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New room-temperature ionic liquids with C_2-symmetrical imidazolium cations†

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New 1,3-dialkylimidazolium hexafluorophosphates with two butyl, pentyl, octyl, nonyl or decyl groups are room temperature ionic liquids.

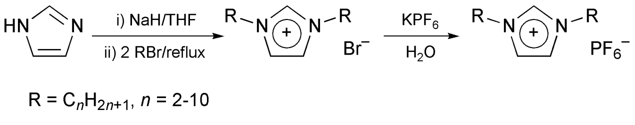
Room-temperature ionic liquids (RTILs),[1] such as 1-alkyl-3-methylimidazolium hexafluorophosphates, are finding ever-expanding applications as alternative reaction media for organic synthesis[2,3] and separation science.[4–6] Although our understanding of why these salts have such low melting points is incomplete, the unsymmetrical nature of the cation is believed to play a major role.[1,7] Thus, the 100 °C lower melting points of 1-ethyl-3-methylimidazolium salts than their *N*-butylpyridinium analogues have been attributed to the C_2 symmetry of the latter.[1]

By extension of such reasoning, 1,3-dialkylimidazolium salts that also have C_2 symmetry would seem to be poor candidates as RTILs. In agreement, 1,3-dialkylimidazolium hexafluorophosphates are reported to be solids at room temperature when the two alkyl groups are hexadecyl.[8] The salts with elongated alkyl groups are of interest because they exhibit liquid crystalline behavior above their melting points.[8,9]

We now report the synthesis of ten 1,3-dialkylimidazolium hexafluorophosphates $[(C_n)_2\text{-Im}]PF_6$ with dialkyl moieties ranging from dimethyl to didecyl and their phase transition behavior. Surprisingly, 1,3-dialkylimidazolium hexafluorophosphates with dibutyl, dipentyl, dioctyl, dinonyl, and didecyl substituents are found to be RTILs.

The $[(C_1)_2\text{-Im}]PF_6$ was prepared by reaction of commercially available 1-methylimidazole with iodomethane to form $[(C_1)_2\text{-Im}]I$[10] followed by its metathesis with potassium hexafluorophosphate in water.‡ Since higher homologues of 1-methylimidazole are not available commercially, a method was sought to convert imidazole directly into a 1,3-dialkylimidazolium halide. (Reported methods for the preparation of 1,3-dialkylimidazolium halides require multiple steps, long reactions times, and/or special precautions.[8,9,11,12]) We have found that reaction of imidazole with one equivalent of sodium hydride in THF followed by addition of two equivalents of a 1-bromoalkane and refluxing (Scheme 1) gives high yields (75–89%) of $[(C_n)_2\text{-Im}]Br$ with $n = 2–10$. Metathesis of the imidazolium bromide salts with potassium hexafluorophosphate in water gave high yields (89–95%) of $[(C_n)_2\text{-Im}]PF_6$ with $n = 2–10$.†‡

The phase transition temperatures (mid-points of glass transitions and/or melting points) for $[(C_n)_2\text{-Im}]PF_6$ with $n = 1–10$ as determined by differential scanning calorimetry (DSC)§ are presented in Table 1. As the alkyl groups are changed from methyl to ethyl to propyl, the melting point drops from 89 to 70 to 43 °C. This suggests poorer packing into the crystal lattice as the alkyl group is elongated. With dibutyl and dipentyl substituents, the salts are RTILs with glass transitions, but no melting points. In sharp contrast when the alkyl groups are elongated to hexyl, a melting point of 73 °C, but no glass transition, is observed. There is a remarkable, greater than 140 °C difference between the phase transition temperatures for $[(C_5)_2\text{-Im}]PF_6$ and $[(C_6)_2\text{-Im}]PF_6$. Apparently the hexyl groups pack into the crystal lattice almost as well as methyl and ethyl groups. As the alkyl groups are lengthened from hexyl to heptyl, the 73 °C melting point for the former diminishes to 47 °C. For octyl and nonyl groups, both glass transitions and melting points are observed. When the alkyl groups are decyl, there are two melting points. Since their melting points are below room temperature, $[(C_8)_2\text{-Im}]PF_6$, $[(C_9)_2\text{-Im}]PF_6$, and $[(C_{10})_2\text{-Im}]PF_6$ are also RTILs. Studies are currently underway to compare the other physical properties of these readily accessible $[(C_n)_2\text{-Im}]PF_6$ RTILs with the more common 1-alkyl-3-methylimidazolium hexafluorophosphates.



Scheme 1 Synthesis of 1,3-dialkylimidazolium bromides and hexafluorophosphates.

Table 1 Structure and phase transition temperatures of 1,3-dialkyimidazolium ionic liquids

		Phase transition temperature	
IL	Alkyl group	T/°C (ΔC_p/J g^{-1} K^{-1})	T_m/°C (ΔH/kJ mol^{-1})
1	CH_3	—	89 (6.8)
2	C_2H_5	—	70 (6.6)
3	C_3H_7	—	43 (6.3)
4	C_4H_9	−69 (0.3)	—
5	C_5H_{11}	−72 (0.2)	—
6	C_6H_{13}	—	73 (8.8)
7	C_7H_{15}	—	47 (5.2)
8	C_8H_{17}	−80 (0.2)	19 (5.2)
9	C_9H_{19}	−70 (0.2)	11 (5.4)
10	$C_{10}H_{21}$	—	−27 (0.4) 16 (6.7)

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† Electronic supplementary information (ESI) available: ^{1}H NMR and IR spectra and elemental analysis results consistent with the indicated structures for all of the $[(C_n)_2\text{-Im}]Br$ and $[(C_n)_2\text{-Im}]PF_6$ compounds. See http://www.rsc.org/suppdata/cc/b1/b104512c/

Notes and references

‡ Representative procedures for the preparation of $[(C_n)_2\text{-Im}]Br$ and $[(C_n)_2\text{-Im}]PF_6$. *Synthesis of 1,3-dinonylimidazolium bromide.* A flask containing a magnetically stirred mixture of 95% sodium hydride powder (0.75 g, 29.4 mmol) in THF (20 ml) was cooled in an ice bath and a solution of imidazole (2.00 g, 29.4 mmol) in THF (20 ml) was added dropwise. The ice bath was removed and the mixture was stirred for 2 h at room temperature. Following dropwise addition of 1-bromononane (11.23 ml, 58.8 mmol) at room temperature, the mixture was refluxed for 7 h and filtered. The precipitate was thoroughly rinsed with THF. The filtrate was evaporated *in vacuo* and the residue was dissolved in dichloromethane. The mixture was filtered and the filtrate was evaporated *in vacuo*. The residue was rinsed with diethyl ether (20 ml) and dried *in vacuo* to give 10.40 g (82% yield) of the product as a waxy-like solid. *Synthesis of 1,3-dinonylimidazolium hexafluor-*

ophosphate. To a magnetically stirred solution of the imidazolium bromide prepared above (1.17 g, 3.69 mmol) in water (20 ml) was added potassium hexafluorophosphate (0.68 g, 3.39 mmol). After 30 min, the lower ionic liquid layer was separated and dissolved in dichloromethane (20 ml). The dichloromethane solution was washed with water (2 × 40 mL) and evaporated *in vacuo*. Benzene was added to the residue and the solution was dried using a Dean–Stark apparatus. After removal of the benzene *in vacuo*, the residue was dried *in vacuo* (0.5 Torr) at 100 °C overnight to give 1.27 g (90%) of $[(C_9)_2\text{-Im}]PF_6$.

For the synthesis of $[(C_2)_2\text{-Im}]Br$ and $[(C_3)_2\text{-Im}]Br$, 3.0 and 1.5 molar excess of ethyl bromide and propyl bromide were used, respectively.

§ Phase transition measurements. A Shimadzu DSC-50 differential scanning calorimeter with a LTC low temperature assembly was utilized. The sample (5–25 mg), that had been stored at room temperature before analysis, was sealed in an aluminum pan under air and cooled to about −130 °C by pouring liquid nitrogen into the LTC unit under helium (30 ml min^{-1}). Cooling to this temperature usually took 20–25 min. As soon as all of the liquid nitrogen had evaporated from the LTC unit and the temperature started to rise spontaneously, heating was initiated at 30 °C min^{-1}. Heating was continued to 70 °C for liquid samples and to 130 °C for solid samples.

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