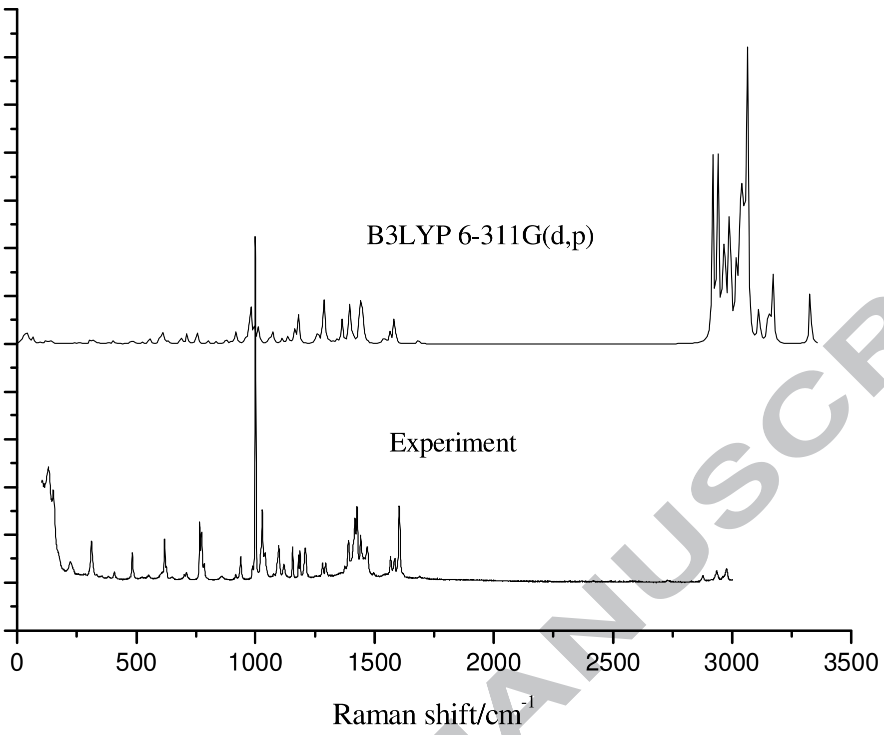

B3LYP 6-311G(d,p)
Experiment
0
500
1000
1500
2000
2500
3000
3500
Raman shift/cm^{-1}

Fig. 4

Table 1. Hydrogen-bond geometries in crystal structure

D-H[a]	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N3-H3	0.860	2.312	157.87	3.126	F4B
N3-H3	0.860	2.537	144.10	3.273	F1A
N3-H3	0.860	2.226	155.67	3.030	F2A
C5-H5A	0.970	2.564	157.44	3.480	F1A
C5-H5A	0.970	2.339	155.16	2.245	F1B
C5-H5B	0.970	2.628	150.13	3.503	F2B
C3-H3	0.930	2.508	137.24	3.253	F2B
C3-H3	0.930	2.353	146.21	3.168	F3B
C3-H3	0.930	2.451	170.18	3.371	F3A
C8-H8A	0.960	2.575	127.95	3.254	F4B
C1-H1	0.930	2.210	165.05	3.117	F3B
C1-H1	0.930	2.284	156.49	3.159	F3A
C2-H2	0.930	2.329	164.74	3.236	O1

[a] Secondary CH2 refined with riding coordinates: C5(H5A,H5B); Idealized Me refined as rotating group: C8 (H8A, H8B, H8C)

Table 2. Optimized and experimental geometric parameters

Parameters[a]	Experimental	Calculated B3LYP/6-311g (d,p) in gas
Bond Angle/°		
C3-N2-C5	126.1(6)	126.63008
C1-N2-C5	126.0(5)	123.90704
C1-N2-C3	107.7(5)	108.95419
C6-N3-C7	123.6(5)	121.79130
C1-N1-C4	126.3(6)	123.83634
C1-N1-C2	108.7(5)	108.64956
C2-N1-C4	124.9(6)	127.44838
N2-C5-C6	110.8(4)	108.05976
C12-C11-C10	120.6(8)	120.00076
C11-C12-C13	120.4(7)	119.58433
C2-C3-N2	105.8(6)	106.68904
N3-C7-C8	109.5(5)	108.93679
N3-C7-C9	112.9(5)	111.73334
C9-C7-C8	110.9(5)	112.43056
C10-C9-C7	119.7(6)	119.96585
C14-C9-C7	122.5(6)	121.09933
C14-C9-C10	117.7(6)	118.92404
N1-C1-N2	109.6(5)	108.57449
C11-C10-C9	121.0(7)	120.78933
N1-C2-C3	108.2(6)	107.13038
C12-C13-C14	119.6(8)	120.42753
C9-C14-C13	120.6(8)	120.27112
O1-C6-N3	124.0(5)	125.94898
O1-C6-C5	121.1(5)	119.18984
N3-C6-C5	114.9(4)	114.81752
F2B-B1-F4B	98.1(18)	
F3B-B1-F2B	118.7(15)	106.66833(F1-B-F4)
F3B-B1-F4B	92.7(19)	111.74136(F3-B-F4)
F1A-B1-F4A	97.9(9)	108.23259(F1-B-F2)
F2A-B1-F1A	112.2(9)	111.35174(F1-B-F3)
F2A-B1-F3A	122.7(9)	112.15269(F2-B-F3)
F2A-B1-F4A	108.0(12)	106.38279(F2-B-F4)
F3A-B1-F1A	118.8(10)	
F3A-B1-F4A	89.6(9)	
F1B-B1-F2B	107(2)	
F1B-B1-F4B	117.5(16)	
F1B-B1-F3B	120(2)	
Bond length/ Å		
O1-C6	1.216(6)	1.22423
N2-C5	1.438(7)	1.47497
N2-C3	1.389(8)	1.38509
N2-C1	1.317(7)	1.33418
N3-C7	1.459(8)	1.47009
N3-C6	1.313(7)	1.34425

N1-C4	1.453(9)	1.46635
N1-C1	1.316(7)	1.33354
N1-C2	1.338(9)	1.38601
C5-C6	1.540(9)	1.54101
C11-C12	1.338(12)	1.39231
C11-C10	1.382(10)	1.39411
C12-C13	1.377(13)	1.39464
C3-C2	1.354(10)	1.36002
C8-C7	1.546(8)	1.53370
C7-C9	1.509(8)	1.52577
C9-C10	1.393(9)	1.40056
C9-C14	1.379(9)	1.39618
C13-C14	1.399(13)	1.39411
F1B-B1	1.26(3)	
F2B-B1	1.33(3)	
F4B-B1	1.36(3)	
F3B-B1	1.28(3)	
F1A-B1	1.420(15)	1.42968
F2A-B1	1.316(13)	1.36536
F3A-B1	1.350(12)	1.42235
F4A-B1	1.436(15)	1.44048

[a] Uanis(F2A) = Uanis(F2B); Uanis(F4A) = Uanis(F4B); Uanis(F3A) = Uanis(F3B); Uanis(F1A) = Uanis(F1B)

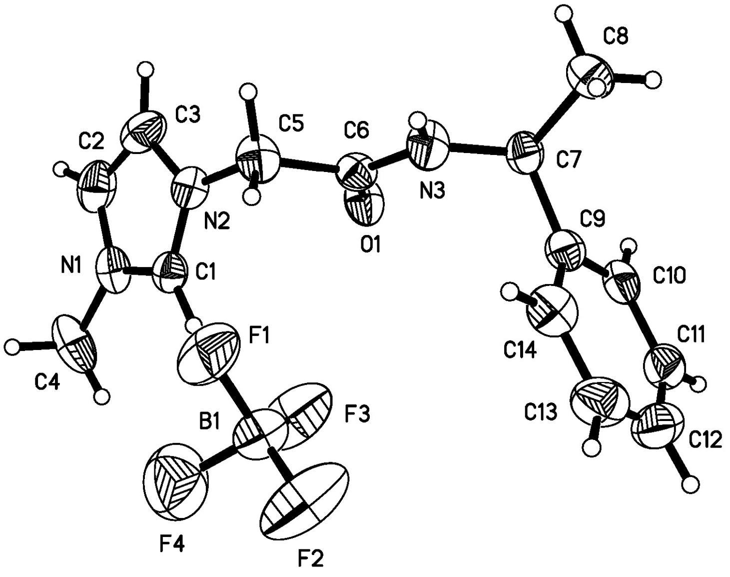
Table 3. Theoretical and experimental wavenumbers (cm^{-1}) ^{a}

Experimental		Theoretical			Approximate assignments
IR	Raman	Frequency	I (IR)	I (Raman)	
3195		3326	276.6	62.1	νN3H
3141		3170	6.8	73.2	νC2H+νC3H
3107		3153	12.1	40.9	νC2H+νC3H
3045		3110	222.2	36.7	νC1H
	2980	3062	22.2	290.9	νCH(Ar)
		3056	5.7	28.1	νCH(Ar)
2993		3048	28.4	77.3	νCH(Ar)
		3039	6.1	108.8	νCH(Ar)
		3035	1.6	33.6	ν_{as}C4H$_3$
		3031	1.3	31.96	νCH(Ar)
		3030	3.6	51.98	ν_{as}C5H$_2$
		3016	5.88	72.4	ν_{as}C4H$_3$
		2995	16.8	51.9	ν_{as}C8H$_3$+νC7H
2966		2986	27.8	99.9	ν_{as}C8H$_3$+νC7H
		2968	10.5	114.6	ν_{s}C5H$_2$
		2959	3.8	45.5	νC7H
2925	2940	2939	21.2	172	ν_{s}C4H$_3$
	2882	2918	20.6	161.2	ν_{s}C8H$_3$
1683		1680	262.7	3.1	νC6=O1
1579	1603	1582	2.42	19.6	νC=C (Ar)
	1567	1564	1.7	6.7	νC=C (Ar)
		1544	23.9	2.8	νC=C (imidazolium)
		1535	47.9	2.2	νC=C (imidazolium)+ρN3H+δC5H$_2$
1550		1534	205.2	0.9	ρN3H
1492		1470	10.3	0.5	νC=C (Ar)
	1468	1451	11.3	15.2	τC4H$_3$
	1441	1444	1.4	4.9	τC4H$_3$+τC5H$_2$

1446	1425	1442	32.1	10.4	τC4H$_3$+δC5H$_2$
	1418	1435	9.6	10.4	δC8H$_3$
1427		1430	10.0	0.4	νC=C (Ar)
		1406	4.8	7.1	ωC4H$_3$
	1390	1393	3.7	25.9	νC=C (imidazolium) +τC5H$_2$
		1363	2.7	14.5	νC=C (imidazolium)+ ωC5H$_2$
1375		1360	10.3	1.3	ωC8H$_3$
1348		1343	5.9	2.3	ωC7H+ρCH(Ar)
		1322	7.5	1.3	ρCH(imidazolium)+ ωC5H$_3$
		1308	3.6	1.5	ρC10H+ρC14H+ωC7H
1294	1281	1289	23.1	21.4	δC1N1+δC1N2+ωC7H
		1283	2.9	11.4	ωC5H$_2$+ωC7H+δC1N1+δC1N2
		1261	36.6	5.7	δC1N1+δC1N2+ωC5H$_2$+ρN3H
		1255	7.8	1.1	ωC7H+ρCH(Ar)+ρCH(imidazolium)
1253		1253	22.9	3.1	ρCH(imidazolium)+ ρN3H
1203	1208	1179	28.4	16.7	νC7C9+ωC8H$_3$+τC5H$_2$
	1155	1165	5.4	5.4	ρCH(Ar) +τC5H$_2$
		1164	13.4	2.1	ρCH(Ar) +τC5H$_2$+ρC1H
1174		1150	519	0.4	νBF$_4$+νC5N2
		1137	172.9	1.37	ρC1H+ρC3H+ ρC2H
		1135	0.1	3.5	ρCH(Ar)
	1107	1112	6.9	2.3	ωC4H$_3$
	1097	1107	21.8	1.3	τC8H$_3$+ρCH(Ar)
		1074	6.7	3.6	ρC2H+ρC1H+ωC4H$_3$
1053		1073	14.8	2.9	τC8H$_3$+ρC11H+ρC14H+ρC7N3+
	1063	1068	22.4	3.7	ρC2H+ρC3H+ωC4H$_3$
		1056	4.6	2.2	ρC2H+ρC3H+ωC4H$_3$
	1028	1012	4.9	7.8	ρC10H+ρC11H+ρC13H+ρC14H
1032		1010	26.1	1.8	ρC2C3+ωC5H$_2$
		996	2.4	3.0	ρC5H+τC8H$_3$+ρC6N3
		992	17.3	8.3	ρC2H+ρC3H+ωC8H$_3$+ρC5N2
	999	977	6.1	27.6	τC=C (Ar)
		973	6.4	0.8	τC11H +τC12H +τC13H +τC14H
966		965	246	0.7	τCH (Ar) +ωC1H+νBF$_4$
937		922	238.2	1.43	ωC1H+νBF$_4$+ωC5H$_2$+ρC5N3+ρC5C6+τ CH (Ar)
918	938	916	128.2	7.2	νBF$_4$+ρC6O1+ρC5C6
		903	9.9	0.1	ωC1H +τCH (Ar)
		894	28.2	0.8	ωC1H
858		876	4.6	3.4	ρC5H+ρC 7H+τC8H$_3$+ωC1H
		834	0.7	0.4	ωC2H+ωC3H
		833	0.7	0.6	τCH (Ar)
792		802	4.5	1.5	ωC1H+ωC2H+ωC3H+ωC6O1
	765	756	7.4	5.0	ωCH (Ar)

761		750	15.5	2.6	ωC11H +ωC12H +ωC13H +ωC=C(Ar)
		719	31.4	0.1	ωC2H +ωC3H
		712	29.6	4.8	ωN3H +νBF$_4$
702		710	93.9	0.4	ωN3H +νBF$_4$+ωC2H +ωC3H
		691	25.1	0.9	ωCH (Ar) +ωC=C(Ar)+ ωC3H
		685	12	2.8	ρC1H+ρC5N2
623		632	25.4	1.5	τCH (imidazolium)
		620	16.8	1.2	τCH (imidazolium)
		611	2.1	1.6	τC2H+τC3H
	618	607	0.1	5.5	τCH (imidazolium)+ ρC=C(Ar)
		598	6.1	2.8	τCH (imidazolium)+ ρC=C(Ar)
563		554	10.5	3.6	τCH (Ar)
542		526	20.1	0.6	τC=C(Ar)
521		492	12.0	0.6	νBF$_4$
		487	1.5	0.5	νBF$_4$
		480	4.5	0.4	νBF$_4$
	483	475	3.2	1.1	ρC5H+τC8H$_3$
		405		1.6	ρC5H+ρC4N1
		398		0.1	τC10H+τC11H+τC13H+τC14H+
		383		0.9	ρC4H$_3$+ρC6O1+τC=C(imidazolium)
		341		0.4	δBF$_4$
		328		0.5	τBF$_4$
	311	320		1.6	ωC5H
		306		2.4	ωN2C5+τCC(imidazolium) +τC=C(Ar)
		255		0.6	ωC8H$_3$+τCC(imidazolium) +τC=C(Ar)
	223	221		0.3	ωC8H$_3$

[a] imidazolium (C1N1C2C3N2); Ar (C9-C14); ν_s: symmetry stretching vibration; ν_{as}: asymmetry stretching vibration; δ: scissor in plane; ρ: twisting in plane; ω: rock out of plane; τ: twisting out of plane.


C8
C3
C5
C6
C2
N3
C7
N2
O1
C9
N1
C1
C10
F1
C11
C14
C4
F3
C13
B1
C12
F4
F2

Highlights

- A new chiral ionic liquid was synthesized from (S)-1- phenylethylamine.
- The structure was studied by IR, Raman, NMR and X-ray crystal diffraction.
- The vibrational modes were assigned with the support of DFT calculations.