

# Designing ionic liquids with boron cluster anions: alkyl-pyridinium and imidazolium ortho- and closo-carborane salts

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A range of new alkylpyridinium and imidazolium orthocarborane, closo-carborane and alkyl-carborane salts have been prepared and characterized by physical and thermal methods, including the solid state structures of five of the salts determined by single crystal X-ray diffraction. The tendency of the salts to form low melting ionic liquids has been assessed; all the ortho-carborane salts studied melted below 100 °C and, significantly, have melting points that are 25-85 °C lower than those of the corresponding closo-carborane analogs demonstrating that a wider range of boron-rich ionic liquid materials can be readily accessed.

## 15 Introduction

The field of ionic liquids has been attracting much attention in the recent decade<sup>1</sup> with the number of publications related to ionic liquids increasing dramatically, and currently exceeding 2500 per year. The ionic liquid state offers many interesting and useful opportunities, not least the ability to control (and tune) the physical and chemical properties of liquid environments.<sup>2</sup>

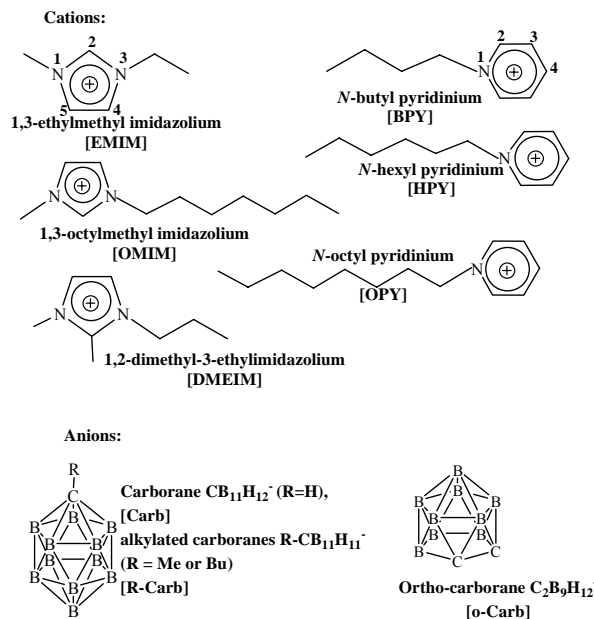
Although ionic liquid materials were first reported in 1914,<sup>3</sup> current developments can be traced back to the development of low temperature molten salt electrolytes for batteries in the 1970s and 80s.<sup>4</sup> However, the highly aggressive and reactive nature of these Cl/AlCl<sub>3</sub>-based systems was somewhat restrictive<sup>5</sup> and the first air- and moisture-stable ionic liquids with tetrafluoroborate and hexafluorophosphate anions were reported in the early 1990s.<sup>6</sup> These are relatively poorly coordinating anions and can yield hydrophobic liquids, however they are still prone to undesirable decomposition leading to release of HF.<sup>7</sup> Improved hydrolytic stability is found with perfluorinated sulfonate and sulfonylimide anions have subsequently been widely used to prepare stable hydrophobic ionic liquids.<sup>8,9</sup>

Non-coordinating inert anions are important across a range of chemical applications and the non-coordinating carboranes are good examples that have been used in catalysis,<sup>10</sup> structural studies of metal-coordination environments and in the investigation of super-acidity.<sup>11</sup> We, and other researchers, recently introduced inert non-coordinating boron-carbon cluster anions - carboranes - in the repertoire of ionic liquids.<sup>12,13</sup> The characteristics of the carborane cage and the ability to derivatize the cage allowed a systematic study into the factors governing the low-melting behavior of the imidazolium-based salts.

These ionic liquid carborane salts have relatively high boron contents and physical properties that can be readily manipulated. There is significant interest in materials of this type in the biomedical field as neutron-capture targets<sup>14</sup> and as

potential liquid neutron moderators with respect to applications in future nuclear-processing.<sup>15</sup>

Here, we report the results of studies to expand the ionic liquid forming salts with carborane anions to systems containing alkyl-pyridinium and imidazolium cations, and also introduce a different, open-face carborane cluster anion – derived from ortho-carborane precursor (Scheme 1); dodecahydro-dicarbido-undecaborate ‘dicarbollide’ anion, used as the [Co(dicarbollide)<sub>2</sub>]<sup>2-</sup> complex anion in nuclear fuel processing.<sup>16</sup>



**Scheme 1.** Structures and abbreviations for the cations and anions

We describe the preparation, characterization and comparison of new ionic liquids containing both ortho- and closo-carborane anions. In addition to di- and trialkylimidazolium cations that were investigated previously<sup>12</sup> with closo-carboranes, alkyl-pyridinium cations have been systematically explored in this study in their combinations with both ortho- and closo-carboranes yielding a

number of new ionic liquid materials. The single crystal X-ray structures of five salts; 1-butylpyridinium ortho-carborane, 1-hexylpyridinium ortho-carborane, 1-octylpyridinium

ortho-carborane, 1-ethyl-3-methylimidazolium ortho-carborane, and 1-butylpyridinium carborane, have been determined.

**Table 1** Melting points and elemental analysis

Compound:	Abbreviation	mp /°C	Analysis, found (calc.) %		
			C	H	N
1 1-butylpyridinium C <sub>2</sub> B <sub>9</sub> H <sub>12</sub>	BPY o-Carb	49	49.29 (49.00)	9.76 (9.72)	5.17 (5.20)
2 1-hexylpyridinium C <sub>2</sub> B <sub>9</sub> H <sub>12</sub>	HPY o-Carb	72	52.92 (52.45)	10.19 (10.16)	4.66 (4.71)
3 1-octylpyridinium C <sub>2</sub> B <sub>9</sub> H <sub>12</sub>	OPY o-Carb	80	55.59 (55.31)	10.57 (10.52)	4.28 (4.30)
4 1-octyl-3-methylimidazolium C <sub>2</sub> B <sub>9</sub> H <sub>12</sub>	OMIM o-Carb	47	51.36 (51.15)	10.79 (10.73)	8.46 (8.52)
5 1-ethyl-3-methylimidazolium C <sub>2</sub> B <sub>9</sub> H <sub>12</sub>	EMIM o-Carb	97	38.79 (39.28)	9.09 (9.48)	11.02 (11.46)
6 1-butyl-2,3-dimethylimidazolium C <sub>2</sub> B <sub>9</sub> H <sub>12</sub>	BDMIM o-Carb	47	46.36 (46.09)	10.26 (10.20)	9.74 (9.77)
7 1-butylpyridinium CB <sub>11</sub> H <sub>12</sub>	BPY Carb	134	43.28 (43.01)	9.40 (9.39)	4.94 (5.02)
8 1-hexylpyridinium CB <sub>11</sub> H <sub>12</sub>	HPY Carb	114	47.37 (46.90)	9.89 (9.84)	4.49 (4.56)
9 1-octyl pyridinium CB <sub>11</sub> H <sub>12</sub>	OPY Carb	112	50.42 (50.14)	10.27 (10.22)	4.05 (4.18)
10 1-butylpyridinium 1-butyl CB <sub>11</sub> H <sub>11</sub>	BPY Bu-Carb	70	49.55 (50.14)	10.20 (10.22)	4.11 (4.18)
11 1-hexylpyridinium 1-methyl CB <sub>11</sub> H <sub>11</sub>	HPY Me-Carb	85	48.42 (48.59)	9.82 (10.04)	4.47 (4.36)
1-octyl-3-methylimidazolium carborane CB <sub>11</sub> H <sub>12</sub>	OMIM Carb	70 (from lit <sup>5</sup> )			
1-ethyl-3-methylimidazolium CB <sub>11</sub> H <sub>12</sub>	EMIM Carb	122 (from lit <sup>5</sup> )			
1-butyl-2,3-dimethylimidazolium CB <sub>11</sub> H <sub>12</sub>	BDMIM Carb	129 (from lit <sup>5</sup> )			

**Table 2.** <sup>1</sup>H NMR chemical shifts (δ ppm, J Hz) in acetone-*d*<sub>6</sub>.<sup>a</sup> See Table 1 and Scheme 1 for the numbered compounds names and structures.

		C <sup>2</sup> H	C <sup>3</sup> H	C <sup>4</sup> H	C <sup>5</sup> H	N <sup>1</sup> CH <sub>2</sub>	N <sup>1</sup> CH <sub>2</sub> (CH <sub>2</sub> ) <sub>m</sub>	N <sup>1</sup> (CH <sub>2</sub> ) <sub>n</sub> CH <sub>3</sub>
1	BPY o-Carb	9.22 (d, J=5.5)	8.30 (t, J=7.8)	8.76 (t, J=7.6)		4.87 (t, J=6.9)	1.73-1.39 (m=2, 4H)	0.95 (t, J=8.3)
2	HPY o-Carb	9.23 (d, J=6.0)	8.30 (t, J=7.1)	8.76 (t, J=8.3)		4.87 (t, J=7.8)	1.39-1.19 (m=4, 8H)	0.84 (t, J=6.0)
3	OPY o-Carb	9.22 (d, J=5.5)	8.30 (t, J=8.6)	8.76 (t, J=7.8)		4.87 (t, J=9.5)	1.53-1.18 (m=6, 12H)	0.84 (t, J=6.9)
4	OMIM o-Carb	9.07 (s)		7.79 (d, J=1.4)	7.73 (d, J=1.8)	4.37 (t, J=9.2)	1.57-1.18 (m=6, 12H)	0.84 (t, J=8.6)
5	EMIM o-Carb	9.09 (s)		7.80 (d, J=1.8)	7.73 (d, J=2.3)	4.41 (q, J=7.4)		N <sup>3</sup> CH <sub>3</sub> : 4.07 (s) 1.56 (t, J=7.3)
6	BDMIM o-Carb			7.65 (d, J=2.3)	7.62 (d, J=1.4)	4.30 (t, J=7.5)	1.86-1.36 (m=2, 4H)	0.92 (t, J=9.2) C <sup>2</sup> CH <sub>3</sub> : 2.77 (s) N <sup>3</sup> CH <sub>3</sub> : 3.96 (s)
7	BPY Carb	9.21 (d, J=5.5)	8.30 (t, J=6.9)	8.76 (t, J=9.7)		4.87 (t, J=7.6)	1.59-1.32 (m=2, 4H)	0.96 (t, J=9.2)
8	HPY Carb	9.22 (d, J=5.5)	8.30 (t, J=6.9)	8.75 (t, J=7.6)		4.86 (t, J=7.8)	1.48-1.21 (m=4, 8H)	0.83 (t, J=6.9)
9	OPY Carb	9.22 (d, J=5.5)	8.30 (t, J=6.9)	8.75 (t, J=7.6)		4.86 (t, J=7.3)	1.58-1.19 (m=6, 12H)	0.84 (t, J=8.6)
10 <sup>b</sup>	BPY Bu-Carb	9.21 (d, J=5.5)	8.31 (t, J=6.2)	8.76 (t, J=8.0)		4.86 (t, J=7.6)	1.48-1.21 (m=2, 4H)	0.95 (t, J=9.2)
11 <sup>c</sup>	HPY Me-Carb	9.22 (d, J=5.5)	8.30 (t, J=8.9)	8.75 (t, J=7.8)		4.87 (t, J=7.6)	1.47-1.24 (m=4, 8H)	0.85 (t, J=8.8)

<sup>a</sup> <sup>1</sup>H {<sup>11</sup>B} NMR also shows broad peaks for H on carborane at δ 1.55 and 1.78.; <sup>b</sup> <sup>1</sup>H NMR also shows resonances for the butyl group on the carborane at δ 0.79, 1.10, 1.24, and 1.75; <sup>c</sup> <sup>1</sup>H NMR also shows peaks for the methyl group at δ 1.49.

## Results and Discussion.

### Synthesis

15 1-Alkylpyridinium (butyl, hexyl and octyl), 1-alkyl-3-methylimidazolium (ethyl and octyl), and 1-butyl-2,3-dimethylimidazolium salts were prepared with ortho-carborane, closo-carborane, and alkylcarborane (butyl- and hexyl) anions by the metathesis reaction of pyridinium or  
20 imidazolium halides with the corresponding cesium carborane salt (or lithium alkylcarborane salts) in dichloromethane. The cations and anions used are shown in Scheme 1, the salts prepared are listed in Table 1 along with the experimental melting points and CHN elemental analysis data on the  
25 isolated salts, proton NMR data is shown in Table 2.

After crude filtration to remove inorganic salts, the reaction mixtures were passed through celite and alumina and the solvent removed *in vacuo* to give the crude products. Recrystallization from ethanol/hexane by vapor diffusion at  
30 ambient or low temperatures gave the salts as colorless, sometimes slightly waxy, solids at room temperature with

melting points between 47-134 °C.

The cations were chosen in order to assess the effects of changing the alkyl chain length and also substituting between  
35 pyridinium and imidazolium cations. Anion effects were examined by comparing the ortho- and closo-carborane salts with equivalent cations. It should be noted that the starting cesium ortho-carborane can be readily prepared in one step from the neutral ortho-carborane<sup>17</sup> compared to the three step  
40 procedure starting with costly decaborane<sup>18</sup> required to synthesize cesium closo-carborane. This makes the nido-carborane anion derived from ortho-carborane much more attractive in terms of the synthetic availability (and potential cost).

45 All the salts form air stable colorless crystalline solids that were characterized by <sup>11</sup>B and <sup>1</sup>H NMR spectroscopy in acetone-*d*<sub>6</sub> solution, elemental analysis (Table 1), and where suitable crystals could be obtained, by single-crystal X-ray crystallography. The <sup>11</sup>B NMR spectra were comparable to  
50 those of other salts with the same anions; <sup>1</sup>H data are shown in Table 2. All the salts prepared were soluble in dichloromethane and acetone, insoluble in hexane, and, in

spite of being somewhat hygroscopic, do not dissolve in water.

### Spectroscopic Characterization.

Proton nuclear magnetic resonance solution spectra in acetone were rationalized by structural composition of the salts (Table 2). The aromatic region shows imidazolium and pyridinium ring proton resonances.

The chemical shifts for the C<sup>2</sup>-H position of the imidazolium ring show a dependence on the anion when comparing CB<sub>11</sub>H<sub>12</sub> salts (reported earlier)<sup>12</sup> versus C<sub>2</sub>B<sub>9</sub>H<sub>12</sub> salts, demonstrating a small change in the case of the OMIM salts (from  $\delta = 9.10$  to 9.07) and a somewhat larger change (from  $\delta = 9.09$  to 9.32) in the case of the EMIM salts.

Infra-red spectra of the ortho-carborane salts show characteristic C-H and B-H stretches in 2800-2900 cm<sup>-1</sup> and 2500-2530 cm<sup>-1</sup> ranges, respectively.<sup>19</sup> In the case of alkyl-pyridinium carborane salts the C-H stretch of the carborane is observed in the 3040-3060 cm<sup>-1</sup> range, similar to the imidazolium compounds (with the notable exception of alkylated carboranes in **10** and **11**). Vibrations of the aromatic C-H bonds in the pyridinium cations are found in the 3080-3100 cm<sup>-1</sup> range, and in the 3110-3180 cm<sup>-1</sup> region for the imidazolium cations.

### Thermal Characterization.

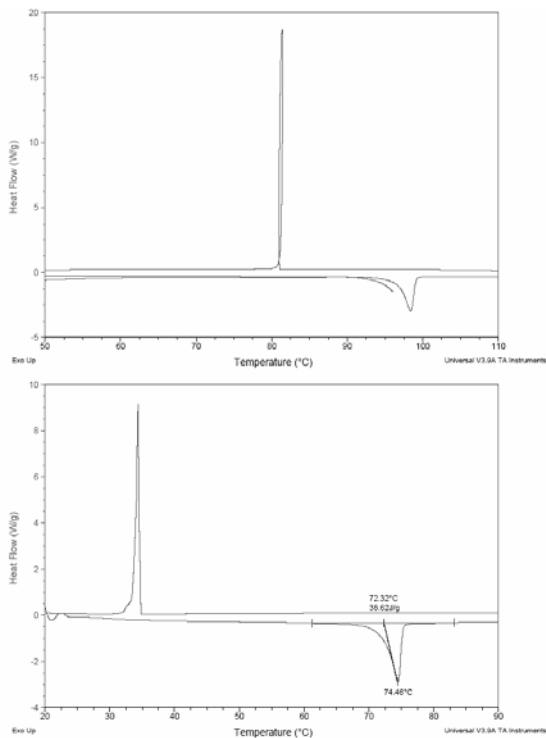
The thermal behavior of the salts was measured by differential scanning calorimetry (see Table 1 for the determined melting points, calculated from the second heating cycle). All the salts investigated melted between 47-134 °C. DSC showed well defined exothermic crystallization peaks on cooling from the molten state. On subsequent heating of samples, a first order melting transition with broadened onset to melting was observed in all cases. Figure 1 shows representative DSC heating and cooling curves for **2** and **5**.

These heating and cooling profiles are typical of ionic liquids and are indicative of pre-melting alkyl-chain mobility and formation of disorder plastic phases as part of the melting transition; in our previous study of ionic liquids with carborane anions, the majority of samples which were isolated and characterized crystallographically had disordered cations consistent with the mobility of the cations even in the solid state of these salts. This form of disorder was also observed in the single-crystal X-ray structures of three of the salts determined here and is described later. Super-cooling behavior is also typical for these compounds (see representative DSC trace for **2** on Figure 1, where crystallization occurs 40 degrees below the melting point.)

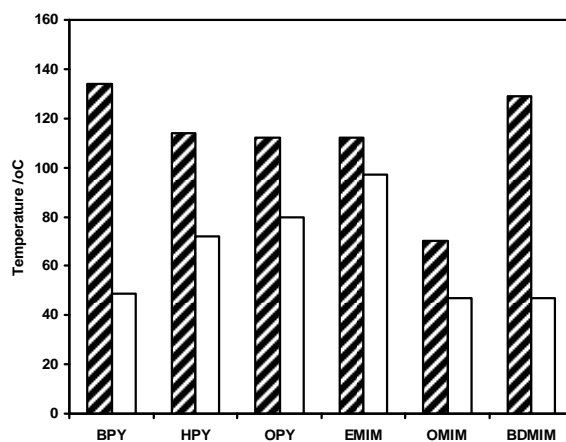
There is a significant lowering of the melting points for all the salts with the ortho-carborane anion (**1-6**) compared to the corresponding closo-carborane salts. The reduction in melting points range between 25 °C ([EMIM]<sup>+</sup>) to 85 °C ([BPY]<sup>+</sup>), and are shown graphically in Figure 2.

The reduction in melting point is most pronounced with the [BPY]<sup>+</sup> and [BDMIM]<sup>+</sup> cations. In both of these cases, the

melting points of the salts were reduced from ~130 °C to less than 50 °C. It is also worth noting that the melting points for the three 1-alkylpyridinium ortho-carboranes (**1-3**) increase with increasing alkyl chain length from butyl through hexyl to octyl. This contrasts with the usual decrease in melting point with increasing alkyl-chain length observed for ionic liquids.<sup>20</sup>



**Figure 1.** DSC traces for HPY o-Carb (**2**, bottom) and EMIM o-Carb (**5**, top) showing the characteristic broad melting point transitions (down) and extensive super cooling of the ionic liquid before undergoing sharp, well defined crystallisation (up) to the solid state.



**Figure 2.** Comparison of the melting points of the pyridinium and imidazolium closo-carborane (hashed bars) and ortho-carborane (clear bars) salts by cation type.

**Table 3.** Crystallographic Data

	<b>1</b>	<b>2</b>	<b>3</b>	<b>5</b>	<b>7</b>
crystal system	ortho.	mono.	tri.	tri.	ortho.
space group	$P2_12_12_1$	Cc	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
<i>a</i> (Å)	9.2643(9)	7.1828(14)	7.3776(15)	7.1768(6)	9.4426(7)
<i>b</i> (Å)	12.1189(14)	31.617(6)	8.3032(17)	8.3083(7)	10.6450(8)
<i>c</i> (Å)	14.5636(17)	8.3874(17)	17.229(3)	12.562(11)	34.386(3)
$\alpha$ (deg)	90	90	89.15(3)	87.761(1)	90
$\beta$ (deg)	90	96.45(3)	81.17(3)	84.001(1)	90
$\gamma$ (deg)	90	90	85.96(3)	82.906(1)	90
<i>V</i> (Å <sup>3</sup> )	1635.1(3)	1892.7(7)	1040.3(4)	739.0(1)	3456.4(4)
<i>Z</i>	4	4	2	2	8
Fw	269.62	296.66	325.72	244.57	279.23
<i>D<sub>c</sub></i> (g/cm <sup>3</sup> )	1.095	1.041	1.04	1.10	1.073
temp (K)	173(2)	173(2)	173(2)	125(2)	100(2)
GOF on <i>F</i> <sup>2</sup>	1.045	1.125	1.065	1.068	1.015
<i>R</i> 1 ( <i>I</i> > 2 $\sigma$ <i>I</i> )	0.0496	0.0515	0.0611	0.0887	0.0353
<i>R</i> 1 (all)	0.0687	0.0803	0.01029	0.1253	0.0375
<i>wR</i> 2 ( <i>I</i> > 2 $\sigma$ <i>I</i> )	0.1040	0.1213	0.1586	0.2396	0.0962
<i>wR</i> 2 (all)	0.1121	0.1350	0.1892	0.2661	0.099
diff. pk/ho (e/Å <sup>3</sup> )	0.185/-0.22	0.171/-0.143	0.306/-0.222	1.334/-0.570	0.482/-0.172

Symmetry-breaking (in cations) is considered to be a key driver to the formation of lower melting ionic liquids, however these two observations suggest that in these salts the larger anion has a dominant role in organizing the solid state. The lower symmetry of the *ortho*-carborane compared to *closo*-carborane anions destabilizes the crystalline form, while increasing the chain-length on the cation here leads to more efficient space-filling around the relatively large anions. Similarly, incorporation of an alkyl-substituent into the carborane anion (**10** and **11**) decreases the anion symmetry and also leads to a reduction in the melting point of the salts relative to the corresponding *closo*-carboranes (**7** and **8**), although the melting points are still higher than those of the corresponding *ortho*-carborane analogs (**1** and **2**).

### X-ray Structures.

Crystals suitable for X-ray structure analysis were obtained for five of the salts; two with the BPY cation (**1** and **7**), one with HPY (**2**), one with OPY (**3**), and one EMIM salt (**5**) by trituration and slow crystallization from ethanol/hexane. Structure solutions were carried out using direct methods and crystallographic data for all the salts is shown in Table 3. All non-hydrogen atoms were readily located upon solution or found in the Fourier difference maps. The disordered groups, where present, were modelled with two components and refined with standard methods. Hydrogen atoms were added at calculated positions and allowed to refine unconstrained (except where noted for located hydrogens, which were allowed to refine unconstrained but riding on bonded atoms). Four *ortho*-carborane structures were obtained for the three alkyl-pyridinium homologues; **1**, **2** and **3**, and the 1-ethyl-3-methylimidazolium salt **5** (with a positionally disordered anion). Data collected for OPY *o*-Carb **3** were of poor quality; nonetheless it was possible to confirm the connectivity and general packing in the crystal. These data are reported for completeness and for comparison with the two related structures from the homologous series with 1-alkylpyridinium cations. In addition, a carborane, BPY Carb **7** is also reported. Two of the salts exhibited disorder in the structures; OPY

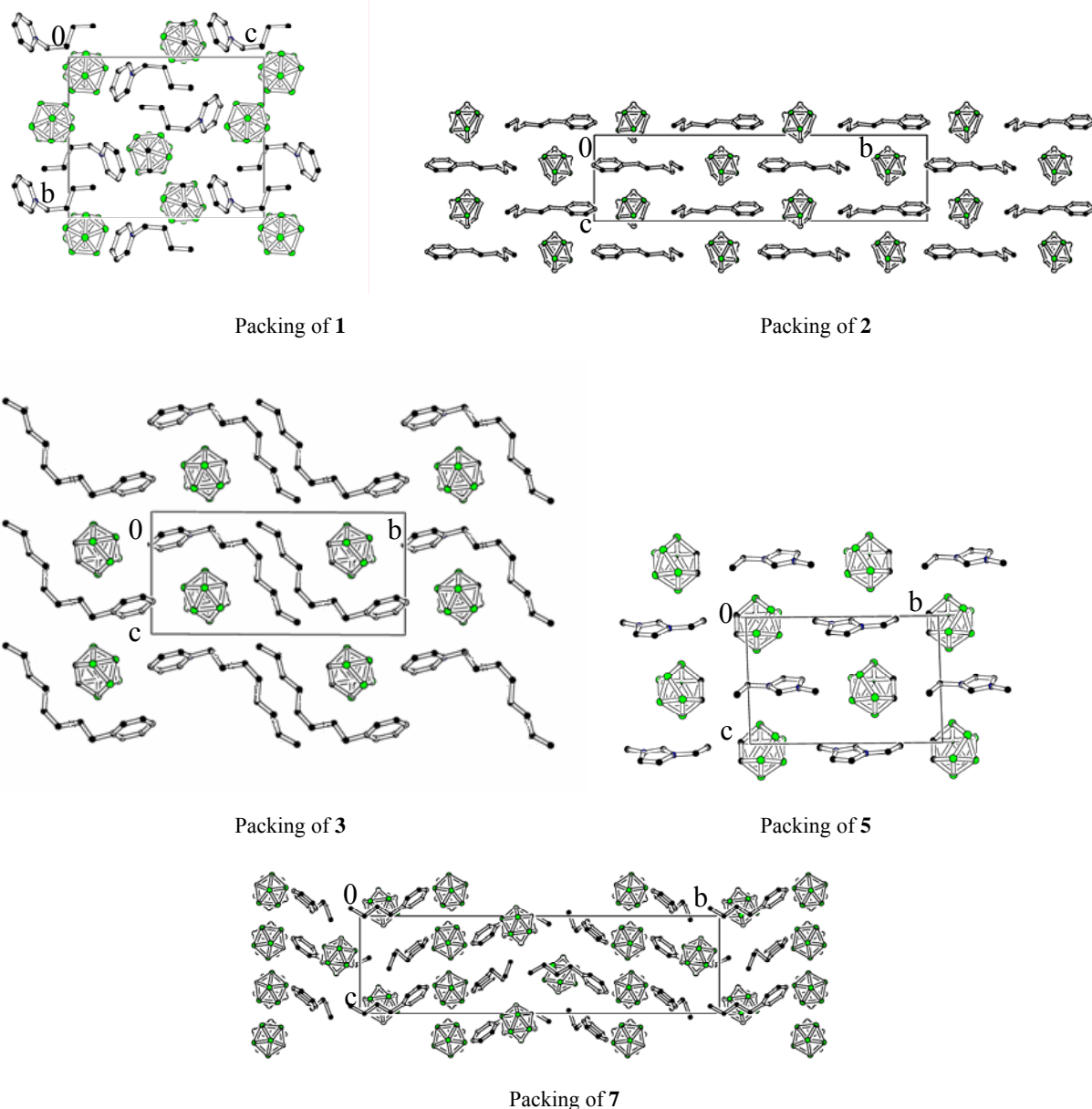
*o*-Carb **3** has a disordered cation, with alkyl-chains modeled over two positions with 63.8(4):36.2(4) % occupancies, and EMIM *o*-Carb **5** has positionally disordered anion with occupancies of 50:50%. This was not explicitly modelled and it probably represents a case similar to that of the analogous 1-ethyl-3-methylimidazolium methylcarborane salt previously reported.<sup>12</sup> BPY *o*-Carb **1** and HPY *o*-Carb **2** crystallized as simple salts with a single ion pair in the asymmetric unit, whereas BPY Carb **7** crystallized with two different ion pairs per unit cell.

Packing diagrams are depicted in Figure 3. The most obvious feature, common for all the structures, is that the salts, whether they are *ortho*-carboranes or *closo*-carboranes, crystallize in layered structures with parallel linear alignment of the anions. In the resultant plane orthogonal to this axis, sheets of anions and cations close-pack in arrays at the van der Waals separation distances.

From the packing diagrams in Figure 3, it is evident, especially for the salts in which the cations contain longer alkyl-substituents, that segregation of polar and apolar functionality in the structure occurs. The ionic lattice of the salts is punctuated by hydrocarbon-rich domains formed by association of the alkyl-groups from the cations. This is a common feature in the crystal structures of alkyl-substituted imidazolium and pyridinium cations (see for example reference 21) and leads, with further elongation of the alkyl-substituents to layered entirely microphase separated structures.

The ions in BPY *o*-Carb **1** pack in the plane with two anions forming a 'cluster' surrounded by four cations. The open face of each *ortho*-carborane anion is capped by a pyridinium cation (closest approach 3.4 Å) forming an ion-pair. In contrast, on lengthening the alkyl-chain of the cation, a shift in the packing motif emerges.

In the structure of HPY *o*-Carb **2**, in the plane, each anion isolated, surrounded by four cations with three pyridinium-head groups from cations which form a pocket in which the anion resides with the open face of the *ortho*-carborane anion capped by a terminal methyl group of the fourth cation in the plane.



**Fig. 3** Packing diagrams from the single crystal X-ray structures of **1**, **2**, **3**, **5**, and **7**, showing the two anion environments: formation of sheets sandwiched by pyridinium cations and isolated anions in an alkyl-chain rich local environment. In all diagrams all H-atoms (and second component of the disordered atoms in **3** and **5**) are omitted for clarity and the view is projected down the a-axis.

For OPY o-Carb **3**, on increasing the alkyl-chain length compared to the BPY and HPY analogs, this biphasic separation becomes more pronounced and, while a similar packing arrangement around the anions is observed, the unit cell lengthens to accommodate the increased hydrocarbon volume of the cation which form a distinct bilayer and also displays disorder in the packing of the flexible octyl-chains.

EMIM Carb **5** also forms isolated anions surrounded in the plane by four cations, with a local packing environment around the anion that closely resembles that of the longer chain pyridinium salts **2** and **3** rather than that of BPY o-Carb **1**. Thermal motion in the crystal is evident from the large thermal ellipsoids for the N-CH<sub>2</sub>CH<sub>3</sub> groups of the cation and

from the anion disorder observed which was modelled with 0.5:0.5 positional disorder of the whole anion. It is also notable that the ethyl-group in this structure is in the plane of the imidazolium ring, unusual in imidazolium salt structures.

In contrast to BPY o-Carb **1**, the corresponding closo-carborane salt, **7**, crystallizes with two unique ion pairs per unit cell, each with a different conformation of the cation butyl-chains, which result in the formation of two unique anion environments in the structure.

## Experimental

### General Considerations

All synthetic procedures were carried out in a fumehood. IR spectra were recorded on a Thermo Nicolet Magna-IR 550 spectrometer. <sup>1</sup>H NMR spectra in acetone-*d*<sub>6</sub> solutions were recorded on a JEOL 400 MHz NMR spectrometer. Microanalyses were performed by Atlantic Microlab, Inc. Melting points were determined by differential scanning calorimetry (DSC) at 5 °C/min heating/cooling rate on 5-10 mg samples on a TA Instruments Q1000 Modulated Differential Scanning Calorimeter. Quoted values were taken from the first peak of the second heating cycle, i.e., all samples were first melted and re-solidified before taking data. Some samples showed more than one peak on the heating trace, indicative of polymorphic crystal phase formation. Re-solidification temperatures upon cooling were frequently significantly lower than the melting points upon re-heating. This hysteresis is consistent with the supercooling of the ionic liquids before crystallisation.

### Synthesis

Cesium carborane salts were synthesized as described elsewhere.<sup>22,23</sup> Isolated yields of the alkyl-pyridinium and dialkyl-imidazolium salts greater than 90%. Elemental analyses and melting points are given in Table 1, NMR spectroscopic data are presented in Table 2, and X-ray data overview in Table 3.

**Cesium ortho-carborane.** Following the reported procedure,<sup>17</sup> in a round bottom flask ethanol (150 mL) and NaOH (3.60 g, 0.09 mol) was placed. Stock ortho-carborane, C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, (10.09g, 0.07 mol) was added to the solution and stirred. Using water cooled condenser and under a N<sub>2</sub> atmosphere the solution was refluxed for 4 days. The solution was allowed to cool to room temperature. Using dry ice, CO<sub>2</sub> was bubbled through the solution for 25 minutes to remove any excess NaOH. The solution was filtered through dry celite and washed 4 times with ethanol (50 mL) to remove the precipitate that formed. The remaining solution was reduced by using a rotoevaporator until an oily liquid remained. CsCl (1.92 g, 0.01138 mol) was dissolved in H<sub>2</sub>O and then added to the round bottom flask. A white precipitate formed and it was isolated and dried on a Buchner funnel (11.906g, 0.0447 mol, 63.87 % yield).

**1-Butylpyridinium ortho-carborane (1).** In a small flask dried cesium o-carborane (0.212g, 7.96×10<sup>-4</sup> mol) was dissolved in dichloromethane (13 mL) and a minimum of acetone (2 mL) mixture. In another flask 1-butylpyridinium chloride (7.96×10<sup>-4</sup> mol) was dissolved in dichloromethane (13 mL). The 1-butylpyridinium chloride solution was then added to o-carborane solution and a white precipitate formed. The solution was then filtered through celite and evaporated to dryness. The remaining solid is then dissolved in dichloromethane, filtered through celite and evaporated again, yielding white waxy solid 1-butylpyridinium o-carborane (0.194g, >90% crude yield). The product is re-crystallized from absolute ethanol by vapor diffusion of hexane at -20° C.

**1-Hexylpyridinium ortho-carborane (2).** Synthesis and

purification was carried out according to the procedure described for 1-butylpyridinium o-carborane above from Cs[C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>] and n-hexyl pyridinium bromide.

**1-Octylpyridinium ortho-carborane (3).** Synthesis and purification was carried out according to the procedure described for 1-butylpyridinium o-carborane above from Cs[C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>] and 1-octylpyridinium bromide.

**1-Octyl-3-methylimidazolium ortho-carborane (4).** Synthesis and purification was carried out according to the procedure described for 1-butylpyridinium o-carborane above from Cs[C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>] and 1-octyl-3-methylimidazolium chloride.

**1-Ethyl-3-methylimidazolium ortho-carborane (5).** Synthesis and purification was carried out according to the procedure described for 1-butylpyridinium o-carborane above from Cs[C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>] and 1-ethyl-3-methylimidazolium chloride.

**1-Butyl-2,3-dimethylimidazolium ortho-carborane (6).** Synthesis and purification was carried out according to the procedure described for n-butyl pyridinium o-carborane above from Cs[C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>] and 1-butyl-2,3-dimethylimidazolium chloride.

**1-Butylpyridinium carborane (7).** Synthesis and purification was carried out according to the procedure described for 1-butylpyridinium o-carborane above from Cs[CB<sub>11</sub>H<sub>12</sub>] and 1-butylpyridinium chloride.

**1-Hexylpyridinium carborane (8).** Synthesis and purification was carried out according to the procedure described for 1-butylpyridinium o-carborane above from Cs[CB<sub>11</sub>H<sub>12</sub>] and 1-hexylpyridinium bromide.

**1-Octylpyridinium carborane (9).** Synthesis and purification was carried out according to the procedure described for 1-butylpyridinium o-carborane above from Cs[CB<sub>11</sub>H<sub>12</sub>] and 1-octylpyridinium bromide.

**1-Butylpyridinium 1-butyl-carborane (10).** The synthesis of n-butyl pyridinium 1-butyl carborane was carried out according to the procedure described for 1-butylpyridinium o-carborane above from Li[1-Butyl-CB<sub>11</sub>H<sub>11</sub>] / dichloromethane solution and 1-butylpyridinium chloride. Starting Li[1-Butyl-CB<sub>11</sub>H<sub>11</sub>] was obtained from treatment of [NMe<sub>3</sub>H][CB<sub>11</sub>H<sub>12</sub>] in THF under a N<sub>2</sub> atmosphere with *n*-BuLi, followed by addition of 1-bromobutane, according to the reported procedure for the ethylation of carborane salts. Reaction completion was confirmed by <sup>11</sup>B NMR spectroscopy. The reaction mixture was evaporated to dryness yielding yellow oil, which was dissolved in dichloromethane/acetone mixture. Insoluble yellowish solid residue (LiBr) was filtered off at this point. The remaining solution was estimated to contain 90% yield of Li[1-Butyl-CB<sub>11</sub>H<sub>11</sub>] based on initial amount of carborane salt and was used directly in the exchange reaction with 1-butylpyridinium chloride.

**1-Hexylpyridinium 1-methyl-carborane (11).** The synthesis and purification of 1-hexylpyridinium 1-methyl carborane was carried out according to the procedure described for 1-butylpyridinium o-carborane above from Cs[1-Me-CB<sub>11</sub>H<sub>11</sub>] and 1-hexylpyridinium bromide. Cs[1-Me-CB<sub>11</sub>H<sub>11</sub>] was obtained from treatment of [NMe<sub>3</sub>H][CB<sub>11</sub>H<sub>12</sub>] in THF under a N<sub>2</sub> atmosphere with *n*-BuLi, followed by addition of CH<sub>3</sub>I according to literature procedure, where the product was

recrystallized from isopropyl alcohol/water mixture saturated with cesium chloride.

### X-ray Structure Determinations.

**1-Butylpyridinium ortho-carborane (1), 1-hexylpyridinium ortho-carborane (2), 1-octylpyridinium ortho-carborane (3).** Crystals were mounted on a Bruker APEX II diffractometer (MoK $\alpha$  radiation) using a nylon loop and cooled to -100°C. Data collection and reduction were performed using Bruker APEX2<sup>24</sup> and SAINT+<sup>25</sup> software packages. An empirical absorption correction was applied with SADABS.<sup>26</sup> Structures were solved by direct methods and refined on F<sup>2</sup> by full matrix least-squares techniques using SHELXTL<sup>27</sup> software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found in a difference Fourier map and refined isotropically. For compounds **2** and **3** numerous recrystallization from a variety of solvents did not yield large crystals of high X-ray quality. Relatively small crystals of 0.4×0.15×0.3 mm (**2**) and 0.4×0.25×0.2 mm (**3**) in size were selected for the study. The data were truncated at ~42° degrees in two theta since no diffraction was observed at higher angles. In the case of compound **2** the doubly bridging H atom between atoms B2 and B3 could not be located. A refinement of a hydrogen atom in a chemically reasonable bridging position between B2 and B3 was not computationally stable. Thus, the structure was refined without this H atom; however the formula corresponds to the proper composition.

In compound **3**, the carbon atoms of the alkyl chain of the pyridinium cations were disordered over two positions each in a 63.8(4):36.2(4) ratio. The disorder was modelled with restraints and constraints.

**1-Ethyl-3-methylimidazolium ortho-carborane (5).** Diffraction data were collected on a Bruker APEX II diffractometer (Mo K $\alpha$  radiation) at -150 °C using a crystal mounted in a nylon loop. The structure was solved by direct methods and standard difference map techniques, refined by full-matrix least-squares procedures on F<sup>2</sup> with SHELXTL.<sup>26</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model, except for methyl group hydrogens which were included in calculated positions and refined with a rotating model. Hydrogen atoms on boron were included in calculated positions and were refined using a riding model, except for the bridging hydrogens which were located and refined. The structure exhibits a whole molecule disorder of the carborane anion; each atom of every disordered atom pair was assigned with an occupancy of 0.5. The disorder was refined with the help of similarity restraints on displacement parameters, and with rigid bond restraints on 1-2 and 1-3 distances and anisotropic displacement parameters.

**1-Butylpyridinium carborane (7).** Diffraction data was collected on a Bruker CCD-1000 diffractometer (MoK $\alpha$ ) radiation using a crystal mounted on a nylon loop and cooled to 100 K. The space group was assigned as P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> on the basis of the systematic absences in the diffraction data and yielded a chemically reasonable and computationally stable

refinement. Most non-hydrogen atoms were found by direct methods, with the remaining non-hydrogen atoms located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were refined with isotropic displacement coefficients.

### Conclusions

In continuation of our studies of ionic liquids utilizing carborane cluster anions, a new family of ortho-carborane based species has been synthesized and spectroscopically and structurally characterized. Both alkyl-pyridinium and di-alkyl imidazolium cations have been employed. It has been shown that the ortho-carborane salts melting points are reduced by between 25-85 °C compared to the corresponding carborane analogues. Ortho-carborane salts are less expensive and easier prepared than other functionalized carboranes, and can be used as analogs to prepare ionic liquids without sacrificing the benefits of these low melting anion classes. Thus, these new materials with ortho-carboranes have a number of advantages compared to their closo-carborane counterparts, both in terms of their physico chemical behavior, and in terms of general synthetic accessibility. The synthetic studies of the derivatized ortho-carborane analogs are planned for the near future, along with electrochemical investigation of the ortho- and closo-carborane-based melts.

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† Electronic Supplementary Information (ESI) is available, including IR spectra and DSC traces at XXXX. The X-ray structures .cif files have been submitted to the Cambridge Data Base under the CCDC reference numbers 649241, 649997, 649998, 651142 and 676575. See DOI: 10.1039/b000000x/

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