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Tunable aryl alkyl ionic liquids with weakly coordinating bulky borate anion

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A B S T R A C T

A series of 1-aryl 3-alkyl imidazolium tetrakis[bis-3,5(trifluoromethyl)phenyl]borate $[BArF_{3,5}]$ ionic liquids were synthesized and characterized. Increasing the alkyl chain length leads to lower melting points even resulting in room temperature ionic liquids (RTILs). In comparison to their corresponding alkyl imidazolium $[BArF_{3,5}]$ counterparts these aryl imidazolium $[BArF_{3,5}]$ ionic liquids show significantly lower melting points.

Introduction

Tetraarylborate anions with many fluoro or fluoromethyl groups on the phenyl part have attracted great interest as weakly coordinating bulky counterions.[1,2] The tetrakis[3,5-bis(trifluoromethyl)phenyl]borate $[BArF_{3,5}]$ anion was first introduced in 1983 by Kobayashi et al. and was originally used for anion catalyzed phase transfer catalysis for diazo-coupling reactions.[3–5] In contrast Brookhart et al. prepared oxonium acid $[H(OEt_2)_2][BArF_{3,5}]$ from $Na[BArF_{3,5}]$ in ether and HCl and used the $[BArF_{3,5}]$ anion as stabilization reagent for electrophilic cationic transition metal complexes,[6] e.g., to stabilize the palladium catalyst in the synthetic copolymerization of olefins and carbon monoxide.[7,8] Also in organometallic chemistry the bulky [BArF] anions have frequently been used.[9–11] It was observed that the generally weakly coordinating anions tetrafluoroborate ($[BF_4]$) or hexafluorophosphate ($[PF_6]$) reacted with highly reactive electrophilic complexes and that abstraction of fluorine from the anion to the cationic complex occurred. By using bulky fluorinated tetraarylborate anions the fluoro transfer onto the metal center could be avoided.[2,9–11]

Weakly coordinating anions recently became more and more important for ionic liquids (ILs) because they show a much lower tendency to coordinate to the cation than the halide counterions.[2] Due to the weaker interaction between the cation and the bulky anion the properties of ILs like melting point, viscosity, high thermal stability, or acidity can be modified.[12] By definition ionic liquids are salts that contain organic cations and inorganic or organic anions and have a melting point below 100 °C. ILs which are even liquid below 25 °C are called room temperature ionic liquids (RTILs).[12] ILs attract interest in a lot of different applications like plating,[13–18] as solvents in organic synthesis or catalysis,[12,19–24] as extracting agents,[25–28] for the dissolution of cellulose,[29–34] or as electrolytes in dye sensitized solar cells.[35–41] In 2006 the first ionic liquids with the $[BArF_{3,5}]$ anion were synthesized based on ammonium, imidazolium, pyridinium, and isochinolinium cations.[42]

These $[BArF_{3,5}]$ ILs were used in the investigation of ion transfer across polarized water/IL interfaces,[42,43] as ionic liquid salt bridges[44,45] that isolate the working from the reference electrode in electrochemistry cells or to prepare poly(IL) functionalized particles[46] where the polymerization is carried out via the functional

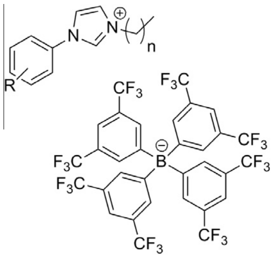

Figure 1. General structure of the investigated aryl alkyl imidazolium $[BArF_{3,5}]$ ILs.

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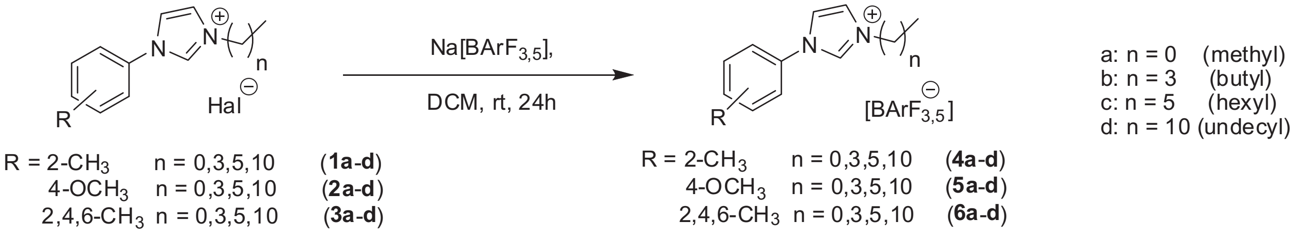

Scheme 1. Synthesis of borate TAAILs by anion metathesis.

group at the cation. Even redox active [BArF$_{3,5}$] ILs containing a ferrocenyl alkyl ammonium cation were synthesized.[47]

We focus on imidazolium based ILs, so-called tunable aryl alkyl ionic liquids (TAAILs) that feature a (substituted) phenyl ring together with an alkyl chain on the other nitrogen atom of the heterocycle.[48–50] Through the aryl ring additional mesomeric and steric effects change the properties of the ionic liquids. Variation of the substituent at the phenyl ring leads to different melting points using the same alkyl chain length and anion depending on the mesomeric or inductive effects of the substituent. Generally, electron donating substituents show lower melting points than electron withdrawing substituents as previously reported.[49] The exchange of the anion also has an influence on the properties of the TAAILs. Coordination of small anions (Br, I) leads to higher melting points compared to the bigger anions ([BF$_4$], [PF$_6$]).[48] Ionic liquids with *N*,*N*-dialkyl imidazolium cations and [BArF$_{3,5}$] anion have been found to exhibit interesting properties. Therefore we investigated the influence of the [BArF$_{3,5}$] anion on different aryl alkyl imidazolium cations by combining the large cations with bulky weakly coordinating anions. In this Letter we report the syntheses and characterization of 1-aryl 3-alkyl imidazolium [BArF$_{3,5}$] ILs. The acronym [Ph$_R$C$_n$Im][BArF$_{3,5}$] describes TAAILs **4a**–**6d** where Ph$_R$ characterizes type and position of the substituent R at the phenyl ring and C$_n$ the length of the alkyl chain at the imidazolium core (Im). The general structure is given in Figure 1.

Results and discussion

The imidazolium halide salts **1a**–**3d** were synthesized from the commercially available anilines using previously described reactions.[48] The aryl imidazoles were accessible via a ring closing reaction using a one-pot procedure with glyoxal, formaldehyde, ammonium chloride, and the respective anilines, followed by a nucleophilic substitution with an alkyl halide. The aryl imidazolium [BArF$_{3,5}$] salts **4a**–**6d** were synthesized by anion metathesis with Na[BArF$_{3,5}$] from the aryl imidazolium halide salts **1a**–**3d** as shown in Scheme 1. After addition of an equimolar amount of Na[BArF$_{3,5}$][51] to the solution of the halide salts **1a**–**3d** in dichloromethane the reaction mixture was stirred at room temperature for 24 h. After removal of the sodium halide salt and solvent, TAAILs **4a**–**6d** were obtained in excellent yields between 88% and 99%.[52] The synthesized TAAILs show no transformation when exposed to air and can be washed with water. They are air and water stable and do not need to be handled or stored in a glovebox. The sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (Na[BArF$_{3,5}$]) was synthesized through a modified route according to Smith et al. using a Grignard reaction.[53] Because of the high and sometimes explosive reactivity of the Grignard reactant the reaction should be handled with care. No problems with the reaction could be observed following the instructions. The azeotropic distillation was carried out with toluene instead of benzene and provided the Na[BArF$_{3,5}$] salt as a colorless solid.

We investigated the influence of the substituent at the aryl ring and the alkyl chain length of the cations in comparison to the influence of the anion on the melting points of the TAAILs. We used different alkyl chain lengths (small, medium, and long) and three different electron donating substituents (2-Me, 4-OMe, 2,4,6-Me [Mes]) which have a different influence of the electron density of the phenyl ring. The methyl and mesityl groups exhibit an +I effect that donates electrons through the sigma bonds into the ring, while mesityl also has an additional steric influence. The +M effect of the methoxy group results in an electron donation through the π-system. To visualize the electronic effects we calculated the electrostatic surface potential (ESP)[54] of the substituted 1-aryl 3-butyl imidazolium cations **4b**, **5b,** and **6b** as shown in Figure 2. To compare the ESP's of the imidazolium cations with different substituents (2-Me, 4-OMe, Mes) we kept the chain length (C$_4$H$_9$) constant. Cations carry a positive charge all over the molecule, the ESP representations differentiate between a more positive potential at the imidazolium core (blue) and a negative potential at the end of the alkyl chain and/or at the functional groups (red). Substituents in *para* position at the aryl ring, especially OMe, show a more negative potential than the methyl group at the *ortho* position.

TAAILs with mesityl substituents **6a**–**d** lead to higher melting points due to the steric influence of the methyl groups at the phenyl ring (Table 1). If there are two methyl groups in *ortho* position to the imidazolium ring the planes of the phenyl ring and of the imidazolium ring[55] are orthogonal to each other as could be demonstrated by quantum chemical calculations (Fig. 2). [BArF$_{3,5}$] ILs **4a**–**5d** with mono substituted 2-Me and 4-OMe show lower melting points than the sterically hindered mesityl [BArF$_{3,5}$] ILs, certainly due to minor steric influences between the aryl ring and the imidazolium core.

The melting points of the imidazolium halide salts with 2-Me **1a**–**d** and 4-OMe **2a**–**d** show a minimum for the medium sized hexyl chain length whereas for the mesityl imidazolium halide salts **3a**–**d** the melting points decrease by increasing alkyl chain length.

By exchanging the halide anion with [BArF$_{3,5}$] the behavior of the methyl imidazolium ILs **4a**–**d** changed, leading to generally lower melting points with increasing chain length as can also be

Table 1
Melting points of 1-aryl 3-alkyl imidazolium [BArF$_{3,5}$] ionic liquids **4a**–**6d** and 1-aryl 3-alkyl-imidazolium halide salts **1a**–**3d**

Anion	R	Me (C$_1$)	Bu (C$_4$)	Hex (C$_6$)	Undec (C$_{11}$)
[BArF$_{3,5}$]	2-Me	71	70	41	−27[d]
	4-OMe	83	44	68	−23[d]
	2,4,6-Me	102	86	70	−21[d]
Halide	2-Me	119[a]	61[b]	*l*[b,c]	47[b]
	4-OMe	127[a]	56[a]	*l*[a,c]	46[b]
	2,4,6-Me	160[a]	90[a]	68[a]	60[b]

[a] Imidazolium salts with iodide counterions.

[b] Imidazolium salts with bromide counterions.

[c] Ionic liquids are liquid (*l*) at room temperature.

[d] Glass transition temperature upon cooling; all melting points are given in °C.

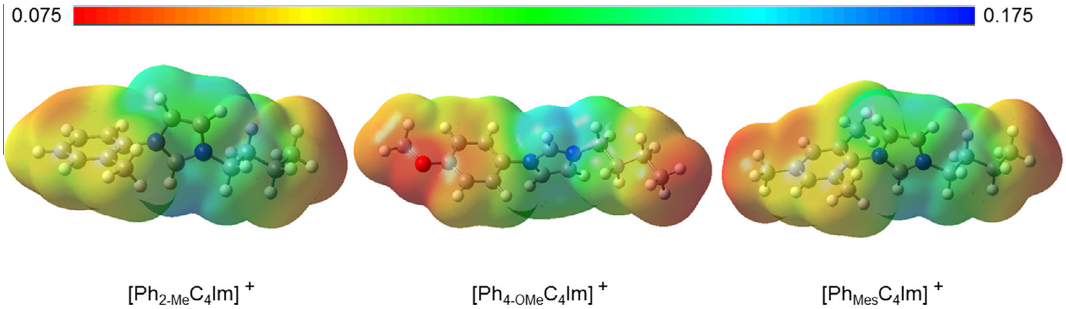

Figure 2. Electrostatic surface potential (ESP) of 1-aryl 3-butyl imidazolium cations **4b**, **5b,** and **6b**.

observed for the mesityl imidazolium $[BArF_{3,5}]$ salts **6a–d**. Only for the methoxy imidazolium ILs **5a–d** no dependence from the chain length could be determined. The free rotation of the –OMe group could favor different kinetic hindrance leading to alternating melting points with increasing alkyl chain length. At long chain lengths the influence of the substituent at the aryl ring becomes less important.

Apart from the 1-mesityl 3-methyl imidazolium $[BArF_{3,5}]$ IL **6a** all other synthesized borate salts fulfill the formal definition and are ionic liquids, the TAAILs with *n*-undecyl chain are even RTILs but appear to be highly viscous liquids. In DSC measurements TAAILs **4d**, **5d,** and **6d** show glass transition temperatures between −27 and −21 °C. Around −70 to −50 °C a strong exothermic effect could be observed due to recrystallization/post-crystallization effects. Upon heating the formation of a melt around −24 to −17 °C could be detected. The reason for the relatively high melting points of the TAAILs can be explained by the interaction between the CF_3 group and the phenyl ring of the borate anion which benefits an easier crystallization. In comparison to the alkyl imidazolium $[BArF_{3,5}]$ ILs[42] derived from methylimidazole (MIM), they show surprisingly lower melting points for the same chain lengths (Table 2). For example the $[C_{10}MIM]$ $[BArF_{3,5}]$ or $[C_{12}MIM]$ $[BArF_{3,5}]$ ILs have melting points around 70–85 °C whereas the $[Ph_{Mes}C_{11}Im]$ $[BArF_{3,5}]$ IL **6d** is liquid at room temperature causing a temperature difference of over 80 K. This can be traced back to the expansion of the π-system as it was also observed for pyridinium versus isochinolinium $[BArF_{3,5}]$ ILs.[42] The additional phenyl ring in combination with the $[BArF_{3,5}]$ anion leads to lower melting points. This could also be confirmed for mesityl substituted $[Ph_{Mes}C_nIm]$ $[BArF_{3,5}]$ ILs **6a–6d** in comparison to $[Ph_{Mes}C_nIm]$ $[BF_4]$ ILs. The sterically more demanding $[BArF_{3,5}]$ anion leads to lower melting points for mesityl ILs with C_1–C_6 alkyl chain lengths compared to the smaller $[BF_4]$ anion, whereas for the long *n*-undecyl chain both mesityl substituted $[Ph_{Mes}C_nIm]$ ILs are liquid at room temperature. For different counterions it could be shown that the behavior of ionic liquids with mesityl substituents is mostly predictable given that the melting points decrease with increasing chain length. This could be shown for halides, $[BF_4]$, $[PF_6]$[48] and now also for the $[BArF_{3,5}]$ anion. The only exception so far are $[Ph_{Mes}C_nIm]$ ILs with $[NTf_2]$ counterion[48] showing melting points near room temperature independent from the alkyl chain length (Tables 1 and 2). This behavior was only observed for the mesityl substituted $[Ph_{Mes}C_nIm]$ ILs, other substituents show a different behavior depending on the anion used as was presented above for the methyl and methoxy substituents.

Table 2
Melting points (mp) of alkyl imidazolium $[BArF_{3,5}]$[42] and aryl imidazolium $[NTf_2]$/$[BF_4]$ ILs[48]

Alkyl imidazolium ILs	Mp in °C	Aryl imidazolium ILs	Mp in °C
$[EMIM]$ $[BArF_{3,5}]$	134	$[Ph_{Mes}C_1Im]$ $[NTf_2]$	71
$[BMIM]$ $[BArF_{3,5}]$	104	$[Ph_{Mes}C_4Im]$ $[NTf_2]$	26
$[C_6MIM]$ $[BArF_{3,5}]$	82	$[Ph_{Mes}C_6Im]$ $[NTf_2]$	40
$[C_{10}MIM]$ $[BArF_{3,5}]$	85	$[Ph_{Mes}C_{11}Im]$ $[NTf_2]$	0
$[C_{12}MIM]$ $[BArF_{3,5}]$	72	$[Ph_{Mes}C_1Im]$ $[BF_4]$	137
$[C_{12}Py]$ $[BArF_{3,5}]$	64	$[Ph_{Mes}C_4Im]$ $[BF_4]$	92
$[C_{12}Iq]$ $[BArF_{3,5}]$	72	$[Ph_{Mes}C_6Im]$ $[BF_4]$	74
		$[Ph_{Mes}C_{11}Im]$ $[BF_4]$	−49

All TAAILs proved to be stable under the applied conditions in TGA experiments (rt-850 °C, heating rate 5 K min^{-1}, air) up to temperatures between 308 and 373 °C. All salts show multiple degradation processes with at least four to six degradation steps with the exception of **5c** which only showed three steps with a major loss of 78 mass % in the first decomposition step. Details of the TGA experiments are given in the Supporting information.

It could be shown that the anion has a considerable influence on the properties of the ionic liquids but also the substituent or alkyl chain length play an important role in varying the melting points of the TAAILs.

Conclusion

In conclusion a series of 1-aryl 3-alkyl imidazolium $[BarF_{3,5}]$ ionic liquids were synthesized. These air and water stable TAAILs show relatively low melting points in comparison to the large anions and cations used. The melting points can be lowered by increasing the alkyl chain length even leading to RTILs for the long *n*-undecyl chain length. The aryl imidazolium $[BarF_{3,5}]$ ILs show significantly lower melting points than their alkyl imidazolium $[BArF_{3,5}]$ ionic liquid counterparts and have decomposition temperatures between 308 and 373 °C. Electrostatic surface potentials for the 1-aryl 3-butyl imidazolium cations were calculated to gain insight into the electron density distribution.

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Supplementary data

Supplementary data (experimental and characterization data, ^1H, ^{13}C, and ^{19}F NMR chemical shift values, elemental analyses, DSC, and TGA data) for compounds **4a–6d** are provided together with the details of the quantum chemical calculations) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2016.06.082.

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51. 1 equiv imidazolium iodide salt was dissolved in 14 ml dichloromethane and 1 equiv Na[BArF$_{3,5}$] was added. After stirring the reaction mixture at room temperature for 24 h the precipitate was filtered off and the remaining solvent was removed. The product was dried in vacuo.
52. Characterization data of selected compounds: compound **4a**: mp 71 °C, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.07 (s, 1H, NCHN), 7.69 (s, 8H, B-Ar-H), 7.51 (s, 5H, Ar-H + B-Ar-H), 7.38 (d, J = 8.0 Hz, 1H, Ar-H), 7.31 (t, J = 8.0 Hz, 1H, Ar-H), 7.25 (s, 1H, NCHCHN), 7.13 (s, 1H, NCHCHN), 7.09 (d, J = 7.5 Hz, 1H, Ar-H), 3.80 (s, 3H, NCH_3), 2.07 (s, 3H, *o*-CH_3) ppm, ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.7 (q, J_B = 50 Hz, 4C$_i$-B), 134.7 (s, 8B-Ar-C), 134.3 (NCHN), 132.8 (C$_i$-*o*-CH_3), 132.5 (Ar-C), 132.4 (C$_i$-N), 132.4 (Ar-C), 129.0 (qq, J_F = 31 Hz, J_B = 2.4 Hz, 8C$_i$-CF_3), 128.2 (Ar-C), 125.5 (Ar-C), 124.7 (NCHCHN), 124.5 (q, J_F = 272 Hz, CF_3), 123.7 (NCHCHN), 117.5 (m, 4B-Ar-C), 36.6 (NCH_3), 16.8 (*o*-CH_3) ppm, ^{19}F NMR (283 MHz, $CDCl_3$): δ = −63.0 (CF_3) ppm, Elemental analysis for $C_{43}H_{25}N_2BF_{24}$: calcd C, 49.83; H, 2.43; N, 2.70, found C, 49.79; H, 2.25; N, 2.71. Compound **5b**: mp 44 °C, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.19 (s, 1H, NCHN), 7.69 (s, 8H, B-Ar-H), 7.51 (s, 4H, B-Ar-H), 7.28 (t, J = 1.8 Hz, 1H, NCHCHN), 7.15 (d, J = 9.3 Hz, 2H, Ar-H), 7.13 (t, J = 1.9 Hz, 1H, NCHCHN), 6.99 (d, J = 9.1 Hz, 2H, Ar-H), 4.05 (t, J = 7.3 Hz, 2H, NCH_2), 3.82 (s, 3H, *p*-OCH_3), 1.82 (m, 2H, NCH_2CH_2), 1.32 (m, 2H, CH_2CH_3), 0.91 (t, J = 7.2 Hz, 3H, CH_2CH_3) ppm, ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 162.0 (C$_i$-*p*-OCH_3), 161.6 (q, J_B = 50 Hz, 4C$_i$-B), 134.7 (s, 8B-Ar-C), 131.8 (NCHN), 129.0 (qq, J_F = 31 Hz, J_B = 2.8 Hz, 8C$_i$-CF_3), 126.0 (C$_i$-N), 124.5 (q, J_F = 272 Hz, CF_3), 123.7 (2Ar-C), 123.0 (NCHCHN), 122.7 (NCHCHN), 117.5 (m, 4B-Ar-C), 116.0 (2Ar-C), 55.8 (*p*-OCH_3), 50.8 (NCH_2) 31.6 (NCH_2CH_2), 19.3 (CH_2CH_3), 12.9 (CH_2CH_3) ppm, ^{19}F NMR (283 MHz, $CDCl_3$): δ = -63.0 (CF_3) ppm, Elemental analysis for $C_{46}H_{31}N_2OBF_{24}$: calcd C, 50.48; H, 2.85; N, 2.56, found C, 50.14; H, 2.75; N, 2.82. Compound **6d**: mp liquid at rt, ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.43 (s, 1H, NCHN), 8.09 (s, 1H, NCHCHN), 7.93 (s, 1H, NCHCHN), 7.62 (s, 12H, B-Ar-H), 7.10 (s, 2H, Ar-H), 4.26 (t, J = 7.0 Hz, 2H, NCH_2), 2.28 (s, 3H, *p*-CH_3), 1.98 (s, 6H, *o*-CH_3), 1.87 (m, 2H, NCH_2CH_2), 1.15 (m, 16H, alkyl-CH_2), 0.75 (t, J = 6.4 Hz, 3H, CH_2CH_3) ppm, ^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 161.0 (q, J_B = 50 Hz, 4C$_i$-B), 140.2 (C$_i$-*p*-CH_3), 137.2 (NCHN), 134.2 (2C$_i$-*o*-CH_3), 134.0 (s, 8B-Ar-C), 131.1 (C$_i$-N), 129.2 (2Ar-C), 128.4 (qq, J_F = 32 Hz, J_B = 2.8 Hz, 8C$_i$-CF_3), 124.0 (q, J_F = 272 Hz, CF_3), 124.0 (NCHCHN), 123.2 (NCHCHN), 117.5 (m, 4B-Ar-C), 49.3 (NCH_2), 31.2 (NCH_2CH_2), 29.0, 28.8, 28.8, 28.7, 28.6, 28.2, 25.3 (alkyl-CH_2), 21.9 (CH_2CH_3), 20.4 (*p*-CH_3), 16.7 (2*o*-CH_3), 13.6 (CH_2CH_3) ppm, ^{19}F NMR (283 MHz, DMSO-d_6): δ = −62.6 (CF_3) ppm, Elemental analysis for $C_{55}H_{49}N_2BF_{24}$: calcd C, 54.83; H, 4.10; N, 2.33, found C, 54.85; H, 4.00; N, 2.52.
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54. All calculations were performed with Gaussian03 using the density functional/Hartree–Fock hybrid model Becke3LYP and the split valence triple-z (TZ) basis set 6-311++G(d,p). No symmetry or internal coordinate constraints were applied during optimizations. Details and references are given in the Supporting information.
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