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The effect of the anion on the chemical shifts of the aromatic hydrogen atoms of liquid 1-butyl-3-methylimidazolium salts

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ABSTRACT: The NMR chemical shifts of the aromatic hydrogen atoms of 1-*n*-butyl-3-methylimidazolium tetrafluoroborate $(BMI^+BF_4^-)$ and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate $(BMI^+PF_6^-)$ have been determined in nine deuterated solvents. The aromatic hydrogen atoms of $BMI^+PF_6^-$ are more sensitive to solvation effects than the hydrogen atoms of $BMI^+BF_4^-$. The interaction of the hydrogen atoms of the imidazolium cation with the relatively small and basic BF_4^- anion is more intimate than the interaction with the fairly large, polarizable and less basic PF_6^- anion. For both salts, the interaction involving the anion and the hydrogen atoms of the imidazolium cation is more intimate for H2, compared with H4 or H5. Owing to the intimate interaction of the ions of $BMI^+BF_4^-$, its aromatic hydrogen atoms are less sensitive to solvation effects than the hydrogen atoms of $BMI^+PF_6^-$. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: ionic liquids; hydrogen bonding; solvation effects; ^{1}H NMR spectroscopy; *ab initio* calculations

INTRODUCTION

A large percentage of organic reactions, including those catalyzed by transition metals, are performed in nonaqueous media, even though a polar medium, such as the one provided by water, would be an ideal medium for most of these reactions. Conventional polar solvents, such as dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF), have been used to provide polar environments for most organic reactions, but tremendous difficulties are often encountered in the separation of the products from the reaction mixtures. Also, the cost to dispose of these solvents is extremely high, approximately 5 billion dollars per year.[1] Ionic liquids, which are now becoming the solvents of choice for a large array of organic reactions,[2] including those that use homogeneous catalysts,[3] have properties that make them recyclable and environmentally benign solvents. They are thermally stable over a very wide temperature range, and they maintain their liquid state at temperatures as high as 200 °C. Ionic liquids have no measurable vapor pressure, and they are recyclable solvents. A major advantage for using ionic liquids as solvents for organic reactions is that organic products are easily and efficiently extracted from the reaction mixtures.

Owing to the unique properties of the class of ionic liquids known as organochloroaluminates,[4] they have been used as solvents for different reactions.[5] 1-Ethyl-3-methylimidazolium chloride-aluminum $[EMI^+AlCl_4^-]$[1] has a tremendous influence on the outcome of reactions in a number of ways, including higher reaction rates and better reaction control.[6] A major drawback in the use of organochloroaluminates, however, is that they are often air- and moisture-sensitive and they have the tendency to react with some reactants.[3] Thus, the use of this specific class of ionic liquids as solvents has been limited to a narrow range of reactions.[7] Recently, a wider range of similar ionic liquids, which have different side chains bonded to the imidazolium cations and different anions, have been investigated for their use as solvents for organic reactions. It was shown that these ionic liquids are fully stable under most reaction conditions, which is a property lacking in the organochloroaluminates. Initial results indicate that these modifications result in ionic liquids that have remarkable effects on the outcome of different reactions.[8]

Since the use of ionic liquids as solvents for organic reactions is increasing tremendously, a thorough understanding of how they affect reactions is urgently needed.

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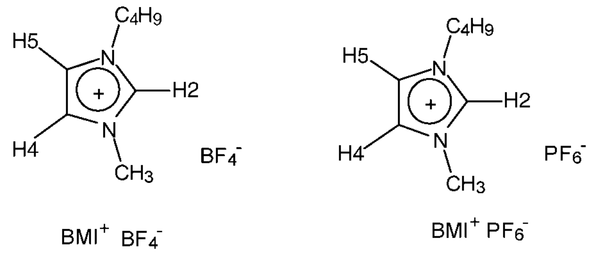

Figure 1. Structures of 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ($BMI^+BF_4^-$) and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($BMI^+PF_6^-$)

Gaining such an understanding will assist chemists to be better able to predict how ionic liquids affect reaction rates and outcomes. The task of analyzing the properties of ionic liquids is a gigantic one, since the effects that conventional solvents have on reactions are still being actively studied, even though they have been studied for over a century.[9,10] It is known that the different hydrogen atoms of 1-*n*-ethyl-3-methylimidazolium (EMI^+) salts are capable of the formation of hydrogen bonds,[11] but the effects that different anions have on the relative strengths of such hydrogen bonds are not known. In this study, the nature of the interaction that exists between the anions and the aromatic hydrogen atoms of 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ($BMI^+BF_4^-$) and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($BMI^+PF_6^-$) is analyzed in deuterated solvents. Figure 1 shows the structure of these salts.

EXPERIMENTAL SECTION

The synthesis of *1-butyl-3-methylimidazolium hexafluorophosphate* [$BMI^+PF_6^-$] and *1-butyl-3-methylimidazolium tetrafluoroborate* [$BMI^+BF_4^-$] was carried out as described in the literature.[12] For each salt, water and other volatile solvents were removed by six cycles of freeze, pump and thaw (8 mm Hg and 77 K), followed by the preparation of NMR solutions in a dry-atmosphere glovebox. The concentration of both salts was 0.45 ± 0.01 mol l^{-1}. The NMR and IR spectra of these compounds matched those reported in the literature.[12] ^{1}H NMR spectra were recorded on an IBM (Bruker) NR/300 FT-NMR spectrometer. The Minitab multilinear regression analysis computer program was used to obtain the correlation equations.[13] The *ab initio* calculations were executed with Gaussian 94 using standard basis sets with no modification.[14] Calculations were performed on our Silicon Graphics Indigo computer. Convergence was to the limits imposed internally by Gaussian 94. Vibrational frequencies were calculated and used to determine the nature of the structure (minima, saddle points, or second-order saddle points). The conformation studied was a minimum at the level of theory examined.

RESULTS AND DISCUSSION

From Table 1, the chemical shifts of the aromatic hydrogen atoms of 1-*n*-butyl-3-methylimidazolium (BMI) salts vary in solvents of different properties. Since the concentrations of the solutions are the same, the chemical shifts of the aromatic hydrogen atoms are solvent dependent. From Table 1, the chemical shift variation of H4 is similar to that of H5, but H2 exhibits a much broader chemical shift variation than either H4 or H5. If two hydrogen atoms of a particular molecule are affected differently by solvation effects, plots of the chemical shifts of such hydrogen atoms, obtained in different solvents, exhibit a non-unity slope. Shown in Table 2 are the statistics for the relationships that exist between the aromatic hydrogen atoms in different solvents. Owing to the closeness of the slope to unity for Eqn. (1), the implication is that solvation effects affect H4 and H5 similarly. This observation is reason-

Table 1. H^1 chemical shift values of 1-*n*-butyl-3-methylimidazolium (BMI) salts in different deuterated solvents at 298 K. Solution concentrations are 0.45 ± 0.01 mol l^{-1} for both compounds

	$BMI^+BF_4^-$			$BMI^+PF_6^-$		
Solvent-*d*	H2	H4	H5	H2	H4	H5
AN	8.46	7.37	7.34	8.37	7.35	7.32
Water[a]	8.54	7.34	7.30	–	–	–
TFA	8.59	7.47	7.45	8.63	7.56	7.53
HOAc	8.67	7.51	7.47	8.60	7.48	7.44
EtOH[b]	8.77	7.57	7.50	–	–	–
MeOH	8.78	7.58	7.51	8.72	7.54	7.48
Acetone	8.89	7.70	7.65	8.88	7.69	7.64
DMSO	9.07	7.77	7.69	9.07	7.73	7.66
DMF	9.15	7.87	7.80	9.20	7.88	7.81

AN, acetonitrile; TFA, trifluoroacetic acid; HOAc, acetic acid; EtOH, ethanol; MeOH, methanol; DMSO, dimethyl sulfoxide; DMF, dimethyl formamide.

[a] $BMI^+PF_6^-$ is insoluble in water.

[b] $BMI^+PF_6^-$ is partially soluble in ethanol.

Table 2. Statistics for the correlation equations ($y = mx + c$), which show the relationships between the chemical shifts for the aromatic hydrogen atoms of 1-butyl-3-methyl imidazolium salts

Eqn	Salt	y	x	m (slope)	c	R	SD
(1)	$BMI^+BF_4^-$	δH4	δH5	1.09	−0.60	0.996	0.02
(2)		δH2	δH4	1.30	−1.06	0.984	0.04
(3)		δH2	δH5	1.40	−1.73	0.970	0.06
(4)	$BMI^+PF_6^-$	δH4	δH5	1.08	−0.56	0.998	0.01
(5)		δH2	δH4	1.61	−3.44	0.982	0.06
(6)		δH4	δH5	1.72	−4.20	0.969	0.08

able, since the environments of these two hydrogen atoms are similar. Similar relationships for the chemical shifts of H2 versus H4 and H2 versus H5 give different slopes, as shown in Eqns (2) and (3) in Table 2. H2 is bonded to a carbon that is located between two electronegative nitrogen atoms, and hence H2 should be more acidic and more sensitive to solvation effects than H4 or H5 — hence, non-unity slopes result for Eqns (2) and (3). The differences in slope shown in Eqns (2) and (3) reflect the slightly different environments of H4 and H5 owing to the different substituents bonded to the nitrogen atoms.

In order to determine the relative difference in acidity of the aromatic hydrogen atoms of the imidazolium cation, the partial charges of the hydrogen atoms were determined from *ab initio* calculations. The results are consistent with the experimental results, in that H2 is more positive than H4 or H5, as shown in Fig. 2.

The different slopes observed in Eqns (2) and (3), compared with the slope for Eqn. (1), clearly indicate that H2 is more sensitive to changes in solvent properties than H4 or H5. Also, the different slopes indicate that H2 is approximately 1.30 and 1.40 times more sensitive to changes in solvation properties than H4 and H5 respectively.

Since the slope for Eqn. (4) is approximately unity, the indication is that different solvents affect H4 and H5 similarly, and these hydrogen atoms of both salts exhibit similar sensitivity to solvation effects. Owing to the different environments of H4 and H5 for $BMI^+PF_6^-$, compared with H2, the slopes shown for Eqns (5) and (6) are slightly different. Based on the magnitude of the slopes, the implication is that the chemical shift of H2 is approximately 1.61 times more sensitive to changes in solvent properties, compared with H4, and 1.72 times more sensitive than H5. Since the slopes for similar relationships for $BMI^+BF_4^-$, [Eqns (2) and (3)] are different than those of Eqns (5) and (6), the anion plays a role in the chemical shift variation of H2 for both compounds. Since the slopes for Eqns (5) and (6) ($BMI^+PF_6^-$) are larger than the slopes for Eqns (2) and (3) ($BMI^+BF_4^-$), the implication is that H2 of $BMI^+PF_6^-$ is more sensitive to a change in the nature of the solvent compared with that of $BMI^+BF_4^-$.

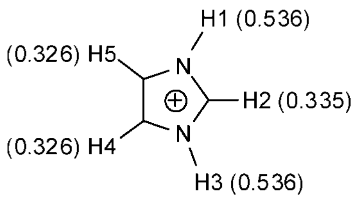

Figure 2. RHF/6 − 31 + G* partial charges (shown in parentheses) for the hydrogen atoms of the imidazolium cation

Typically, the formation of hydrogen bonds from basic solvents to acidic hydrogen atoms,[15] such as H2, moves the chemical shifts of these hydrogen atoms downfield.[16] H2 is situated between two heteroatoms, whereas H4 and H5 are each located adjacent to one. The greater range of chemical shifts for H2 is indicative of its greater hydrogen bonding abilities, compared with H4 and H5. Also, the chemical shifts of H2 are farther downfield in basic solvents, relative to acidic solvents (Table 1). For $BMI^+BF_4^-$, a strong interaction between the aromatic hydrogen atoms, primarily H2, with its counter ion results in the chemical shift of H2 being less sensitive to solvation effects than $BMI^+PF_6^-$, which has a weaker interaction between the aromatic hydrogen atoms, primarily H2. Since the BF_4^- ion is a less polarizable and a harder base than the PF_6^- ion, it has the ability to form a tighter interaction with the hydrogen atoms of the imidazolium cation than PF_6^-.

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