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# Novel ionic liquids based on the benzimidazolium cation

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A new series of salts, based on the benzimidazolium cation (Bim) and some common anions have been prepared. The salts were characterised by DSC, NMR, IR, elemental analysis and thermogravimetric analysis. They showed different properties such as melting point, thermal stability, multiple phase behaviour, and solubility properties compared to salts of the imidazolium cation.

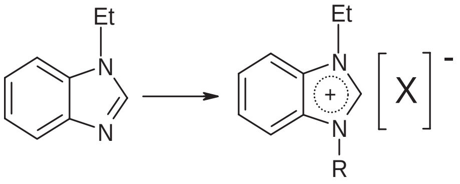
**Keywords**: ionic liquids, benzimidazolium, cation

Ionic liquids, also known as room temperature molten salts with melting point under 100˚C or 150˚C,[1] have attracted increasing attention over recent years since the discovery of air and water stable 1-ethyl-3-methylimidazolium-based ionic liquids by Wilkes in 1992.[2] Typically, they are composed of organic cations and a variety of anions, the most popular of them are those based on 1, 3-dialkylimidazolium cations and inorganic anions such as tetrafluoroborate, $BF_4^-$, and hexafluorophosphate, $PF_6^-$. Many ionic liquids with special properties based on [im] have been prepared by introducing a functional group into the alkyl chain.[3] These solvents possess a number of interesting properties such as negligible vapour pressure, high polarity, good thermal stability, anti-microbial activities,[4] radiochemical stability,[5] large electrochemical window, potential to be reused and easy to handle. Thus, room temperature ionic liquids (RTILs) have been used in many areas of chemistry including organic and inorganic synthesis,[6] biphasic catalysis,[6] separation processes,[7] and electrochemistry.[8] Here, we report one series of RTILs based on the benzimidazolium cation with potential use as catalysts and solvents in alkylation reactions of benzene with other alkenes.

These new salts have been characterised by DSC, elemental analysis, NMR, IR spectroscopy, and thermogravimetric analysis.

In the differential scanning calorimetry (DSC) curves, $C_4$EBimBr (Fig.1) showed multiple phase behavior. In this case, the sample seemed to have quenched, without crystallisation, to a glass state. A glass transition was observed at –34°C, and then a broad crystallisation peak appeared at 31°C on warming, as was commonly observed in "marginal glass formers". At 61°C, $C_4$EBimBr exhibited a solid–solid transition and finally melted at 74°C. A similar phenomenon has been reported for the N-methyl-N-butyllpyrrolidinium Hexafluorophosphate salts[9] and quaternary ammonium imide salts.[10] $C_5$EBimBr only displayed a glass transition at –30°C and its melting point was not observed in the DSC curve when heated. The melting points of new salts are listed in Table 1. From Table 1, it was clear that both the cation and anion significantly influenced the melting point of these compounds. The melting points of salts containing lower symmetry such as $C_5$EBimX were lower than that of $C_4$EBimX containing higher symmetry. For each cation, the melting point followed the trend $BF_4^- < Br^- < PF_6^-$, which was somewhat different from imidazolium salts.

The thermogravimetric data of new ionic liquids were shown in Table 1 and in Fig. 2. Although the studies indicated that the new salts began to decompose at slightly lower temperature than that for the [Im] series,[11] they also displayed high thermal stability. $C_5EBimPF_6$ showed no weight loss to 340°C (Fig. 2). Relative anion stabilities shown in Table 1 were in the same order as the [Im] series and followed the anion order[11] $Br^- < BF_4^- < PF_6^-$. Additionally, the alkyl chains length of the cation had no evident effect on the thermal stability.



**Scheme 1** Structure of new salts. 1 X = Br 2 X = $BF_4$ 3 X = $PF_6$ a: R = n-$C_4H_9$ b: R = n-$C_5H_{11}$.

**Table 1** Thermal analysis data of new salts

| Entry | ILs | M.p./˚C | *T*d/˚C | Water content (W/W) |
|---|---|---|---|---|
| **1a** | $C_4$EBimBr | 74 | 246 | Soluble |
| **1b** | $C_5$EBimBr | – | 254 | Soluble |
| **2a** | $C_4EBimBF_4$ | 57 | 320 | 1.30% |
| **2b** | $C_5EBimBF_4$ | 38 | 340 | 1.15% |
| **3a** | $C_4EBimPF_6$ | 135 | 357 | 0.60% |
| **3b** | $C_5EBimPF_6$ | 72 | 349 | 0.54% |

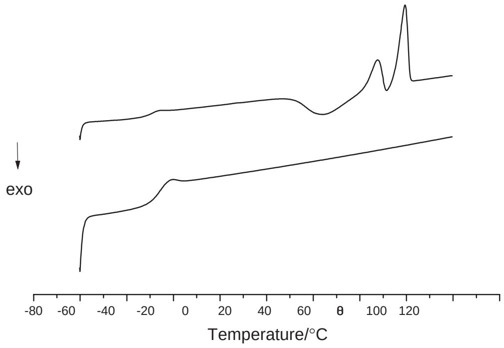


**Fig. 1** The DSC curve for [$C_4$EBim][Br] and [$C_5$EBim][Br].

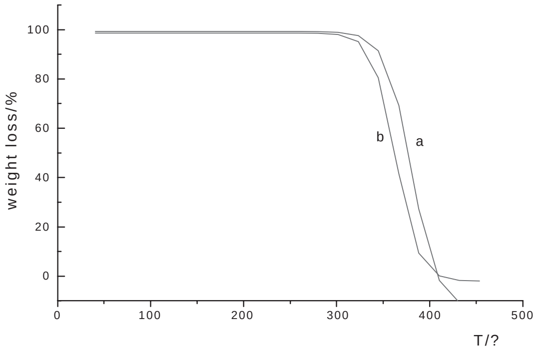


**Fig. 2** Thermogravimetric curve for (a) $C_5EBimPF_6$ and (b) $C_4EBimBF_4$.

The solubility properties of the the new ionic liquids in some common solvents were studied. The bromide salt was completely miscible with water. However, the $PF_6^-$ salts were sparingly water-soluble. It was indicated that water content of

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the ionic liquids with different anions decreased in the order $Br^- > BF_4^- > PF_6^-$ . All the ionic liquids were completely soluble in ethanol, methanol, acetonitrile, chloroform and acetone, but they were immiscible with toluene, benzene, cyclohexane, tetrachloride and diethyl ether. Ethyl acetate appeared to constitute the borderline; bromide salts were immiscible with ethyl acetate, while $BF_4^-$ and $PF_6^-$ were soluble with this solvent. Some of these solubility properties were quite different from the reported [Im] series.[3]

In summary, the new benzimidazolium-based ionic liquids in this paper have low melting point and interesting phase behavior. They also show unusual solubility and thermal properties, which can expand the knowledge of RTILs chemistry.

## Experimental

IR spectra were recorded using KBr pellets on a NEXUS 670 FT-IR infrared spectrometer (Nicolet). Elemental analysis were performed by a Vario EL instrument. The water content of each RTILs was determined by a Karl-Fischer titrator. The differential scanning calorimetry (DSC) experiments were performed using a Pyris 1 DSC(PERKIN ELMER) with a ramp temperature of 10°C min$^{-1}$. The melting points were determined by Melting Point Apparatus $X_4$. The thermal stability of each RTIL was determined by thermogravimetric analysis using a TGA/SDTA851 thermogravimetric analyzer at a heating rate 10°C min$^{-1}$ with nitrogen as the purge gas.

### *Synthesis of new ionic liquids*

*C$_4$EBimBr*: 1-Ethylbenzimidazolium was added to a 100 ml three-necked flask with a reflux condenser followed by the addition of toluene (50ml). Then equal molar freshly distilled bromobutane was added dropwise and the solution was stirred at 70°C for 24h until two phase formed, the upper phase, containing unreacted starting material, was decanted and the bottom phase was washed with fresh toluene(25ml×2). In the end, any remaining toluene was removed by rotary evaporation at 70°C for 6h.

IR(KBr) ν: 3125.83, 3023.55, 2964.64, 2871.76, 1612.63, 1562.57, 1465.36, 1429.99, 1383.70, 1349.09, 1216.73, 766.96, 560.74, 427.00cm$^{-1}$; $^1$H NMR (500Hz, $CDCl_3$): δ = 0.97(m, *J*(H, H) = 18Hz, 3H), δ = 1.44(t, *J*(H, H) = 15Hz, 2H), δ = 1.76(t, *J*(H, H) = 15Hz, 3H), δ = 2.04(t, *J*(H, H) = 14Hz, 2H), δ = 4.66 (t, *J*(H, H) = 15Hz, 2H), δ = 4.73(m, *J*(H, H) = 22Hz, 2H), δ = 7.70(m, *J*(H, H) = 25Hz, 2H), δ = 7.74(m, *J*(H, H) = 14Hz, 2H), δ = 11.57(s, 1H); elemental analysis calcd(%) for $C_{12}H_{18}N_2Br$C 55.12, H 6.71, N 9.9. Found C 54.87, H 6.49 N 10.3.

*C$_4$EBimPF$_6$*: C$_4$EBimBr was transferred to a plastic container followed by the addition of deionised water. The magnetically stirred solution was cooled in an ice bath and 60% $HPF_6$ in a 1:1.1 molar ratio was added slowly. The mixture was stirred in the ice bath for 12h. The product precipitated as a white waxy solid and was collected by filtration. The white solid was washed with quantitative fresh deionised water and then dried *in vacuo* at 70°C for 6h.

IR(KBr) ν: 3167.81, 3114.53, 2964.87, 2879.25, 1623.30, 1569.74, 1465.50, 1430.95, 1384.66, 1346.09, 1211.45, 843.34, 558.43, 418.67 cm$^{-1}$; $^1$H NMR (500Hz, $CDCl_3$): δ = 0.97 (m, *J*(H, H) = 18Hz, 3H), δ = 1.44(t, *J*(H, H) = 15Hz, 2H), δ = 1.76(t, *J*(H, H) = 15Hz, 3H, δ = 2.04(t, *J*(H, H) = 14Hz, 2H), δ = 4.66(t, *J*(H, H) = 15Hz, 2H), δ = 4.73(m, *J*(H, H) = 22Hz, 2H), δ = 7.70(m, *J*(H, H) = 25Hz, 2H), δ = 7.74(, *J*(H, H) = 14Hz, 2H), δ = 11.57(s, 1H); elemental analysis calcd(%) for $C_{12}H_{18}N_2PF_6$ C 44.83 H 5.46 N 8.1 Found C 45.00 H 5.41 N 8.0

*C$_4$EBimBF$_4$*: The same procedure was used as indicated for C$_4$EBimPF$_6$ with the exception of the use of 40% $HBF_4$ instead of 60% $HPF_6$.

IR(KBr) ν: 3129.95, 3020.03, 2960.96, 2873.31, 1615.12, 1563.99, 1461.95, 1430.05, 1380.82, 1348.19, 1211.50, 1081.87, 759.54, 563.12, 427.07 cm$^{-1}$; $^1$H NMR(500Hz, $CDCl_3$): δ = 0.99(t, *J*(H, H) = 5Hz, 3H), δ = 1.44(m, *J*(H, H) = 23Hz, 2H), δ = 1.68(m, *J*(H, H) = 39Hz, 3H), δ = 2.00(t, *J*(H, H) = 15Hz, 2H), δ = 4.49(t, *J*(H, H) = 15Hz, 2H), δ = 4.55(d, *J*(H, H) = 7Hz, 2H), δ = 7.67 (m, *J*(H, H) = 25 Hz, 2H), δ = 7.74(m, *J*(H, H) = 13Hz, 2H), δ = 9.61(s, 1H); elemental analysis calcd(%) for $C_{12}H_{18}N_2BF_4$ C 53.83 H 6.56 N 9.7 Found C 53.79 H 6.64 N 9.5

*C$_5$EBimBr:* The synthesis followed the same procedure as for C$_4$EBimBr described above with the exception of the bromopentane instead of bromobutane.

IR(KBr) ν: 3128.02, 3017.96, 2957.91, 2867.39, 1614.38, 1563.32, 1460.73, 1379.96, 1348.64, 1220.43, 1139.67, 756.69, 561.70, 426.91 cm$^{-1}$; $^1$H NMR (500Hz, $CDCl_3$): δ = 0.91(t, *J*(H, H) = 15Hz, 3H), δ = 1.41(m, *J*(H, H) = 16Hz, 4H), δ = 1.75(t, *J*(H, H)14Hz, 3H), δ = 2.08(t, *J*(H, H) = 15Hz, 2H), δ = 4.63(t, *J*(H, H) = 15Hz, 2H), δ = 4.73(m, *J*(H, H) = 22Hz, 2H), δ = 7.67(m, *J*(H, H) = 10Hz, 2H), δ = 7.73(m, *J*(H, H) = 21Hz, 2H), δ = 11.57(S, 1H) elemental analysis calcd(%) for $C_{13}H_{20}N_2Br$ (284 ) C 56.57 H 7.07 N 9.4 Found C 55.96 H 7.02 N 10.5

*C$_5$EBimBF$_4$*: The same procedure was used as indicated for C$_4$EBimBF$_4$.

IR(KBr) ν: 3129.95, 3020.03, 2958.04, 2866.12, 1617.82, 1563.43, 1461.60, 1379.38, 1346.70 1249.67, 1118.53, 1082.02, 758.86, 528.16, 425.78cm$^{-1}$; $^1$H NMR(500Hz, $CDCl_3$): δ = 0.91 (t, *J*(H, H) = 14Hz, 3H), δ = 1.40(m, *J*(H, H) = 14Hz, 4H), δ = 1.70(m, *J*(H, H) = 37Hz, 3H), δ = 2.03(t, *J*(H, H) = 14Hz, 2H), δ = 4.50(t, *J*(H, H) = 15Hz, 2H), δ = 4.59(m, *J*(H, H) = 22Hz, 2H), δ = 7.67(m, *J*(H, H) = 32Hz, 2H) δ = 7.75(m, *J*(H, H) = 20Hz, 2H), δ = 9.56(S, 1H); elemental analysis calcd(%) for $C_{13}H_{20}N_2BF_4$ C 55.30 H 6.91 N 9.2 Found C 55.33 H 6.94 N 9.1

*C$_5$EBimPF$_6$:* The same procedure was used as indicated for C$_4$EBimPF$_6$.

IR(KBr) ν: 3165.96, 3114.34, 2964.27, 2873.72, 1616.70, 1570.20, 1463.51, 1390.45, 1348.38 1253.68, 1139.63, 838.68, 558.03, 425.19 cm$^{-1}$;$^1$H NMR(500Hz, $CDCl_3$): δ = 0.92(m, *J*(H, H) = 13Hz, 3H), δ = 1.39(m, *J*(H, H) = 17Hz4), δ = 1.70*J*(m, (H, H)) = 14Hz, 3H), δ = 2.02(t, *J*(H, H) = 14Hz, 2H), δ = 4.48(t, *J*(H, H) = 15Hz, 2H), δ = 4.56(m, *J*(H, H) = 22Hz, 2H), δ = 7.68(m, *J*(H, H) = 10Hz, 2H) δ = 7.74(m, *J*(H, H) = 19Hz, 2H), δ = 9.65(S, 1H); elemental analysis calcd(%) for $C_{13}H_{20}N_2PF_6$ C 46.41 H 5.81 N 7.7 Found C 46.38 H 5.87 N 7.6

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