

# Exploiting isolobal relationships to create new ionic liquids: novel room-temperature ionic liquids based upon (*N*-alkylimidazole)(amine)BH<sub>2</sub><sup>+</sup> “boronium” ions†

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**Readily prepared imidazole-based boronium ions form stable, hydrophobic, room-temperature ionic liquids (RTIL) with unique electronic and spectroscopic characteristics.**

It is probably safe to say that five years ago most chemists had never heard of ionic liquids. But in that short period of time interest in these unorthodox materials has grown at a phenomenal rate.<sup>1</sup> The scope of demonstrated or proposed applications of IL is extraordinary, ranging from their use as non-volatile, non-flammable solvents to advanced heat transfer fluids, lubricants and anti-statics.<sup>2</sup> Surpassing in magnitude the number of potential uses is the number of possible IL compositions, estimated by Seddon to be in the billions.<sup>3</sup>

In the absence of predictive computational methods to direct their design, the discovery-based development of new IL will remain vital to the field. This is especially the case *vis-à-vis* heretofore unknown or unused classes<sup>4</sup> of ions when such entities are easily prepared and provide access to potentially unique structural or electronic attributes. In light of these considerations we report here that an obscure cation type – the “boronium”<sup>5</sup> ion – is a versatile platform for creating hydrophobic, room-temperature ionic liquids.

Our new IL are of the general type [L<sup>1</sup>L<sup>2</sup>BH<sub>2</sub>]<sup>+</sup>Tf<sub>2</sub>N<sup>-</sup> where L<sup>1</sup> and L<sup>2</sup> are tertiary amines and *N*-alkylimidazoles respectively. To the best of our knowledge these are the first boronium ions of this type to be reported.<sup>6,7</sup> The generalized structure of each bears a striking similarity to *N,N'*-dialkylimidazolium ions, the latter being ubiquitous IL-forming cations. The –H<sub>2</sub>B–NR<sub>3</sub> fragments of the boronium ions are isolobal with N-bound neopentyl-type –H<sub>2</sub>C–CR<sub>3</sub> structures. Yet, as structural elements the former are considerably easier to access, principally requiring the capacity to form a BH<sub>3</sub> complex of the desired tertiary amine; even bulky species such as quinuclidine (e.g. **6**) may be incorporated as a side chain in this fashion. The compositions of select examples of the new IL are given in Table 1. Significantly, all manifest the highly

**Table 1** Select [(*N*-alkylimidazole)(amine)BH<sub>2</sub>]<sup>+</sup>Tf<sub>2</sub>N<sup>-</sup> RTIL<sup>a</sup>

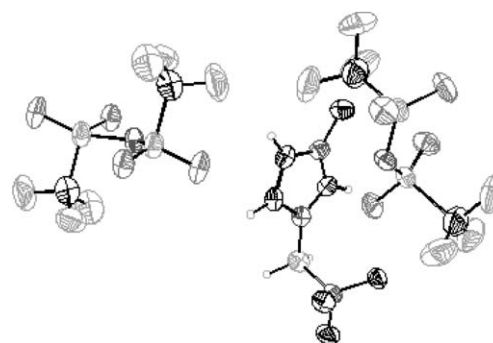
Compound	Imidazole	Tertiary amine	C <sup>2</sup> -H δ <sup>b</sup>
<b>1</b>	1-methyl	trimethyl	8.14
<b>2</b>	1-methyl	triethyl	8.14
<b>3</b>	1-methyl	di( <i>n</i> -butyl)methyl	8.21
<b>4</b>	1-butyl	trimethyl	8.28
<b>5</b>	1-butyl	triethyl	8.21
<b>6</b>	1-butyl	quinuclidine	8.20
<b>7</b>	1,2-dimethyl	trimethyl	n/a
<b>8</b>	1-decyl-2-methyl	trimethyl	n/a

<sup>a</sup> Compound **1** is the only one of these IL which is not a room-temperature liquid. DSC (10 °C/min) of crystalline **1** gave a sharp mp at 60.2 °C. <sup>b</sup> Imidazolium ring C<sup>2</sup>-H proton, 300 MHz, 0.5 M acetone-*d*<sup>6</sup>.

valued property of hydrophobicity and most are mobile room-temperature liquids.

In order to confirm the general structures of the cations we undertook a single-crystal X-ray study of **1**, the simplest of the salts (Fig. 1).<sup>8</sup> The asymmetric unit in the crystal consists of a fully ordered cation and two independent halves of anions disordered about centers of inversion. Though resolved, the anion disorder is extensive and indicative of very weak interactions between the cation H-atoms and the anion.

The overall structure and packing are not remarkable. An analysis of the bond distances and angles† within the imidazolium ring reveals little effect from the boronium substituent. The ring parameters are quite similar to previously reported dialkyl-substituted imidazolium cations.<sup>9</sup> The anion is in the more



**Fig. 1** ORTEP of **1** showing the boronium cation and disordered anion set.

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† Electronic supplementary information (ESI) available: full X-ray crystallographic data, representative synthetic procedures, additional spectroscopic information. See <http://dx.doi.org/10.1039/b504631a>

common, low energy *trans* conformation, which is similar to that observed in  $[(C_2)_3im][NTf_2]$ .<sup>9d</sup> A comparison of all intermolecular contacts less than van der Waals† reveals very few and very weak interactions between the cations and anions, similar to those observed in  $[C_1mim][NTf_2]$ ,  $[(C_2)_3im][NTf_2]$ ,<sup>9d</sup> and  $[C_2C_1benzylim][NTf_2]$ .<sup>9a</sup> The closest ring-H contact is 2.382 Å from the C<sup>2</sup>-H atom to one disordered oxygen position of one of the independent anions. There is also a contact between the C<sup>2</sup>-H and the nitrogen of the same anion at a distance of 2.52 Å. As observed previously with  $[imidazolium]^+ Tf_2N^-$  salts, there are no strong hydrogen bonds to direct the packing in the crystal lattice.

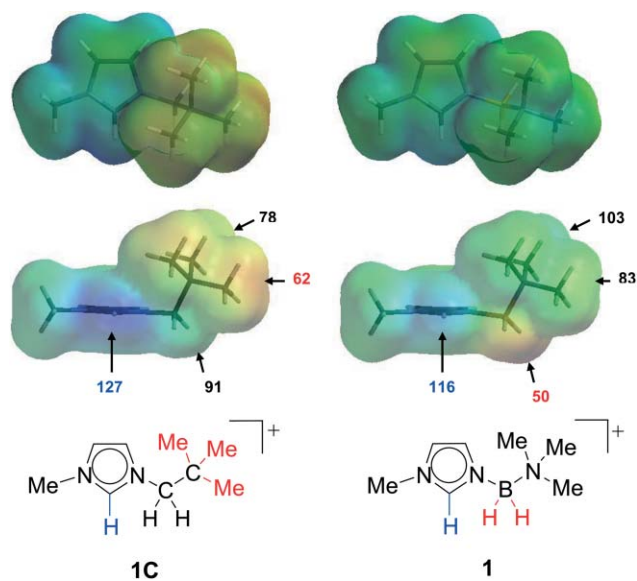
The syntheses of the imidazole-boronium cations are accomplished using careful modifications of earlier protocols.<sup>10</sup> Conceptually, all are based on the modular assembly of commercially available units, *e.g.* a tertiary amine, an N-heterocycle and a source of  $BH_2^+$  (commonly an amine-borane complex).<sup>7</sup> In all cases, isolation of precursor iodide salts is followed by anion metathesis in water using  $LiTf_2N$ ; the final products separate as hydrophobic phases. While conventional imidazolium IL are often initially isolated as highly coloured materials,<sup>11a,b</sup> the boronium  $I^-$  and  $Tf_2N^-$  compounds are completely colourless. Salts of  $[(1-butylimidazole)(trimethylamine)BH_2]^+$  are typical in this regard, the  $I^-$  species manifesting no absorption > 270 nm ( $\lambda_{max} = 237$  nm) and the  $Tf_2N^-$  salt not absorbing > 245 nm ( $\lambda_{max} = 225$  nm). This behavior is conceivably the result of a difference in susceptibility on the part of boronium ions towards interionic charge-transfer.<sup>11c,d</sup>

The new IL are capable of solubilizing a number of substrate types. Consequently, we conducted the Diels-Alder coupling of cyclopentadiene and methyl acrylate in **4** as a simple test of their use as solvents for organic reactions. The reaction proceeded cleanly, giving the expected bicyclic product in quantitative yield. The distribution of *endo/exo* isomers was 4.6, in accord with results previously reported for this reaction in other IL.<sup>12</sup>

The simplicity with which the boronium ions are prepared and the structural diversity readily embodied in them each provide an important pragmatic basis for their use in formulating IL. Further, based upon an earlier computational study<sup>13</sup> we anticipated that significant variations in electron density and charge distribution would be manifest in imidazole-boronium cations *versus* an *N,N'*-dialkylimidazolium norm, providing a fundamental rationale for our work as well. In order to validate this premise, we performed high-level calculations on the cation of **1** as well as **1C**, a putative isostructural conventional analog.<sup>14</sup>

As shown in Fig. 2, the distribution of electron density in **1** is strikingly different from that in **1C**. In the former the area of lowest electropositive potential (50 kcal/mol) is associated with the B-H atoms, those being close to the imidazole ring. In **1C**, the lowest potential (62 kcal/mol) is linked to the methyl H-atoms of the ring-appended neopentyl moiety. The latter are distal to the imidazole ring, which in both cations has the maximum electropositive potential at the C<sup>2</sup>-H positions (116 and 127 kcal/mol respectively).

Differences are also observed in the electrostatically-derived charges of each ion. In **1**, the charges on the three nitrogen atoms ( $N^{im-Me}$ ,  $N^{im-BH_2}$  and  $N^{amine}$ ) are 0.23, 0.23 and 0.36 au, respectively. In **1C**, a much larger localized charge (0.57 au) is carried by a single atom, the neopentyl methylene carbon, which is the structural counterpart of the  $N^{amine}$  atom of **1**. In turn, the



**Fig. 2** Computed cation structures of **1C** and **1** showing select electropositive potentials. The muted colour extremes of the latter make its greater charge delocalization visually apparent.

imidazole N atoms of **1C** are assigned smaller values (0.21 and 0.20) than their analogs in **1**. Globally, the electronic differences between **1** and **1C** are non-trivial and corroborate our initial supposition. Specifically, they suggest that the imidazole-boronium ion – like bis(amine) $BH_2^+$  cations<sup>13</sup> – has a greater degree of charge delocalization than a conventional counterpart. Interestingly, complementary calculations of the gas phase reduction potentials of **1** and **1C** indicate that the boronium ion is also more difficult to reduce by  $\sim 0.5$  V.<sup>18</sup>

The <sup>13</sup>C-, <sup>11</sup>B- and <sup>19</sup>F-NMR spectra of the boronium IL are unremarkable and comport with established data on other boronium ions and imidazolium  $Tf_2N^-$  salts.<sup>7,19</sup> However, the <sup>1</sup>H-NMR spectra of the compounds exhibit a major difference compared to those of conventional imidazolium IL. Specifically, there is a marked *dissimilarity* in the absolute same-anion imidazole ring-H  $\delta$  values for the boronium systems *versus* those of normal imidazolium IL.<sup>4,19</sup> Notably, the C<sup>2</sup>-H  $\delta$  of the boronium  $I^-$  salts is in the 9–9.5 range, while for the  $Tf_2N^-$  RTIL this resonance is just above 8 ppm. These values are significantly shifted from those observed in same-anion conventional imidazolium salts. For example, in **1** the C<sup>2</sup>-H resonance is at 8.14 ppm, while those in  $[C_1mim]Tf_2N$  and  $[C_2mim]Tf_2N$  are at 8.94 and 9.03 ppm respectively, differences of 0.80 and 0.89  $\delta$ . The C<sup>2</sup>-H in the *iodide* salt of the same boronium cation comes at 9.09 ppm! Such results are highly suggestive of weaker solution state cation-anion H-bonding<sup>4,19</sup> in the boronium salts than in common imidazolium IL and are in accord with both the X-ray results and the lower electropositive potential computed for C<sup>2</sup>-H in **1** *versus* **1C**.

Interestingly, the <sup>1</sup>H-NMR spectrum of **3** as isolated revealed an unexpected feature, namely that it is clearly composed of a mixture of cations incorporating two chemically distinct types of methyl di-*n*-butyl amine ( $L^1$ ) and 1-methylimidazole ( $L^2$ ) fragments. We considered two possible explanations, one invoking the existence of two conformers of  $L^1L^2BH_2^+$  (imposed by the steric bulk of the

amine) and the other which posited a redistribution reaction resulting in a mixture of cations of formulas  $L^1L^2BH_2^+$ ,  $L^1_2BH_2^+$  and  $L^2_2BH_2^+$ . However, after extensive computational evaluations and an exhaustive VT, multinuclear and multidimensional NMR study of this system, we favor the former scenario. The clearest evidence in support of this arises from the proton decoupled  $^{11}B$ -spectrum of the mixture, which exhibits only two peaks ( $-3.82$  and  $-7.98$  ppm, rel.  $Et_2OBF_3$ ). Note that the  $^{11}B$ -resonance from a separately prepared sample of the salt  $L^2_2BH_2^+ Tf_2N^-$  (itself a mobile RTIL) is observed at  $-8.46$  ppm. Finally, we observe that the minor cation component of the system is cleanly and irreversibly converted into the major component cation upon thermolysis in  $dmsO-d_6$ . Despite the existence of  $dmsO$ -supported boronium ions,<sup>20</sup> no additional peaks were observed in the  $^{11}B$ -NMR during this procedure, also militating against a redistribution reaction.

Overall, the present results demonstrate that imidazole-derived boronium ions constitute a useful complement to the more familiar dialkylimidazolium ions for the formulation of new ionic liquids. Preliminary work (*vide supra*) has also now revealed that bis(alkylimidazole)BH<sub>2</sub><sup>+</sup> ions are also capable of forming RTIL, and work is in progress to evaluate bis(amine)BH<sub>2</sub><sup>+</sup> ions for this purpose as are studies on other boronium ion variants and applications.

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