Synthesis, Crystal Structures and Electrical Conductivities of the Ionic Liquid Compounds Butyldimethylimidazolium Tetrafluoroborate, Hexafluorophosphate and Hexafluoroantimonate

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The crystal structures of three very low-melting ionic liquid (IL) salts containing the 1-butyl-2,3-dimethylimidazolium cation and the fluoro anions BF_4^-, PF_6^- and SbF_6^- are reported. These are considered model compounds for ambient temperature ionic liquids, which are currently being explored as solvents for various types of synthetic reactions. All three compounds adopt significantly different structures in the solid state, highlighting the influence of counterion size in a series comprising a common cation. The crystal structures are discussed with respect to the possible existence of polar and non-polar domains, which are considered to be involved with the solvation of polar and non-polar substrates. The melting points of all three compounds are within the range 40–45 °C. A comparative measurement of conductivities of the molten salts in the vicinity of 20–50 °C has been made, including the new IL 1-allyl-2,3-dimethylimidazolium tetrafluoroborate and the widely applied 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF$_4$).

Introduction

The solvent properties of ionic liquids (IL) have attracted a lot of interest with respect to applications as reaction media for both polar and non-polar solvates.[1a−1f] Homogeneous catalysis using organometallic or coordination compound catalysts is one prominent example where ILs based on 1,3-substituted imidazolium cations in particular have been employed, not only because of their non-volatility, but also due to their variability with respect to the possible adjustment of solvent properties.[1g] The degree of polarity can be varied by adapting the length of the 1-alkyl chain and the counterion to the desired reaction conditions. The investigation of structural properties in the liquid state requires considerable experimental effort (as for example in X-ray absorption spectroscopy[2]), and little information can be gained if heavy elements are missing. Model compounds that are crystalline at ambient temperature have therefore been used for structural investigations. It has been known for some time that salts C_nMeImX incorporating a common anion X^- will usually exhibit low melting points with medium-length alkyl chains ($n = 4-9$),[3] as in these cases crystal packing forces are not strong enough to raise melting points above 300 K. Lower chain-length salts are often readily crystallized, and structural studies have mainly focused on 1-ethyl-3-methylimidazolium (EMIM) salts with various counterions. The EMIM cation, which is asymmetric but rather small, is readily crystallized not only with high charge-density anions such as chloride, but even with hexafluorophosphate, a typical counterion for the liquid-state salts. The crystal structure of EMIMPF$_6$ (melting point 331 K) has been reported by Fuller et al.[4] EMIMBF$_4$, on the other hand, which is liquid at ambient temperature, may serve as an example for the influence of counterion size, since the higher charge density of BF_4^- vs. PF_6^- is expected to increase the Coulombic part of the lattice energy and therefore the melting point. An example of a long chain-length salt has been reported by Seddon et al. who solved the crystal structure of C_{12}MIMPF$_6$.[5]

Long-chain IL salts have attracted some interest due to their liquid crystalline (LC) properties. The origin for these can be found in the formation of domains, "Coulombic" layers where the ionic head-groups interact with the counterions, and "van der Waals" layers built from (anti)parallel stacking of the alkyl chains. Hexafluorophosphate salts with cations up to C_{20}MIM have been investigated by differential thermal analysis (DTA) and show one or more LC transitions. Melting to isotropic liquids occurs at rather high temperatures (>100 °C) .[5] The phase behavior of long chain-length imidazolium and pyridinium chlorides, tetrachlorocobaltates and tetrachloronickelates showing LC properties has also been reported.[6]

Larsen et al. have reported the synthesis and crystal structures of several EMIM, ethyldimethylIM, octylMIM and BDMIM alkylboranes, and the authors rationalized trends in melting points according to the packing efficiency of the asymmetrically substituted cation.[7] More recently, Dupont et al. investigated C−H-π interactions in the solid

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state and in solution of BMIM tetraphenylborate,[8] and van den Broeke et al. introduced substituents at the phenyl rings of this salt and reported their influence on the structural and physical properties.[9]

A thorough investigation into the electrochemical and rheological properties of various substituted imidazolium/anion combinations by Bonhôte et al.[10] revealed some general trends for melting/glass transition points. One of the most notable findings in this respect was that methylation at the 2-position of the heteroaromatic ring generally raised melting points by more than 50 K. This was observed even with anions which were expected to be strong hydrogen-bond acceptors for the "acidic" hydrogen at C(2) and for which the opposite effect might have been expected. The influence of ion size and viscosity of IL melts on their electric conductivity is also reported by these authors and was more recently investigated by McEwen et al.[11] Increasing the volume of either cation or anion has generally been found to result in lower absolute values and higher activation energies for conductivity.

The present work is focused on the influence of counterion size on the solid-state structures and liquid-state mobilities of IL compounds comprising the medium chain-length cation 1-butyl-2,3-dimethylimidazolium (BDMIM).

Results and Discussion

All IL compounds reported in this work contain the cation 1-butyl-2,3-dimethylimidazolium (BDMIM). The cation adopts slightly different conformations in the different compounds with respect to the butyl chain, which is kinked from the plane of the imidazolium ring in all cases studied here.

The two crystallographically independent BF_4^- ions in the structure of BDMIMBF$_4$ **I** were both found to be disordered. The type of disorder was investigated by means of three-dimensional Fourier maps, and is depicted in Figure 1. For $BF_4^-(1)$, the two different orientations are related by a (non-crystallographic) mirror plane and for $BF_4^-(2)$ by a (non-crystallographic) threefold axis, which corresponds to the B(2)−F(9) bond. For both BF_4^- sites, the type of disorder appears to be maintained at 298 K as suggested by the corresponding Fourier maps. Disorder is not observed with the cations, thus apparent disorder originating from the use of twinned data can be excluded.

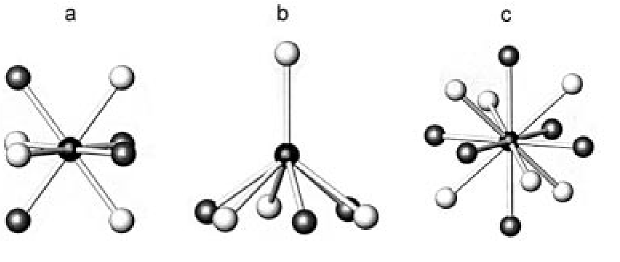

Figure 1. Disorder observed for the BF_4^- ions in BDMIMBF$_4$ at 213 K (a, b) and for the PF_6^- ions at 298 K in BDMIM PF$_6$ (c), as observed from difference Fourier syntheses; the two disorder components are shown with different shadings

The title compound **I** is the first IL tetrafluoroborate to be structurally characterized. The structure can be described as being composed of two different types of double layers extending in the crystallographic (0 1 0) plane (Figure 2). The anionic parts of these two layers are very similar, showing the tetrahedral ions in two different orientations with shortest center-to-center distances of 690 pm within the layers. The cationic part composed of the two crystallographically independent imidazolium cations is, however, markedly different for the two double layers, leading to different environments for the BF_4^- sites. The butyl chains extend roughly in the direction of the *b* axis, away from the charged centers of the layers. Pairwise shortest contacts of 402 and 409 pm between the outer methyl/methylene groups of the butyl chain are found along the *b* axis, which roughly correspond to the sum of the van der Waals radii.

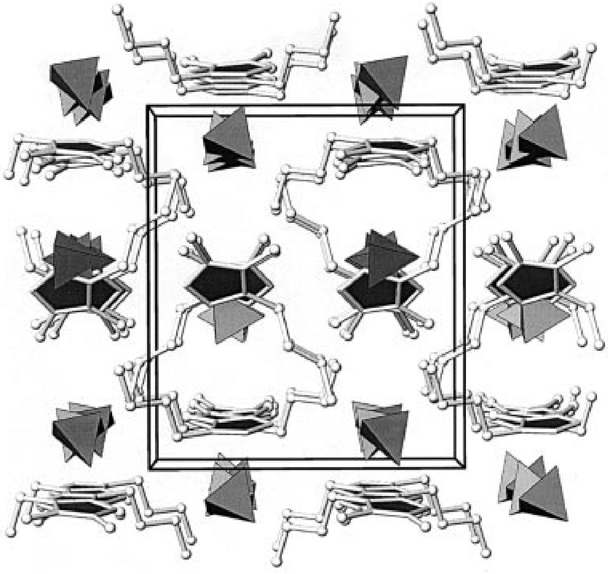

Figure 2. View of the crystal structure of BDMIMBF$_4$ along the crystallographic *c*-axis; BF_4^- ions are shown as grey tetrahedra; all hydrogen atoms of the imidazolium cation have been omitted for clarity; anions and cations in the central double layer are crystallographically equivalent, a second set of crystallographically equivalent molecules can be distinguished above and below

Pronounced anisotropy as found in **I** has been observed in crystal structures of ionic liquid salts before. Relatively high-melting EMIM halides exhibit hydrogen-bonded 3-D networks.[12] The formation of layered structures recently reported for BMIMCl is, however, promoted by strong hydrogen bonds between cation and anion.[13,14] Intermolecular H···F interactions are considered to be very weak in compounds of the type reported here as indicated by the crystallographic disorder observed for BF_4^- and PF_6^-. This issue is discussed further below. Consequently, arrangements of the BDMIM cation and the low charge-density fluoro anions result from a balance of weak Coulombic and dispersive interactions, whereas hydrogen bonding in IL chlorides is always strong, as indicated by their much higher melting points. Compound **I** exhibits channels between the cationic layers where the anions are accommodated, similar to those observed in BMIMCl. In the former case, the "structure-directing principle" (close packing of the molecules maximizing non-directional interactions) leads to flat layers which, on the other hand, are corrugated in the BMIMCl structure, driven by maximizing the strongly directional C−H···Cl H-bonds.

The coordination environments of the BF_4^- ions are depicted in Figure 3. Closest distances between fluoride and C/N atoms of the ring are summarized in Table 1. Carbon/nitrogen-fluorine distances of 300−350 pm roughly correspond to the sum of the van der Waals radii $r_F + r_{C/N}$ (147, 175 and 155 pm respectively[15,16]). Four of these contacts are found for $BF_4^-(1)$, whereas there are only three, slightly larger ones for $BF_4^-(2)$. This is probably the reason why the disorder found for $BF_4(2)$ is more pronounced than for $BF_4(1)$.

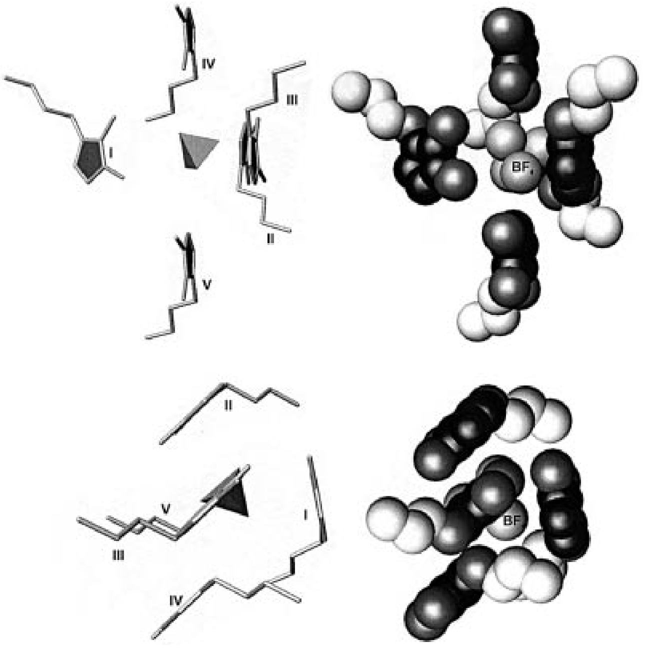

Figure 3. Coordination environments of the BF_4^- ions in BDMIMBF_4; cations are numbered sequentially with increasing center-to-center distances to the BF_4^- ion; the closest contacts between ring atoms and BF_4^- fluorides are summarized in Table 1; in the space-filling models, atoms are shown with different shadings, according to parts of the molecule of increasing polarity (ring C,N atoms as black spheres, methyl/methylene directly bound to the ring as grey spheres, the three outer butyl carbons as white spheres)

Table 1. Closest contacts (pm) between EF_x^- (E = B, P, Sb; x = 4, 6) fluorines and ring atoms of the cations in BDMIMEF_x, as shown for the BF_4^- ions in Figure 3

	$BF_4(1)$	$BF_4(2)$	PF_6	SbF_6
I	308 (C−F)	348 (N−F)	310 (C−F)	345 (C−F)
II	305 (C−F)	318 (C−F)	319 (N−F)	325 (C−F)
III	315 (C−F)	407 (N−F)	323 (C−F)	356 (C−F)
IV	329 (C−F)	334 (C−F)	356 (C−F)	342 (C−F)
V	454 (C−F)	423 (C−F)	451 (C−F)	447 (N−F)
VI			446 (C−F)	475 (N−F)

Due to the pronounced asymmetry of the cation, a naive analysis of intermolecular distances is probably not justified here. None of the C(4)−H, C(5)−H ring hydrogen atoms, however, shows an orientation which would suggest hydrogen bonding to the fluorines of BF_4^-.

The crystals of BDMIM PF_6 **II** were obtained from the melt as described in the Exp. Sect. They were typically 0.5−1 mm in diameter; twinning was never observed. The compound adopts an acentric monoclinic structure in space group *Cc* with four formula units per unit cell. The hexafluorophosphate ion is entirely ordered at 213 K while disorder, as in the case of the BF_4^- compound, is observed only at 298 K. The two orientations of the disordered ion are related to each other by a 60° rotation around the threefold axis of the octahedron (Figure 1). The crystal structure of **II** is composed of alternating layers of cations and anions extending in the crystallographic (0 1 1) plane, with all imidazolium ring planes coplanar (roughly perpendicular to the *a* axis) and all butyl chains aligned in one direction, roughly parallel to the *a* axis, as can be seen from Figure 4. As there are only translational symmetry elements (a single glide plane and centering translations), the structure is noncentrosymmetric and no double layers as in the case of **I** are formed. Shortest contacts of 432 pm between the butyl chains are found among adjacent rows of cations in direction of the *c* axis. The hexafluorophosphate ion is surrounded by six cations with the centers forming a distorted trigonal prism.

The PF_6^- group with its surrounding imidazolium ions is depicted in Figure 5. Cations **I**−**IV** all make contacts to fluorine atoms within distances of 310 to 356 pm, summarized in Table 1. The contacts with the two remaining cations are considerably longer (451 and 446 pm). As in the structure of **I**, the butyl chains are kinked from the ring planes, and a closer approach of cations and anions along the *a*

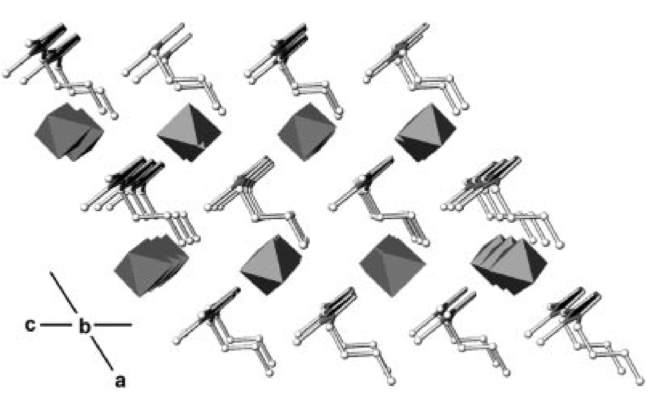

Figure 4. View of the crystal structure of BDMIMPF_6 along the crystallographic *b*-axis; PF_6^- ions are shown as grey octahedra; all hydrogen atoms of the imidazolium ring have been omitted for clarity

axis is obviously restricted by the butyl chains. The distance between the terminal methyl carbon and the ring plane of the adjacent layer in the direction of the *a* axis is only 355 pm such that a tighter surrounding of the anion is prevented. Although C−H···F contacts involving the ring hydrogens can be found which adopt a close to linear arrangement, generally considered a prerequisite for hydrogen bonding, the distances involved are rather long: C−F distances of 337 and 355 pm and H···F distances of 248 and 267 pm, with both angles being virtually 160°. However, these distances are within the sum of the van der Waals radii for H and F (125 + 147 pm), and weak hydrogen bonding could well be present according to the definition of Taylor and Kennard.[16] Very similar H···F distances have also been found in the structure of EMIMPF_6,[4] but hydrogen bonding was suggested to be extremely weak or absent, due to the absence of red shifts of the ν_{CH} bands in the IR spectrum. Evidence from the present structure is entirely consistent with this observation. Comparing the structure of **II** with that of EMIMPF_6 is instructive. Whereas the former compound exhibits a pronounced layer structure, the latter shows cations in a pairwise arrangement and a much less discerned hydrophobic region resulting from the shorter ethyl chains. Although the acentric cation arrangement in **II** is not expected to exist in the melt, the greater tendency to separate into non-polar (very often referred to as hydrophobic, although this is not adequate in pure ILs) and ionic domains as compared to EMIMPF_6 is obvious.

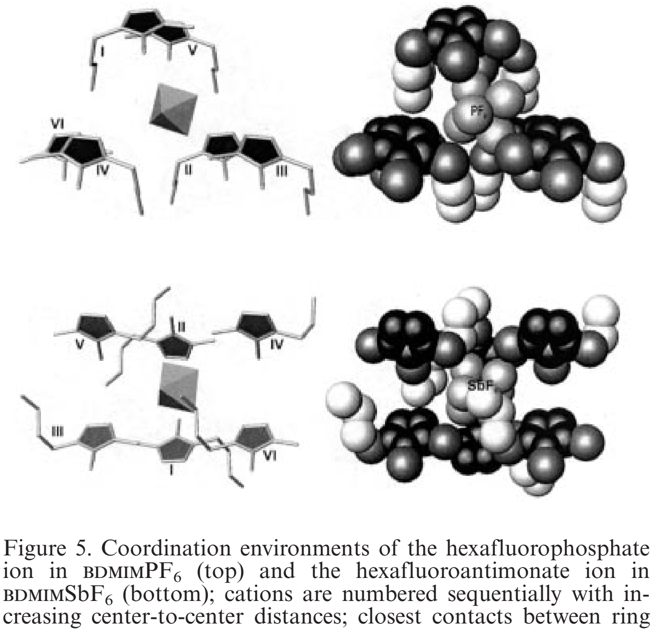

Figure 5. Coordination environments of the hexafluorophosphate ion in BDMIMPF_6 (top) and the hexafluoroantimonate ion in BDMIMSbF_6 (bottom); cations are numbered sequentially with increasing center-to-center distances; closest contacts between ring atoms are summarized in Table 1; shading of the ring atoms is analogous to the scheme adopted in Figure 3

No disorder is observed for the hexafluoroantimonate ion in the structure of BDMIMSbF_6 **III** even at ambient temperature. The crystal lattice is again distinctly different from the two previous compounds; a view of the structure along the *a* axis is depicted in Figure 6. There is no more orientational preference in the cation sub-lattice. The imidazolium moieties are in fact oriented with ring planes parallel to the (0 1 1), (0 $\bar{1}$ $\bar{1}$), (0 1 $\bar{1}$) and (0 $\bar{1}$ 1) crystallographic planes. The packing of cations and anions can be described as being reminiscent of the NiAs structure type, with the SbF_6^- octahedra surrounded by six nearest neighbor cations in a distorted trigonal prismatic coordination, and the cations being surrounded by six SbF_6^- ions in a distorted octahedral arrangement. The NiAs structure type may of course only serve as a schematic rationale for the true structure, as can be judged from large differences in the center-to-center distances between cations and anions. There are no short contacts between carbon atoms of the butyl chains, and thus short-range repulsive interactions between the cations are further diminished with respect to the hexafluorophosphate compound.

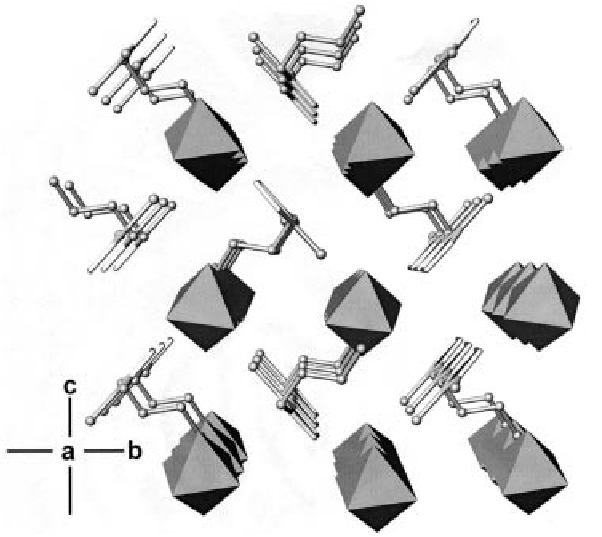

Figure 6. View of the structure of BDMIMSbF_6 along the crystallographic *a*-axis; SbF_6-ions are shown as grey octahedra; all hydrogen atoms of the imidazolium cation have been omitted for clarity; the SbF_6^- ions make a close to hexagonal packing with the imidazolium ions located in the "octahedral holes"

The existence of polar and non-polar domains in liquid BMIMBF_4 has been proposed from diffusion studies of ions and neutral molecules by Schröder et al.[17] The accelerated diffusion of $Fe(CN)_6^{4-}$ as well as the diffusion of neutral molecules was attributed to formation of a "nanostructure" of polar (ionic) and non-polar domains which became even more pronounced upon the addition of water to the IL phase. The formation of polar and non-polar domains, as found in the long chain-length IL compounds, can be recognized, at least to some extent, in the double-layer structure of **I** and the structure of **II**, whereas no such domains can be distinguished in the structure of **III**. This is due to the difference in packing modes, determined by anion size in the present series. The influence of anion size in these non hydrogen-bonded IL compounds can be rationalized by comparing the two compounds **II** and **III** with the BDMIM carborane compounds reported by Larsen et al. Packing in the structure of **I** is obviously determined by the arrangement in the cation sub-lattice, the influence of which prevails for the structure of **II**. By further increasing the size of the anion as in **III**, vacancies in the anion sub-lattice expand such as to accommodate the cations in a way that cation−cation contacts are no longer observed, despite their asymmetry. With even larger anions such as the carboranes, packing will be entirely dominated by the anions, such that close-packing of cations is prevented and disorder of the latter becomes frequent.

The presence of hydrogen bonding in solid IL salts incorporating weakly coordinating anions has been a cause for debate for some time because shifts of the corresponding IR bands indicative of H-bonding are weak or absent within experimental error. Whereas there is no doubt as to the existence of strong H-bonding in IL halides and weaker H-bonding in EMIMNO_3,[18] for example, it has been considered absent in haloaluminates,[19] and the results for anions like BF_4^- and PF_6^- are inconclusive. The closest H···F bond in EMIMPF_6 is reported as being 256 pm, clearly below the sum of the van der Waals radii. Several investigations of liquid EMIMBF_4, BMIMBF_4 and BMIMPF_6 [20−22] by NMR spectroscopy (including intermolecular ^{1}H-^{19}F NOE) established a close proximity between the hydrogens of the heteroaromatic core and the fluorines of the anion. The hydrogen-bonding interaction can be extended to include rather weak contacts as was recently shown by Seddon and co-workers for the C−H···Cl bond.[23] The absence of *significant* hydrogen bonding in all compounds of the present series is supported by infrared spectroscopy. Although the charge density of the anion varies considerably in the series, the wavenumbers of the two principal absorption bands of the aromatic hydrogens remain virtually constant. The three compounds exhibit a common pattern in this region, with a strong band at 3156 cm^{-1} and an associated weak band at 3187 cm^{-1}. Further support of this interpretation is lent by the low melting points of the present compounds as compared to truly H-bonded structures.[24]

The molecular volumes of the fluoro-anions EF_x^- have been calculated assuming a spherical geometry. Volumes are calculated as $V = 4/3\pi(d_{EF} + r_F)^3$, where d_{EF} is the interatomic distance and r_F is the "packing radius" of fluorine, as derived by Gavezzotti.[25] The bias introduced by this arbitrary choice of atomic radii is considered to be tolerable, as comparison is made only between the members of the present series of compounds. The molecular volumes of the BDMIM cation in the crystal were then calculated from the difference of the cell volumes and the respective anion volumes according to Equation (1).

$$V_{BDMIM} = V_{cell}/Z - V_{EF_x^-} \qquad (1)$$

The molecular volumes V_{BDMIM} are found to be very similar, namely 230, 225 and 232 Å^3 for **I**, **II** and **III** respectively. This suggests a similar "packing coefficient" k for the three structures, as defined in Equation (2).[26]

$$k = ZV_{mol}/V_{cell} \qquad (2)$$

All three structures can therefore be regarded as being fairly close-packed, a notion that is further supported by the absence of cation disorder, contrary to the carboranes reported by Larsen et al., where disorder of the cations was observed in most of the crystal structures.

The melting points and the temperature-dependent electrical conductivities of the melts were measured for compounds **I**−**III**. The melting points of the three BDMIM salts are found within a narrow range around 315 K, about 100 K above the glass-transition points reported for the respective BMIM compounds (Table 2).

Table 2. Melting points (K) of BDMIMEF_x salts determined in this work as compared to those of respective EMIM salts taken from ref.[4] and glass transition (T_g) points of the respective BMIM salts taken from ref.[20]

	BF_4^-	PF_6^-	SbF_6^-
BDMIM	312.8(5)	313.0(5)	317.5(5)
EMIM	288	331	
BMIM	192 (T_g)	212 (T_g)	

The conductivities of the low-melting IL salts BDMIMX (X = BF_4^-, PF_6^-, SbF_6^-), some of which have been reported previously,[27] were measured using a conventional conductivity cell as described below. In order to elucidate the influence of viscosity and the substitution pattern at the imidazolium ring, conductivities of BMIMBF_4 and the new ionic liquid 1-allyl-2,3-dimethylimidazolium tetrafluoroborate (ADMIMBF_4) were measured as well. The temperatures were chosen such that a range of about 10 K above and below the respective melting points was covered, except for the latter two compounds which are far above their glass-transition points at ambient temperature. Conductivities were found to follow linear ln(σ) vs. $1/T$ behavior in the narrow temperature range covered here, whereas the Vogel−Tamman−Fulcher equation has been previously found to describe the temperature-dependent conductivity of several ionic liquids in a wider temperature range.[11] The conductivities are depicted in Figure 7 and summarized in Table 3.

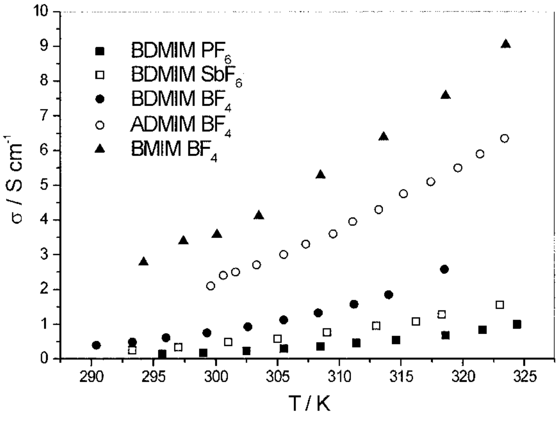

Figure 7. Plot of conductivity vs. temperature of the molten salts; the BDMIM compounds of BF_4^- and PF_6^- and of SbF_6^- are in the supercooled state below 313 and 318 K respectively

Table 3. Conductivities σ (S cm^{-1}) of the molten salts at 298 K depicted in Figure 7, and activation energies E_A (kJ/mol) obtained from the corresponding Arrhenius plots

	σ	E_A
BMIMBF_4	3.4	31.6(7)
ADMIMBF_4	2.1	36.0(8)
BDMIMBF_4	0.7	50.1(6)
BDMIMSbF_6	0.4	47(1)
BDMIMPF_6	0.2	54.1(9)

A comparison of the conductivities was first made among the three BDMIM compounds. Since the viscosities could not be determined, only the effect of ion size can be taken into account. Compound **I** has the highest conductivity and the lowest is observed for **II**, although the difference between **II** and **III** is not large. The conductivities of the latter two compounds are reversed as to what would be expected from their anion size and melting points. It has been shown previously that large anions can produce melts of low viscosity if they have low charge-density and if hydrogen bonding is absent.[10] The slightly lower conductivity of the PF_6^- salt as compared to that of SbF_6^- could still be due to the latter effect as discussed above. An unusually low conductivity of EMIMPF_6 as compared to the much larger EMIM bis(trifluoromethylsulfonyl)imide has been previously reported by McEwen et al.[11] The values obtained in this work for **I** and **II** are similar, although reversed in order with respect to those reported by Sutto et al., determined using the complex impedance method.[27]

The activation energies for conductivity decrease in the order $PF_6^- > BF_4^- > SbF_6^-$, with absolute values consistent with that reported for the similar compound dimethylpropylimidazolium hexafluorophosphate (DMPIPF_6).[11]

The second series compared are the BF_4^- salts of BMIM, BDMIM and ADMIM. The ADMIM compound was synthesized in order to verify whether trisubstituted imidazolium salts with this types of anion are generally solid at ambient temperature. ADMIMBF_4 turned out to be a liquid of rather low viscosity even at approx. 260 K, thus methylation in the 2-position cannot be exclusively responsible for the large increase of melting points. Conductivities of the BF_4^- salts increase in the order BMIM > ADMIM > BDMIM. This order could otherwise be described as: a) exchange of an allyl for a butyl group at the nitrogen plus methylation in the 2-position, resulting in lower mobility of the cation, and b) reverse exchange of butyl for allyl, decreasing the mobility even further. The large effect produced by the second step (cf. Figure 7) is a particularly unexpected result, and is probably explained by weaker van der Waals bonding with the allyl group as compared to butyl, rather than a large increase in the overall size of the cation.

Conclusion

From the present work we conclude that packing inefficiency as a prerequisite for the low melting points of ionic liquid salts, reflected by frequent crystallographic disorder, can be ruled out for the present compounds, contrary to the IL carboranes reported by Larsen et al. Instead, the low-melting compounds containing the BDMIM cation and fluoro anions suggest a certain degree of cation−cation repulsive interaction for compounds with smaller anions (BF_4^- and PF_6^-) which is no longer influential in the case of SbF_6^- owing to lattice expansion. The existence of polar and non-polar domains, believed to be associated with the unique "amphiphilic" solvent properties of ILs, are found in the structures of the BF_4^- and PF_6^- salts. A similar trend as with melting points is observed with ionic mobilities in the respective molten salts, inferred from measurements of electric conductivities. However, since the charge densities of the conducting species are low and dispersive interactions make up an important part of the adhesive forces in these melts, factors other than ion size, especially polarizability, have to be taken into account. Introducing unsaturated side chains at the imidazolium ring (possibly perfluorinated ones in order to reduce reactivity) might be a worthwhile issue with respect to the design of low viscosity melts, as suggested by the new IL ADMIMBF_4.

Experimental Section

Preparations: BMIMCl and BDMIMCl were obtained from *n*-chlorobutane and 1,2-dimethylimidazole (Aldrich 98%) as reported previously.[18] The BF_4^-, PF_6^- and SbF_6^- salts were prepared by a modified procedure according to Suarez et al.[20] The imidazolium chloride was stirred with a 1.1-fold excess of $NaBF_4$, KPF_6 or $NaSbF_6$ in dry acetone at ambient temperature for 48 hours. Sodium chloride was then filtered from the solution, and most of the acetone was removed under reduced pressure. Dichloromethane was then added in order to precipitate the remaining sodium salts, and the mixture was kept at −10 °C for 24 hours. The precipitates were filtered from the solution and the organic solvents were removed under reduced pressure. The resulting ionic liquid was then heated at 70 °C/10^{-2} bar for 12 hours to remove any remaining volatiles. Purity was checked by NMR spectroscopy and elemental analysis; chloride impurities were generally below the detection limit with silver ions. Some of these ionic liquid salts are now commercially available.[28] 1-Allyl-3-methylimidazolium bromide was synthesized from allyl bromide and 1,2-dimethylimidazole and bromide ions were exchanged for tetrafluoroborate as described above.

Crystal Growth: Suitable crystals for X-ray single crystal diffraction of BDMIMBF_4 (**I**) and BDMIMPF_6 (**II**) could only be obtained from the molten salts. Crystals of BDMIMSbF_6 (**III**) were obtained from solution. The crystal growth of the imidazolium salts from the melt was performed in Schlenk tubes (approx. 10 cm in length and 1 cm in diameter) equipped with a septum through which a wire ending in a loop with seed crystals was immersed into the melt. The tubes were kept in a water bath maintained about 1 °C below the melting point. Crystals started growing at the loop and were separated from the melt typically after a couple of hours by slowly lifting the wire out of the liquid. Crystals of **III** were obtained from mixtures of MeCN/Et_2O typically within less than 24 hours.

Conductivity Measurements: AC conductivities of the molten salts were measured using a conventional conductivity cell equipped with 1 cm^2 platinum electrodes with a nominal cell constant of 0.7

Table 4. Crystallographic data of BDMIMBF$_4$, BDMIMPF$_6$ and BDMIMSbF$_6$

	$C_9H_{17}BF_4N_2$	$C_9H_{17}F_6N_2P$	$C_9H_{17}F_6N_2Sb$
a (Å)	13.080(3)	15.389(3)	9.100(2)
b (Å)	11.270(2)	8.604(2)	12.510(2)
c (Å)	16.930(3)	11.730(2)	13.000(3)
β (°)	93.14(4)	122.46(3)	100.14(3)
V (Å^3)	2491.79(8)	1310.4(5)	1457.27(5)
T (K)	213(1)	213(1)	293(3)
Molecular weight (g/mol)	240.05	298.21	371.86
Space group	$P2_1/c$ (No. 14)	*Cc* (No. 10)	$P2_1/n$ (No. 14)
Z	8	4	4
λ (Å)	0.71069	0.71069	0.71069
$\rho_{calcd.}$ (g/cm^3)	1.307	1.512	1.773
*R*1	0.080	0.062	0.040
*wR*2 (all data)	0.230	0.175	*0.107*

cm^{-1}. The cell was calibrated with a 0.01 M aqueous solution of KCl and connected to a WTF conductivity analyzer model LF 410, operating at 4 MHz ac current. The temperature of the cell was maintained constant within 0.5 °C using a thermostatted water bath. The compounds were cautiously dried at 70 °C under reduced pressure before measurement and transferred to the cell inside an argon-filled glove box.

NMR and Infrared Spectra: Both NMR spectra in CD_2Cl_2 solution, recorded on a Varian Mercury 200 spectrometer (200 MHz), as well as IR spectra of solid samples run as KBr pellets with a Nicolet FTIR spectrometer (model Avatar), are virtually identical for the three BDMIM compounds. NMR and IR spectroscopic data for **III** and for the new compound ADMIMBr are summarized below. Compounds **I**−**III** and ADMIMBr were also submitted to elemental analysis.

1-Butyl-2,3-dimethylimidazolium Hexafluoroantimonate (III): ^{1}H NMR: δ = 1.0 [t, C(11)H3], 1.3 [tt, C(10)H2], 1.7 [tt, C(9)H2], 2.5 [s, C(8)H3], 3.7 [s, C(7)H3], 4.0 [t, C(6)H2], 7.2 [dd, C(4)H, C(5)H] ppm. ^{13}C NMR: δ = 10.0 (C-8), 14.0 (C-11), 20.0 (C-10), 32.0 (C-9), 35.0 (C-7), 49.0 (C-6), 121.0 (C-4), 123.0 (C-5), 144.0 (C-2) ppm. IR (600−4000 cm^{-1}, KBr pellets): $\tilde{\nu}$ = 3186, 3153 aromatic ν(C−H); 2968−2881 aliph. ν_s(C−H); 1608−1469 ν_s(C=C/C=N ring); 1426−1080 aliph. δ_{as}(C−H), ν_s(ring), δ(C−H ring); 950 δ(in plane ring C−H); 750 δ_{as}(out of plane ring). $C_9H_{17}N_2F_6Sb$ (388.91): calcd. C 27.8, H 4.4, N 7.2; found C 27.5, H 4.7, N 6.8.
I: $C_9H_{17}N_2F_4B$ (239.91): calcd. C 45.0, H 7.1, N 11.7; found C 44.8, H 8.0, N 11.2.
II: $C_9H_{17}N_2F_6P$ (298.11): calcd. C 36.2, H 5.7, N 9.4; found C 36.2, H 6.0, N 9.1.

1-Allyl-2,3-dimethylimidazolium Bromide: ^{1}H NMR: δ = 2.58 [s, C(7)H3], 3.79 [s, C(6)H3], 4.95 [dt, C(8)H2], 5.28 [d/m, C(10)H-*E*], 5.38 [d/m, C(10)H-*Z*], 5.98 [m, C(9)H], 7.61 [d, C(4)H], 7.73 [d, C(5)H] ppm. ^{13}C NMR: δ = 11.08 (C-7), 27.69 (C-8), 36.30 (C-6), 120.65 (C-9), 120.65 (C-5), 121.77 (C-4), 123.22 (C-10), 130.4 (C-9), 144.66 (C-2) ppm. IR (600−4000 cm^{-1}, KBr pellets): $\tilde{\nu}$ = 3169 (w), 3106 (m), 3056 (3014) (s) aromatic/allyl ν(C−H); 2929−2860 aliph. ν_s(C−H); 1586−1461 ν_s(C=C/C=N ring/allyl); 1410−1170 aliph. δ_{as}(C−H), ν_s(ring), δ(C−H) ring; 950 δ(in plane ring C−H); 750 δ_{as}(out of plane ring). $C_8H_{13}N_2Br$ (216.99): calcd. C 44.2, H 6.4, N 12.9; found C 44.6, H 6.2, N 12.9.

X-ray Structure Determinations: Single crystal diffraction was performed with a Bruker diffractometer equipped with graphite monochromator and a Smart-Apex CCD detector (Siemens) using Mo-K_α radiation. A complete hemisphere was recorded in 600, 435 and 230 frames, at φ angles of 0°, 90° and 180°, respectively. A scan width of 0.3° was used. Indexing was done using the program SMART, frame integration and data reduction using the SAINTPLUS suite. Absorption correction was performed using the program SADABS (all ©Bruker AXS). Sample crystals were placed into glass capillaries and sealed under argon atmosphere. Recording temperatures and crystallographic parameters for compounds **I**−**III** are summarized in Table 4. Crystals of **I** were obtained as two-component twins in all cases. The crystals, however, were large and of excellent quality, thus a sufficient number of non-overlapping reflections could be collected to allow for separation of contributions from the two components, structure solution and batch scaling of the data according to the degree of overlap during least-squares refinement. Diffraction data were collected at 213 K and indexed with a monoclinic unit cell containing eight formula units, which had previously been obtained from a powder diffraction pattern where twinning is not of concern.
CCDC-221752 (for BDMIMBF$_4$), -221753 (for BDMIMPF$_6$) and -221754 (for BDMIMSbF$_6$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] [1a] P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* **2000**, *39*, 3772. [1b] R. Sheldon, *Chem. Commun.* **2001**, 2399. [1c] C. M. Gordon, *Appl. Catal. A* **2001**, *222*, 101. [1d] P. Dyson, *Trans. Metal Chem.* **2001**, *27*, 353. [1e] J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667. [1f] C. Baudequin, J. Baudoux, J. Levillain, D. Cahard, A.-C. Gaumont, J.-C. Plaquevent, *Tetrahedron Asymmetry* **2003**, *14*, 3081. [1g] Y. Chauvin, L. Mußmann, H. Olivier, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2698.

[2] A. J. Dent, K. R. Seddon, T. Welton, *J. Chem. Soc., Chem. Commun.* **1990**, 315.

[3] J. D. Holbrey, K. R. Seddon, *J. Chem. Soc., Dalton Trans.* **1999**, 2133.

[4] J. Fuller, R. T. Carlin, H. C. D. Long, D. Haworth, *J. Chem. Soc., Chem. Commun.* **1994**, 299.
[5] C. M. Gordon, J. D. Holbrey, A. R. Kennedy, K. R. Seddon, *J. Mater. Chem.* **1998**, *8*, 2627.
[6] C. J. Bowlas, D. W. Bruce, K. R. Seddon, *Chem. Commun.* **1996**, 1625.
[7] A. S. Larsen, J. D. Holbrey, F. S. Tham, C. A. Reed, *J. Am. Chem. Soc.* **2000**, *122*, 7246.
[8] J. Dupont, P. A. Z. Suarez, R. F. De Souza, R. A. Burrow, J.-P. Kintzinger, *Chem. Eur. J.* **2000**, *6*, 2377.
[9] J. van den Broeke, M. Stam, M. Lutz, H. Kooijman, A. L. Spek, B.-J. Deelman, G. van Koten, *Eur. J. Inorg. Chem.* **2003**, 2798.
[10] P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Graetzel, *Inorg. Chem.* **1996**, *35*, 1168.
[11] A. B. McEwen, H. L. Ngo, K. LeCompte, J. L. Goldman, *J. Electrochem Soc.* **1999**, *146*, 1687.
[12] A. Elaiwi, P. B. Hitchcock, K. R. Seddon, N. Srinivasan, Y.-M. Tan, T. Welton, J. A. Zora, *J. Chem. Soc., Dalton Trans.* **1995**, 3467.
[13] S. Saha, S. Hayashi, A. Kobayashi, H. Hamaguchi, *Chem. Lett.* **2003**, *32*, 740.
[14] J. D. Holbrey, W. M. Reichert, M. Nieuwenhuyzen, S. Johnston, K. R. Seddon, R. Rogers, *Chem. Commun.* **2003**, 1636.
[15] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 461.
[16] R. Taylor, O. Kennard, *J. Am. Chem. Soc.* **1982**, *104*, 5063.
[17] U. Schröder, J. D. Wadhawan, R. G. Compton, F. Marken, P. A. Z. Suarez, C. S. Consorti, R. F. de Souza, J. Dupont, *New J. Chem.* **2000**, *24*, 1009.
[18] J. S. Wilkes, M. Zaworotko, *J. Chem. Soc., Chem. Commun.* **1992**, 965.
[19] P. B. Hitchcock, K. R. Seddon, T. Welton, *J. Chem. Soc., Dalton Trans.* **1993**, 2639.
[20] S. E. P. A. Z. Suarez, J. E. Dullius, R. F. de Souza, J. Dupont, *J. Chim. Phys.* **1998**, *95*, 1626.
[21] J.-F. Huang, P.-Y. Chen, I.-W. Sun, S. P. Wang, *Inorg. Chim. Acta* **2001**, *320*, 7.
[22] A. Mele, C. D. Tran, S. H. De Paoli Lacerda, *Angew. Chem. Int. Ed.* **2003**, *36*, 4364.
[23] C. B. Aakeröy, T. A. Evans, K. R. Seddon, I. Palinko, *N. J. Chem.* **1999**, 145.
[24] P. Kölle, R. Dronskowski, *Inorg. Chem.*, in press.
[25] A. Gavezzotti, in *Structure Correlation Vol. 2* (Eds.: H. B. Bürgi, J. D. Dunitz), VCH: Weinheim, **1994**.
[26] A. I. Kitaigorodski, *Molecular Crystals and Molecules*, Academic Press: New York **1973**.
[27] T. E. Sutto, H. L. De Long, P. C. Trulove, *Progress in Molten Salt Chemistry 1* (Eds.: R. W. Berg, H. A. Hjuler), Elsevier: Paris, **2000**, 511.
[28] Solvent Innovation GmbH, Köln (www.solvent-innovation.com).

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