Raman and ab Initio Studies of Simple and Binary 1-Alkyl-3-methylimidazolium Ionic Liquids

Rolf W. Berg,*,† Maggel Deetlefs,‡ Kenneth R. Seddon,‡ Irene Shim,† and Jillian M. Thompson‡

Department of Chemistry, Technical University, DK-2800 Lyngby, Denmark, and QUILL Centre, Queen's University of Belfast, Stranmillis Road, Belfast BT9 5AG, Northern Ireland, U.K.

Raman spectra of the ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate ([C$_4$mim][PF$_6$]), 1-hexyl-3-methylimidazolium chloride ([C$_6$mim]Cl), and 1-hexyl-3-methylimidazolium hexafluorophosphate ([C$_6$mim][PF$_6$]), and binary mixtures thereof, have been assigned using ab initio MP2 calculations. The previously reported anti and gauche forms of the [C$_4$mim]$^+$ cation have been observed, and this study reveals this to be a general feature of the long-chain 1-alkyl derivatives. Analysis of mixtures of [C$_6$mim]Cl and [C$_6$mim][PF$_6$] has provided information on the nature of the hydrogen bonding between the imidazolium headgroup and the anions, and the invariance of the essentially 50:50 mixture of the predominant conformers informs on the nature of glass formation in these systems.

Introduction

Ionic liquids have been defined as species that are composed entirely of ions and are liquid at or near room temperature.[1] They have been used for many applications, ranging from media for organic synthesis[2] and catalysis[3] to lubricants,[4,5] and more recently have generated much academic and industrial interest as replacements for environmentally damaging volatile organic solvents.[6–11] It has been recently demonstrated that the outcome of organic reactions can be controlled by the choice of ionic liquid[12] and that both the anion and cation can interact specifically with catalysts or substrates.[13–17]

One of the most interesting (and potentially most useful) properties of ionic liquids is that it is possible to tune their physical properties, such as miscibility with other solvents or substrates; this can be utilized in process development for product isolation, either by decantation, filtration, or solvent extraction.[18] For example, the melting point, water miscibility, density, and viscosity of ionic liquids vary with the anion and with the alkyl chain length on the cation.[19,20] Moreover, many industrial processes will rely upon binary mixtures of two ionic liquids for optimal performance,[21] and it has been estimated that there are at least a billion (10^{12}) such ionic liquids.[22] The nature of intermolecular interactions in ionic liquids is of great importance for their general use as solvents, and yet relatively little is understood about the million simple ionic liquids. As for binary ionic liquid systems, some early studies probed the nature of interactions in so-called first-generation chloroaluminate ionic liquids,[23] but far less information is available for second generation, air-stable systems such as the [C$_6$mim]-Cl/[C$_6$mim][PF$_6$] mixtures investigated in this work, where anions are independent of each other.

Previous studies into the structure of ionic liquids have included the use of vibrational spectroscopy. Reports from Hamaguchi's group[24–26] have described the [C$_4$mim]$^+$ (1-butyl-3-methylimidazolium) cation with a number of different anions using Raman spectroscopy, and the polymorphism of [C$_4$mim]-Cl has been independently verified by two groups.[24,27–29] (In

other papers, the abbreviation [bmim]$^+$ is used as an alternative to [C$_4$mim]$^+$, and [hmim]$^+$ has been used instead of [C$_6$mim]$^+$; both schemes are common and acceptable.) Infrared spectroscopy and X-ray crystallography have been used to study imidazolium cations, containing alkyl chains ranging from [C$_2$mim]$^+$ to [C$_{18}$mim]$^+$, although these studies have focused predominantly on the solid state.[26,28,30–32] There have also been a number of X-ray scattering[25,33–36] and neutron diffraction and scattering studies,[29,37–39] although neutron diffraction studies, by their nature, have had [C$_1$mim]$^+$ and [C$_2$mim]$^+$ as their cynosure.

IR spectroscopy has provided detailed information on the nature of the interaction between water and ionic liquids. Kazarian, Welton, and co-workers[16,40] reported the presence of hydrogen-bonded, non-self-associated water molecules in [C$_4$mim][PF$_6$] and [C$_4$mim][BF$_4$], with the water hydrogen bonding more strongly to the [BF$_4$]$^-$ anion than to the [PF$_6$]$^-$. Hydrogen bonding is also known to occur between the cations and anions in an ionic liquid, as demonstrated by mass spectrometry in the gas phase,[41] by ^{1}H NMR studies in solution,[42–46] and by X-ray and IR studies in the solid state.[43,45–48] The net conclusions from this wealth of studies are that the 1-alkyl-3-methylimidazolium cation will form, often multiple, hydrogen bonds from the cation—usually the H(2), H(4), H(5), H(6), H(7) and the terminal methyl group on the alkyl chain—to even weak hydrogen bond acceptors, such as tetrafluoroborate and hexafluorophosphate, and that there was some evidence for the presence of conformers in the liquid state. It therefore seemed of interest to see whether the conformers were confined to a butyl chain, or a more general phenomenon, to explore the relationship between the solid and solution structures, and to see how two anions of differing hydrogen bond acceptor ability, viz., chloride and hexafluorophosphate, would compete in a binary mixture with a common cation.

---
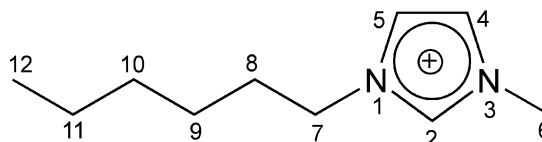
* Corresponding author: fax, +45 4588 3136; tel, +45 4525 2412; e-mail, rwb@kemi.dtu.dk.

† Department of Chemistry, Technical University.

‡ QUILL Centre, Queen's University of Belfast.

Ionic Liquid Study

J. Phys. Chem. B, Vol. 109, No. 40, 2005 **19019**

TABLE 1: Approximate Descriptions^a of Vibrational Frequencies Discussed in the Text as Determined in MP2 Calculations for the [C$_4$mim]$^+$ Cation with the Butyl Group either in the AA (anti−anti) or in the GA (gauche−anti) Conformation

	butyl group in the **AA** (anti−anti) conformation		butyl group in the **GA** (gauche−anti) conformation	
mode	ν/cm^{-1}	approximate description	ν/cm^{-1}	approximate description
12	441.0	N−C7 oopl bend + N−C6 oopl ooph bend + chain bend + CH$_2$ wag + ring rot	503.7	N−C7 oopl bend + N−C7−C8−C9 angles bend
13	619.6	ring oopl def + C7H$_2$ rock + C7−C8−C9 bend	603.9	N−C6 N−C7 iph str + ring oopl def + C8H$_2$ rock + N−C7−C8 bend
14	636.2	ring def (C2−H oopl bend) + N−C6 N−C7 iph str + C7H$_2$ rock + C7−C8−C9 bend	622.8	ring def (C2−H C4−H iph oopl bend) + C8H$_2$ rock + N−C7−C8 bend
15	670.2	N−C6 str + ring def (N1 and H on C2 oopl ooph departure) + C8H$_2$ wag + N−C7−C8 bend	662.8	ring def (bend around line NN) + C8H$_2$ rock + N−C7−C8 bend
16	725.5	ring C−H oopl bend (bend around NN line)	712.8	N−C6 N−C7 ooph str + ring ipl def + C8H$_2$ rock + C7−C8 tor
17	748.8	N−C6 N−C7 ooph str + ring ipl def + N−C7−C8 and C7−C8−C9 bend	725.1	ring C−H oopl bend (bend around NN line)

^{a} Key of approximate group vibrations: asym = asymmetric, bend = angle bending (scissoring), breathing = all ring bonds iph, def = more complicated deformation of skeleton, ipl = in plane, iph = in phase (symmetric), oopl = out of ring plane, ooph = opposite motion, out of phase (asymmetric), ring = imidazole core, rot = ring rotation, as a wheel, with carbon H atoms, rock = rocking (like V to *V* by rotation around an axis out of the paper), sci = nonconnected scissoring, str = bond stretching, sym = symmetric, tor = torsion around specified bond, twi = twisting of CH$_2$ group or chain, wag = wagging (like V to v by rotation around an axis in the paper, →).
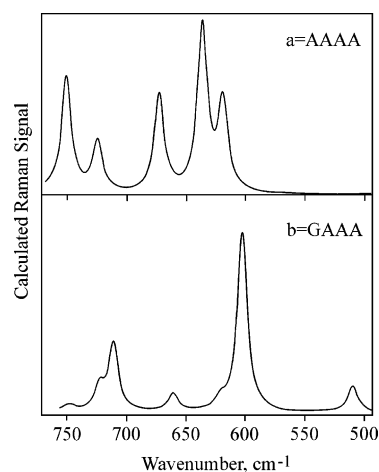
TABLE 2: Experimentally Observed Spectral Bands Discussed in the Text for the Investigated Ionic Liquids, Given in cm^{-1}, and Their Approximate Assignments

ν/cm^{-1}				
[C$_4$mim][PF$_6$]	[C$_4$mim][BF$_4$]	[C$_6$mim][PF$_6$]	[C$_6$mim]Cl	assignments^a
498	500			[C$_4$mim]$^+$ N−C7 opl bend + N−C7−C8−C9 angles bend (GA12)
568		568		ν_2(PF$_6^-$) stretching
601	601	600	600	N−C6 N−C7 iph str + ring oopl def + C8H$_2$ rock + N−C7−C8 bend (GA13, GAAA17)
624	625	623	627	ring def (C2−H oopl bend) + N−C6 N−C7 iph str + C7H$_2$ rock + C7−C8−C9 bend (AA14, AAAA18)
656	658	658	656	N−C6 str + ring def (N1 and H on C2 oopl ooph departure) + C8H$_2$ wag + N−C7−C8 bend (AA15, AAAA19) + ring def (bend around line NN) + C8H$_2$ rock + N−C7−C8 bend (GA15, GAAA19)
698	699	698	698	N−C6 N−C7 ooph str + ring ipl def + C8H$_2$ rock + C7−C8 tor (GA16, GAAA20)
730 ? hidden	∼735		732	N−C6 N−C7 ooph str + ring ipl def + N−C7−C8 and C7−C8−C9 bend (AA17, AAAA22)
741		741		ν_1(PF$_6^-$) stretching

^{a} Key for descriptions of approximate group vibrations, see Table 1; **AA**, **GA**, **AAAA**, and **GAAA** mode numbers given in parentheses.
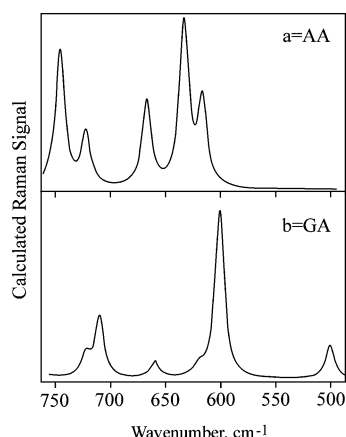
Figure 1. Calculated Raman spectra of two conformers between 750 and 500 cm^{-1} of the [C$_4$mim]$^+$ cation: a, all-anti conformer; b, gauche−anti conformer.

Figure 2. The calculated Raman spectra of two conformers of the [C$_6$mim]$^+$ cation between 750 and 500 cm^{-1}: a, all-anti conformer; b, gauche−anti−anti−anti **(GAAA)** conformer.

Recently, [C$_4$mim]Cl has been found to form two different crystal polymorphs at room temperature, monoclinic (mp 41 °C)[28] and orthorhombic (mp 66 °C),[28] and [C$_4$mim]Br (mp >70 °C) was also reported.[28] The structure of the monoclinic polymorph has been independently solved:[26] The chloride ion is very close (2.55 Å) to the hydrogen H(2) in the ring and to the two H(7) methylene protons (2.72 and 2.73 Å),[28] meeting the criteria for relatively strong hydrogen bonds.[49,50] Similar strong hydrogen bonds are observed in the orthorhombic form.[28]

TABLE 3: Approximate Descriptions[a] of Vibrational Frequencies Discussed in the Text As Determined in MP2 Calculations for the $[C_6mim]^+$ Cation with the Hexyl Group either in the all-anti (AAAA) or in the gauche−anti−anti−anti (GAAA) Conformation

	hexyl group in the all-anti (**AAAA**) conformation			hexyl group in the gauche-anti-anti-anti (**GAAA**) conformation	
mode	ν/cm^{-1}	approximate description		ν/cm^{-1}	approximate description
16	458.4	N−C7 oopl bend + C6H$_3$ oopl bend + C8−C9−C10−C11 bend		511.4	N−C7 opl bend + N−C7−C8−C9 angles bend
17	619.6	ring oopl def + C7H$_2$ rock + C7−C8−C9 bend		604.4	N−C6 N−C7 iph str + ring ipl def + C8H$_2$ rock + N−C7−C8 bend
18	636.7	ring def (C2−H oopl bend) + N−C6 N−C7 iph str + C7H$_2$ rock + C7−C8−C9 bend		622.7	ring def (C2−H C4−H iph oopl bend) + C8H$_2$ rock + N−C7-C8 bend.
19	673.2	N−C6 str + ring def (N1 and H on C2 oopl ooph departure) + C8H$_2$ wag + N−C7−C8 bend		662.8	ring def (bend around line NN) + C8H$_2$ rock + N−C7−C8 bend
20	725.4	ring C−H oopl bend (bend around NN line)		713.0	N−C6 N−C7 ooph str + ring ipl def + C8H$_2$ rock + C7−C8 tor
21	746.6	chain CH$_2$ rock		724.7	ring C−H oopl bend (bend around NN line)
22	751.4	N−C6 N−C7 ooph str + ring ipl def + N−C7−C8 and C7−C8−C9 bend		750.4	chain CH$_2$ rock

[a] For key of approximate group vibrations, see Table 1.

TABLE 4: Comparison of Selected Vibrational Frequencies As Determined in MP2 Calculations for the $[C_4mim]^+$ and $[C_6mim]^+$ Cations in AA and AAAA Conformations, Respectively[a]

	$[C_4mim]^+$ **AA** cation				$[C_6mim]^+$ **AAAA** cation			
mode	ν/cm^{-1}	IR intens/ km mol^{-1}	R activity/ Å^4 amu	mode	ν/cm^{-1}	IR intens/ km mol^{-1}	R activity/ Å^4 amu^{-1}	approximate description[b]
13	620	0.52	1.34	17	620	0.54	1.47	ring oopl def + C7H$_2$ rock + C7−C8−C9 bend
14	636	9.40	2.59	18	637	9.88	2.74	ring def (C2−H oopl bend) + N−C6 N−C7 iph str + C7H$_2$ rock + C7−C8−C9 bend
15	670	12.23	1.36	19	673	12.60	1.62	N−C6 str + ring def (N1 and H on C2 oopl ooph departure) + C8H$_2$ wag + N−C7−C8 bend
17	749	13.06	2.13	22	751	12.84	1.90	N−C6 N−C7 ooph str + ring ipl def + N−C7−C8 and C7−C8−C9 bend

[a] Also included are the predicted relative IR and Raman intensities as well as descriptions of the selected modes. [b] For key of approximate group vibrations, see Table 1.

TABLE 5: Comparison of Selected Vibrational Frequencies As Determined in MP2 Calculations for the $[C_4mim]^+$ and $[C_6mim]^+$ Cations in GA and GAAA Conformations, Respectively[a]

	$[C_4mim]^+$ cation				$[C_6mim]^+$ **GAAA** cation			
mode	ν/cm^{-1}	IR intens/ km mol^{-1}	R activity/ Å^4 amu^{-1}	mode	ν/cm^{-1}	IR intens/ km mol^{-1}	R activity/ Å^4 amu^{-1}	approximate description[b]
12	504	0.6543	1.1920	16	511	0.2962	0.8334	N−C7 opl bend + N−C7−C8−C9 angles bend
13	604	1.46	5.9919	17	604	1.41	5.6691	ring ipl def + C8H$_2$ rock + N−C7−C8 bend
14	623	2.82	0.3563	18	623	2.85	0.3405	ring def (C2−H C4−H iph oopl bend) + C8H$_2$ rock + N−C7-C8 bend
15	663	15.62	0.5566	19	663	15.92	0.5652	ring def (bend around line NN) + C8H$_2$ rock + N−C7−C8 bend
16	713	6.65	2.1455	20	713	6.88	2.1136	N−C6 N−C7 ooph str + ring ipl def + C8H$_2$ rock + C7−C8 tor

[a] Also included are the predicted relative IR and Raman intensities as well as descriptions of the selected modes. [b] For key of approximate group vibrations, see Table 1.

The $[C_4mim]^+$ cations were found to differ in their conformation in the two polymorphs: In the monoclinic form, the butyl chain is all anti, and in the orthorhombic form the chain is gauche around C7−C8. This most notably reveals itself in the rotation of the butyl chain around the C7−C8 bond, differing by 106.16° between the two conformers.[28] In a convenient notation, these conformers are referred to here as the **AA** and the **GA** forms. Furthermore, the FT-Raman spectra of these compounds differ considerably,[24,27] when recorded at room temperature.

In the present work, we build on the earlier work from our own groups and from Japan[24,27,28] (n.b. during the preparation of this paper, a paper from Carper and co-workers appeared,[51] which neither cited nor added much to these earlier papers, all of which were published in the year prior to its submission) and demonstrate that similar analysis of $[C_4mim]$Cl can be obtained using Raman and ab initio MP2 calculations using Gaussian 03,[52] with the equilibrium geometries of the C7−C8

anti and gauche conformers of the cation being optimized using the basis set 6-31G*. Vibrational frequencies and the intensities of the infrared and Raman bands have been derived. Once verified, this methodology was used to assign the peaks in the previously unreported $[C_6mim]$Cl and $[C_6mim][PF_6]$ liquids and to determine the presence of any conformers in the $[C_6mim]^+$ cation, and then this information was used to study the interactions between $[C_6mim]$Cl and $[C_6mim][PF_6]$ in a series of binary ionic liquids. The $[C_6mim]^+$ cation was chosen, as 1,3-dialkylimidazolium cations are perhaps the most frequently used cations in the literature, and the 1-hexyl-3-methyl- derivative lies in the lowest melting point region of the series, allowing both these simple anions to form liquids at room temperature.

Experimental Section

1-Methylimidazole (99%), 1-chlorobutane (99%), and 1-chloro-hexane (99%) were obtained from Aldrich and used as received.
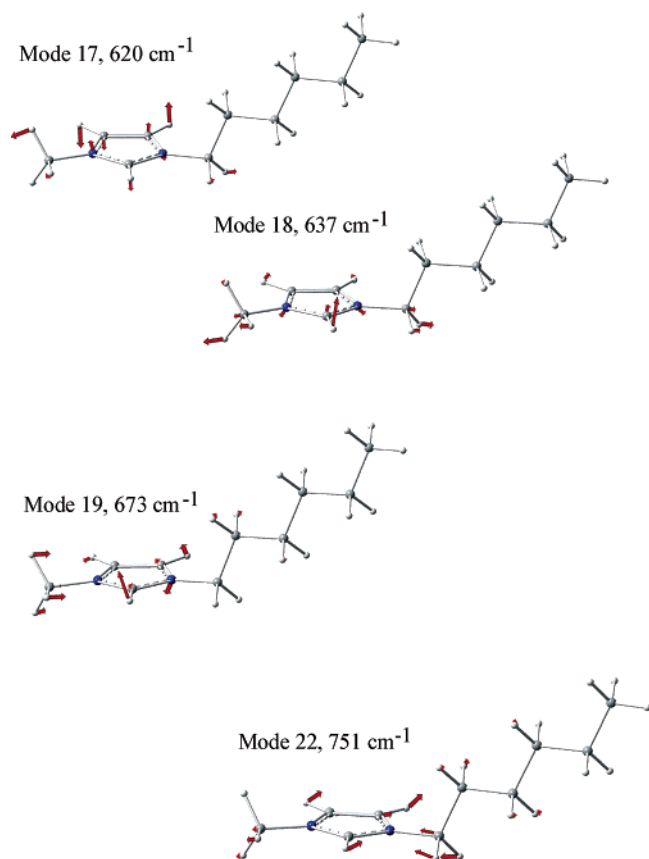
Ionic Liquid Study

J. Phys. Chem. B, Vol. 109, No. 40, 2005 **19021**

Figure 3. Displacement vectors for the characteristic modes for **AAAA** conformer of the [C$_6$mim]$^+$ cation: a, mode 17, 620 cm^{-1}; b, mode 18, 637 cm^{-1}; c, mode 19, 673 cm^{-1}; d, mode 22, 751 cm^{-1}.

Figure 4. Displacement vectors for the characteristic modes for **GAAA** conformer of the [C$_6$mim]$^+$ cation: a, mode 16, 511 cm^{-1}; b, mode 17, 604 cm^{-1}; c, mode 18, 623 cm^{-1}; d, mode 19, 663 cm^{-1}; e, mode 20, 713 cm^{-1}.

1-Butyl-3-methylimidazolium chloride was prepared according to literature methods,[53] and 1-hexyl-3-methylimidazolium chloride and 1-hexyl-3-methylimidazolium hexafluorophosphate were prepared by related procedures. They were all dried in vacuo at 50 °C for several hours before use after predrying under high vacuum at 60 °C for several hours. This drying technique typically affords water contents of ca. 30 ppm (w/w) for [C$_6$mim][PF$_6$].[54] Mixtures of [C$_6$mim]Cl and [C$_6$mim][PF$_6$] were prepared under an inert atmosphere and transferred to capillary tubes which were then sealed before analysis.

Preparation of [C$_6$mim]Cl. A mixture of 1-methylimidazole and 1-chlorohexane (1:1.1 molar ratio) was heated to 70 °C with stirring until complete consumption of the imidazole (by ^{1}H NMR spectroscopy) was achieved. The liquid was cooled and washed with ethyl ethanoate (3 × one-third the volume of ionic liquid) and then dried on a rotary evaporator and then in vacuo, at 60 °C for 5 h.

Preparation of [C$_6$mim][PF$_6$]. [C$_6$mim]Cl was dissolved in deionized water and treated with an aqueous solution of HPF$_6$ in an ice bath. The mixture was stirred at room temperature overnight before the ionic liquid was extracted into dichloromethane and then washed with deionized water until the washings were neutral. The [C$_6$mim][PF$_6$] was isolated by evaporation of the dichloromethane and dried in vacuo at 60 °C for 5 h.

Preparation of [C$_6$mim]Cl−[C$_6$mim][PF$_6$] Mixtures. In a glovebox charged with dinitrogen, mixtures of [C$_6$mim]Cl−[C$_6$mim][PF$_6$] (X([C$_6$mim]Cl) = 0, 0.1, 0.2, 0.3, ..., 1) were prepared by accurately weighing appropriate amounts of each ionic liquid into a glass vial, stirring the sample vigorously, an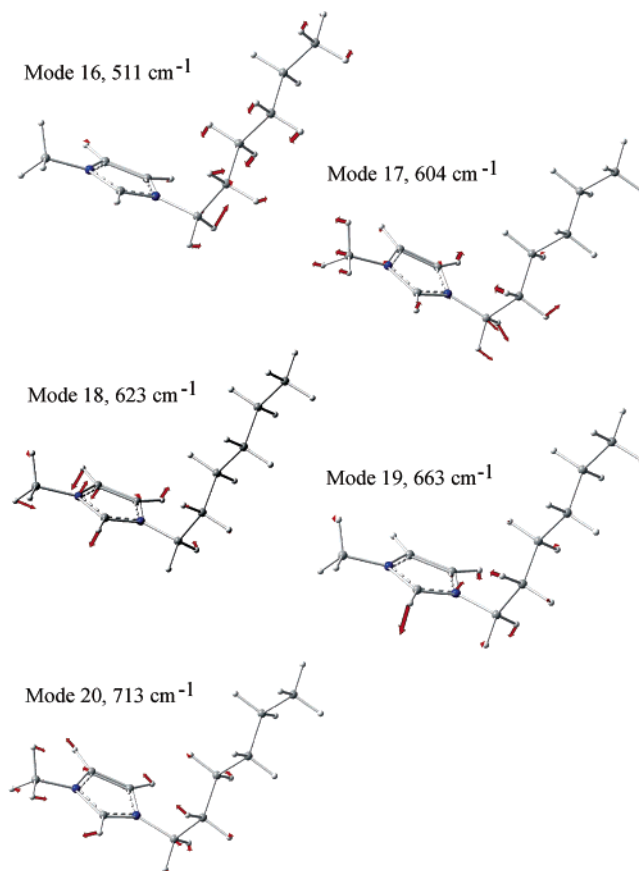d subsequently transferring the ionic liquid mixture into a glass capillary tube. The capillary tubes were transferred from the glovebox in a Schlenk flask, where they were quickly sealed (using a propane flame) before Raman spectra of the samples were recorded.

FT-Raman Spectroscopy Instrumentation. Spectra were obtained using a Bruker IF S66 FRA-106 Fourier transform spectrometer with a Raman attachment. The exciting source was a 1064 nm near-infrared Nd:YAG laser with a nominal power of 100 mW. It should be noted that use of visible laser light (green 514.5 nm or red 784 nm) resulted in strong fluorescence. The scattered light was filtered and collected at a liquid N$_2$ cooled Ge−diode detector, giving a resolution of approximately 2 cm^{-1} between individual pixels. FT-Raman spectra were collected over the range 3500 cm^{-1} (Stokes) to −1000 cm^{-1} (anti-Stokes). All spectra were measured at approximately 23 °C in small glass capillary tubes. The spectra were not corrected for the small changes in instrument response.

MP2 Calculated Vibrations. The wavenumber (frequency) scale in an ab initio MP2 calculation was calculated as too high, due to the lack of modeling of the surroundings. In the gas phase an empirical "MP2" scale factor of 0.9434 has sometimes been used in order to, by experience, calculate fairly accurate vibrational wavenumbers. A scaling factor of 1 was used in the current work; calculation details are provided in the relevant Supporting Information tables.

Results and Discussion

The calculated Raman spectra between 750 and 500 cm^{-1} for the anti and gauche conformers of [C$_4$mim]Cl are shown in

TABLE 6: Observed Spectral Bands Given in cm⁻¹ and Approximate Assignments

[C₆mim]Cl	[C₆mim](Cl,[PF₆]) (1:1)	[C₆mim][PF₆]	assignments[a]
220	220	220	chain def + N−C6H₃ out of plane bend (AA9)
265	266	266	N−C6H₃ + N−C7H₂ oopl ooph bend (GA11)
292	294	294	ring wag + chain def (AA13)
345	346	340	chain def. (GA13)
410	407	405	ring rot + chain def (AA14 + GA14)
	471	469	$\nu_5(PF_6^-)$ symmetric bending [C₄mim]⁺ N−C7 opl bend + N−C7−C8−C9 angles bend (GA12)
	567	568	$\nu_2(PF_6^-)$ stretching
600	602	600	N−C6 N−C7 iph str + ring oopl def + C8H₂ rock + N−C7−C8 bend. (GA17)
627	624	623	ring def (C2−H oopl bend) + N−C6 N−C7 iph str + C7H₂ rock + C7−C8−C9 bend (AA18)
656	657	658	N−C6 str + ring def (N1 and H on C2 oopl ooph departure) + C8H₂ wag + N−C7−C8 bend (AA19) + ring def (bend around line NN) + C8H₂ rock + N−C7−C8 bend (GA19)
698	700	698	N−C6 N−C7 ooph str + ring ipl def + C8H₂ rock + C7−C8 tor (GA20)
732	732		N−C6 N−C7 ooph str + ring ipl def + N−C7−C8 and C7−C8−C9 bend (AA22)
	741	741	$\nu_1(PF_6^-)$ symmetric stretching
765	766	762	ring C−H oopl iph bend (umbrella) (GA23)
817	820	817	C7H₂ and chain rock (GA26)
		852	C7H₂ rock and chain def (GA27)
870	870	870	chain def (AA28 & GA28)
892	893	892	chain def (AA29 & GA29)
955	957	958, 1004	chain def (AA30 & GA30)
1022	1023	1026	ring elongation (C3) + N−C6 str (AA31 & GA31)
1064	1064	1065	ring elongation (C2) + N−C iph str + C4−H C5−H ipl bend (sci) (AA32 & GA32)
1080	1081	1079	chain ooph C−C str (AA33)
1121	1120	1119	chain ooph C−C str (AA34)
1170	1170	1169	chain ooph C−C str (AA35 & GA35)
1187	1190	1190	chain def (AA38)
1224	1227	1227	C2−H ipl bend, C6H₂ def, CH₂ rock + chain tor (AA40 & GA40 & GA42)
		1257	chain def, CH₂ twi (GA43)
		1283	chain CH₂ wag (AA46 & GA46)
1306	1309	1311	chain (CH₂ twi) + ring CH iph ipl bend (AA47 + AA48)
1338	1339	1339	chain (CH₂ twi) (GA47 & GA48)
1385	1387	1389	ring breathing + C7H₂ twi (AA50 & GA50)
1416	1419	1421	ring asym str + C7H₂ twi + C6H₃ def (AA53 & GA54)
1442	1443	1445	C6H₃ def (AA58 & GA59)
1458	1456	1460	C7H₂ + C8H₂ + C9H₂ + C10H₂ def (AA60, GA60 & AA61)
1565	1568	1570	C12H₃ def & C6H₃ def (AA63 & AA65)
2732	2734	2734	combination
2862	2862	2866	methylene CH₂ str + combination
2872	2872	2873	methylene CH₂ str + combination
2901	2906	2909	methylene CH₂ str + combination
2933	2935	2937, 2927	methylene CH₂ str + combination
2951	2960	2968	methyl CH₃ sym.str. + combination
3062	-	3115	C−H str. (position 2)
3142	3170	3180	C−H str. (position 4,5)

[a] Key for descriptions of approximate group vibrations, see Table 1; assignments mostly for [C₆mim]⁺, with conformer **AA** and **GA** mode numbers given in parentheses.

Figure 1, and the band assignments discussed here for Figure 1 are listed in Table 1. (Detailed Raman spectra and approximate band descriptions are given in the Supporting Information.) The obtained experimental Raman signals for the [C₄mim]⁺ and [C₆mim]⁺ cation ionic liquids that are discussed here are given in Table 2.

The peak positions and relative intensities obtained from the ab initio MP2 calculations compare well with those experimentally derived and with those obtained by DFT calculations by Ozawa et al.[24] The Raman spectra for the [C₄mim]⁺ cation also compared well with the results obtained by Ozawa et al.:[24] their measured bands at 701, 625, 603, and 500 cm⁻¹ correspond within experimental error to our [C₄mim][PF₆] liquid bands at 698, 624, 601, and 498 cm⁻¹. These bands also compare well with the new results for the hexyl system (vide infra), with bands at 698, 623, and 601 cm⁻¹, but no band was seen at ∼498 cm⁻¹.

In the new calculations, Raman bands characteristic of the **AA** conformer appeared at ∼636 and ∼749 cm⁻¹ (Table 1), as compared to the experimental values of 624 and 730 cm⁻¹ (Table 2). In addition, two modes at ∼620 and ∼670 cm⁻¹ were identified that appear to be characteristic for the **AA** conformer, but these modes have lower Raman activities than the modes at ∼636 and ∼749 cm⁻¹; see Figure 1. Furthermore, they are rather close to two modes of the **GA** conformer, found experimentally at 624 and 656 cm⁻¹ (Table 2). The corresponding characteristic frequencies of this **GA** conformer were calculated as ∼504, ∼604, and ∼713 cm⁻¹ (Table 1), as compared to the experimental values of ∼500, ∼602, and ∼699 cm⁻¹ (Table 2).

The calculated energies, E_e, of the two conformers show that the **GA** conformer is more stable than the **AA** conformer by 0.767 kJ mol⁻¹, but at 298.15 K the Gibbs energy of the **AA** conformer is less than that of the **GA** conformer by 0.168 kJ mol⁻¹, indicating almost equal amounts of the two conformers at equilibrium at room temperature, 52% of anti−anti vs 48% of gauche−anti. These results are consistent with the observation of both conformers being simultaneously present in the spectrum of a [C₄mim][BF₄] liquid as observed by Ozawa et al.[24] We

Ionic Liquid Study

J. Phys. Chem. B, Vol. 109, No. 40, 2005 **19023**

conclude from our spectra (vide infra) that this is also the case in the [C$_4$mim][PF$_6$] liquid.

[C$_6$mim]X was studied in a similar manner to determine the presence of any such conformers in the hexyl chain and hence whether the phenomenon is general, or specific, to the [C$_4$mim]X ionic liquids. The calculated Raman spectra for the two conformers of the 1-hexyl-3-methylimidazolium cation between 750 and 500 cm^{-1} are shown in Figure 2, and the modes discussed here are approximately described in Table 3. (Detailed Raman spectra and approximate band descriptions are given in the Supporting Information.) Again, the calculated peak positions agreed well with those obtained experimentally. The most characteristic normal modes in the 500–800 cm^{-1} range of the cations 1-butyl-3-methylimidazolium and 1-hexyl-3-methylimi-dazolium are compared in Table 4 for the all-anti conformers. The corresponding data for the **GA** and **GAAA** conformers are shown in Table 5.

The characteristic frequencies calculated for the all-anti conformer of the 1-hexyl-3-methylimidazolium cation were ~620, ~637, ~673, and ~751 cm^{-1}, and those of the **GAAA** conformer were ~511, ~604, ~623, ~663, and ~713 cm^{-1}, respectively. Figures 3 and 4 show the calculated displacement vectors associated with these characteristic frequencies for the two conformers of the [C$_6$mim]$^+$ cation.

It is recognized, both from the spectra in Figures 1 and 2 and the data in Tables 1 and 3, that the characteristic frequencies do not change significantly when the butyl group is exchanged for a hexyl group.

According to the calculated E_e values, the **GAAA** conformer of the [C$_6$mim]$^+$ cation is more stable than the all-anti conformer by 1.221 kJ mol^{-1}, and at 298.15 K, the calculated Gibbs energy of the **GAAA** conformer is 0.181 kJ mol^{-1} less than that of the **AAAA** conformer, indicating almost equal amounts of the two conformers at room temperature, 52% of **GAAA** vs 48% of **AAAA**.

A thorough assignment of the peaks in both the [C$_4$mim]$^+$ and [C$_6$mim]$^+$ cations having been obtained, this information was then used to study the effects on the nature of the hydrogen bonding in mixtures of [C$_6$mim]Cl and [C$_6$mim][PF$_6$]. Raman spectra of the prepared mixtures are shown, and details are given in Table 6 and Figures 5–7. The spectra have been normalized with respect to the area of the C–H band peak at 2900–3000 cm^{-1}, making the relationship among the spectra readily apparent.

The observed spectral bands are given in Table 6, in which assignments are given based on the MP2 calculations described above, on prior IR and Raman spectroscopy studies on 1-methyl-imidazole and deuterated versions thereof,[55] and on spectra of the [PF$_6$]$^-$ ion.[56,57] For 1-methylimidazole in an assumed C_s symmetry, the methyl group should contribute 9 vibrations (5A′ and 4 A″), the three aromatic CH groups should contribute 9 vibrations (6A′ and 3 A″), and the ring should give 12 ring modes (9A′ and 3 A″).[55] The butyl or hexyl group contributes further a number of vibrations, much like in hexane, such that a total of 69 and 87 normal modes exist in the [C$_4$mim]$^+$ and [C$_6$mim]$^+$ ions, respectively. In the 1-methylimidazole molecule, ring C–H vibrations occur at 3128 and 3103 cm^{-1}, well assigned by deuteration studies,[55] and these bands are shifted in our [C$_6$mim]$^+$ spectra to 3142 and 3062 cm^{-1} in the chloride ionic liquid and to 3180 and 3115 cm^{-1} in the [PF$_6$]$^-$ ionic liquid (Figure 5). The degree of hydrogen bonding between the anion and ring-bound hydrogen atoms H(2), H(4), and H(5) seems to change significantly when the anion is exchanged from the neat chloride to the hexafluorophosphate. Thus, Figure 5
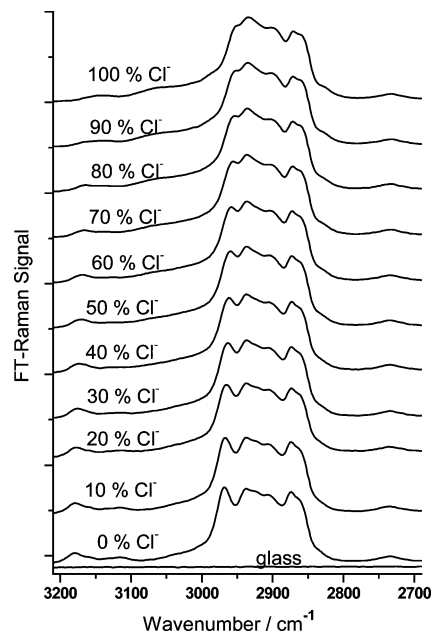

Figure 5. Detail of FT-Raman spectra of a binary room-temperature ionic liquid system, with [C$_6$mim]Cl (top) and [C$_6$mim][PF$_6$] (bottom). The mole percentage of chloride is shown as well as the background spectrum obtained on the empty capillary glass material.
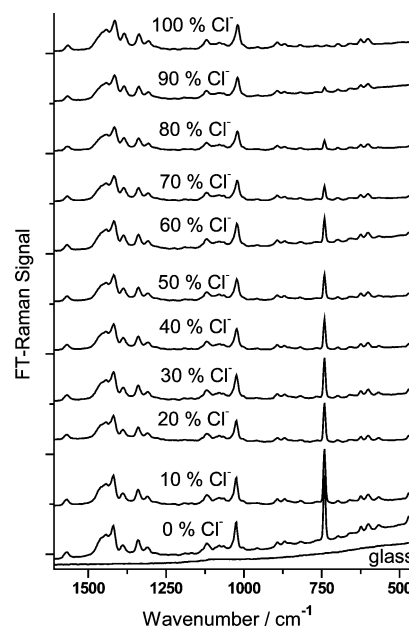

Figure 6. Detail of FT-Raman spectra of a binary room-temperature ionic liquid system, with [C$_6$mim]Cl (top) and [C$_6$mim][PF$_6$] (bottom). The mole percentage of chloride is shown as well as the background spectrum obtained on the empty capillary glass material.

and Table 6 clearly show that as the chloride concentration increases with respect to the hexafluorophosphate concentration, the bands due to hydrogen-bond C–H groups shift to lower frequency within the intense complex system of bands in the range 3000–2850 cm^{-1} (due to methyl and methylene C–H stretching frequencies, probably partly enhanced by Fermi resonance with overtones of the CH$_2$ angle bending modes). This shift to lower frequency with increasing chloride concentration is in line with previous chloroaluminate spectroscopy studies where hydrogen bonding was found to increase with increasing chloride concentration.[23,58–60]

In Figure 6, the expected trend is observed: as the concentration of the [PF$_6$]$^-$ ion increases, so does the intensity of the
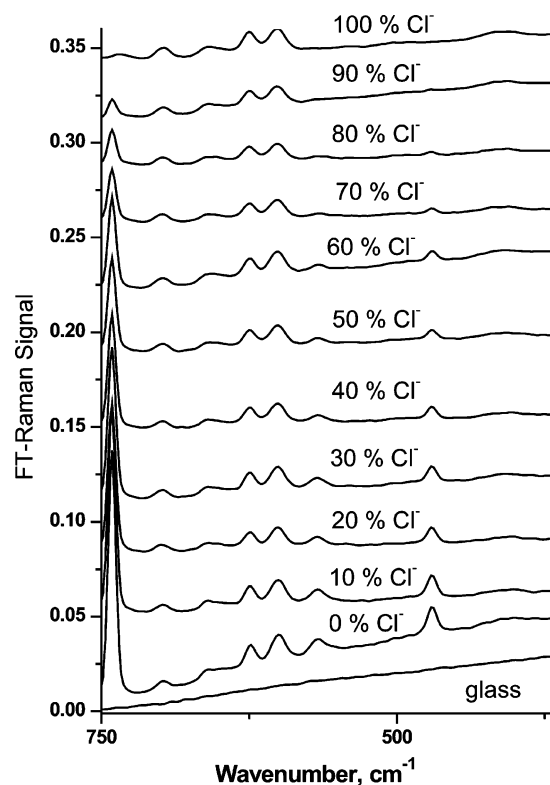
Figure 7. Detail of FT-Raman spectra of a binary room-temperature ionic liquid system, with [C$_6$mim]Cl (top) and [C$_6$mim][PF$_6$] (bottom). The mole percentage of chloride is shown as well as the background spectrum obtained on the empty capillary glass material.

ν_1([PF$_6$]$^-$) symmetric stretching band at 741 cm^{-1}, and the same is true for the ν_2([PF$_6$]$^-$) stretching peak at 568 cm^{-1} and the ν_5([PF$_6$]$^-$) symmetric bending peak at 470 cm^{-1}, whereas the rest of the major bands in the 2000−700 cm^{-1} range are largely undisturbed. More remarkable is that, in Figure 7, it is demonstrably clear that the region from 400 to 700 cm^{-1} (neglecting the anion band) is essentially invariant. As the crystal structures of the two polymorphs both revealed hydrogen bonding to the longer alkyl chain in the crystalline state, this cannot be affecting the equilibrium between the two conformers in solution.

Conclusion

The results show that the Raman bands identified by Ozawa et al.[24] as characteristic for the conformer of the 1-butyl-3-methylimidazolium cation are also characteristic for the conformers of the 1-hexyl-3-methylimidazolium cation. Moreover, the vibrational analysis of the binary system reveals that neither the changes in hydrogen bonding to the ring hydrogen atoms nor the change in Coulombic environment has any detectable effect upon the essentially 50:50 distribution of the two conformers. This observation, although surprising, adds weight to the theory that one of the drivers for the extensive glass formation which is observed in these systems is the frustration of the crystallization process by the existence of an equimolar mixture of low symmetry (C_1) conformers, preferring to form eutectics to conformationally pure crystals.[28]

Supporting Information Available: A listing and figures showing NMR spectral data for [C$_6$mim][PF$_6$] and tables listing vibrational frequencies for 1-butyl-3-methylimidazolium cation with the butyl group in the anti−anti and gauche−anti conformations and 1-hexyl-3-methylimidazolium with the hexyl group in the all-anti and gauche−anti−anti−anti comformations. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) *Ionic Liquids in Synthesis*; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, 2003; pp 364 + xvi.

(2) Earle, M. J. In *Ionic Liquids*: *Industrial Applications for Green Chemistry*; Rogers, R. D., Seddon, K. R., Eds.; American Chemical Society: Washington DC, 2002; Vol. 818; pp 90−105.

(3) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3773−3789.

(4) Ye, C. F.; Liu, W. M.; Chen, Y. X.; Yu, L. G. *Chem. Commun.* **2001**, 2244−2245.

(5) Ionic Liquids are good lubricants, In *Chem. Eng. News* **2001**, *79*, Nov 12, 23.

(6) Atkins, M. P.; Davey, P.; Fitzwater, G.; Rouher, O.; Seddon, K. R.; Swindall, J. *Ionic Liquids*: *A Map for Industrial Innovation*; Q001; QUILL: Belfast, 2004.

(7) *Ionic Liquids IIIB*: *Fundamentals, Progress, Challenges, and Opportunities−Transformations and* Processes; Rogers, R. D., Seddon, K. R., Eds.; American Chemical Society: Washington DC, 2005; Vol. 902.

(8) *Ionic Liquids IIIA*: *Fundamentals, Progress, Challenges, and Opportunities−Properties and Structure*; Rogers, R. D., Seddon, K. R., Eds.; American Chemical Society: Washington DC, 2005; Vol. 901.

(9) *Ionic Liquids as Green Solvents*: *Progress and Prospects*; Rogers, R. D., Seddon, K. R., Eds.; American Chemical Society: Washington DC, 2003; Vol. 856.

(10) *Green Industrial Applications of Ionic Liquids*; Rogers, R. D., Seddon, K. R., Volkov, S., Eds.; Kluwer: Dordrecht, 2002; Vol. 92.

(11) *Ionic Liquids*: *Industrial Applications for Green Chemistry*; Rogers, R. D., Seddon, K. R., Eds.; American Chemical Society: Washington DC, 2002; Vol. 818.

(12) Earle, M. J.; Katdare, S. P.; Seddon, K. R. *Org. Lett.* **2004**, *6*, 707−710.

(13) Lancaster, N. L.; Welton, T.; Young, G. B. *J. Chem. Soc., Perkin Trans. 2* **2001**, 2267−2270.

(14) Lancaster, N. L.; Salter, P. A.; Welton, T.; Young, G. B. *J. Org. Chem.* **2002**, *67*, 8855−8861.

(15) Fischer, T.; Sethi, A.; Welton, T.; Woolf, J. *Tetrahedron Lett.* **1999**, *40*, 793−796.

(16) Cammarata, L.; Kazarian, S. G.; Salter, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192−5200.

(17) Aggarwal, A.; Lancaster, N. L.; Sethi, A. R.; Welton, T. *Green Chem.* **2002**, *4*, 517−520.

(18) Rooney, D. W.; Seddon, K. R. In *Handbook of Solvents*; Wypych, G., Ed.; ChemTech Publishing: Toronto, 2001; pp 1459−1484.

(19) Seddon, K. R.; Stark, A.; Torres, M. J. In *Clean Solvents*: *Alternative Media for Chemical Reactions and Processing*; Abraham, M., Moens, L., Eds.; American Chemical Society: Washington DC, 2002; Vol. 819; p 34−49.

(20) Seddon, K. R.; Stark, A.; Torres, M.-J. *Pure Appl. Chem.* **2000**, *72*, 2275−2287.

(21) Abdul-Sada, A. K.; Seddon, K. R.; Stewart, N. J. WO 95 21872, 1995.

(22) Seddon, K. R. In *The International George Papatheodorou Symposium*: *Proceedings*; Boghosian, S., Dracopoulos, V., Kontoyannis, C. G., Voyiatzis, G. A., Eds.; Institute of Chemical Engineering and High Temperature Chemical Processes: Patras, 1999; pp 131−135.

(23) Tait, S.; Osteryoung, R. A. *Inorg. Chem.* **1984**, *23*, 4352−4360.

(24) Ozawa, R.; Hayashi, S.; Saha, S.; Kobayashi, A.; Hamaguchi, H. *Chem. Lett.* **2003**, *32*, 948−949.

(25) Katayanagi, H.; Hayashi, S.; Hamaguchi, H. O.; Nishikawa, K. *Chem. Phys Lett.* **2004**, *392*, 460−464.

(26) Saha, S.; Hayashi, S.; Kobayashi, A.; Hamaguchi, H. *Chem. Lett.* **2003**, *32*, 740−741.

(27) Hayashi, S.; Ozawa, R.; Hamaguchi, H. *Chem. Lett.* **2003**, *32*, 498−499.

Ionic Liquid Study

J. Phys. Chem. B, Vol. 109, No. 40, 2005 **19025**

(28) Holbrey, J. D.; Reichert, W. M.; Nieuwenhuyzen, M.; Johnston, S.; Seddon, K. R.; Rogers, R. D. *Chem. Commun.* **2003**, 1636−1637.

(29) Triolo, A.; Russina, O.; Arrighi, V.; Juranyi, F.; Janssen, S.; Gordon, C. M. *J. Chem. Phys.* **2003**, *119*, 8549−8557.

(30) Gordon, C. M.; Holbrey, J. D.; Kennedy, A. R.; Seddon, K. R. *J. Mater. Chem.* **1998**, *8*, 2627−2636.

(31) Holbrey, J. D.; Seddon, K. R. *J. Chem. Soc., Dalton Trans* **1999**, 2133-2159.

(32) Hardacre, C.; Holbrey, J. D.; McCormac, P. B.; McMath, S. E. J.; Nieuwenhuyzen, M.; Seddon, K. R. *J. Mater. Chem.* **2001**, *11*, 346−350.

(33) Roche, J. D.; Gordon, C. M.; Imrie, C. T.; Ingram, M. D.; Kennedy, A. R.; Celso, F. L.; Triolo, A. *Chem. Mater.* **2003**, *15*, 3089−3097.

(34) Hardacre, C.; Holbrey, J. D.; McMath, S. E. J.; Nieuwenhuyzen, M. In *Ionic Liquids*; American Chemical Society: Washington, DC, 2002; Vol. 818, pp 400−412.

(35) Firestone, M. A.; Dzielawa, J. A.; Zapol, P.; Curtiss, L. A.; Seifert, S.; Dietz, M. L. *Langmuir* **2002**, *18*, 7258.

(36) Bradley, A. E.; Hardacre, C.; Holbrey, J. D.; Johnston, S.; McMath, S. E. J.; Nieuwenhuyzen, M. *Chem. Mater.* **2002**, *14*, 629−635.

(37) Bowers, J.; Vergara-Gutierrez, M. C.; Webster, J. R. P. *Langmuir* **2004**, *20*, 309−312.

(38) Hardacre, C.; Holbrey, J. D.; McMath, S. E. J.; Bowron, D. T.; Soper, A. K. *J. Chem. Phys.* **2003**, *118*, 273−278.

(39) Hardacre, C.; McMath, S. E. J.; Nieuwenhuyzen, M.; Bowron, D. T.; Soper, A. K. *J. Phys.: Condes. Matter* **2003**, *15*, S159−S166.

(40) Welton, T.; Kazarian, S.; Crowhurst, L.; Perez-Arlandis, J. M.; Salter, P. *Abstr. Pap. Am. Chem. Soc.* **2002**, *224*, 139.

(41) Abdul-Sada, A. K.; Elaiwi, A. E.; Greenway, A. M.; Seddon, K. R. *Eur. Mass Spectrom.* **1997**, *3*, 245−247.

(42) Avent, A. G.; Chaloner, P. A.; Day, M. P.; Seddon, K. R.; Welton, T. In *Proceedings of the Seventh International Symposium on Molten Salts*; Hussey, C. L, Wilkes, J. S., Felngas, S. N., Ito, Y., Eds.; The Electrochemical Society Inc.: Pennington, NJ, 1990; Vol. PV 90-17, pp 98−133.

(43) Elaiwi, A.; Hitchcock, P. B.; Seddon, K. R.; Srinivasan, N.; Tan, Y. M.; Welton, T.; Zora, J. A. *J. Chem. Soc., Dalton Trans.* **1995**, 3467−3472.

(44) Avent, A. G.; Chaloner, P. A.; Day, M. P.; Seddon, K. R.; Welton, T. *J. Chem. Soc., Dalton Trans.* **1994**, 3405−3413.

(45) Hitchcock, P. B.; Seddon, K. R.; Welton, T. *J. Chem. Soc., Dalton Trans.* **1993**, 2639−2643.

(46) Abdul-Sada, A. K.; Al-Juaid, S.; Greenway, A. M.; Hitchcock, P. B.; Howells, M. J.; Seddon, K. R.; Welton, T. *Struct. Chem.* **1990**, *1*, 391−394.

(47) Abdul-Sada, A. K.; Greenway, A. M.; Hitchcock, P. B.; Mohammed, T. J.; Seddon, K. R.; Zora, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1753−1754.

(48) Hitchcock, P. B.; Mohammed, T. J.; Seddon, K. R.; Zora, J. A.; Hussey, C. L.; Ward, E. H. *Inorg. Chim. Acta* **1986**, *113*, L25-L26.

(49) Aakeröy, C. B.; Evans, T. A.; Seddon, K. R.; Pálinkó, I. *New J. Chem.* **1999**, *23*, 145−152.

(50) van den Berg, J.-A.; Seddon, K. R. *Cryst. Growth Des.* **2003**, *3*, 643−661.

(51) Talaty, E. R.; Raja, S.; Storhaug, V. J.; Dolle, A.; Carper, W. R. *J. Phys. Chem. B* **2004**, *108*, 13177−13184.

(52) Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; J. A. Montgomery, J.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

(53) Holbrey, J. D.; Reichert, W. M.; Nieuwenhuyzen, M.; Johnston, S.; Seddon, K. R.; Rogers, R. D. *Chem. Commun.* **2003**, 1636.

(54) Torres, M.-J. Ph.D. Thesis, The Queen's University of Belfast, 2001.

(55) Perchard, C.; Novak, A. *Spectrochim. Acta, Part A* **1967**, *23*, 1953−1968.

(56) Shurvell, H. F. *Can. Spectrosc.* **1967**, *12*, 156−162.

(57) Heyns, A. M. *Spectrochim. Acta, Part A* **1977**, *33*, 315−322.

(58) Dieter, K. M.; Dymek, C. J., Jr.; Heimer, N. E.; Rovang, J. W.; Wilkes, J. S. *J. Am. Chem. Soc.* **1988**, *110*, 2722−2726.

(59) Dymek, C. J., Jr.; Stewart, J. P. P. *Inorg. Chem.* **1989**, *28*, 1472−1476.

(60) Tahahashi, S.; Curtiss, L. A.; Gosztola, D.; Koura, N.; Saboungi, M.-L. *Inorg. Chem.* **1995**, *34*, 2990.