VARIATION OF THE CATION OF IONIC LIQUIDS: THE EFFECTS ON THEIR PHYSICOCHEMICAL PROPERTIES AND REACTION OUTCOME

Rebecca R. Hawker, Ronald S. Haines and Jason B. Harper
School of Chemistry, University of New South Wales, 2052 Sydney, Australia
(e-mail: j.harper@unsw.edu.au)

Abstract. *A large number of ionic liquids containing cations derived from different heterocycles have been compared, particularly noting the differences in physicochemical properties and how they affect reaction outcome. Where possible, trends were identified and the potential to modify the cation of an ionic liquid to alter properties and/or control reaction outcome in a rational fashion is discussed.*

Contents

1. Introduction

Ionic liquids are defined as salts which have a normal melting point below 100 °C.[1] Common ionic liquids include those containing imidazolium, pyridinium, pyrrolidinium, ammonium and phosphonium cations. As they are made up solely of charged species, ionic liquids have a range of unique properties including negligible vapour pressure,[2] the ability to dissolve a large number of organic and inorganic materials and high thermal stability.[3] The utility of ionic liquids is increased by the fact that through changing the constituent ions, physical properties can be altered to fit a particular need; these properties include melting point, viscosity and miscibility with other solvents.[4] There is even the potential to use ionic liquids composed of mixtures of multiple cations and multiple anions to give a wider range of solvents,[5] though such mixtures are rarely well characterised[6] and will not be discussed further in this review. The ability to vary their properties has led ionic liquids to be considered as 'designer solvents'[7,8] and allows for 'task specific'[9] ionic liquids to be developed.

A large number of ionic liquid cations contain heterocycles, including imidazolium, thiazolium, triazolium, pyridinium, pyrrolidinium, thiolanium, oxazolidinium, piperidinium, morpholinium and pyrazolium systems (Figure 1); it is worth noting that cations containing both saturated and unsaturated heterocycles are common.[10] In this review, only modifications to the ionic liquid cation are discussed.[i] Such modifications are more common in the literature because they can be targeted at specific properties of the cation, such as shape, size, or charge distribution. In contrast, modification of the anion often leads to changes in several of its properties, complicating the interpretation of observations.

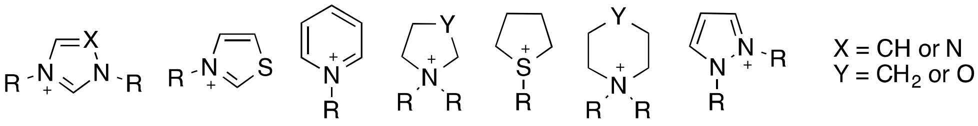
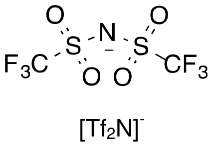


Figure 1. A range of heterocyclic cations found in ionic liquids.

Common modifications to the above cations include variation of the alkyl chain length on the heteroatoms and adding alkyl groups to the heterocyclic ring. Rarer modifications, which are slowly becoming more prevalent, include functionalization of the alkyl chains on the heteroatoms along with modification of the electronic properties of the heterocycle, particularly through the addition of electron-withdrawing groups.

Regrettably there are many, often inconsistent, abbreviations used in the literature for naming the cations common in ionic liquids. This review, where possible, uses a consistent approach to naming with naming conventions introduced at the beginning of each section.

To isolate the effect of varying the cation, comparisons of properties will only be made for ionic liquids containing a common anion.[ii] The *bis*(trifluoromethanesulfonyl)imide anion ($[Tf_2N]^-$) is particularly common in the ionic liquid literature, due to the favourable properties it imparts to ionic liquids including lower viscosity



$[Tf_2N]^-$

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[i] By the nature of this review, the focus will be on cations containing heterocyclic moieties; given their prevalence this is not unreasonable. Reference to related acyclic systems is only made where it will aid the discussion.

[ii] For example surface tension value is affected by both the cation and anion because they are present in the interface layer.[11]

and greater electrochemical stability.[4] Because of this, the majority of the comparisons in this review involve ionic liquids containing this anion.

The properties that will be discussed in this review are melting point, glass transition temperature, density, viscosity, thermal stability, surface tension, electrical conductivity and molar volume. The melting point and glass transition temperatures of ionic liquids are important, not least because varying the cation may turn an ionic liquid into an 'ordinary' salt (due to the arbitrary definition of an ionic liquid requiring a melting point below 100 °C) but also the applications of ionic liquids will be limited by their liquidus range. Density is the property of ionic liquids measured most often, as many applications require knowledge of density and, once more, the practicality of using ionic liquids is often dependent on this property.[3] For example, a larger density difference between an ionic liquid and a conventional solvent would be optimal to hasten phase separation.[12] The viscosities of ionic liquids[iii] are important as a high viscosity may decrease an ionic liquids utility, due to a reduction in mass transfer.[3] The miscibility of an ionic liquid with traditional solvents is significant as it will determine the practicality of using these salts either as extractants or as cosolvents. Surface tension has a well-known connection to cohesive energies of liquids,[13] so is of interest as this can relate to other properties (including viscosity) but also may determine how species interact in solution.

It should be noted that there are other reviews covering the physicochemical aspects of ionic liquids in the literature,[3,14] particularly the very comprehensive review by Zhang *et al.*[15] which covers the literature up to and including 2004. The present review serves as an update, adding new data and new ionic liquids but also differs in two important respects. Firstly, it makes a series of comparisons between groups of ionic liquids where the cation varies in a systematic fashion. Secondly, the effect of varying the ionic liquid cation on reaction outcome is incorporated.

Ionic liquids are potential alternatives to molecular solvents not only because of their lack of volatility[2] and potential for recycling,[8] but also because they can alter reaction outcomes (rate, selectivity, *etc*) in a desired fashion. Whilst modifying the physicochemical properties of ionic liquids through variation of the component ions is of interest, changing the cation may also affect how reactions proceed in these solvents. At this stage, ionic liquid solvent effects are not well understood[8] and significant work is underway to develop principles to predict their effects on reaction outcomes.[3,16–18] In this review, the effect of changing the cation of an ionic liquid on reaction outcomes will be discussed.

This review includes measured properties of ionic liquids from many sources[iv] and the interpretation of these data requires attention to three aspects of the measurements.

(i) The conditions under which measurements were made. A number of the properties that will be discussed, including density and viscosity, vary significantly with temperature. To overcome this, where possible, only data obtained at the same temperature will be compared.

(ii) The range of methods used to obtain the data. Differences in instrument precision for these methods (say for density measurements, which can vary from three to five significant figures) may lead to trends being observable in some cases but not in others. With instrument precision comes the issue of

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[iii] Viscosities of ionic liquid may be reported as either dynamic or kinematic viscosity, which are related through density. In this review, only dynamic viscosity will be discussed.

[iv] Of course there is also the issue that some research groups may not report a particular property; that is, the combined data set may be incomplete.

uncertainties in the data, which will vary based on the method used. Perhaps surprisingly, often uncertainties are not reported and hence care must be taken using these values; throughout this review, where no uncertainties are reported it is because none are contained in the original publication.

(iii) It has been shown previously that the purity of ionic liquids can dramatically affect their properties;[19] this has been particularly demonstrated for ionic liquids containing halide impurities[v] and those with water present. Whilst frequently not reported (particularly in the early literature), the assumption is made throughout this review that all the ionic liquids are free of impurities.

2. Physicochemical properties of ionic liquids containing heterocyclic cations

To aid the reader, the discussion of the effects of varying the cation of an ionic liquid is broken down into sections based on the parent heterocycle. The order approximately parallels the prevalence of the cation type in the literature and within each section, the order in which the modifications are presented is kept as consistent as is practical. Note that the discussion is limited to ionic liquids containing monocationic cations; biscationic ionic liquids are also being developed,[20–23] particularly for liquid crystal applications,[24] but are not widespread at this stage.

2.1. Ionic liquids containing imidazolium cations

Ionic liquids containing an imidazolium cation are amongst the most studied of the modern ionic liquids[25] and by far the most common in the literature.[15] Imidazolium based ionic liquids are easily synthesized through alkylation of an *N*-alkylimidazole and subsequent anion metathesis to incorporate the desired anion.[10,18,26] The most common modifications to imidazolium cations in ionic liquids involve changes to the *N*-alkyl substituents, however a number of other modifications have been reported. The range of imidazolium cations discussed here includes those with variations to the *N*-alkyl chain length, cyclic and aromatic *N*-alkyl substituents, addition of silicon to the *N*-alkyl chain, addition of ether groups to the *N*-alkyl chain and substitution of the imidazolium ring.

Imidazolium cations are frequently abbreviated to the form $[xy\text{im}]^+$, where x and y are the first letters of the names of the alkyl chains on the nitrogen atoms.[vi] For example, the very common cation 1-butyl-3-methylimidazolium is abbreviated to $[\text{bmim}]^+$. While other, possibly less ambiguous,[vii] abbreviations are used, the $[xy\text{im}]^+$ nomenclature is more common and used in this review. Any abbreviation system becomes more complicated as the size, shape and functionality of the compound becomes more complex so, along with presenting structures to aid understanding, effort has been made to make the abbreviations straightforward.

Consider the ionic liquids **1-11**, a series in which one *N*-alkyl substituent on the imidazolium core (methyl) is held constant whilst the other increases in length. For each of the properties listed in Table 1, a number of trends can be observed.

For the glass transition temperature of the ionic liquids **1-11** there is no obvious correlation between this property and increasing the alkyl chain length on the cation. A decrease in the density of the ionic

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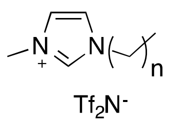
[v] Halide ions are likely impurities given many ionic liquids are synthesized *via* metathesis of the corresponding halide salts.

[vi] To avoid ambiguity, pentyl is abbreviated p_e, heptyl h_e and dodecyl, dod.

[vii] For example, the imidazolium series can be abbreviated in the form $[C_xC_y\text{im}]^+$, where x and y are the number of carbons in the alkyl chains on the heterocyclic ring; 1-butyl-3-methylimidazolium is abbreviated to $[C_4C_1\text{im}]^+$. This, of course, is only practical for the linear alkyl systems.

liquids **1-11** is observed when the length of the *N*-alkyl chain is increased while the opposite trend is observed for viscosity, with a longer aliphatic chain resulting in an increase in the viscosity. The trend in density can be rationalised in terms packing efficiency of the molecules, which will determine the mass per volume. As the alkyl chain increases in length, there is a decrease in the charge density on the cation and an increase in molar volume,[33] because the ions are unable to pack effectively due to the flexible alkyl chain; it is this that causes the decrease in density.



1, n = 0
2, n = 1
3, n = 2
4, n = 3
5, n = 4
6, n = 5
7, n = 6
8, n = 7
9, n = 8
10, n = 9
11, n = 11

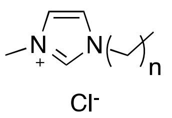
Table 1. The glass transition temperature (T_g), density (ρ), dynamic viscosity (η), electrical conductivity (κ) and molar volume (V_m) of the ionic liquids **1-11** at 298.15 K.

	Ionic liquid	**T_g / K** [a]	**ρ / g cm^{-3}**	**η / mPa s**	**κ / mS cm^{-1}**	**V_m / cm^3 mol^{-1}** [c]
1	[mmim][Tf_2N] **1**[b]	-	1.570	38.0	9.0	
2	[emim][Tf_2N] **2**	195	1.519[a,b] / 1.5147[c]	32.6[b] / 33.3[d] / 33.0[f]	9.0[b] / 7.13[d]	258.35
3	[pmim][Tf_2N] **3**	186	1.475[a]	47.0[d] / 45.75[f]	4.24[d]	-
4	[bmim][Tf_2N] **4**	186	1.436[a,c] / 1.437[b]	49.9[b] / 52.3[d] /50.62[f]	3.8[b] / 3.16[d]	292.04
5	[$p_e$mim][Tf_2N] **5**	188	1.403[a]	63.3[d] / 57.8[f]	2.24[d]	-
6	[hmim][Tf_2N] **6**	189	1.372[a,e] / 1.371[b,c]	69.7[b] / 66.96[e] /70.61[f]	2.2[b]	326.35
7	[$h_e$mim][Tf_2N] **7**	188	1.344[c,e]	77.25[e] / 81.11[f]	-	-
8	[omim][Tf_2N] **8**	189	1.320[a,b] / 1.3189[c]	90.0[b] / 93.053[f]	1.3[b]	360.51
9	[nmim][Tf_2N] **9**	190	1.299[a]	106.41[f]	-	-
10	[dmim][Tf_2N] **10**	190	1.271[a] / 1.2783[c]	120.18[f]	-	393.88
11	[dodmim][Tf_2N] **11**	-	1.2447[c]	154.33[f]	-	427.07

[a] From Dzyuba *et al.*[27] [b] From Tokuda *et al.*[28] [c] From Tariq *et al.*,[29] uncertainties for density reported as ± 0.0003 g cm^{-3}. [d] From Bulut *et al.*[30] [e] From Mandai *et al.*[31] [f] From Tariq *et al.*,[32] uncertainties for density reported as ± 0.4%.

The origin of the trend in viscosity is likely more subtle; viscosity is a measure of the internal friction in a system[14] however a number of parameters contribute to this, including molar mass, shape and size of the ions and the forces between the ions.[28] In this case, it is likely that a combination of the increase in the alkyl chain length (and the associated flexibility) restricts the movement of one component of the ionic liquid past another along with the increase in dispersion forces due to the increased molecular volume. There is a general inverse relationship between the length of the *N*-alkyl chain on the cation and the electrical conductivity.[34] This is due to increased ionic mobility (correlating with low viscosity).

Melting points are available for only a limited number of ionic liquids **1-11**, however data for the corresponding chlorides are available and are shown in Table 2. Note that the parent salt **12** in this system is not an ionic liquid, having a melting point above 100°C, however it is relevant to include to allow comparison across the series.



12, n = 0
13, n = 1
14, n = 2
15, n = 3
16, n = 7
17, n = 9
18, n = 11
19, n = 13
20, n = 15
21, n = 17

Table 2. The melting temperature (T_m) of the ionic liquids **12-21**.

	Ionic liquid	**T_m / K**
1	[mmim][Cl] **12**	398.15[a,b]
2	[emim][Cl] **13**	360.15[a] / 357.15[b]
3	[pmim][Cl] **14**	333.15[b]
4	[bmim][Cl] **15**	338.15[a,b] / 341.95[c]
5	[omim][Cl] **16**	285.41[c]
6	[dmim][Cl] **17**	311.17[c]
7	[dodmim][Cl] **18**	369.78[c] / 270.35[d]
8	[tedmim][Cl] **19**	292.55[d]
9	[hedmim][Cl] **20**	315.15[d]
10	[ocdmim][Cl] **21**	326.35[d]

[a]From Sheldon.[35] [b]From Fannin *et al.*[36] [c]From Domańska *et al.*[37] [d]From Bradley *et al.*[38]

These data show that there is not a simple relationship between the melting points in ionic liquids **12-21** and the alkyl chain length. There is an initial decrease in melting point from the symmetrical parent **12**, likely as a result of a decrease in symmetry affecting the packing of the components of the salt, but further increases do not give any significant correlation after the propyl system **14**. Any interpretation is made more difficult by the inconsistent reported data for the ionic liquid **18**.

The ionic liquids **22-29**, whose properties are summarised in Table 3, represent those with cycloalkyl chain modifications to the substituents on the nitrogen atoms of the imidazolium ring, without the incorporation of any heteroatoms. As such, they make the logical next comparison because of the independent variation of substituent size and flexibility. The linear systems **5-7** are also included with data at the relevant temperatures.[viii]

It is of interest to compare the properties of ionic liquids with cycloalkyl groups attached to the imidazolium ring with their linear counterparts introduced earlier. In the ionic liquids with a five-carbon *N*-alkyl chain ([$p_e$mim][Tf_2N] **5** and [cyclopentylmim][Tf_2N] **22**) the ionic liquid with the linear pentyl group has a lower glass transition temperature and density compared at the same temperature (293 K rather than 298 K). Given the lack of uncertainties, it is not possible to compare the viscosities of the ionic liquids

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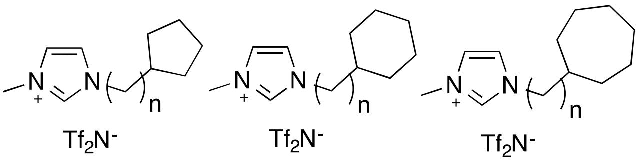
[viii] The ionic liquids **5-7** with linear alkyl chains have been specifically included in this Table as comparisons between the linear and cyclic systems are useful and require temperature dependent data not presented in Table 1.

5 and **22**. The same trends are observed for the C_6 ionic liquids **6** and **25** and C_7 ionic liquids **7** and **29** except that the viscosities of the cycloalkyl systems are much increased relative to the linear cases here.



22, n = 0
23, n = 1
24, n = 2

25, n = 0
26, n = 1
27, n = 2
28, n = 3

29, n = 0

Table 3. The glass transition temperature (T_g), density (ρ) and dynamic viscosity (η) of the ionic liquids **5-7** and **22-29** at either 293.15 K or 298.15 K.

	Ionic liquid	T_g / K	ρ / g cm^{-3} [a,b]	ρ / g cm^{-3} [i]	η / mPa s [a,b]	η / mPa s [c]
1	[$p_e$mim][Tf_2N] **5**	189.6[a]	1.408	1.403[b]	78.74	57.8[c]
2	[hmim][Tf_2N] **6**	189.8[a]	1.376	1.372[d,g]	86.04	70.61[e]
3	[$h_e$mim][Tf_2N] **7**	190.3[a]	1.349	1.344[g]	99.89	81.11[e]
4	[cyclopentylmim][Tf_2N] **22**[a]	194.3	1.483	-	81.18	-
5	[(cyclopentyl)$m_2$im][Tf_2N] **23**[f]	200.2	-	1.438	-	106.4
6	[(cyclopentyl)emim][Tf_2N] **24**[f]	198.9	-	1.408	-	119.1
7	[cyclohexylmim][Tf_2N] **25**	211.8[a,g]	1.451	1.446[g]	273.5	193.3[g]
8	[(cyclohexyl)$m_2$im][Tf_2N] **26**	212.1[f] / 210.8[h]	-	1.414[f] / 1.417[h]	-	306.6[f]
9	[(cyclohexyl)emim][Tf_2N] **27**[f]	207.1	-	1.386	-	218.0
10	[(cyclohexyl)pmim][Tf_2N] **28**[f]	207.5	-	1.358	-	240.4
11	[cycloheptylmim][Tf_2N] **29**[a]	209.6	1.432	-	284.6	-

[a]From Mandai *et al.*[33] [b]Values measured at 293.15 K [c]Values measured at 298.15 K. [d]From Dzyuba *et al.*[27] [e]From Tariq *et al.*[32] [f]From Mandai *et al.*[39] [g]From Mandai *et al.*[31] [h]From Tao *et al.*,[40] where uncertainties in the density are reported as ± 0.001 g cm^{-3}.

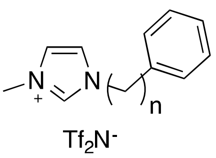
For density, the cycloalkyl systems **22**, **25** and **29** will have fewer degrees of freedom than their linear counterparts **5-7**; the result is a larger molar volume in the linear alkyl ionic liquids, which explains the increase in density on moving to the cycloalkyl systems. In the case of the viscosity measurements, the origin of the increase in viscosity for the cyclohexyl and cycloheptyl derivatives relative to their linear counterparts is not as clear and suggests greater interactions between the components of the ionic liquids containing the larger ring systems.

Looking at the ionic liquids **22-25** that contain a cyclopentyl group, as the distance between the cyclopentyl ring and the imidazolium system is increased, no trend in glass transition is seen but a decrease in density is observed. The same is observed for the ionic liquids **26-28** containing the cyclohexyl group. Again, this is reasonable as this would be a similar trend to increasing the alkyl chain length described above for the ionic liquids **1-11**, where there is less efficient packing accompanying a longer chain length, causing the density to decrease.

The viscosity of ionic liquids **22-25** increases with added methylene groups between the ring and the imidazolium system. It would be assumed that the same trend observed for these salts would be observed for the cyclohexyl cases **26-28**. This is not the case, with the viscosity of [(cyclohexyl)mmim][Tf_2N] **26** being significantly higher than [(cyclohexyl)emim][Tf_2N] **27** and any of the other ionic liquids observed in this section. This may be due that the extra flexibility in ionic liquid **27** due to the methylene spacer, allowing the ions to move past each other more easily than in the analogue **26** where the cation is significantly more rigid, overcoming any effects due to increased dispersion forces in these cases.

Similar trends to that seen for the linear systems described in Table 1 are observed as the ring size of the cycloalkyl system on the cation changes in ionic liquids **22**, **25** and **29**, where the density decreases and the viscosity increases. It would appear that the reasons for these trends are the same as suggested for the simple imidazolium systems **1-11**; with an increasing alkyl chain length, the larger the side chain, the lower the packing efficiency, causing a decreased density and increasing flexibility of the nitrogen substituent decreases molecular mobility, along with an increase in the dispersion forces.

The ionic liquids **30-34**, whose properties are summarised in Table 4, are representative of those with aromatic side chain modifications to the substituents on the nitrogen atoms of the imidazolium ring, without the incorporation of any heteroatoms. Thus this group makes a ready comparison to the cycloalkyl systems presented above.



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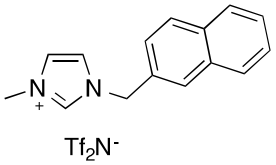
32, n = 3



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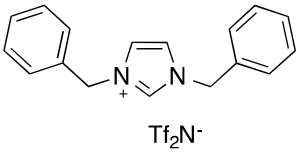

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Table 4. The glass transition temperature (T_g), decomposition temperature (T_d), density (ρ), dynamic viscosity (η) and molar volume (V_m) of the salts **30-34** at 298.15 K (unless otherwise specified).

	Ionic liquid	T_g / K	T_d / K	ρ / g cm^{-3}	η / mPa s	V_m / cm^3 mol^{-1}
1	[(Ph)mmim][Tf_2N] **30**[a]	215[b] / 215.8[c] / 214.9[d]		1.504[b]	190[b]	301.5[b]
2	[(Ph)mmim][Tf_2N] **30**		694[d]	1.489[c] / 1.493[d]	125.0[c]	-
3	[(Ph)emim][Tf_2N] **31**[c]	214.4	-	1.456	222.0	-
4	[(Ph)pmim][Tf_2N] **32**[c]	212.7	-	1.434	224.4	-
5	[(Naph)mmim][Tf_2N] **33**[d]	234.8	679	1.482	-	339.7
6	[BnBnim][Tf_2N] **34**[d]	228.5	683	1.434	-	369.2

[a] Values were measured at 293.15 K. [b] From Shirota *et al.*[41] [c] Mandai *et al.*[39] [d] From Tao *et al.*,[40] where uncertainties in the density are reported as ± 0.001 g cm^{-3}.

The first thing to consider in this section is how the properties change as the distance between the phenyl ring and the imidazolium system is increased in ionic liquids **30-32**. No trend in glass transition is seen but a decrease in density is observed paralleling the decrease in density for ionic liquids **1-11** where increasing the alkyl side chain length led to decreased density due to less efficient packing. The viscosity of ionic liquids **30-32** increases with added methylene groups between the phenyl ring and the imidazolium system.[ix] The origins of this difference may either be similar to the case with the ionic liquids **1-11** (with the increasing alkyl chain length restricting the movement of one component of the ionic liquid past another along increasing dispersion forces), due to the aromatic system introducing further interactions or most likely a combination of both of these effects.

The ionic liquids **26** ([(cyclohexyl)mmim][Tf_2N], Table 3, entry 8) and **30** contain the same number of carbon atoms in the cation, with the same connectivity but the latter ionic liquid contains an aromatic system on the *N*-substituent. Similar relationships exist between ionic liquids **27** (Table 3, Entry 9) and **31**, and between **28** (Table 3, entry 10) and **32**.

For the ionic liquid **30** with the aromatic side chain the glass transition temperature is higher than in the ionic liquid **26** (Table 3, entry 8). The same is observed for ionic liquids **27** (Table 3, Entry 9) and **31**, and between **28** (Table 3, entry 10) and **32**. This suggests greater interaction between the components, which might be accounted for by the change in electronic distribution in the *N*-substituent; incorporating an aromatic component introduces a significant quadrupole moment.[x]

A higher density is observed for the phenyl ionic liquid **30** than the non-aromatic derivative **26** (Table 3, entry 8); again this is observed for other comparable ionic liquids **27** (Table 3, Entry 9), **28** (Table 3, entry 10) and **31**. These results show that it is likely the aromatic nature of the cation side chain of the ionic liquids **30-32** that causes the density to increase. Whilst the more rigid aromatic groups would increase the molecular volume, the increased intermolecular forces due to the presence of the π system outweigh this.

Comparison of the viscosity of the ionic liquids containing either cycloalkyl or aromatic components in the nitrogen substituent is more complicated. The cyclohexyl ionic liquid **26** has a much larger viscosity (473 mPa s compared with 190 mPa s at 293 K) than the phenyl derivative **30** with only one methylene between the cyclic system and the imidazolium ring. When comparing the similar systems with ethylene linkers **27** and **31** the difference is not so clear with the cyclohexyl ionic liquid **27** having a slightly lower viscosity (218.0 mPa s compared to 222.0 mPa s at 298 K). Then when looking at the similar systems with a three carbon linker, the cyclohexyl ionic liquid **28** has a larger viscosity than the phenyl derivative **32** (240.4 mPa s compared to 224.4 mPa s at 298 K). No trend is apparent and hence it is difficult to make any rationalisations based upon the incorporation of an aromatic component.

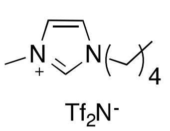
The cation of the ionic liquid **33** is related to the cation in ionic liquid **30** but with a larger aromatic substituent on the imidazolium ring; based solely on the size of the side chain, this would be expected to result in a decrease in density. This is what is observed, confirming that these trends are seen across a range of systems. An increase in viscosity would also be expected, however as this has not been reported, a comparison cannot be made. The glass transition temperature for the naphthyl containing ionic liquid **33** is higher than for the ionic liquid containing a phenyl substituent **30** suggesting greater interactions between the components. The ionic liquid **33** containing a naphthyl group is less chemically stable with it having a lower decomposition temperature than the corresponding ionic liquid **30** with a phenyl substituent suggesting a decomposition pathway facilitated by the larger substituent.

[ix] It is worth noting the difference between the viscosities measured for salt **30** at different temperatures; while it is reasonable that the viscosity is greater at lower temperature, the magnitude of the difference is large. Irrespective, the trend discussed in the text holds.

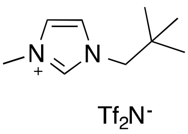
[x] The quadrupole moment of benzene is approximately ten times that of cyclohexane.[42,43]

All of the systems compared so far have had cations based on methylimidazole; that is, they are of the form [xmim]$^+$. The ionic liquid **34** has a symmetric cation with two benzyl substituents, and thus the comparison to the methyl benzyl system **30** is of interest. Adding a second phenyl group causes a decrease in density, however it is difficult to explain the exact cause of this. It would be reasonable to think that the bulkier side chains will cause less efficient packing of molecules causing the decrease in density. However the observed change in density could also be rationalised as the cation of ionic liquid **34** is symmetric.

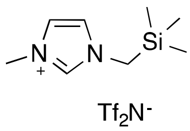
In order to reduce the viscosity of ionic liquids, a study has varied the side chain by replacing a neopentyl group in ionic liquid **35** with one containing silicon to give ionic liquid **36**. Comparison of properties with those of the linear pentyl derivative **5** is clearly of interest, but is made slightly more difficult by the differences in the temperatures at which the data is recorded (Table 5). Fortunately, from the data presented several trends are clear.



5



35



36

Table 5. The density (ρ), dynamic viscosity (η) and molar volume (V_m) of the ionic liquids **5**, **35** and **36**.

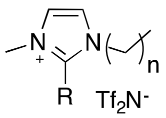
	Ionic liquid	Temperature / K	ρ / g cm^{-3}	η / mPa s	V_m / Å^3
1	[p$_e$mim][Tf$_2$N] **5**	293	1.407^a	77.734^a / 80.6^b	-
2	[p$_e$mim][Tf$_2$N] **5**	298	1.403^c	63.3^b / 57.8^d	-
3	[(Np$_e$)mim][Tf$_2$N] **35**^{e}	295	1.50	161	312.7
4	[(TMS)mmim][Tf$_2$N] **36**^{e}	295	1.46	98.3	326.1

^{a}From Bini *et al.*[44] ^{b}From Bulut *et al.*[30] ^{c}From Dzyuba *et al.*[27] ^{d}From Tariq *et al.*[32] ^{e}From Shirota *et al.*,[45] uncertainties are reported as ± 3% for density and ± 5% for viscosity.

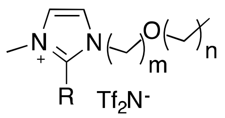
Initial comparison of the data for the branched system **35** and the parent ionic liquid **5** shows a large increase in density and viscosity on moving to the branched system **35**. The former is reasonable as the neopentyl group occupies a smaller volume than a linear pentyl chain, increasing the packing efficiency of ionic liquid **35**. The increase in viscosity is not so readily explained as the more branched system would be expected to have fewer degrees of freedom yet similar interactions with other components of the liquid.

Both the density and viscosity in the ionic liquid **36** are significantly lower than the carbon analogue **35**. The former might be accounted for through a decrease in packing efficiency due to silicon being larger than carbon. Shirota *et al.* proposed that it is likely that in the silicon-containing ionic liquid **36**, the torsional potentials are lower than in the ionic liquid **35**, which may lead to a greater multiplicity of orientations, further inhibiting ion packing in the liquid.[45] The authors also attribute differences in viscosity to a number of factors including different electrical interactions with neighbouring ions.[45]

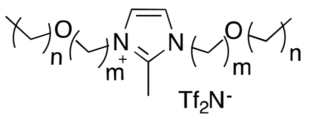
Ether groups have also been introduced into the nitrogen substituents of imidazolium-based ionic liquids in order to reduce viscosities and melting points, without reduction in the electrochemical stability which is observed in addition of other electron-withdrawing groups such as nitriles and ester moieties;[13] their properties are shown in Table 6. This series includes the first ionic liquids in which substitution of the imidazolium ring occurs at a site other than a nitrogen centre along with incorporating functionality in the substituents. The inclusion of a numeral in the abbreviation indicates that the following substituent is at that position on the imidazolium ring, whilst a substituent listed as (*x*O*y*), where *x* and *y* are the first letters of the names of the alkyl chains, contains an ether functionality. For example, the cation 1-(methoxyethyl)-3-methylimidazolium is abbreviated to [(mOe)mim]$^+$. Similar abbreviations are used for the incorporation of other functionalities throughout this section.



3, n = 2, R = H
4, n = 3, R = H
5, n = 4, R = H
37, n = 3, R = CH_3
38, n = 4, R = CH_3



39, m = 1, n = 0, R = H
40, m = 2, n = 0, R = H
41, m = 1, n = 1, R = H
42, m = 2, n = 1, R = H
43, m = 1, n = 0, R = CH_3
44, m = 2, n = 0, R = CH_3
45, m = 1, n = 1, R = CH_3
46, m = 2, n = 1, R = CH_3



47, m = 2, n = 0, R = H
48, m = 2, n = 1, R = H
49, m = 2, n = 0, R = CH_3
50, m = 2, n = 1, R = CH_3

Table 6. The decomposition temperature (T_d), density (ρ), dynamic viscosity (η) and electrical conductivity (κ) of the imidazolium ionic liquids **3-5** and **37-50** at 298.15 K.

	Ionic liquid	T_d / K	ρ / g cm^{-3}	η / mPa s	κ / mS cm^{-1}
1	[pmim][Tf_2N] **3**[a]	676.4	1.47	40.5	5.66
2	[bmim][Tf_2N] **4**[a]	673.9	1.44	47.0	3.96
3	[$p_e$mim][Tf_2N] **5**	-	1.403[b]	63.3[c] / 57.8[d]	2.24[c]
4	[b2$m_2$im][Tf_2N] **37**[e]	687.6	1.40	89.7	2.22
5	[p_e2$m_2$im][Tf_2N] **38**[e]	682.9	1.42	100.4	1.66
6	[(mOm)mim][Tf_2N] **39**[a]	568.5	1.50	49.8	4.49
7	[(eOm)mim][Tf_2N] **40**[a]	539.0	1.46	47.0	4.07
8	[(mOe)mim][Tf_2N] **41**[a]	663.0	1.45	41.8	4.62
9	[(eOe)mim][Tf_2N] **42**[a]	667.3	1.39	34.8	4.37
10	[(mOm)2$m_2$im][Tf_2N] **43**[f]	578.3	1.48	92.6	2.34
11	[(mOe)2$m_2$im][Tf_2N] **44**[e]	651.9	1.41	66.4	2.81
12	[(eOm)2$m_2$im][Tf_2N] **45**[f]	558.7	1.47	86.8	2.28
13	[(eOe)2$m_2$im][Tf_2N] **46**[b]	651.1	1.37	64.0	-
14	[$(mOe)_2$im][Tf_2N] **47**[a]	622.9	1.40	47.1	3.12
15	[$(eOe)_2$im][Tf_2N] **48**[a]	601.9	1.36	41.2	2.67
16	[$(mOe)_2$2mim][Tf_2N] **49**[b]	634.8	-	-	2.46
17	[$(eOe)_2$2mim][Tf_2N] **50**[b]	643.9	1.34	70.6	1.62

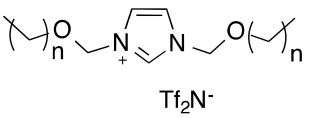
[a]From Zhang *et al.*,[46] uncertainties for density, viscosity and conductivity are reported as ± 5%. [b]From Dzyuba *et al.*[27] [c]From Bulut *et al.*[30] [d]From Tariq *et al.*[32] [e]From Jin *et al.*[47] [f]From Jin *et al.*,[48] uncertainties for density, viscosity and conductivity are reported as ± 5%.

As a first comparison, consider the ionic liquids **39-42** containing one ether group without methylation at the 2-position and compare them with the corresponding ionic liquids **3-5**. A lower decomposition temperature is observed for ionic liquid **39** compared with the parent ionic liquid **3**; the same trend is observed on comparing ionic liquids **40** and **41** with ionic liquid **4**, showing that addition of an oxygen to the alkyl chain facilitates decomposition. Any comparisons of the densities of ionic liquids **39-42** with the corresponding data for the alkylated ionic liquids **3-5** cannot be made due to the large uncertainties reported for these data for the ether derivatives. The viscosity does not show a clear effect of inclusion of an ether moiety with ionic liquid **39** containing an ether substituent having a higher viscosity that ionic liquid **3**. Ionic liquids **40** and **4** have the same viscosity value, while ionic liquid **41** has a lower value than the corresponding ionic liquid **4**. Comparing ionic liquids **40** and **41**, it can be concluded that the position of the oxygen on the alkyl chain can vary the viscosity of the ionic liquid. The viscosity of ionic liquid **42** is lower than that of ionic liquid **5**. The authors[46] rationalise this decrease as being due to the electron-donating effect of the ether group weakening the electrostatic interaction between cation and anion.[49,50] The opposite trends are observed for the electrical conductivity of ionic liquid **39-42**. The ionic liquids with a higher viscosity, have a lower conductivity than the corresponding alkylated derivatives **3-5**, as would be expected.

It is also of interest to compare ionic liquid **39** with **43** and observe what effects methylation at the 2-position of the cation has on the properties of the ionic liquid. This comparison can also be made with ionic liquids **41** and **44**, **40** and **45**, and **42** and **46**. Addition of a methyl substituent at the 2-position of the cation to give ionic liquid **43** causes an increase in the decomposition temperature. This is also observed on comparing ionic liquids **45** and **40**, however not in the comparison of either ionic liquids **44** and **41**, or **46** and **42**; because of this no conclusions can be made. Due to the reported densities of the ionic liquids **39-46** having such large uncertainties, it is impossible to ascertain any trends in the data. For the viscosity, the ionic liquids **43-46** with a methyl substituent at the 2-position has a higher value than the corresponding non-methylated ionic liquids **39-42**, this suggests methylation at the 2-position causes a decrease in the ion mobility of the system and is further discussed below (see Table 11). The conductivities of the methylated ionic liquids **43-46** are lower than ionic liquids **39-42**, which would be explainable by lower ion mobility for the methylated ionic liquids and, once again, correlate with viscosity data.

The next comparison considers the ionic liquids containing one ether group **43-46** with the corresponding alkylated derivatives **37** and **38** (no data is reported for the analogous *N*-propyl ionic liquid containing a methyl group at the C2 position of the imidazolium cation). A lower decomposition temperature is observed for both the ionic liquids **44** and **45** compared with the parent ionic liquid **37**, showing that addition of an oxygen facilitates decomposition. The same is observed on comparing the data for the ionic liquids **46** and **38**. Again, no conclusions based on the densities of ionic liquids **44-46** and comparison with the corresponding data for the alkylated ionic liquids **37** and **38** can be drawn due to the large uncertainties reported for the cases with ether substituents. For the viscosity, both ionic liquids **44** and **45**, containing an ether group, have a lower viscosity than the corresponding alkylated ionic liquid **37**. This is also observed for the ionic liquid **46** when viscosity data is compared with that for ionic liquid **38**. This is interesting, as it indicates that the changes in intermolecular forces on replacement of a methylene unit with an oxygen results in less restricted motion of the ions. The conductivity of the ionic liquid **44** and **45** containing an ether group is higher than the corresponding ionic liquid **37**, which correlates with the trend in viscosity. The ionic liquids **47** and **48**, with an ether functionality present in both *N*-substituents, have also been investigated; again, with either a hydrogen atom or a methyl group at the C2 position. Without data on the corresponding dialkyl substituted ionic liquids, it is difficult to make any conclusion, however comparison with the mono-ether ionic liquids **41** and **42** can be made. The decomposition temperature is lower in ionic liquid **47** with the two ether substituents than in the ionic liquid **41** with one ether substituent. This is also observed for the longer alkyl cases **48** and **42**. Addition of the second ether group to the ionic liquid cation in ionic liquid **47** causes a further decrease in density and an increase in viscosity when compared with the ionic liquid **41** containing one ether group (the same as salts **48** and **42**). This is more likely to be explained by the addition of a larger substituent (compared to the previous methyl group) rather than either symmetry or the addition of another ether moiety. As has been observed for previous systems, increasing the alkyl chain length will decrease the packing efficiency, resulting in a decrease in density and has been shown to increase the viscosity. The ionic liquid **47** containing two ether groups has a lower conductivity than the ionic liquid **41** containing one ether group indicating less effective movement of charge which may be a consequence of an increased viscosity paralleling that in ionic liquid **48** compared to the salt **42**. The same trends are observed for the ionic liquids **49** and **50** methylated at the 2-position compared with the ionic liquids **44** and **46**.

Another series of imidazolium-based ionic liquids containing ether substituents have been studied. Without data for the corresponding alkylated imidazolium salts, the most reasonable comparisons can be made within the series **51-56** as the length of the alkyl chain increases (Table 7).



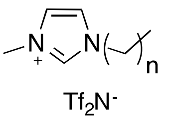
51, n = 2
52, n = 3
53, n = 4
54, n = 5
55, n = 6
56, n = 7

Table 7. The decomposition temperature (T_d), density (ρ) and dynamic viscosity (η) of the imidazolium ionic liquids **51-56** at 298.15 K.[51]

	Ionic liquid	**T_d / K**	**ρ / g cm^{-3}**	**η / mPa s**
1	[(pOm)$_2$im][Tf$_2$N] **51**	508	1.391	82.6
2	[(bOm)$_2$im][Tf$_2$N] **52**	513	1.338	86.7
3	[(p$_e$Om)$_2$im][Tf$_2$N] **53**	503	1.277	95.0
4	[(hOm)$_2$im][Tf$_2$N] **54**	503	1.249	115.0
5	[(h$_e$Om)$_2$im][Tf$_2$N] **55**	513	1.226	144.9
6	[(oOm)$_2$im][Tf$_2$N] **56**	508	1.205	154.0

The trends observed in the properties of the ionic liquids **51-56** above are similar to those trends observed previously; a decrease in density and increase in viscosity with increasing chain length attached to the nitrogen of the imidazolium cation. Once again, this is reasonable and is due to a larger side chains reducing the packing efficiency, causing a lower density and increasing the internal friction along with an increase in dispersion forces. These data show that having an oxygen atom in the side chain does not perturb the correlations observed in such a series. Whilst the decomposition temperatures are also given, no clear trend is observed.

Inclusion of oxygen atoms at the terminal position of the *N*-substituents, thus incorporating hydroxyl groups, has also been examined. Comparison of the properties of the alkylated ionic liquids **2-4** and the hydroxyl derivative **57** show some trends (Table 8).



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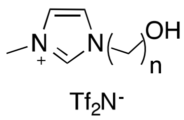
3, n = 2
4, n = 3



57, n = 2

Table 8. The glass transition temperature (T_d), density (ρ), dynamic viscosity (η) and surface tension (σ) of the imidazolium ionic liquids **2-4** and **57** at 298.15 K (unless otherwise noted).

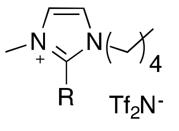
	Ionic liquid	T_g / K ^{a}	ρ / g cm^{-3}	η / mPa s	η / mPa s ^{b}	σ / mN m$^{-1\,a}$
1	[emim][Tf_2N] **2**	-	1.519^c	33.3^d	20.3^e / 30.0^f	-
2	[pmim][Tf_2N] **3**	-	1.475^c	47.0^d	-	-
3	[bmim][Tf_2N] **4**	186	1.42^a	49 ± 1^a	27.5^e	33.0
4	[(HOe)mim][Tf_2N] **57**	192	1.51^a	91 ± 3^a	41.8^f	34

^{a}From Jin *et al.*[13] ^{b}Measured at 313.15 K. ^{c}From Dzuyba *et al.*[27] ^{d}From Bulut *et al.*[30] ^{c}From Tokuda *et al.*[28] ^{d}From Song *et al.*[52]

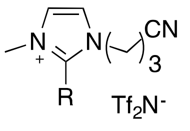
It should be noted that the two studies[13,52] which have prepared ionic liquid **57** have compared it with the alkylated ionic liquids [emim][Tf_2N] **2** and [bmim][Tf_2N] **4**. Looking at the molar masses of the ionic liquids, perhaps a better comparison would be with [pmim][Tf_2N] **3**; irrespective of this, the trends in the data appear to be clear. The hydroxyl containing ionic liquid **57** has a higher glass transition temperature, higher density, higher viscosity and higher surface tension than the corresponding alkylated ionic liquid **3** and, with the exception of density, all data is higher than that for the ionic liquids **2** and **4** also. All of these values are readily rationalised through the incorporation of a group capable of hydrogen bonding with other species, thus increasing the interactions between the components of the ionic liquid.

Related to the ionic liquids where the cation has a hydroxyl group on the *N*-substituents are the cyano ionic liquids **58** and **59**; these also introduce new interactions between components of the liquid that affect the properties (Table 9). The first comparison is between the ionic liquids **58** and **59**, containing a nitrile functional group, with the corresponding alkylated ionic liquids **5** and **38** (due to similar formula weights) though these comparisons are limited somewhat by the availability of data. A higher decomposition temperature is observed for ionic liquid **59** compared with ionic liquid **38**. This demonstrates that addition of a nitrile functional group increases the thermal stability of ionic liquids. A higher glass transition temperature is observed for ionic liquid **58** compared with the alkylated ionic liquid **5**. An increased density is observed for both ionic liquids **58** and **59** when compared with the corresponding alkylated derivatives **5** and **38**. This suggests that addition of a nitrile functional group increases the packing efficiency of the molecules, perhaps due to an increase in the interactions between components of the mixture as a result of the polarity of the introduced nitrile group. The viscosity is higher in ionic liquids **58** and **59** compared with the ionic liquids **5** and **38** while the surface tension also is higher in ionic liquids **58** when compared with **5**; once again, introducing the polar group is likely responsible for these changes.

Other electronegative atoms have also been added to the alkyl chain on the cations of imidazolium ionic liquids, including fluorine. Fluorous ionic liquids are of interest for a number of reasons, typically related to the fact that while fluorine is a small atom that can be a replacement for hydrogen without significantly affecting the overall molecule size, it is also the most electronegative element.[54] It is well established that fluorine substitution can enhance stability and the hydrophobicity of molecules,[54] hence the properties of the series of ionic liquids **60-62** below were considered in Table 10.



5, R = H
38, R = CH$_3$

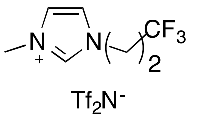


58, R = H
59, R = CH$_3$

Table 9. The glass transition temperature (T_g), decomposition temperature (T_d), density (ρ), viscosity (η) and surface tension (σ) of the ionic liquids **5**, **38**, **58** and **59** at 298.15 K.

	Ionic liquid	T_g / K	T_d / K	ρ / g cm^{-3}	η / mPa s	σ / mN m^{-1}
1	[p$_e$mim][Tf$_2$N] **5**	188[a]	-	1.403[b]	63.3[c] / 57.8[d]	-
2	[p$_e$2m$_2$im][Tf$_2$N] **38**[c]	-	682.85	1.42	100.4	-
3	[(pCN)mim][Tf$_2$N] **58**[b]	202.45	657.45	1.519	286	52.2
4	[(pCN)2m$_2$im][Tf$_2$N] **59**[b]	211.65	697.85	1.483	506	45.2

[a]From Dzuyba *et al.*[27] [b]From Zhang *et al.*[53] [c]From Bulut *et al.*[30] [d]From Tariq *et al.*[32]



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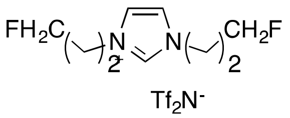

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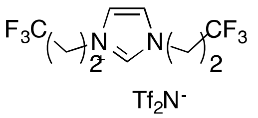


62

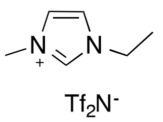
Table 10. The melting temperature (T_m) and density (ρ) of the ionic liquids **60-62**.[55]

	Ionic liquid	T_m / K	ρ / g cm^{-3}
1	[(F$_3$p)mim][Tf$_2$N] **60**	203	1.44
2	[(Fp)$_2$im][Tf$_2$N] **61**	193	1.57
3	[(F$_3$p)$_2$mim][Tf$_2$N] **62**	211	1.85

The temperature at which the density measurements in Table 10 were made was not reported, hence comparison with the non-fluorinated analogues in Table 1 is not possible.[xi] The more fluorine added to the ionic liquids (going from system **61** to system **62**) the larger the density; this is as would be expected given that (as described above), the molecular volume would not be expected to change significantly and fluorine has a higher atomic weight than hydrogen, so any replacement of hydrogen with fluorine should increase the mass per volume. The symmetrical systems **61** and **62** are also more dense than the methylimidazole derivative **60**, which may be a function of the symmetry resulting in greater packing efficiency. Little can be said on the melting point data given the relatively small variation between the compounds.

Modifications of the imidazolium ring of the ionic liquids have also been undertaken. The ionic liquids **63-70** make a useful series in order to consider the effect of substitution both in terms of the site of substitution, extent of substitution, and the size and electronic nature of the substituent. For example, methyl and chloro substituents are of comparable size[56] but differ in their electron donating/withdrawing nature.[57]

[xi] It is assumed that all densities measured in this study were determined at the same temperature.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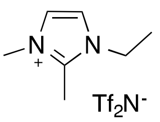
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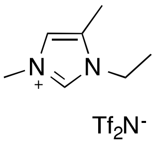
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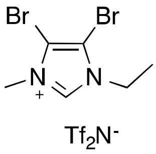
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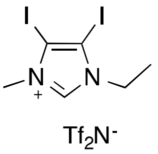
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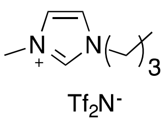
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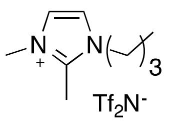
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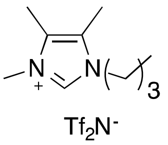
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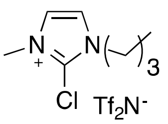
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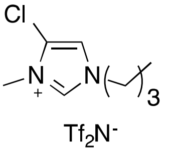
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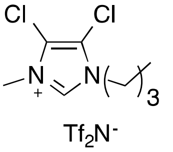
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Table 11. The melting temperature (T_m), density (ρ) and dynamic viscosity (η) of the imidazolium ionic liquids **2**, **4**, **37** and **63-70** at the temperature specified.

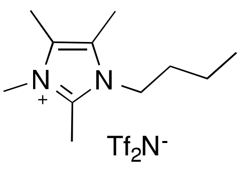
	Ionic liquid	T_m /K	Temperature	ρ / g cm^{-3}	η / mPa s
1	[emim][Tf_2N] **2**		295	1.52[a]	34[a]
2	[emim][Tf_2N] **2**	270[a] / 257.4[b]	298	1.52[b]	33.3[b]
3	[emim][Tf_2N] **2**		363	1.45[b]	6.54[b]
4	[e2m$_2$im][Tf_2N] **63**[a]	293	294	1.495	88
5	[e5m$_2$im][Tf_2N] **64**[a]	267	295	1.470	37
6	[e45Br$_2$mim][Tf_2N] **65**[b]	319	298	1.90	508
7	[e45Br$_2$mim][Tf_2N] **65**[b]		363	1.83	21.4
8	[e45I$_2$mim][Tf_2N] **66**[b]	356.3	363	2.05	47.9
9	[bmim][Tf_2N] **4**[c]	269[d]	298	1.4373[c]	50.34[c]
10	[b2m$_2$im][Tf_2N] **37**[e]	-	298	1.4159	93.33
11	[b45m$_3$im][Tf_2N] **67**[c]	-	298	1.3892 ± 0.0007	70.7 ± 1.6
12	[b2Clmim][Tf_2N] **68**[c]	-	298	1.5005 ± 0.0002	120.52 ± 0.73
13	[b2Clmim][Tf_2N] **68**[c]		323	1.4761± 0.0005	38.40 ± 0.52
14	[b4Clmim][Tf_2N] **69**[c]	315	323	1.4703 ± 0.0002	33.61 ± 0.17
15	[b45Cl$_2$mim][Tf_2N] **70**[c]	-	298	1.5467 ± 0.0004	189.8 ± 2.5
16	[b45Cl$_2$mim][Tf_2N] **70**[c]		323	1.5209 ± 0.0005	49.76 ± 0.49

[a]From Bonhôte *et al.*[4] [b]From Mukai *et al.*[58] [c]From Hawker *et al.*[59] [d]From Tokuda *et al.*[28] [e]From Katsuta *et al.*[60]

There are two comparisons involving addition of methyl groups to the imidazolium ring of the cation that can be made, one between the ionic liquids **2**, **63** and **64** containing an ethyl substituent on the nitrogen and the other involving ionic liquids **4**, **37** and **67** which contain a butyl chain. Looking at the ethyl derivatives **2** and **63**, methylation at the two position causes the density to decrease. This isn't surprising, as addition of a methyl substituent on the imidazolium ring would cause more inefficient packing due to an increase in molar volume. The viscosity of the methylated ionic liquid **63** is higher than **2**, which is not expected. A number of reports[50,61–63] have attempted to determine why the viscosity increases dramatically when methylating at the C2 position. Explaining this in terms of free volume[50,64] or hole theory[65,66] suggests that the less free volume reduces the number of hole carriers for molecular transport, increasing the viscosity.[64]

Addition of a methyl substituent at the 5-position of the imidazolium cation to give the ionic liquid **64** affects properties differently than methylation at the 2-position. The density decreases (more than for the C2 methyl ionic liquid **63**) and the viscosity increases slightly (though not as much as the C2 methyl ionic liquid **63**). This would show that there is less efficient packing in ionic liquid **64** than both the C2 methyl ionic liquid **63** and the parent ionic liquid **2**. All of these properties demonstrate that position of a methyl substituent is important and suggest that the interactions between components of the mixture vary with the site of substitution, perhaps due to the different hydrogen bonding ability of the substituents.

When considering the properties of the butylated imidazolium derivatives **4**, **37** and **67**, similar trends are observed. Introduction of a methyl substituent at the C2 position affects the properties in the same way as for ionic liquids **2** and **63**, with a decrease in density and a large increase in viscosity. Ionic liquid **59** containing two methyl substituents at the C4 and C5 positions has a lower density than both ionic liquids **4** and **37**; again this is as might be expected given these changes would change the shape of the molecule and increase the area of the molecule which will reduce the packing efficiency. The viscosity is interesting; again similar to the ethyl substituted ionic liquids **63** and **64**, the 4,5-dimethyl ionic liquid **67** has a higher viscosity than the parent case **4**, but lower than the C2 methylated ionic liquid **37**. This demonstrates that position of substituents is crucial in terms of viscosity, and blocking the C2 position increases it dramatically. It is interesting to note that the 1-butyl-2,3,4,5-tetramethylimidazolium ionic liquid [b245m$_4$im][Tf$_2$N] **71** has been synthesised,[67] however no physicochemical properties have reported.



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Introduction of electron-withdrawing groups to the aromatic ring also results in changes to the properties of the ionic liquid. First looking at the ionic liquids **65** and **66** with an *N*-ethyl substituent, and comparing them with the protiated ionic liquid **2**, a higher melting temperature is observed. The iodo ionic liquid **66** has a higher melting point than the bromoimidazolium species **65**, likely due to the increased dispersion forces as a result of the larger halogen. For the density, comparing the ionic liquids **2**, **65** and **66** at the one common temperature (363 K), the ionic liquids containing electron-withdrawing groups have higher densities, with the iodo ionic liquid **66** having the highest density; this is likely dominated by introduction of increased dispersion forces though the change in the electronic distribution in the cation on incorporation of an electronegative element is likely also relevant. The same trend is seen in the viscosity of ionic liquids **2**, **65** and **66** as well, with the halogenated ionic liquids having a much larger viscosity than the parent ionic liquid **2**, once again likely due to the increased interactions between components as a result of the introduction of larger, electronegative atoms.

Comparing the chlorinated ionic liquids **68-70** containing electron-withdrawing substituents to the corresponding protiated and methylated ionic liquids **4**, **37** and **67**, shows similar trends to those observed for the ethylated ionic liquids **2** and **63-66**. First looking at the ionic liquid **68** with a chlorine atom at the 2-position and comparing to the protiated and methylated cases **4** and **37** at the only common temperature, a higher density and viscosity is observed for ionic liquid **68**. This isn't surprising as it is the same trend seen above for the other halogenated ionic liquids **65** and **66**, and likely has the same origin. The ionic liquid **69** with the chlorine atom at the 4-position, similar to the cases above, shows that position of a substituent is important in determining properties.

It is difficult to make any comparison for melting points between ionic liquid **69** and any of the other ionic liquids in Table 11, due to insufficient data. However, due to the fact that the ionic liquid **68** containing a chlorine at the C2 position is a liquid at room temperature while ionic liquid **69** is not,[59] it is safe to say that a chlorine at the 4-position in ionic liquid **69** causes the melting point to rise. Because of the increased melting point, the other physicochemical data collected for this ionic liquid are at 323.15 K. For the density, comparing ionic liquid **69** with the protiated ionic liquid **4**, a higher density is observed for the chlorinated case, likely for similar reasons to those described above for the other halogens. Comparing both mono-chlorinated ionic liquids **68** and **69**, small differences are observed for the densities, with a higher value observed for ionic liquid **68**. This might be explained by considering that the addition of a substituent at the C2 position would cause changes to the hydrogen bonding ability of the ionic liquid. For the viscosity, ionic liquid **69** has a lower value compared with ionic liquid **68**, again showing that the position of the substituent is important. When considering the ionic liquid **70** with two chloro substituents it is reasonable to compare the data with those for the parent ionic liquid **4**, the methylated ionic liquid **67** and the mono-chlorinated ionic liquids **68** and **69**. Looking at the density, ionic liquid **70** has the highest density value, compared with the species **4** and **67-69**. Comparing the dichloro system **70** to the methylated ionic liquid **67**, it is interesting to note that although methyl groups and chlorines are similar in size,[56] the differences in mass and in electronic nature causes a large difference in the densities. The presence of the second chorine atom in ionic liquid **70** causes an increase in the density relative to the mono-chlorinated ionic liquids **68** and **69**. The viscosity of ionic liquid **70** is particularly high, with it being almost being four times that of the parent ionic liquid **4**. It is also more than twice the density of the methylated ionic liquid **67** and larger than the mono-chlorinated ionic liquids **68** and **69** at the same temperatures (298.15 K and 323.15 K). These results show that addition of electron-withdrawing chloro substituents to the imidazolium ring will cause an increase in the density and viscosity. Further, all of these results are consistent with the increased mass of a chlorine atom and the increased interactions between components of the ionic liquid due to the electronegativity of the introduced species.

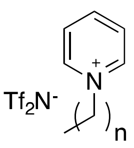
2.2. Ionic liquids containing pyridinium cations

Pyridinium-based ionic liquid cations are becoming more prevalent particularly due to their potential as a lower cost alternative to imidazolium ionic liquids[68] and the fact that their properties, such as thermal stabilities, may be more useful than the related imidazolium systems.[69] They are being applied in a number of different processes including in photoinduced electron transfer,[70] as conductive liquids in electrochemistry and as catalysts in a number of reactions.[11] These ionic liquids are easily synthesized through alkylation of pyridine, and subsequent anion-metathesis depending upon the anion required.[71] Common modifications to the pyridinium cation of these ionic liquids include varying the chain length of the *N*-alkyl substituents and the addition of alkyl substituents around the aromatic ring.[xii] Similar to the fashion in which imidazolium cations are frequently abbreviated, pyridinium cations are commonly abbreviated to the form $[x\text{py}]^+$, where x is the first letter of the name of the alkyl chain on the nitrogen atom.[xiii]

[xii] The latter modification is likely common due to the availability of the corresponding pyridines.

[xiii] With caveats on ambiguity as before.

As for the imidazolium ionic liquids, the most straightforward comparison is for the ionic liquids **72-77** that vary only in the length of the alkyl chain on the nitrogen atom of the cation. Note that only data for the homologues containing an even number of carbons in the chain have been reported.[xiv]



72, n = 1
73, n = 3
74, n = 5
75, n = 7
76, n = 9
77, n = 11

Table 12. The decomposition temperature (T_d), density (ρ), dynamic viscosity (η) and surface tension (σ) of the pyridinium ionic liquids **72-77** at 298.15 K.

	Ionic liquid	T_d **/ K**	ρ **/ g cm^{-3}**	η **/ mPa s**	σ **/ mN m^{-1}**
1	[epy][Tf_2N] **72**^{a}	706	1.532	39.76	35.5
2	[bpy][Tf_2N] **73**	724^a	1.456^a / 1.4476^b	60.55^a / 60.41^b	34.8^a
3	[hpy][Tf_2N] **74**	784^a	1.382^a	245.33^a / 80^c	33.9^a
4	[opy][Tf_2N] **75**^{b}	-	1.3268	114.34	-
5	[dpy][Tf_2N] **76**^{b}	-	1.2835	151.93	-
6	[dodpy][Tf_2N] **77**^{b}	-	1.2488	200.45	-

^{a}From Bittner *et al.*,[11] uncertainties in the density are reported at ± 0.002 g cm^{-3}, uncertainties in the density are reported as ± 0.45 mPa s. ^{b}From Yunus *et al.*,[72] uncertainties in the viscosity are reported as ± 0.35 %. ^{c}From Crosthwaite *et al.*,[69] uncertainties in the density are reported as ± 0.00005 g cm^{-3}, viscosity reported as ± 2 %.

The first comparison is between the imidazolium based ionic liquids and the pyridinium based ionic liquids. Ionic liquid [bmim][Tf_2N] **4** (Table 1, Entry 4) and [bpy][Tf_2N] **73** have very similar molecular weights (419.36 and 416.35 g mol^{-1}, respectively). The pyridinium ionic liquid **73** has a higher density than the imidazolium ionic liquid **4**, which would demonstrate that the pyridinium ionic liquid packs more efficiently than the corresponding imidazolium case. This may be the result of increased charge localisation in the pyridinium cation, though the difference in cation shape will also significantly affect packing efficiency. The pyridinium ionic liquid **73** also has a higher viscosity than the imidazolium ionic liquid **4**, which may be due again to increased charge localisation in the cation.

Clear trends are evident within the alkylpyridinium series of ionic liquids **72-77**. For the decomposition temperatures of ionic liquids **72**, **73** and **74**, a longer aliphatic chain results in a higher decomposition temperature (due to limited data, ionic liquids **75-77** cannot be compared).[11] As was observed for the imidazolium salts with aromatic substituents (Table 4), this suggests that the larger substituents hinder decomposition.

A decrease in the density of ionic liquids **72-77** is observed when the *N*-alkyl chain is increased. Once again, this is consistent with that shown above for the imidazolium series and can be explained by an increase in size of the cation affecting the packing efficiency. The opposite trend is observed for viscosity, with a longer aliphatic chain on the pyridinium cation resulting in an increase in the viscosity of the ionic liquids **72-77**. Once again, this is consistent with the above discussion on the imidazolium systems and these

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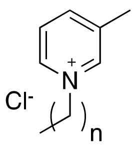
[xiv] No discussion as to why only the even numbered homologues were characterised was presented.

changes can be attributed to decreased mobility of the ions in the ionic liquid as the alkyl chain increases in length due both to flexibility and increased dispersion forces. It is interesting to note the contradictory viscosity data in the literature on the properties of the ionic liquid **74**; one value reported is three times the other![11,69] The discrepancy is discussed,[11] however no origin of the difference was identified. Given the other data available, that reported by Crosswaithe *et al.*[69] better fits the trend present. The larger the *N*-alkyl chain on the cation, the smaller the surface tension for the ionic liquids **72**, **73** and **74** as a result of the increased Coulombic forces between the cation and the anion.

As was the case for the imidazolium species, the melting point data for the above ionic liquids **72-77** is limited, so the corresponding series of chloride ionic liquids **78-85** has been examined (Table 13). It is worth noting that all of this series have a methyl group at the 3-position of the pyridinium ring (and the cations are abbreviated in a fashion analogous to for the imidazolium systems); whilst the effect of this group will be discussed subsequently, the series **78-85** represents an available comprehensive set of melting point data for pyridinium salts.



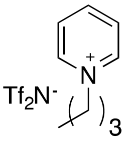
78, n = 3
79, n = 5
80, n = 7
81, n = 9
82, n = 11
83, n = 13
84, n = 15
85, n = 17

Table 13. The melting (T_m) and decomposition temperatures (T_d) of the ionic liquids **78-85**. Uncertainties are reported as ± 0.2 K for T_m and ± 3 K for T_d.[73]

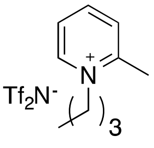
	Ionic liquid	T_m / K	T_d / K
1	[b3mpy][Cl] **78**	384.5	515
2	[h3mpy][Cl] **79**	355.1	511
3	[o3mpy][Cl] **80**	353.2	505
4	[d3mpy][Cl] **81**	352.5	500
5	[dod3mpy][Cl] **82**	360.8	500
6	[ted3mpy][Cl] **83**	366.8	500
7	[hed3mpy][Cl] **84**	383.0	501
8	[ocd3mpy][Cl] **85**	385.4	501

The melting points of ionic liquids **78-85** do not follow a consistent trend; this is similar to that observed previously for the imidazolium chlorides **12-21** (Table 2). There is an initial decrease in melting point on increasing the chain length; then it remains effectively unchanged before increasing from ionic liquid **82** and above. The decomposition temperatures of ionic liquids **78-85** do decrease initially on chain extension, but become invariant for the series from the ten carbon chain case **81** and above.

Given substitution on the aromatic ring has been introduced with the series above, it is worthwhile to also consider the effect of the site of substitution. Alkylation of the parent ionic liquid **73** on the aromatic portion of the cation gives rise to a series of new ionic liquids **86-90** with physical properties as described in Table 14.



73



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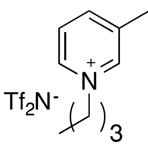

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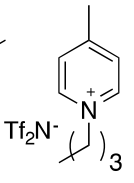

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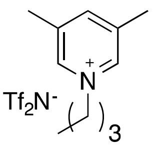

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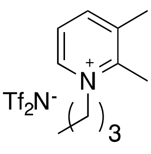

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Table 14. The decomposition temperature (T_d), density (ρ), dynamic viscosity (η) and surface tension (σ) of the ionic liquids **73** and **86-90** at 293.15 K.

	Ionic liquid	**T_d / K**	**ρ / g cm^{-3}**	**η / mPa s**	**σ / mN m^{-1}**
1	[bpy][Tf$_2$N] **73**[a]	724	1.462	75.61	35.0
2	[b2mpy][Tf$_2$N] **86**[a]	721	1.482	143.91	36.5
3	[b3mpy][Tf$_2$N] **87**[a]	727	1.429	81.71	35.8
4	[b4mpy][Tf$_2$N] **88**[a]	724	1.419	65.26	35.4
5	[b3m5mpy][Tf$_2$N] **89**[b]	-	1.386	103	-
6	[b2m3mpy][Tf$_2$N] **90**[b]	-	1.389	186	-

[a] From Bittner *et al.*,[11] uncertainties in the density are reported at ± 0.002 g cm^{-3}, uncertainties in the viscosity are reported as ± 0.45 mPa s. [b] From Papaiconomou *et al.*[74]

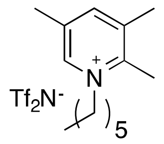
The first comparison is between the ionic liquids **86-88** containing methylated pyridinium cations and the parent ionic liquid **73**. The decomposition temperatures of all four ionic liquids **73** and **86-88** have been measured and no trend is apparent. In terms of density, the position of the methyl group has a significant effect on the density. Compared to the ionic liquid **73**, the ionic liquid **86** with the 2-methylated cation has a higher density, whereas the ionic liquids **87** and **88**, with 3- and 4-methylated cation respectively, both have a lower density. This trends shows that the packing efficiency of these ionic liquids are in the order 2-methyl > protio > 3-methyl > 4-methyl. It is interesting that the variation in effects of the site of substitution here is greater than for the imidazolium cases (Table 11).

The viscosity follows a similar trend; again, the position of the methyl group has a significant effect on the viscosity. Comparing the ionic liquid **86** with the 2-methylated cation with the parent ionic liquid **73**, a large increase in viscosity is observed. Comparing the 3-methylated ionic liquid **87** with the protiated system **73**, an increase is also seen, but not as much as with ionic liquid **86**. In the case of the 4-methylated ionic liquid **88** the viscosity is lower than that of the parent ionic liquid **73**. The changes in mobility of the components of the liquid are unclear, as many things are changing at once, including molar mass, dispersion forces and shape. However the mobility of the components of the ionic liquids vary with the nature of the pyridinium cation in the order of 4-methyl < protio < 3-methyl < 2-methyl and again, the variation in effects is greater and allows more control than the imidazolium series. Similar trends for density and viscosity are found in ionic liquids containing phenyl *N*-substituents (see Mahurin *et al.*[75]).

For ionic liquids **89** and **90** containing multiple methyl substituents, only the density and viscosity can be compared due to limited data for the other properties. Comparing ionic liquid **89** with methyl groups at the 3- and 5- positions with that of the mono-methylated ionic liquid **87** and the protiated ionic liquid **73**, a decrease in density is observed for **89**. This isn't surprising, as addition of a second methyl group would increase the molar volume and cause a decrease in the packing efficiency. The same is observed for ionic liquid **90** with methyl groups in the 2 and 3 positions. There is not a significant difference between the density of ionic liquids **89** and **90**, so no conclusions can be made from this.

The viscosity of ionic liquid **89** is higher than both the mono-methylated ionic liquid **87** and the parent ionic liquid **73**. This is rationalised as there is a change in size of the molecule, which will result in decreased ion mobility. The same is observed for ionic liquid **90**, when compared with **86-87** and **73**. It is interesting to note the differences in viscosity between the ionic liquids **89** and **90**. Ionic liquid **90** has a larger viscosity than **89** (186 compared to 103 mPa s), which is rationalised due to the methyl groups in ionic liquid **90** causing more of a steric hindrance to the nitrogen atom than in ionic liquid **89**.

The length of the alkyl chain appended to the pyridinium rings is also important and can be seen by considering the properties of the pyridinium salts **91-93** (Table 15) which have increasing length of alkyl substitution at the 2-position.



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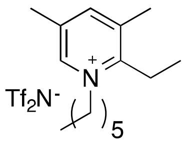

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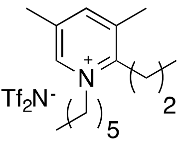

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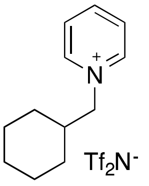
Table 15. The decomposition temperature (T_d), density (ρ), dynamic viscosity (η) and speed of sound (u) of the ionic liquids **91-93** at 298.15 K.

	Ionic liquid	T_d **/ K**	ρ **/ g cm^{-3}**	η **/ mPa s**	u **/ m s^{-1}**
1	[h2m3m5mpy][Tf$_2$N] **91**[a]	643	1.33618	174	1288
2	[h2e3m5mpy][Tf$_2$N] **92**	630[a]	1.31042	236[a]/ 245[b]	1303[a]
3	[h3m5m2ppy][Tf$_2$N] **93**[a]	637	1.25347	278	1291

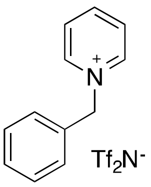
[a]From Verdía *et al.*,[76] uncertainties for density are reported as ± 0.00003 g cm^{-3}, viscosity are reported as ± 2 mPa s, speed of sound reported as ± 1 ms^{-1}. [b]from Crosthwaite *et al.*,[69] uncertainties for viscosity are reported as ± 2 mPa s.

An increase in length of aliphatic chain at the 2-position decreases the density and increases the viscosity of pyridinium ionic liquids. These results are similar to increasing the aliphatic chain on the *N*-substituent and are unsurprising given that increasing the alkyl chain length on the aromatic ring would increase the molar volume, which would change the properties in a similar fashion to that mentioned above for ionic liquids **91-93**. As the decomposition temperatures and speeds of sound of ionic liquids **91-93** are all very similar, no observations can be made. Speed of sound measurements can be related to the interactions between components of solution, with particular opportunity for measuring internal pressure of solvation in ionic liquids.[77] In an effort to determine differences the effects of incorporating cyclic components in the *N*-substituent, cycloalkyl and phenyl groups have also been added to the nitrogen atom of pyridinium ionic liquids, see Table 16.

A comparison of the physical properties of the cyclohexyl ionic liquid **94** with those of the corresponding ionic liquid with the linear *N*-alkyl substituent, would be of interest, however the physicochemical properties of the latter ionic liquid have not been reported. The glass transition temperatures of ionic liquids **94** and **95** are not significantly different.



94



95

Table 16. The glass transition temperature (T_g), melting temperature (T_d), density (ρ) and dynamic viscosity (η) of the ionic liquids **94** and **95** at 293.15 K (unless otherwise noted).[41]

	Ionic liquid	T_g / K	T_m / K	ρ / g cm^{-3}	η / mPa s ^{a}
1	[(cyclohexyl)mpy][Tf$_2$N] **94**	220	314.9	-	65.2
2	[(Ph)mpy][Tf$_2$N] **95**	219	279.6	1.496	32.4

^{a}Viscosity measured at 328.4 K.

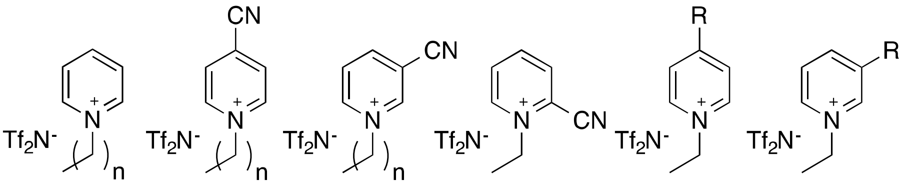
The melting point of ionic liquid **94** containing a cyclohexyl *N*-substituent is higher than the ionic liquid **95** containing a phenyl group suggest that the larger dispersion forces overcome any increased interaction involving the delocalised π system. Due to limited data for ionic liquid **94**, the density of both ionic liquids **94** and **95** cannot be compared. The viscosity for ionic liquid **94** containing the cyclohexyl group is higher than ionic liquid **95** with the aromatic side chain. This has been observed for imidazolium ionic liquids containing cyclohexyl and phenyl substituents (Tables 3 and 4). This is rationalised through the cyclohexyl group having more degrees of freedom and hence less ion mobility, and the differences in the intermolecular forces with ionic liquid **95** containing a π system.

Functionalisation of the pyridinium ring with an electron-withdrawing group such as either a cyano or a trifluoromethyl group also dramatically affects the properties. This is exemplified by the series of ionic liquids **96-105** (Table 17). The data in Table 17 allow comparisons between the parent [epy]$^+$, [bpy]$^+$ and [opy]$^+$ based ionic liquids **72**, **73** and **75**[xv] and those with electron-withdrawing substituents on the pyridinium ring. Due to some large variations in melting temperature of these ionic liquids, the viscosity studies for ionic liquids **96-105** were measured over a range of temperatures; some of the common temperatures have been chosen for some comparison.

For the melting points of ionic liquids **96**, **98**, **99** and **101-103**, only a few comparisons can be made due absence of data for the non-substituted ionic liquids **72**, **73** and **75**. It is difficult to determine any clear trends, as the temperature data are all very similar.

For the density, examining all the ionic liquids **96-101** containing a nitrile group, the density is greater for each of them than for each of the parent cases **72**, **73** and **75**. That is, adding electron-withdrawing substituents causes the density to increase. This is not necessarily surprising as along with a nitrile group having a larger formula weight than a methyl group, the electron-withdrawing nature of the nitrile groups would be expected to introduce additional interactions (along with additional dispersion forces as a result of the larger cation).

[xv] Unfortunately no comparison with the corresponding methylated species is possible due to differing substitution on the nitrogen atom.



72, n = 1 **96**, n = 1 **99**, n = 1 **101** **102**, R = CF_3 **104**, R = CF_3
73, n = 3 **97**, n = 3 **100**, n = 3 **103**, R = CH_3 **105**, R = CH_3
75, n = 7 **98**, n = 7

Table 17. The melting point (T_m), decomposition temperature (T_d), density (ρ) and dynamic viscosity (η) of the pyridinium ionic liquids **72**, **73**, **75** and **96-105**. Densities were measured at 293.15 K. Viscosities were measured at the temperatures noted.

	Ionic liquid	T_m / K	T_d / K	ρ / g cm^{-3}	η / mPa s^{f}	η / mPa s
1	[epy][Tf_2N] **72**[a]	-	706	1.534	39.76	-
2	[bpy][Tf_2N] **73**[a]	-	724	1.456	60.55	-
3	[opy][Tf_2N] **75**[b]	-	-	1.3268	114.34	-
4	[e4CNpy][Tf_2N] **96**[c]	306-308	628	1.567	-	40[g]
5	[b4CNpy][Tf_2N] **97**[c]	-	623	1.474	371	32[g]
6	[o4CNpy][Tf_2N] **98**[c]	303	589	1.348	581	47[g]
7	[e3CNpy][Tf_2N] **99**[c]	346	595	-	-	43[g]
8	[b3CNpy][Tf_2N] **100**[c]	-	593	1.478	1031	75[g]
9	[e2CNpy][Tf_2N] **101**[c]	309-311	541	1.559	610	40[g]
10	[e4CF_3py][Tf_2N] **102**[c]	302-303	591	-	-	16[h]
11	[e3CF_3py][Tf_2N] **103**[c]	301-302	591	-	-	22[h]
12	[e4mpy][Tf_2N] **104**[d]	-	-	1.4919	-	9.9[h]
13	[e3mpy][Tf_2N] **105**[e]	-	-	1.49332	-	10.14[h]

[a]From Bittner *et al.*[11] [b]From Yunus *et al.*[72] [c]From Hardacre *et al.*[78] [d]From Larriba *et al.*,[79] uncertainties in density are reported at ± 0.0006 g cm^{-3}, uncertainties in viscosity are reported as ± 1.3%. [e]From Seoane *et al.*[80] [f]Viscosity measured at 298.15 K. [g]Viscosity measured at 348.15 K. [h]Viscosity measured at 343.15 K.

For ionic liquids **96-103** the temperatures at which the viscosity measurements were taken was dependent on the melting temperatures. The temperatures chosen for comparison (298.15 K for ionic liquids **72**, **73**, **75**, **97**, **98**, **101** and **102**, 343.15 K for ionic liquids **102-105** and 348.15 K for ionic liquids **96-101**) allow for the most correlations to be made. Looking at the ionic liquids measured at 298.15 K, a large increase in viscosity is observed for ionic liquid **101** containing the nitrile substituent relative to the parent case **72**. This is also observed for ionic liquids **73**, **97** and **100** with a *N*-butyl substituent and ionic liquids **98** and **75** with an *N*-octyl substituent. The position of the substituent is also seem to be important, with the ionic liquid **100** (nitrile group at the 3-position) having a significantly higher viscosity than ionic liquid **97** (nitrile substituent at the 4-position). This trend is not evident with ionic liquids **96**, **99** and **101** as all the viscosity measurements at 348.15 K are not significantly different. Throughout these examples, the addition of an electron-withdrawing group (along with resultant change in the shape of the cation and increased dispersion forces) would be expected to increase the interactions between the components of the mixture.

The only comparison for the ionic liquids **102** and **103** containing trifluoromethyl substituents on the pyridinium ring in terms of viscosity is with the corresponding ionic liquids **96** and **99** containing nitrile groups. Although these data is not at the same temperature (343.15 compared to 348.15 K), the comparison is still clear; the ionic liquids **102** and **103** containing trifluoromethyl substituents have a lower viscosity than the ionic liquids **96**, **99** and **101** containing nitrile substituents. This suggests the interactions introduced by the cyano moiety, be they either greater dispersion forces or the result of different charge distributions, are not present in the trifluoromethyl systems.

Another interesting comparison is that between the trifluoromethylated ionic liquids **102** and **103** and the corresponding methylated ionic liquids **104** and **105**. Due to limited data for all of these ionic liquids **102-105**, the viscosity can only be compared at one common temperature; 343.15 K. As was seen for the methylated ionic liquids **87** and **88** above, substitution at the 3-position results in a higher viscosity than substitution at the 4-position. The trifluoromethylated ionic liquids **102** and **103** have higher viscosities than the corresponding methylated salts **104** and **105**, consistent with an increase in dispersion forces.

Functionalisation of the *N*-alkyl chain of pyridinium ionic liquids has also been considered. The series **107-110** below contains nitrile, hydroxyl, ether and ester groups on the alkyl chain attached to the nitrogen.

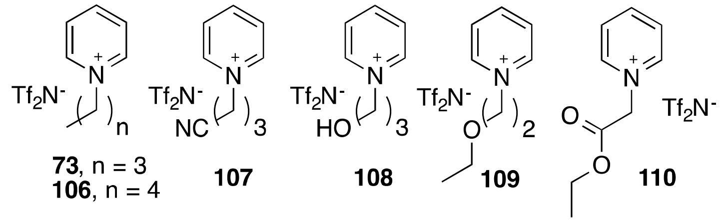


Table 18. The glass transition temperature (T_g), density (ρ) and dynamic viscosity (η) of ionic liquids **73**, **74** and **106-110** at 293.15 K.

	Ionic liquid	T_d / K	ρ / g cm^{-3}	η / mPa s
1	[bpy][Tf$_2$N] **73**[a]	724	1.456	60.55
2	[p$_e$py][Tf$_2$N] **106**[b]	-	1.4259	-
3	[hpy][Tf$_2$N] **74**	784[a]	1.382[a]	245.33[a] / 80[c]
4	[(pCN)py][Tf$_2$N] **107**[d]	547.05	1.534	409
5	[(HOp)py][Tf$_2$N] **108**[e]	-	1.551	160
6	[(eOe)py][Tf$_2$N] **109**[f]	-	1.4667	52.3
7	[(mCOOe)py][Tf$_2$N] **110**[e]	-	1.532	786

[a]From Bittner *et al.*,[11] uncertainties in density are is reported at ± 0.002 g cm^{-3}, uncertainties in viscosity are reported as ± 0.45 mPa s. [b]From Liu *et al.*,[81] uncertainties in density are reported as ± 0.0002 g cm^{-3}. [c]From Crosthwaite *et al.*[69] [d]From Zhang *et al.*[53] [e]From Deng *et al.*,[82] uncertainties in density reported as ± 0.01%, uncertainties in viscosity are reported as ± 2%. [f]From Chen *et al.*,[50] uncertainties in density reported as ± 0.0002 g cm^{-3}, uncertainties in viscosity are reported as ± 2 mPa s.

Each of the ionic liquids **107-110** can be compared to the corresponding alkyl derivative **73**, **74** and **106**; where the molar masses of the cation most closely match. For ionic liquid **107** containing a nitrile group on the *N*-alkyl chain, the corresponding alkyl derivative is the pentyl-substituted ionic liquid **106**. Due to limited data for the pentyl ionic liquid **106**, only density can be compared. Ionic liquid **107** has a higher density than the corresponding ionic liquid **106** with an alkyl *N*-substituent. This is reasonable given the electron-withdrawing nature of the nitrile group and the arguments already presented above. It is important to note that this is the same trend observed for all the other ionic liquids containing nitrile substituents, both on the aromatic ring for ionic liquids **96-101** and the imidazolium ionic liquids **50** and **51**.

For the hydroxylated ionic liquid **108**, the corresponding alkyl system is the butylated ionic liquid **73**. For the density, ionic liquid **108** containing a hydroxyl substituent has a higher density than the alkyl system **73**, likely due to the added hydrogen bonding ability of the cation, increasing the packing efficiency resulting in an increased mass per volume. The hydroxyl based ionic liquid **108** also has a higher viscosity than the corresponding alkylated ionic liquid **73**. Again, these are the same trends observed for the imidazolium ionic liquid **49** containing a hydroxyl group and are likely due to increased interactions between species in the liquid.

For the ionic liquid **109** containing an ether substituent, the corresponding alkyl system is the pentyl ionic liquid **106**. The density for ionic liquid **109** is higher than the alkylated ionic liquid **106**; which is consistent with introduction of an oxygen atom increasing the packing efficiency. The viscosity of **109** cannot be compared with the ionic liquid **106**, due to the lack of data for salt **106**.

It is difficult to compare ionic liquid **110** to an alkylated ionic liquid, due to it containing an ester group. In terms of the length of side chain, the ionic liquid **106** containing a pentyl group seems fitting, based upon molecular mass of the cation it is the ionic liquid **74** containing a hexyl chain that is most relevant. The ionic liquid **110** containing an ester substituent has both a higher density and higher viscosity than both of the corresponding alkylated ionic liquids **74** and **106**. This could be for a number of reasons including the polar nature of the ester substituent.

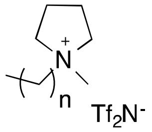
2.3. Ionic liquids containing pyrrolidinium cations

Pyrrolidinium-based ionic liquids can be thought of as tetralkylammonium ionic liquids in which two of the alkyl units are tethered together. They are quite prevalent in the literature[83–85] and are the first series discussed here which does not involve a delocalised π system. They are typically prepared from the corresponding pyrrolidines through alkylation followed by subsequent metathesis.[86] In pyrrolidinium ionic liquids, the most common modifications to the cation involve changes to the length of the *N*-alkyl chain with the addition of functionality on these chains less prevalent. No functionalisation of heterocyclic ring has been recorded, likely due to reactivity of the resultant species. Similar to the fashion in which the ionic liquids used previously are abbreviated, pyrrolidinium cations are commonly abbreviated to the form $[xy\text{pyr}]^+$, where *x* and *y* are the first letters of the names of the alkyl chains on the nitrogen centre.[xvi]

Once again, the most straightforward comparison to be considered is the effect of varying the length of the alkyl chains on the nitrogen centre. This can be done through consideration of the properties of the ionic liquids **111-117**, which are summarised in Table 19. The first comparison is between the different types of heterocycles, particularly the imidazolium and pyrrolidinium systems since the latter can be thought of as the saturated version of the former. The ionic liquids **4** (Table 1, Entry 4), **73** (Table 12, Entry 2) and **112**

[xvi] With caveats on ambiguity as before.

will be compared as they all contain a butyl chain substituent and have similar molecular weights. Each of the ionic liquids **4**, **73** and **112** with different heterocycles will be compared all at the same temperature (298.15 K). For melting temperature, the ionic liquids are in the order of [bpy][Tf$_2$N] **73** > [bmim][Tf$_2$N] **4** > [bmpyr][Tf$_2$N] **112**.



111, n = 2
112, n = 3
113, n = 4
114, n = 5
115, n = 6
116, n = 7
117, n = 9

Table 19. The melting point (T_m), density (ρ), dynamic viscosity (η), surface tension (σ) and electrical conductivity (κ) of the ionic liquids **111-117** at 303.15 K (unless otherwise noted).

	Ionic liquid	T_m / K[a]	ρ / g cm^{-3} [b]	ρ / g cm^{-3} [a]	η / mPa s	σ / mN m^{-1} [b,d]	κ / mS cm^{-1} [a]
1	[pmpyr][Tf$_2$N] **111**	282.1	1.40	1.43	47 ± 3[a]	34.4	3.88 ± 0.06
2	[bmpyr][Tf$_2$N] **112**	266.7	1.39	1.39	60 ± 3[a]/74.9[c,d]	33.0	2.59 ± 0.04
3	[p$_e$mpyr][Tf$_2$N] **113**	283.4	-	1.38	65 ± 4[a]	-	2.07 ± 0.04
4	[hmpyr][Tf$_2$N] **114**	271.4	1.32	1.33	76 ± 4[a]	31.7	1.52 ± 0.03
5	[h$_e$mpyr][Tf$_2$N] **115**	285.3	-	1.30	85 ± 5[a]	-	1.22 ± 0.02
6	[ompyr][Tf$_2$N] **116**	257.8	-	1.27	100 ± 5[a]	-	0.87 ± 0.02
7	[dmpyr][Tf$_2$N] **117**	279.1	1.25	1.26	127 ± 7[a]	31.4	0.62 ± 0.01

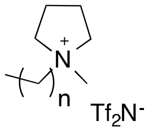
[a]From Appetecchi *et al.*,[87] uncertainties in the melting point are reported as ± 0.1 K, uncertainties in density are reported as ± 0.01 g cm^{-3}. [b]From Jin *et al.*,[13] uncertainties in the density are reported as ± 0.02 g cm^{-3}. [c]From Tokuda *et al.*[28] [d]Results were obtained at 298.15 K.

For the decomposition temperature, the opposite trend is observed with the pyrrolidinium ionic liquid **112** having the highest thermal stability and the pyridinium ionic liquid **73** having the lowest. For the density, the trend is as follows; [bpy][Tf$_2$N] **73** > [bmim][Tf$_2$N] **4** > [bmpyr][Tf$_2$N] **112**. In the case of viscosity, the trend is [bmpyr][Tf$_2$N] **112** > [bpy][Tf$_2$N] **73** > [bmim][Tf$_2$N] **4** which is different again, showing that the imidazolium has a higher mobility of the ions than the other two heterocycles. Whilst rationalising each of these trends is not necessarily straightforward, the trends are of interest as they allow an ionic liquid cation to be chosen based upon the properties required for the ionic liquid.

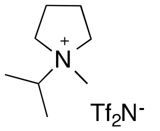
Within the series of ionic liquids **111-117**, there is no trend in melting point with length of the alkyl chain on the pyrrolidinium core though generally the cases with an even number of carbon atoms in the variable *N*-substituent (butyl, hexyl, *etc*) have lower melting points than those with an odd number of carbon atoms on the variable *N*-substituent.

The effect on density and viscosity of modifying the alkyl chain length is very similar for the pyrrolidinium series **111-117** as for the previous imidazolium and pyridinium cases. A decrease in density is observed when the *N*-alkyl chain is increased in length, while the opposite trend is observed for the viscosity of ionic liquids **111-117** with a longer chain length resulting in an increased viscosity. Once again, this is as expected given that the increased alkyl chain length will increase molecular volume and the dispersion forces. The surface tension results for ionic liquids **111-117** show that with a longer chain the surface tension decreases, consistent with a decrease in the strength of inter-particle forces. For the electrical conductivity of ionic liquids **111-117**, a longer aliphatic chain results in a lower conductivity, again due to decreased ion mobility which is consistent with the higher viscosity observed. Importantly, all of the above results are similar to the results previously observed for imidazolium and pyridinium ionic liquids demonstrating that these trends hold for ionic liquids containing the cations discussed so far.

As well as ionic liquids containing pyrrolidinium with straight-chained alkyl substituents on the nitrogen, some ionic liquids with cations having branched alkyl chain substituents have been investigated. The following ionic liquids **118-120** are compared (Table 20) with their corresponding *N*-alkyl ionic liquids **111-112**; the branched nature is indicated by the italicised superscript prefix.



111, n = 2
112, n = 3



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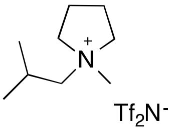
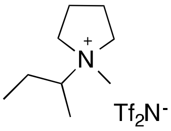


119



120

Table 20. The melting point (T_m), density (ρ), dynamic viscosity (η) and electrical conductivity (κ) of the ionic liquids **111-112** and **118-120** at 303.15 K.[87]

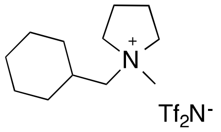
	Ionic liquid	T_m / K	ρ / g cm^{-3}	η / mPa s	κ / mS cm^{-1}
1	[pmpyr][Tf_2N] **111**	282.1	1.43	47 ± 3	3.88 ± 0.06
2	[bmpyr][Tf_2N] **112**	266.7	1.39	60 ± 3	2.59 ± 0.04
3	[^{i}pmpyr][Tf_2N] **118**	372.8	1.46	50 ± 3	2.79 ± 0.05
4	[^{i}bmpyr][Tf_2N] **119**	275.9	-	-	-
5	[^{s}bmpyr][Tf_2N] **120**	291.3	-	-	-

Uncertainties in the melting point are reported as ± 0.1 K, density are reported as ± 0.01 g cm^{-3}.

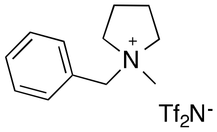
Comparing the melting points of ionic liquids **118-120** with branched alkyl chains with the straight-chained derivatives **111-112**, the branched derivatives have a higher melting temperature with ionic liquid **118** having a significantly larger value that ionic liquid **111**, with a smaller increase for the butyl chain case **120** compared to its linear counterpart **112**.

Due to limited data for the ionic liquids **119-120**, only the properties of propyl-chained ionic liquids **111** and **118** will be compared. For the density, ionic liquid **118** containing an isopropyl group has a higher density than ionic liquid **111** with the linear propyl chain. This is consistent with a higher packing efficiency due to the isopropyl group having fewer degrees of freedom. The viscosity data for the two ionic liquids are the same within uncertainty. The isopropyl ionic liquid **118** has a lower conductivity than the corresponding ionic liquid **111**, presumably due to the lower mobility as a result of the linear alkyl chain.

Ionic liquids containing a pyrrolidinium cation with cycloalkyl and phenyl substituents have been characterised. The properties of ionic liquids **121** and **122** are presented in Table 21.It would be of interest to compare the ionic liquid **121**, with the corresponding heptyl-chained ionic liquid **115**; due to differences in temperatures at which the properties were measured, these two ionic liquids cannot be compared. Looking at the glass transition temperature, ionic liquid **122** containing the phenyl group has a higher temperature than the cyclohexyl ionic liquid **121**. This has been observed with the imidazolium ionic liquids (Table 4) and is rationalised through greater interactions between the components of the aromatic ionic liquid **122**. The melting point data cannot be compared, as there is no measured data for ionic liquid **122**. Ionic liquid **122** containing the aromatic group has a higher density that the corresponding ionic liquid **121**, suggesting there is a higher packing efficiency for the ionic liquid **122** containing the π system. This has also been observed previously for the imidazolium ionic liquids (Table 4).



121



122

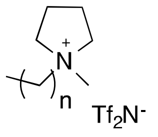
Table 21. The melting temperature (T_m), glass transition temperature (T_g), decomposition temperature (T_d), density (ρ), dynamic viscosity (η) and surface tension (σ) of the ionic liquids **121-122** at 293.15 K.[41]

	Ionic liquid	T_g **/ K**	T_m **/ K**	ρ **/ g cm**$^{-3}$	η **/ mPa s**	σ **/ mN m**$^{-1}$
1	[(cyclohexylm)mpyr][Tf_2N] **121**	205	283.7	1.379	388	35.1
2	[(Phm)mpyr][Tf_2N] **122**	213	-	1.438	567	38.6

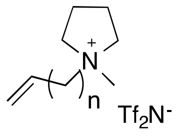
The viscosity of ionic liquid **122** containing the phenyl ring, is higher than that of ionic liquid **121** containing the cyclohexyl ring paralleling trends for some of the imidazolium ionic liquids (Table 4) and for the pyridinium ionic liquids (Table 16). It is rationalised that this may be due to the differences in intermolecular forces of the ionic liquid **122** containing the phenyl group causing a decrease in the ion mobility, though subtle difference in the shape of the cation likely also contribute. The surface tension of ionic liquid **122** containing a phenyl group is higher than that of the ionic liquid **121** containing a cyclohexyl group, again suggesting greater intermolecular forces in the ionic liquid **122**.

Allyl substituents have also been added to the nitrogen atom of pyrrolidinium based ionic liquids as seen in ionic liquids **123-125**. Properties are presented in Table 22 and are compared with alkylated ionic liquids **111** and **113**. Looking at the properties of the ionic liquid **123** containing an unsaturated alkyl chain and comparing those with the properties of the corresponding saturated ionic liquid **111** a number of conclusions can be made, though only data obtained at the same temperature can be compared. In the cases where temperature was not reported, it is assumed that within that work, properties were measured at a single temperature, so that data can be compared. Considering ionic liquids **111** and **123**, the substance containing the unsaturated alkyl chain has a higher glass transition temperature and melting point. The decomposition temperature of ionic liquid **123** containing the allyl chain is lower than ionic liquid **111**, which is not surprising as the allyl substituent would be expected to be more reactive, facilitating decomposition. For the density, the ionic liquid **123** has a higher value than the corresponding saturated ionic liquid **111** (at both 303.15 K and the unspecified temperature). This suggests that the unsaturated chain causes a higher packing efficiency than the saturated chain, most likely due fewer degrees of freedom though there are also likely differences in dispersion forces.

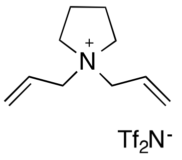
The viscosity of ionic liquid **123** containing an unsaturated alkyl chain is lower than that of the corresponding saturated ionic liquid **111**, presumably due to few degrees of freedom in the unsaturated case. As a corollary to the change in viscosity, the conductivity holds the opposite trend, with **123** having a higher value than **111**, where a higher conductivity is observed with increased ion mobility. Due to large differences in the temperatures at which the properties have been recorded, none of the properties of ionic liquids with a longer alkyl chain **123** and **124** can be compared.



111, n = 2
113, n = 4



123, n = 1
124, n = 3



125

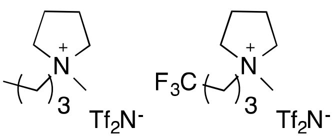
Table 22. The glass transition (T_g), melting (T_m) and decomposition temperatures (T_d), density (ρ), dynamic viscosity (η) and conductivity (κ) of the salts **111**, **113** and **123-125** at 303.15 K (unless otherwise noted).

	Ionic liquid	T_g / K	T_m / K	T_d / K	ρ / g cm^{-3}	η / mPa s	κ/ mS cm^{-1}
1	[pmpyr][Tf$_2$N] **111**	222[a]	281[a]	698[a] / 690[b]	1.426[a] / 1.27[c]	44.7[a]	4.61[a]
2	[p$_e$mpyr][Tf$_2$N] **113**[b]	-	283.4	-	1.38	65 ± 4	2.07 ± 0.04
3	[(allylm)mpyr][Tf$_2$N] **123**	225[a]	284[a]	654[a] / 594[c]	1.447[a] / 1.43[c]	39.5[a]	4.72[a]
4	[(allylp)mpyr][Tf$_2$N] **124**[d]	-	269.3	678	-	90.6	1.15
5	[(allylm)$_2$pyr][Tf$_2$N] **125**[c]	-	-	575	1.40	-	-

[a]From Wu *et al.*,[88] uncertainties in the density are reported as ± 0.01 g cm^{-3} [b]From Appetecchi *et al.*,[87] uncertainties in the melting point are reported as ± 0.1 K, density are reported as ± 0.01 g cm^{-3}. [c]From Yim *et al.*,[84] temperatures not reported. [d]From Baek *et al.*,[89] properties measured at 293.15 K.

Addition of a second allyl chain to give the ionic liquid **125** results in a lower decomposition temperature than for the ionic liquid **123** with one allyl chain, which is reasonable given the argument above about the reactivity of allyl groups facilitating decomposition. The density of ionic liquid **125** is lower than the ionic liquid **123**, consistent with addition of a larger group to the nitrogen atom compared with the previous methyl substituent in ionic liquid **123**. A larger cation will decrease the packing efficiency causing a smaller mass per volume. Limited data prevents any of the other properties being compared.

Fluorine atoms have also been included in the alkyl chain of ionic liquid **126** containing a pyrrolidinium cation, similar to the imidazolium ionic liquids **60-62** described above (Table 10). The properties of these ionic liquids are presented in Table 23.



112 **126**

Table 23. The melting point (T_m), glass transition temperature (T_g), decomposition temperature (T_d), density (ρ), dynamic viscosity (η) and electrical conductivity (κ) of the ionic liquids **112** and **126** at 298.15 K (unless otherwise noted).[90]

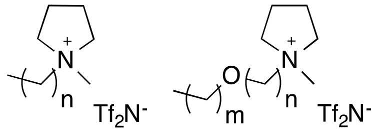
	Ionic liquid	T_g / K	T_m / K	T_d / K	ρ/ g cm^{-3} [a]	η/ mPa s	κ/ mS cm^{-1}
1	[bmpyr][Tf$_2$N] **112**	186	268	691	1.39	81	2.6
2	[(F$_3$b)mpyr][Tf$_2$N] **126**	205	300	697	1.49	288	0.7

[a]Density values measured at 293.15 K, with uncertainties reported as ± 0.01 g cm^{-3}.

Comparing the ionic liquids **112** and **126**, the ionic liquid **126** containing an alkyl chain with fluorine atoms has a higher glass transition temperature, melting temperature and decomposition temperature. This would demonstrate that addition of electron-withdrawing fluorine atom causes changes in the intermolecular forces associated with melting, likely increasing the dispersion forces, and makes the cation more chemically stable than the corresponding ionic liquid **112**, as is consistent with the stability of the carbon-fluorine bond.[54]

The fluorinated ionic liquid **126** has a higher density than the corresponding protiated ionic liquid **112**. This isn't surprising, as the increased formula weight and differences in intermolecular forces, including dispersion, would cause an increase in the mass per volume. The viscosity is also significantly increased in ionic liquid **126** containing a fluorine atom than the corresponding ionic liquid **112**, demonstrating that a decrease in ion mobility is observed. This is consistent with the reduced conductivity of ionic liquid **126** when compared with the protiated ionic liquid **112**, and is likely due to the increased interactions between the components of the solution.

Ether groups have also been added to the cation of pyrrolidinium ionic liquids **127-129**, analogous to the introduction of the ethers in substituents in imidazolium ionic liquids. It should be noted that comparisons here are somewhat limited due to lack of available data.



111, n = 2
112, n = 3
113, n = 4

127, m = 0, n = 1
128, m = 0, n = 2
129, m = 1, n = 1
130, m = 1, n = 2

Table 24. The glass transition temperature (T_g), melting temperature (T_m), decomposition temperature (T_d), density (ρ), dynamic viscosity (η) and electrical conductivity (κ) of the ionic liquids **111-113** and **127-130**.

	Ionic liquid	T_g / K	T_m / K	T_d / K	ρ / g cm^{-3}	η / mPa s	κ / mS cm^{-1}
1	[pmpyr][Tf$_2$N] **111**	222^{a}	281^{a}	669^{a}	$1.40^{b,h}$	$44.7^{a,g}$	$4.61^{a,g}$
2	[bmpyr][Tf$_2$N] **112**	186^{b}	266.7^{c}	-	$1.39^{b,h}$ / $1.387^{d,j}$	$87^{d,i}$	$2.28^{d,i}$
3	[p$_e$mpyr][Tf$_2$N] **113**	283.4^{c}	-	-	$1.351^{d,j}$	$113^{d,i}$	$1.48^{d,i}$
4	[(mOm)mpyr][Tf$_2$N] **127**^{b}	-	252	542	1.4827^{h}	40^{h}	5.5^{h}
5	[(mOe)mpyr][Tf$_2$N] **128**	185^{a} / 182^{b}	-	685^{a} / 689^{b}	$1.4539^{b,h}$ / $1.4546^{f,h}$	$53^{b,h}$ / $54.8^{f,h}$	3.7^{bh}
6	[(eOm)mpyr][Tf$_2$N] **129**	-	-	-	$1.4375^{f,h}$	$38.7^{f,h}$	-
7	[(eOe)mpyr][Tf$_2$N] **130**^{e}	-	-	-	$1.4104^{f,h}$ / 1.41^{j}	$51.8^{f,h}$ / 60^{k}	-

[a]From Wu *et al.*[91] [b]From Zhou *et al.*[92] [c]From Appetecchi *et al.*,[87] uncertainties in the melting point are reported as ± 0.1 K. [d]From Slattery *et al.*[93] [e]From Shirota *et al.*[94] [f]From Chen *et al.*,[50] uncertainties in the viscosity are reported as ± 1.0 %. [g]Results measured at 303.15 K. [h]Results measured at 298.15 K. [i]Results measured at 294.15 K. [j]Results measured at 295.15 K. [k]Results measured at 296.15 K.

The first pair of ionic liquids compared are salt **127**, containing an ether group, and salt **111**, containing a propyl group. Ionic liquid **127** has a lower melting point than ionic liquid **111**. The decomposition temperature for ionic liquid **127** is also lower than that of **111** suggesting that the added oxygen substituent makes the ionic liquid less stable. Looking at the density of ionic liquids **127** and **111**, the ionic liquid **127** containing an ether group has a higher density than the corresponding ionic liquid **111** (at 298.15 K), which demonstrates a greater packing efficiency in the ionic liquid **127** containing an ether group. The viscosity and conductivity data for both ionic liquids **127** and **111** cannot be compared due to the large difference in temperature at which the properties were measured.

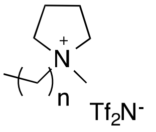
The next comparison is between ionic liquid **128** and **129** with the larger cation and the corresponding ionic liquid **112** containing a butyl group. For ionic liquid **129** only the density and viscosity can be compared, due to limited data reported. Ionic liquid **112** has a lower glass transition temperature than ionic liquid **128**. The ionic liquid **128** and **129** containing an ether group has a higher density than **112** (at 298.15 K), which is the same as for ionic liquids **127** and **111**, suggesting that addition of an ether group on the nitrogen atom causes a greater packing efficiency. For the viscosity, both ionic liquids **128** and **129** have a lower value than the alkylated ionic liquid **112**. This suggests that there is greater ion mobility for the ionic liquids containing ether substituents. It is interesting to directly compare ionic liquids **128** and **129**, with the same chain length but the oxygen atom in different positions. A higher density is observed for the ionic liquid **128** with the oxygen atom further away from the nitrogen atom, then the ionic liquid **129** with the oxygen atom is closer to the nitrogen. This suggests a greater packing efficiency for ionic liquid **128**, compared with salt **129**, perhaps due to the short spacer length of one methylene between the oxygen and the nitrogen on the pyrrolidinium ring.[50] The viscosity of ionic liquids **128** and **129** has a similar trend, with ionic liquid **128** having a higher value than **129**. This suggests that an increase in ion mobility is observed for the ionic liquid **129** with the oxygen closer to the pyrrolidinium ring compared with **128**.

The final comparison is between the ether-containing ionic liquid **130** and the **113**, containing a pentyl substituent. The ionic liquid **130** containing an ether group has a larger density than the corresponding ionic liquid **113** (at 295.15 K). This is the same trend observed for the other ionic liquids **127-129** with likely the same origin. For the viscosity, the ionic liquid **130** containing the ether group has a lower viscosity than the corresponding ionic liquid **113**, this suggests that addition of the oxygen increases ion mobility.

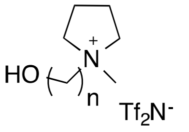
Substituents on the nitrogen atom containing hydroxyl groups have also been investigated in the pyrrolidinium ionic liquids **131-133**, and are summarised in Table 25.

The first comparison to be made is between ionic liquid **131** containing a hydroxyl group and the corresponding alkyl ionic liquid **111**, which has the closest molar mass. A lower glass transition temperature is observed for ionic liquid **131** containing the hydroxyl group than ionic liquid **111** and this has been attributed to a disruption of crystal packing with increasing flexibility of the alkyl chain and reduction of the lattice energy.[91] The melting temperature follows the same trend and shows that these effects override any introduction of hydrogen bonds as a result of the hydroxyl group. The decomposition temperature of ionic liquids **131** and **111** have conflicting trends depending upon the source of the data, so no conclusions can be drawn. Ionic liquid **131** containing a hydroxyl group has a higher density (at both temperatures reported) and viscosity than the corresponding ionic liquid **111**, which isn't surprising as the hydroxyl group is capable of hydrogen bonding, so increased packing efficiency and decrease in ion mobility is readily rationalised. A decrease in the conductivity of ionic liquid **131** containing the hydroxyl group compared with ionic liquid **111** is consistent with the higher viscosity, due to the decrease in ion mobility.

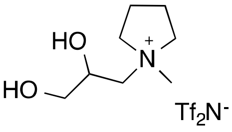
For ionic liquids **132** and **112** with a longer alkyl chain the opposite trends are observed for glass transition temperature and melting point, where ionic liquid **132** containing a hydroxyl group has a higher value than the corresponding ionic liquid **112**; in these systems the introduced hydrogen bonds clearly have a more significant effect.



111, n = 2
112, n = 3
113, n = 4



131, n = 2
132, n = 3



133

Table 25. The glass transition temperature (T_g), melting temperature (T_m), decomposition temperature (T_d), density (ρ), dynamic viscosity (η) and electrical conductivity (κ) of the ionic liquids **111-113** and **131-133**.

	Ionic liquid	T_g / K	T_m / K	T_d / K	ρ / g cm^{-3} a	ρ / g cm^{-3} b,c	η / mPa s a	κ / mS cm^{-1} a
1	[pmpyr][Tf$_2$N] **111**	222^d	281^d	669^d / 707^b	1.4253^d	1.40	44.7^d	4.61^d
2	[bmpyr][Tf$_2$N] **112**	186^b	266.7^e	-	1.39^e	1.39	60 ± 3^e	2.59 ± 0.04^e
3	[p$_e$mpyr][Tf$_2$N] **113**^{e}	283.4	-	-	1.38	-	65 ± 4	2.07 ± 0.04
4	[(HOe)mpyr][Tf$_2$N] **131**	176^d	248^d	682^d / 679^b	1.5044^d	1.51	51.5^d	3.64^d
5	[(HOp)mpyr][Tf$_2$N] **132**^{d}	189	285	642	1.4773	-	90.7	0.585
6	[(p(OH)$_2$)mpyr][Tf$_2$N] **133**^{b}	223	-	645	-	1.61	-	-

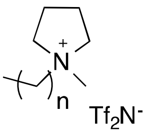
[a]Measured at 303.15 K. [b]From Jin *et al.*,[13] uncertainties for temperatures are reported as ± 2 K [c]Measured at 298.15 K [d] From Wu *et al.*,[91]uncertainties for density are reported as ± 0.001 g cm^{-3} [e] From Appetecchi *et al.*,[87] uncertainties for melting points are reported as ± 0.1 K, density values are reported as ± 0.02 g cm^{-3}.

The same trends are observed for density, viscosity and conductivity as for the ionic liquids **131** and **111**, where the ionic liquid **132** with a hydroxyl group has a larger density (at the common temperature 303.15 K) and viscosity, along with a smaller value for conductivity, than the parent ionic liquid **112** and the origins are likely the same. It is interesting to note that trends in physicochemical properties on hydroxylation are the same as have been observed for the imidazolium ionic liquid **49** (Table 8, Entry 4), showing that these trends occur irrespective of the heterocycle.

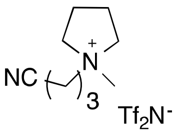
Ionic liquid **133** has a second hydroxyl group added to the alkyl chain and should be compared to ionic liquid **113** which has a similar molar mass. Due to limited reported data, only the glass transition temperature and density can be compared. When comparing these two ionic liquids, the ionic liquid **133** containing the multiple hydroxyl groups has a lower glass transition temperature and a higher density (even though values are measured at different temperatures) than the corresponding ionic liquid **113**, presumably due to greater interactions as a result of the addition of hydroxyl groups.

Other substituents have also been considered with nitrile and ester groups found in pyrrolidinium ionic liquids. The properties for ionic liquids **134** and **135** are presented in Table 26 with the *N*-alkyl ionic liquids **112** and **113**.

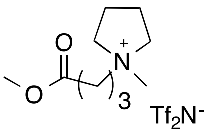
The first comparison is between ionic liquid **134** containing a nitrile functional group and the corresponding ionic liquid **113** (with a similar molecular weight). There is a difference in the temperatures at which the density and viscosity data were collected for the ionic liquids **113** and **134** (293.15 K compared to 295.15 K). This is not be ideal, however, the data clearly shows that the viscosity of the ionic liquid **134** with a cation containing a nitrile group is larger than that of ionic liquid **113**. Addition of a nitrile group would cause differences in the intermolecular forces (including dispersion), so a decrease in ion mobility is reasonable. The opposite trend is also observed for the conductivity of ionic liquids **134** and **113**, in line with what would be expected based on viscosity.



112, n = 3
113, n = 4



134



135

Table 26. The decomposition temperature (T_d), dynamic viscosity (η) and conductivity (κ) of the ionic liquids **112**, **113**, **134** and **135** at 293.15 K (unless otherwise noted).

	Ionic liquid	T_d **/ K**	η **/ mPa s**	κ **/ mS cm^{-1}**
1	[bmpyr][Tf$_2$N] **112**[a]	710	91.8	1.69
2	[p$_e$mpyr][Tf$_2$N] **113**[b,c]	-	113	1.48
3	[(NCp)mpyr][Tf$_2$N] **134**[a]	715	399.0	0.46
4	[(mCOOp)mpyr][Tf$_2$N] **135**[a]	660	211.2	0.79

[a] From Baek *et al.*[89] [b]From Slattery *et al.*[93] [c]Measured at 295.15 K.

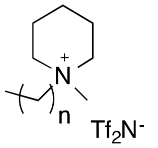
It is difficult to compare the ionic liquid **135** with the corresponding alkyl chained ionic liquid, especially as the ester group is bulky. Perhaps the best ionic liquid would be one with a similar molecular weight, such as ionic liquid **114**, containing a hexyl chain, however density and viscosity data are not available for this ionic liquid at the same temperature as for the ester case **135**; rather here and in literature the comparison is made with the parent butyl case **112**. The viscosity of ionic liquid **135** containing an ester group is large compared with the ionic liquid **112** (and the conductivity is likewise lower). Due to the difference size of the substituents it is difficult to isolate the origin of this changes, which may be due to increased size of the *N*-substituent, because of the electronic properties of an ester group or a combination of both.

2.4. Ionic liquids containing piperidinium cations

Piperidinium cations are clearly related to the pyrrolidinium cations; they are tetraalkylammonium ionic liquids with an extra methylene unit in the ring system. They are readily synthesized through the alkylation of piperidine and subsequent anion metathesis to give the desired ionic liquids.[95] The most common modifications to the cations of this class of ionic liquids arise through variation of the length of the alkyl chain on the nitrogen atom, although vinyl groups, ether moieties and fluorine atoms have also been added. The abbreviation convention used for the piperidinium ionic liquids here is [*xy*pi][Tf$_2$N], where *x* and *y* are the first letters of the names of the alkyl chains on the nitrogen centre.[xvii]

[xvii] With caveats on ambiguity as before.

Similar to the other heterocycles, the first series of ionic liquids considered contains an *N*-alkyl substituent of increasing chain length; the data is presented in Table 27.



136, n = 0
137, n = 1
138, n = 2
139, n = 3
140, n = 4
141, n = 5
142, n = 6
143, n = 7

Table 27. The melting temperature (T_m), density (ρ), dynamic viscosity (η) and conductivity (κ) of the ionic liquids **136-143** at 293.15 K.[95]

	Ionic liquid	T_m / K	ρ / g cm^{-3}	η / mPa s	κ / mS cm^{-1}
1	[mmpi][Tf$_2$N] **136**	400.2	-	-	-
2	[empi][Tf$_2$N] **137**	363.1	-	-	-
3	[pmpi][Tf$_2$N] **138**	285.5	1.414	190 ± 10	0.92
4	[bmpi][Tf$_2$N] **139**	-	1.384	240 ± 10	0.65
5	[p$_e$mpi][Tf$_2$N] **140**	269.7	1.356	280 ± 10	0.54
6	[hmpi][Tf$_2$N] **141**	290.9	1.329	270 ± 10	0.36
7	[h$_e$mpi][Tf$_2$N] **142**	279.4	1.306	330 ± 20	0.26
8	[ompi][Tf$_2$N] **143**	-	1.285	370 ± 20	0.22

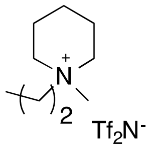
Uncertainties in the melting temperature are reported as ± 0.5 K, uncertainties in the density are reported as ± 0.002 g cm^{-3}, uncertainties in viscosity are as listed, uncertainties in the conductivity are reported as ± 0.01 mS cm^{-1}.

The first comparison to be made is between the piperidinium cations and the other heterocyclic cations discussed above. Comparing the conductivity of the propyl chain piperidinium ionic liquid **138** with ionic liquids **4** (Table 1, Entry 4), **73** (Table 12, Entry 2) and **112** (Table 19, Entry 2) (chosen due to similar molecular weights) the imidazolium salt **4** has the highest conductivity, with the pyrrolidinium case **112** next then ionic liquid **73** and the piperidinium ionic liquid **138** has the lowest conductivity. This suggests that the piperidinium cation causes reduced ion mobility compared with the other ionic liquids **4**, **73** and **112**.

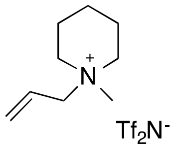
For density, the order is pyridinium **73** > imidazolium **4** > pyrrolidinium **112** > piperidinium **138**, highlighting that piperidinium is by far the least dense. This shows the nature of the packing efficiency of each different heterocyclic cation, with the aromatic cations packing better than the ionic liquids containing a saturated cation. In the case of viscosity, the piperidinium case has a significantly larger viscosity, the order being piperidinium **138** > pyridinium **73** ≈ pyrrolidinium **112** > imidazolium **4**, demonstrating that the anisotropy of the cation is more significant in affecting viscosity.

Increasing the alkyl chain length of the series of ionic liquids **136-143** shows a decrease in density. Again this is consistent with previous cases of increasing alkyl chain length where an increase in size increased dispersion forces and decreased the packing efficiency. For the viscosity the same trend as seen before is observed in these cases, with an increase in alkyl chain length causes an increase in viscosity. In the case of conductivity, an increase in alkyl chain length causes a decrease in conductivity. It is reasonable to suggest that the reasons for these trends are the same as for the ionic liquids containing the other heterocyclic cations discussed above.

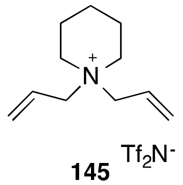
Allyl substituents have also been included in piperidinium ionic liquids **144-145**, with properties of these ionic liquids shown in Table 28.



138



144



145

Table 28. The decomposition temperature (T_d), density (ρ), dynamic viscosity (η) and conductivity (κ) of the ionic liquids **138**, **144** and **145**.

	Ionic liquid	**T_d / K**	**ρ / g cm^{-3}**	**η / mPa s**	**κ / mS cm^{-1}**
1	[pmpi][Tf$_2$N] **138**^{a}	658	1.32	141	2.9
2	[(allylm)mpi][Tf$_2$N] **144**	618^a / 669^b	1.42^a / 1.433^b	108^a / 94.5^b	3.5^a / 2.31^b
3	[(allylm)$_2$pi][Tf$_2$N] **145**^{a}	612	1.45	113	2.3

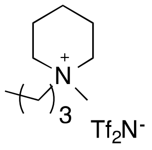
^{a}From Yim *et al.*,[96] temperatures not reported. ^{b}From Wu *et al.*,[88] measured at 303.15 K, uncertainties in the density are reported as ± 0.01 g cm^{-3}.

Comparing the piperidinium ionic liquid **144** to the corresponding pyrrolidinium ionic liquid **123** (Table 22, entry 3) above, the same trends are observed as in the alkyl chain case. A lower decomposition temperature is observed for the pyrrolidinium **123**, compared with the piperidinium **144**, suggesting that the piperidinium case **144** is more stable that the corresponding pyrrolidinium salt **123**. A higher density is observed in the pyrrolidinium ionic liquid **123** compared with the piperidinium ionic liquid **144**, however the values are very similar. A lower viscosity is observed for the pyrrolidinium **123** compared with the piperidinium **144**, suggesting that there is greater ion mobility for the pyrrolidinium ionic liquid **123**. The conductivity for ionic liquid **123** is higher than the corresponding piperidinium **144**, consistent with increased ion mobility for the components of salt **123**.

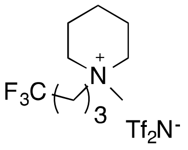
Within the series of ionic liquids **144** and **145** comparisons can be made between a saturated and unsaturated alkyl chain, similar to that shown above with the pyrrolidinium ionic liquids **123-125** (Table 22). Where the temperature at which the readings were taken was not reported, it is assumed that within that work the temperature was consistent, so that data can be compared. Looking at the decomposition temperature, ionic liquid **144** containing the unsaturated alkyl chain has a lower value than the corresponding saturated ionic liquid **138**. This again suggests that addition of the more reactive allyl group facilitates the decomposition. For the density, the ionic liquid **144** containing the allyl substituent has a higher value than the corresponding ionic liquid **138**. This is explained by an increase in packing efficiency, due to fewer degrees of freedom, which is consistent with the trends seen in the pyrrolidinium ionic liquids containing allyl substituents. The viscosity of ionic liquid **144** with unsaturated alkyl chain is lower than the ionic liquid **138** corresponding alkyl substituent, perhaps due to fewer degrees of freedom for ionic liquid **144**. The conductivity holds the opposite trend with ionic liquid **144** containing the unsaturated alkyl chain is higher than the corresponding saturated ionic liquid **138**, as is consistent with its relationship with viscosity.

Addition of a second allyl substituent to the *N*-atom has also been considered following the synthesis of the ionic liquid **145**. No direct comparison to the corresponding saturated ionic liquid with the dipropyl cation can be made due to it not being synthesised at the time of writing. Ionic liquid **145** has a lower decomposition temperature than both the ionic liquids **144** and **138**, suggesting that the addition of a longer alkyl chain offsets any effects of a second vinyl group. Ionic liquid **145** with two unsaturated alkyl chains has a higher density than both **144** and **138**. This perhaps is surprising, as addition of a longer saturated alkyl chain causes the density to decrease in all of the ionic liquids considered so far. This suggests that the symmetrical nature of the ionic liquid facilitates greater packing efficiency. Ionic liquid **145** has a higher viscosity than the ionic liquid **144** with only one allyl substituent. This is readily explained with the addition of a second alkyl chain in ionic liquid **145** changing the intermolecular forces causing a decrease in mobility. The conductivity of ionic liquid **145** with two allyl substituents is lower than both ionic liquid **144** and **138**, which is inconsistent with the trend in their viscosities.

Fluorinated piperidinium ionic liquids have also been investigated in a similar fashion to the pyrrolidinium ionic liquids described in the previous section. The results for ionic liquids **139** and **146** are presented in Table 29; these comparisons are made because the ionic liquids have the same length alkyl chains on the nitrogen centres.



139



146

Table 29. The glass transition temperature (T_g), decomposition temperature (T_d), density (ρ), dynamic viscosity (η) and electrical conductivity (κ) of the ionic liquids **139** and **146** at 298.15 K (unless otherwise noted).[90]

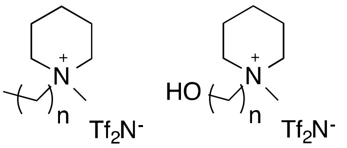
	Ionic liquid	T_g / K	T_d / K	ρ / g cm^{-3} ^{a}	η / mPa s	κ / mS cm^{-1}
1	[bmpi][Tf$_2$N] **139**	196	681	1.34	173	0.6
2	[(F$_3$b)mpi][Tf$_2$N] **146**	216	689	1.48	990	0.2

^{a}Density values measured at 293.15 K, uncertainties in the density are reported as ± 0.01 g cm^{-3}.

It is observed that the effects of adding fluorine are the same as seen previously, with all the properties following the same trends as seen for the pyrrolidinium ionic liquid **126** above. The glass transition temperature of ionic liquid **146** containing fluorine has a higher value than the corresponding protiated ionic liquid **139**. The authors rationalise[90] this as being due to addition of a bulky terminal trifluoromethyl group though the difference in size would not be expected to be large based on previous arguments. The decomposition temperature of the two ionic liquids **139** and **146** follows the same trend, with the fluorinated case **146** being higher than non-fluorinated **139**, this suggests added stability of the ionic liquid when fluorine atoms are included in the cation though it should be noted that the effect is comparatively small, perhaps smaller than might have been expected given the stability of carbon-fluorine bonds.

The density of ionic liquid **146** is higher than the corresponding ionic liquid **139**, which is consistent with previous cases (Tables 10 and 23) with the higher formula weight of the cation and the change in intermolecular forces causing the density to increase. The same trend is observed for the viscosity, with the fluorinated system **146** having a significantly higher viscosity than parent case **139**. The same is observed for the pyrrolidinium ionic liquid **126** where the fluorine causes a decrease in the ion mobility; this is probably again due to changes in the intermolecular forces within the ionic liquid **146** due to the presence of the electronegative fluorine atoms. The conductivity of the fluorinated ionic liquid **146** is lower than that of salt **139**, which would be consistent with the decreased ion mobility observed for the viscosity. It is worth noting that since these trends are similar regardless of nature of the heterocyclic cation, general predictions on properties of the ionic liquids on fluorination of the cation can be made.

Hydroxyl groups have also been added to the alkyl chain of piperidinium cations in ionic liquids. The properties of the ionic liquids **147** and **148** and the corresponding alkyl ionic liquids **138** and **139** with comparable formula weight are presented in Table 30.



138, n = 2
139, n = 3

147, n = 2
148, n = 3

Table 30. The glass transition temperature (T_g), melting point (T_m), decomposition temperature (T_d), density (ρ), dynamic viscosity (η) and electrical conductivity (κ) of the ionic liquids **138**, **139**, **147** and **148** at 303.15 K.

	Ionic liquid	T_g / K	T_m / K	T_d / K	ρ / g cm^{-3}	η / mPa s	κ / mS cm^{-1}
1	[pmpi][Tf_2N] **138**	-	285.5^a	658^b	1.4070^c	110.4^c	-
2	[bmpi][Tf_2N] **139**	196^d	-	681^d	1.3765^c	135.4^c	-
3	[(HOe)mpi][Tf_2N] **147**^{e}	185	250	681	1.4922	82.6	2.16
4	[(HOp)mpi][Tf_2N] **148**^{e}	196	-	649	1.4604	146.5	1.21

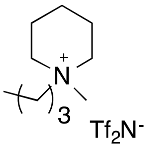
^{a}From Montanino *et al.*,[95] uncertainties in melting point are ± 0.5 K. ^{b}From Yim *et al.*[84] ^{c}From Bhattacharjee *et al.*,[97] uncertainty in the density measurements is reported as ± 0.0005 g cm^{-3}, uncertainty in viscosity is ± 0.35% ^{d}From Le *et al.*,[90] uncertainties for density are reported as ± 0.01 g cm^{-3}. ^{e}From Wu *et al.*,[91] uncertainties for the density are reported as ± 0.001 g cm^{-3}.

A first comparison is between ionic liquid **147** containing a hydroxyl group, with the corresponding ionic liquid **138**. Due to limited data from ionic liquid **138**, the glass transition temperature and conductivity cannot be compared. Looking at the melting point, ionic liquid **147** containing the hydroxyl substituent has a lower melting temperature than the corresponding ionic liquid **138**. The opposite trend is observed for the decomposition temperature of ionic liquids **147** and **138**, with that of salt **147** being higher than that of salt **138**; more extensive chemical functionalization provides alternative decomposition pathways.

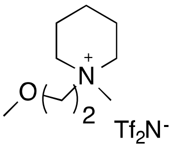
Ionic liquid **147** has a higher density than the corresponding ionic liquid **138**, which is the same results observed for both imidazolium and pyrrolidinium ionic liquids containing hydroxyl groups (Tables 8 and 25). This is rationalised through addition of a group capable of hydrogen bonding causing an increased packing efficiency. For the viscosity, ionic liquid **147** has a lower value than ionic liquid **138**, which was not observed for the imidazolium and pyrrolidinium ionic liquid cations. It is unclear whether this value is an anomaly, or if there is another reason for the difference. Due to limited data for ionic liquid **138**, the conductivity data of the hydroxylated species **147** cannot be compared.

The next comparison to make is between the ionic liquids **139** and **148** with a longer alkyl chain. For the glass transition temperature, both ionic liquids **139** and **148** have the same value, so no conclusions can be made. The decomposition temperatures of ionic liquids **139** and **148** hold the opposite trend observed to ionic liquids **138** and **147**, suggesting the additional functionalization is not as significant in these circumstances.

The density of ionic liquid **148** is higher than the corresponding ionic liquid **139** which is the same as observed for ionic liquids **147** and **138** and also the imidazolium and pyrrolidinium ionic liquids containing hydroxyl substituents (Tables 8 and 25). It is expected that these results have the same origin as previously described. The viscosity is higher for ionic liquid **148** than ionic liquid **139**, which is what is expected based upon addition of a group capable of hydrogen bonding, which would cause a decrease in the ion mobility. Again, due to limited data for ionic liquid **139**, the conductivity data of the hydroxylated species **148** cannot be compared. Alkyl chains containing ether groups have also been included in the cation of piperidinium ionic liquids. The properties of ionic liquid **149** and the corresponding alkyl substituted ionic liquid **139** are presented in Table 31.



139



149

Table 31. The glass transition temperature (T_g), decomposition temperature (T_d), density (ρ), dynamic viscosity (η) and electrical conductivity (κ) of the salts **139** and **149** at 298.15 K (unless otherwise noted).

	Ionic liquid	T_g / K	T_d / K	ρ / g cm^{-3}	η / mPa s	κ / mS cm^{-1}
1	[bmpi][Tf$_2$N] **139**[a]	196	696	1.3786	182	1.1
2	[(mOe)mpi][Tf$_2$N] **149**	191[a] / 193[b]	690[a] / 687[b]	1.4355[a] / 1.4294[b]	102[a] / 79.7[b]	2.0[a] / 2.3[b]

[a]From Zhou *et al.*[92] [b]From Wu *et al.*,[91] properties measured at 303.15 K, uncertainties in the density are reported as ± 0.001 g cm^{-3}.

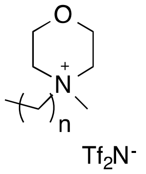
Looking at the glass transition temperature for ionic liquid **149** containing an ether group and comparing that to the data for the corresponding alkyl ionic liquid **139**, a higher temperature is observed for ionic liquid **139** though the differences are small. The same trend is observed for the decomposition temperature, where the ionic liquid **149** containing the ether substituent has a lower value than **139**. This suggests that addition of the oxygen makes the ionic liquid more reactive, assisting in its decomposition. This has also been observed for the imidazolium and pyrrolidinium ionic liquids (Table 7 and 24).

The density of the ionic liquid **149** containing oxygen is higher than that of the ionic liquid **139** with an alkyl group. This effect has been seen with the other ionic liquids containing ether groups (see Tables 7 and 23) and is rationalised by a greater packing efficiency in the ether-containing ionic liquid **149** due to a change in intermolecular forces for the cation. The viscosity is lower for the ether containing ionic liquid **149** than the corresponding ionic liquid **139** demonstrating that the oxygen increases ion mobility, possibly as a result of a change in shape of the cation. As there is greater ion mobility for components of the ionic liquid **149** a larger conductivity value is observed when compared with the parent ionic liquid **139**. Overall, these trends are the same observed for the other ionic liquids examined, irrespective of the nature of the cation.

2.5. Ionic liquids containing morpholinium cations

Morpholinium cations are related to piperidinium cations, however an oxygen atom replaces a methylene group at the 4-position of the heterocycle. These ionic liquids are not very common, but a few studies have investigated their physicochemical properties. Ionic liquids containing morpholinium cations are readily synthesised through alkylation of morpholine and subsequent anion metathesis to give the desired ionic liquids.[98] Variation of the alkyl chain length is the most common modification of the cation of morpholinium ionic liquids, however ionic liquids incorporating cations containing allyl,[xviii] fluoro and ether groups have also been investigated. The abbreviation convention used here for the morpholinium ionic liquids is similar to that used previously; [*xy*mo][Tf_2N], where *x* and *y* are the first letters of the names of the alkyl chains on the nitrogen atoms.[xix]

The first series of morpholinium-containing ionic liquids considered have different length *N*-alkyl substituents. The properties for ionic liquids **150-152** are presented in Table 32.



150, n = 1
151, n = 2
152, n = 3

Table 32. The glass transition temperature (T_g), melting point (T_m), decomposition temperature (T_d), density (ρ) and electrical conductivity (κ) of the ionic liquids **150-152** at 313.15 K (unless otherwise noted).

	Ionic liquid	T_g / K	T_m / K	T_d / K	ρ / g cm^{-3}	κ / mS cm^{-1}
1	[emmo][Tf_2N] **150**[a]	-	309.7	-	1.514	2.4
2	[pmmo][Tf_2N] **151**[b]	235	-	473	1.54	-
3	[bmmo][Tf_2N] **152**[a]	-	308.2	-	1.439	1.2

[a] From Galinski *et al.*[98] [b]From Kim *et al.*,[99] density measured at 298.15 K.

Although there is limited data, some conclusions can be made about the properties above. The first series of comparisons is between the ionic liquids containing the morpholinium cation and ionic liquids containing other heterocyclic cations discussed so far, particularly those containing the piperidinium cation. The morpholinium ionic liquid **151** with the propyl chain will be compared with the corresponding piperidinium ionic liquid **138**, the pyrrolidinium ionic liquid **112**, the pyridinium ionic liquid **73** and the imidazolium ionic liquid **4** as they all have comparable molecular weight.

For the glass transition temperature, the trend is, from the lowest to highest temperature, imidazolium **4** < pyrrolidinium **112** < pyridinium **73** < piperidinium **138** < morpholinium **151**. For the decomposition temperature the trend is morpholinium **151** < piperidinium **138** < pyridinium **73**. Due to limited data for all the other ionic liquids, only the three above can be compared. The results are not surprising with the

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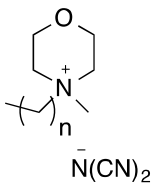
[xviii] Although allyl substituents have been added to morpholinium cations,[88] due to temperature differences, they cannot be compared to the corresponding ionic liquid **151**. Thus, they will not be discussed in this review.

[xix] With caveats on ambiguity as before.

morpholinium containing an oxygen in the ring being more unstable than the corresponding piperidinium ionic liquid. The density of the morpholinium ionic liquid **151** is the highest observed so far of the heterocyclic cations. The order is pyrrolidinium **112** < piperidinium **138** < imidazolium **4** < pyridinium **73** < morpholinium **151**. Comparing ionic liquids **138** and **151** suggests that addition of an oxygen to the ring causes a greater packing efficiency.

Looking at ionic liquids **150-152**, only a few properties can be compared due to limited data and differences in temperature at which the properties were measured. The melting point of ionic liquid **152** is lower than **150**, however no conclusions can be made upon this due to the small differences and the lack of reported uncertainties. Ionic liquid **152** has a lower density than ionic liquid **150** which is what has been observed previously where increasing the alkyl chain length increases the molar volume causing a lower packing efficiency, which outweighs the increasing molar mass. A lower conductivity is observed for ionic liquid **152** than **150**, which is consistent with a decrease in the ion mobility as the alkyl chain increases.

Since the range of morpholinium ionic liquids containing the [Tf$_2$N]$^-$ anion is not extensive, a more comprehensive series containing the dicyanimide anion ([N(CN)$_2$]$^-$).will be considered. The properties for these ionic liquids **153-160** is presented in Table 33.



153, n = 1
154, n = 2
155, n = 3
156, n = 4
157, n = 5
158, n = 6
159, n = 7
160, n = 8

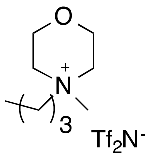
Table 33. The density (ρ), dynamic viscosity (η) and electrical conductivity (κ) of the ionic liquids **153-160** at 298.15 K.[100]

	Ionic liquid	**ρ / g cm$^{-3\,i}$**	**η / mPa s**	**κ / mS cm^{-1}**
1	[emmo][N(CN)$_2$] **153**	1.1682	-	-
2	[pmmo][N(CN)$_2$] **154**	1.1637	410.93	1.340
3	[bmmo][N(CN)$_2$] **155**	1.1183	398.82	1.410
4	[p$_e$mmo][N(CN)$_2$] **156**	1.1224	509.05	0.724
5	[hmmo][N(CN)$_2$] **157**	1.0697	518.24	0.701
6	[h$_e$mmo][N(CN)$_2$] **158**	1.0631	598.20	0.260
7	[ommo][N(CN)$_2$] **159**	1.0347	666.55	0.209
8	[nmmo][N(CN)$_2$] **160**	1.0325	721.09	0.156

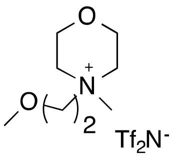
As this series of ionic liquids contain the [N(CN)$_2$]$^-$ anion, the values for density, viscosity and conductivity cannot be compared to any of the ionic liquid containing the [Tf$_2$N]$^-$, anion as it is well known that changing the anion dramatically affects the physicochemical properties.[25]

Within the series **153-160**, as the alkyl chain increases, the density generally decreases, with the exception of ionic liquid **155**. It is unclear whether the butyl case is an anomaly, or this is indicative of the uncertainty in the measurements, given the trends seen previously and the rationale. Similarly for the viscosity, as the alkyl chain increases, so does the value for viscosity except for ionic liquid **155** (and, in parallel, the conductivity decreases with alkyl chain length). The authors did not mention[100] that ionic liquid **155** was an outlier, rather saying that the trend shows odd alkyl chain lengths exhibit viscosity values higher than those of even alkyl chain lengths. They have also mentioned this odd-even effect for both density and conductivity. No rationalisation was given for this observed alternating behaviour.

Ether groups have also been added to the cation of morpholinium-based ionic liquids. The properties of ionic liquid **161** are presented in Table 34, with comparison to the parent system **152** containing simple alkyl substituent on the nitrogen atom.



152



161

Table 34. The glass transition temperature (T_g), decomposition temperature (T_d), density (ρ), dynamic viscosity (η) and electrical conductivity (κ) of the ionic liquids **152** and **161** at 298.15 K.[92]

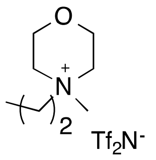
	Ionic liquid	T_g / K	T_d / K	ρ / g cm^{-3}	η / mPa s	κ / mS cm^{-1}
1	[bmmo][Tf_2N] **152**	213	671	1.4405	532	0.4
2	[(mOe)mmo][Tf_2N] **161**	207	660	1.5055	310	0.6

The ionic liquid **161** containing the ether group, has a lower glass transition temperature than the ionic liquid **152**. This is also the case with the decomposition temperature, where ionic liquid **161** containing an ether moiety in the cation is observed to decompose 11 K below the ionic liquid **152** with the alkylated cation. This has been observed previously with the imidazolium ionic liquids (Table 7), pyrrolidinium ionic liquids (Table 24) and piperidinium ionic liquids (Table 31) and is reasonable given that the oxygen in the ether groups makes the cation more reactive, hence assisting in its decomposition. The density of the ionic liquid **161** with the ether group is higher than that of the ionic liquid **152**, consistent with an increased packing efficiency for ionic liquid **161** due to differences in intermolecular forces and has been observed before. The viscosity of the ionic liquid **161** is lower than the corresponding **152** without an ether group in the *N*-substituent. As conductivity and viscosity are inversely related, it is observed that ionic liquid **161** containing the ether group has a higher conductivity than **152**, consistent with increased ion mobility for the ionic liquid containing oxygen.

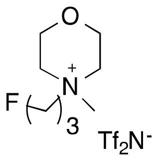
Fluorine has also been incorporated in the alkyl chain of morpholinium cations ionic liquids, both on its own and in conjunction with ether moieties. The properties of the fluorinated ionic liquids **162**, **164** and **166** and the corresponding protiated ionic liquids **151**, **163** and **165** are presented in Table 35, allowing direct comparison and the effects of fluorination to be seen.

Looking at the first two ionic liquids **151** and **162,** ionic liquid **162** with a fluorine atom in the alkyl chain has a lower glass transition temperature than ionic liquid **151**. The decomposition temperature of ionic liquid **162** is significantly higher than the corresponding ionic liquid **151** without a fluorine atom. This suggests that addition of a fluorine atom to the cation causes the ionic liquid to be more chemically stable, which has been observed previous for both the pyrrolidinium ionic liquids (Table 23) and the piperidinium ionic liquids (Table 29). Again, as seen before with addition of fluorine atoms to the cation, the density of **162** is higher than **151**. This is consistent with a larger molecular weight and changes to the intermolecular forces as a result of incorporation of the fluorine atom.

For the ionic liquids **163** and **164** containing ether substituents, similar trends to those described directly above are observed. The glass transition temperature for both ionic liquids **163** and **164** are the same, so no conclusions can be made from this. There is a higher decomposition temperature and density for ionic liquid **164** containing a trifluoromethyl group on the cation, compared with the parent ionic liquid **163**. The origins for these trends are reasonably assumed to be the same as above.



151



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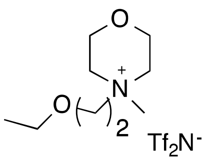

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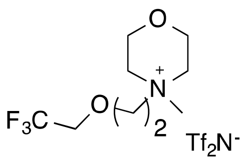

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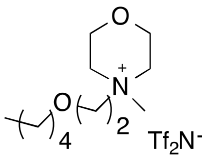

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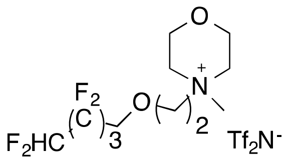


166

Table 35. The glass transition temperature (T_g), decomposition temperature (T_d) and density (ρ) of the ionic liquids **151** and **162-166** at 298.15 K.[99]

	Ionic liquid	T_g / K	T_d / K	ρ / g cm^{-3}
1	[pmmo][Tf$_2$N] **151**	235	473	1.54
2	[(Fp)mmo][Tf$_2$N] **162**	222	615	1.69
3	[(eOe)mmo][Tf$_2$N] **163**	220	662	1.54
4	[(F$_3$CmOe)mmo][Tf$_2$N] **164**	220	685	1.69
5	[(p$_e$Oe)mmo][Tf$_2$N] **165**	220	683	1.38
6	[(F$_2$HC(CF$_2$)$_3$Oe)mmo][Tf$_2$N] **166**	219	673	1.86

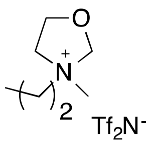
For ionic liquids **165** and **166**, with significantly longer ether chains, slightly different trends are observed. The glass transition temperature of ionic liquid **166** containing the long fluorous ether chain has a lower value than the corresponding protiated ionic liquid **165** though the very small difference limits any conclusions that may be drawn. The opposite trend is also observed for decomposition temperature, where the ionic liquid **166** containing a fluorous chain has a lower value than the ionic liquid **165**. It is uncertain the reason behind this observation though it does suggest that the larger proportion of fluorine atoms facilitates decomposition. The density of ionic liquid **166** follows the predicted trend with a considerably higher density than the corresponding ionic liquid **165**; this is unsurprising given the incorporation of the large number of heavier fluorine atoms.

2.6. Oxazolidinium cations

Oxazolidinium-based ionic liquids are structurally related to both the pyrrolidinium- and morpholinium-based ionic liquids described above; the cations present the same ring size at the pyrrolidinium ionic liquids with an oxygen at the 3-position and can be considered a five-membered version of the morpholinium cation. Although not common in the literature, a number of studies into the physicochemical properties of oxazolidinium ionic liquid has been undertaken. They are readily synthesised by alkylation of oxazolidine and then subsequent anion metathesis to obtain the desired ionic liquid.[99]

Variation of the cation oxazolidinium ionic liquids has been achieved through addition of fluorine and ether groups to the *N*-substituent, however no studies varying the alkyl chain length have been undertaken. The naming convention used for the oxazolidinium ionic liquids here is [*xy*ox][Tf_2N], where *x* and *y* are the first letters of the names of the alkyl chains on the nitrogen centre.[xx]

Addition of a fluorine atom to the *N*-alkyl chain of the cation has been considered for ionic liquids containing oxazolidinium cations, similar to the morpholinium-based ionic liquid **162** described earlier. The properties for ionic liquid **168** and the corresponding non-fluorinated ionic liquid **167** are presented in Table 36.



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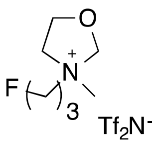

168

Table 36. The glass transition temperature (T_g), decomposition temperature (T_d), density (ρ) and dynamic viscosity (η) of the ionic liquids **167** and **168**.[99] Density data was measured at 298.15 K, viscosity data was measured at 313.15 K.

	Ionic liquid	T_m **/ K**	T_d **/ K**	ρ **/ g cm^{-3}**	η **/ mPa s**
1	[pmox][Tf_2N] **167**	317	620	1.55	340
2	[(Fp)mox][Tf_2N] **168**	-	603	1.63	287

Looking at the decomposition temperature, ionic liquid **168** containing a fluorine atom on the alkyl chain of the cation has a lower value than the parent ionic liquid **167**. This is the opposite to that observed on fluorination of similar, non-ether, species (*cf.* Table 35) and the reason for this is unknown. The density of ionic liquid **168** containing the fluorinated cation is higher than the corresponding ionic liquid **167**; this is what would be expected and is rationalised by the higher formula weight and greater intermolecular forces in the ionic liquid **168**. The viscosity of these ionic liquids does not hold to the expected trend (based on previous series), with the viscosity of ionic liquid **168** containing the fluorine atom in the alkyl chain being lower than ionic liquid **167**. The origin of this is unclear, since the opposite trend in properties of ionic liquids is observed on fluorination of pyrrolidinium (Table 29) and morpholinium cations (Table 35).

Ether moieties have also been incorporated in the *N*-substituent of oxazolidinium-based ionic liquids. The properties of ether-containing ionic liquid **170** and the corresponding ionic liquid **169** (with similar mass) are presented in Table 37. The glass transition temperature of ionic liquid **170** with a cation containing an ether group is higher than the corresponding ionic liquid **169**, though the difference is small; the difference in decomposition temperatures of both ionic liquids **169** and **170** is even smaller and it is difficult to draw conclusions based on these data. For the density, ionic liquid **170** has a higher value than the ionic liquid **169** without the ether group in the cation. This is what has been observed before for ionic liquids containing pyrrolidinium (Table 24), piperidinium (Table 31) and morpholinium cations (Tables 24, 31 and 33) with addition of an oxygen to the alkyl chain causing a greater packing efficiency due to a change in the intermolecular forces. Also, as expected given the data for the ionic liquids considered

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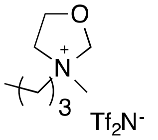
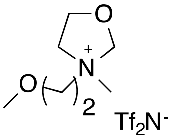
[xx] With caveats on ambiguity as before.

previously (Tables 6, 24, 31 and 33), the ionic liquid **170** containing the ether group has a lower viscosity than the corresponding ionic liquid **169**, consistent with change in the intermolecular forces. It is interesting to note that the conductivity of ionic liquid **170** is lower than the analogous ionic liquid **169** without the ether group as typically conductivity and viscosity are inversely proportional. The reason for the inconsistency in the conductivity and viscosity data is unknown.



169



170

Table 37. The glass transition temperature (T_g), decomposition temperature (T_d), density (ρ), dynamic viscosity (η) and electrical conductivity (κ) of the ionic liquids **169** and **170** at 298.15 K.[92]

	Ionic liquid	T_g / K	T_d / K	ρ / g cm^{-3}	η / mPa s	κ / mS cm^{-1}
1	[bmox][Tf$_2$N] **169**	197	600	1.4645	145	2.1
2	[(mOe)mox][Tf$_2$N] **170**	200	601	1.5127	117	1.8

2.7. Pyrazolium cations

Pyrazolium cations are similar to imidazolium cations, with the nitrogen atoms adjacent to each other in the heterocycle rather than in a 1,3-arrangement. Although this type of cation is uncommon in the ionic liquid literature, some studies have considered ionic liquid containing pyrazolium cations and compared them to the corresponding imidazolium-based ionic liquids. Pyrazolium ionic liquids can be synthesised through the alkylation of pyrazole followed by anion metathesis to give the desired ionic liquid.[101] Modifications of the cation of pyrazolium-based ionic liquids that have been reported include changing the alkyl chain length, methylation of the aromatic ring and the addition of ether groups to the *N*-substituent. The naming convention used for pyrazolium ionic liquids here is [*xy*pz][Tf$_2$N], where *x* and *y* are the first letters of the names of the alkyl chains on the nitrogen centre.[xxi]

The first series of ionic liquids considered here, similar to the other ionic series discussed above, involves variation of the alkyl chain length of the *N*-substituent. The properties of ionic liquids **171-173** are presented in Table 38. It should be noted that these systems have methyl groups attached to the carbon atoms of the heterocyclic ring; no series without such methylation has been studied, restricting comparison to the compounds in Table 38. The effects of methylation will be discussed further below.

For the density of the ionic liquids **171**, **172** and **173**, as the *N*-alkyl substituent increases in length, the density decreases. This is the trend observed for all the other ionic liquids containing heterocyclic cations, where the packing efficiency is decreased due to an additional methylene group. No trend in the viscosities of these ionic liquids is evident. Based on previous cases and the rationale presented, it would be expected that as the length of the alkyl chain on the nitrogen centre is increased, the viscosity would also increase; this is not the case. Similarly, the conductivities of ionic liquids **171-173** do not vary significantly with the length of the alkyl chain on the nitrogen centre. The authors have reported[102] that high values of viscosity

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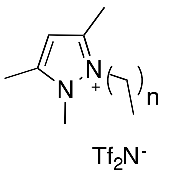
[xxi] With caveats on ambiguity as before.

and low values of conductivity (in imidazolium ionic liquids) result from weak Coulombic forces, high internal mobility and bulky molecular shape. It has also been said that Coulombic forces should be affected by the size of the cation, so this suggests that viscosities the pyrazolium-based ionic liquids are less affected by ionic sizes than those of imidazolium-based ionic liquids.

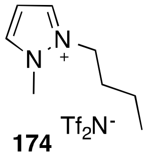


171, n = 1
172, n = 2
173, n = 3

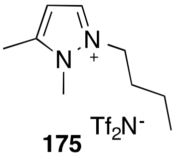
Table 38. The density (ρ), dynamic viscosity (η) and electrical conductivity (κ) of the ionic liquids **171-173** at 303.15 K.[102]

	Ionic liquid	ρ / g cm^{-3}	η / mPa s	κ / mS cm^{-1}
1	[e35m$_3$pz][Tf$_2$N] **171**	1.454	68	3.0
2	[p35m$_3$pz][Tf$_2$N] **172**	1.421	62	2.8
3	[b35m$_3$pz][Tf$_2$N] **173**	1.388	67	2.8

The effect of methylation around the aromatic ring of pyrazolium ionic liquids has been investigated. The properties of ionic liquids **174** and **175** are presented in Table 39. A good comparison of ionic liquids **174** and **175** would be with ionic liquid **173** described above with three methyl substituents. However due to the properties being measured at different temperatures, this is not possible.



174



175

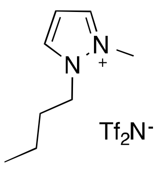
Table 39. The density (ρ), dynamic viscosity (η) and electrical conductivity (κ) of the ionic liquids **174** and **175** at 298.15 K.[101]

	Ionic liquid	ρ / g cm^{-3}	η / mPa s	κ / mS cm^{-1}
1	[bmpz][Tf$_2$N] **174**	1.40	67.1	3.20
2	[b3m$_2$pz][Tf$_2$N] **175**	1.38	76.9	2.60

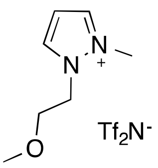
Ionic liquid **174** allows comparisons across a range of ionic liquids **4**, **73**, **112**, **138**, **151** and **169** incorporating different heterocycles (with similar molecular weights). Due to limited data for pyrazolium salt **174** only the density, viscosity and conductivity will be compared with the other heterocycles. For the density, the order is pyrrolidinium **112** ≈ pyrazolium **174** < piperidinium **138** < imidazolium **4** < pyridinium **73** ≈ oxazolidinium **169** < morpholinium **151**. This suggests that ionic liquids containing the pyrazolium cation do not pack very efficiently compared to ionic liquids containing most of the other heterocycles. It is interesting to make a direct comparison between that of isomers **4** and **174**. The pyrazolium ionic liquid **174** has a lower density than the imidazolium **4**, showing that moving either the nitrogen atoms, or the alkyl substituents next to each other will reduce the packing efficiency. For viscosity, the order is imidazolium **4** < pyridinium **73** < pyrazolium **174** < pyrrolidinium **112** < piperidinium **138** < oxazolidinium **169**. It is interesting to note that the ionic liquids with unsaturated heterocyclic cations have lower viscosity than those with saturated heterocyclic cations. For the conductivity, the order for the ionic liquids is piperidinium **138** < oxazolidinium **169** < pyridinium **73** < pyrrolidinium **112** < pyrazolium **174** < imidazolium **4**. The ionic liquids with the higher viscosities have the lower conductivities, due to their relationship.

Looking at how addition of a methyl group to the aromatic ring of the pyrazolium cation in these ionic liquids affects their properties, the same trends are seen with the imidazolium-based ionic liquids (Table 11). The density of methylated ionic liquid **175** is lower than that of the corresponding ionic liquid **174**. This is consistent with a decrease in packing efficiency due to an increase in size of the cation of ionic liquid **175**. The viscosity of ionic liquid **175** is higher than ionic liquid **174** consistent with a decrease in the ion mobility due to a change in ion size and different intermolecular forces. As the viscosity is higher for ionic liquid **175**, the conductivity is, as expected, lower than the corresponding ionic liquid **174**.

Ether groups have also been added to the *N*-substituents of pyrazolium-based ionic liquids. The properties for ionic liquids **176-179** and the corresponding ionic liquid **174** are presented in Table 40.



174



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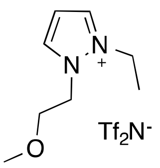

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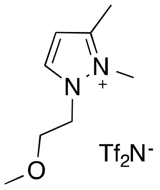
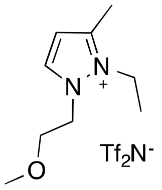


178



179

Table 40. The melting temperature (T_m), decomposition temperature (T_d), density (ρ), dynamic viscosity (η) and electrical conductivity (κ) of the ionic liquids **174** and **176-179** at 298.15 K.

	Ionic liquid	T_m / K	T_d / K	ρ / g cm^{-3}	η / mPa s	κ / mS cm^{-1}
1	[bmpz][Tf$_2$N] **174**[a]	-	-	1.40	67.1	3.20
1	[(mOe)mpz][Tf$_2$N] **176**[b]	<213	614.4	1.43	52.1	3.26
2	[(mOe)epz][Tf$_2$N] **177**[b]	<213	611.5	1.31	41.2	3.31
3	[(mOe)3m$_2$pz][Tf$_2$N] **178**[b]	<213	630.0	1.36	73.0	2.45
4	[(mOe)3mepz][Tf$_2$N] **179**[b]	<213	617.9	1.34	68.3	2.35

[a]From Chiappe *et al.*[101] [b]From Chai *et al.*[103]

With this series of ionic liquids several comparisons can be made. The first of these is what happens when an ether group is added to the alkyl substituent; so comparison is between ionic liquids **174** and **176**. The effects of methylation of the aromatic ring and increased alkyl chain length for the other *N*-substituent can also be readily compared.

When comparing ionic liquid **176** containing an ether group, with the corresponding alkyl ionic liquid **174**, the same trends are observed which have been seen for the other classes of ionic liquids on incorporation of a cation containing an ether moiety. In the case of density, ionic liquid **176** has a higher value than the corresponding ionic liquid **174** containing a simple alkyl substituent. This is consistent with the oxygen in the cation of ionic liquid **176** introducing different intermolecular forces, which result in a lower packing efficiency than ionic liquid **174**. The viscosity for ether-containing ionic liquid **176** is lower than that of ionic liquid **174**. This is also as might be expected and has been observed above for ionic liquids based on other heterocyclic cations. Without uncertainties it is not possible to say whether the conductivities of **174** and **176** are significantly different.

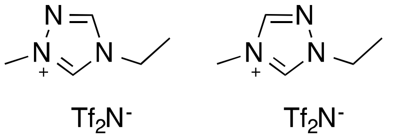
It is useful to subsequently compare ionic liquids **176** and **177** to ascertain any effects of increasing the chain length of the second *N*-substituent from methyl to ethyl has on the properties. Melting temperatures do not vary significantly. The decomposition temperature for ionic liquid **176** containing the ethyl *N*-substituent is lower than that of ionic liquid **177**. This suggests that the increase in alkyl chain length causes the ionic liquid to be less stable, although with other heterocyclic cations no similar trends are observed for this property. When considering the density of the ionic liquids **176** and **177**, increasing the alkyl chain length causes a decrease in the density. This is as would be expected and has been observed for all the ionic liquids, containing a variety of heterocyclic cations, discussed above. The viscosity of ionic liquid **177** containing an ethyl *N*-substituent is lower than that of ionic liquid **176** containing a methyl *N*-substituent; this is unusual given that in previous systems such an increase in the chain length of an *N*-substituent causes an increase in viscosity; the reason for this is unknown. The conductivity for ionic liquid **177** containing the ethyl alkyl chain is higher than the ionic liquid **176** containing the methyl alkyl chain as is consistent with the viscosity data; greater ion mobility gives a higher ionic conductivity. The same trends in density and viscosity are observed for the ionic liquids **178** and **179** also, though the conductivity of ionic liquid **179** is lower than that of ionic liquid **178**; this is anomalous as it is inconsistent with the viscosity data.

The next comparison is between ionic liquids **176** and **178**, to determine if methylation of the aromatic ring has the same effect as described above for the ionic liquids **174** and **175**. The decomposition temperature for ionic liquid **178** containing the additional methyl group on the cation is higher than for the parent ionic liquid **176**. This suggests that the addition of an extra methyl group to the aromatic ring of the cation causes the ionic liquid to be more stable. For density, the ionic liquid **178** containing the cation with the added methyl group has a lower density than the ionic liquid **176**. This is what is described above for the ionic liquids **174** and **175**; it is also observed for the imidazolium and pyridinium ionic liquids (Tables 11 and 14) and the origin (reduced packing efficiency due to an increase in the molar volume) is likely also the same. Ionic liquid **178** has a higher viscosity than the corresponding ionic liquid **176** containing a cation without the extra methyl group. This is also consistent with what has been observed previously (for imidazolium and pyridinium cations). As the viscosity increases, a decrease in the conductivity is observed for ionic liquid **178** containing the extra methyl group when compared with ionic liquid **176**, as would be expected. These trends are also the same with ionic liquids **177** and **179,** except for the density where ionic liquid **179** has a higher value than ionic liquid **177** (1.34 compared with 1.31 g cm^{-1}) and the origin of this difference is not obvious.

2.8. Triazolium cations

Triazolium cations are very similar to imidazolium cations and pyrazolium cations, but with an extra nitrogen atom in the heterocyclic ring; there are two possible arrangements of three nitrogens in the heterocycle giving 1,2,3-triazolium and 1,2,4-triazolium cations; only the latter have been extensively characterised though the former have been prepared.[104] These cations have gained interest as components of ionic liquids useful in energy-rich applications;[105] such salts have greater densities, improved thermal stabilities and reduced vapour pressure relative to other ionic liquids, all of which are advantageous in "energetic" materials.[105,106] Triazolium-based ionic liquids can be synthesized through alkylation of a triazole and subsequent anion metathesis, to the desired anion.[107] The most common modification for these cations is variation to the *N*-alkyl chain length, which will be discussed here.

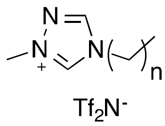
For the cases of unsymmetrical ionic liquids - where there are two different alkyl groups on the nitrogen centres - there are two isomers for the 1,2,4-triazolium cation; this is exemplified in Figure 2 for the two simple ionic liquids. For brevity, these ionic liquids will written as [#*xy*tz][Tf_2N], where *x* and *y* are the first letters of the names of the alkyl chains on the nitrogen atoms,[xxii] and # is the number indicating the position of the *x* substituent.



[4emtz][Tf_2N]   [1emtz][Tf_2N]

Figure 2. Two simple triazolium salts.

The first series of ionic liquids considered is where the *N*-alkyl substituent increases in length. The properties of the ionic liquids **180-185** are presented in Table 41. Also included is the ionic liquid **181**, which allows for the effect of the branching of an alkyl substituent to be considered.



180, n = 1
182, n = 2
183, n = 3
184, n = 5
185, n = 7

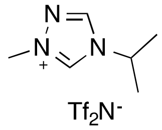


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Table 41. The glass transition temperature (T_g), density (ρ) and dynamic viscosity (η) of the ionic liquids **180-185** at 298.15 K.[107]

	Ionic liquid	T_g / K	T_d / K	ρ / g cm^{-3}	η / mPa s
1	[4emtz][Tf_2N] **180**	203.6	531	-	-
2	[4^{i}pmtz][Tf_2N] **181**	204.9	563	1.484	107 ± 1
3	[4pmtz][Tf_2N] **182**	201.9	624	1.485	102 ± 1
4	[4bmtz][Tf_2N] **183**	207.8	616	1.489	246 ± 3
5	[4hmtz][Tf_2N] **184**	202.4	617	1.372	130 ± 3
6	[4omtz][Tf_2N] **185**	201.8	611	1.314	154 ± 5

The first comparisons for this series of ionic liquids are with previously discussed ionic liquids containing different cations, particularly the imidazolium and pyrazolium series. The triazolium-based ionic liquid **183** will be compared with the other ionic liquids **4**, **73**, **112**, **138**, **151**, **169** and **174** which have similar formula weights. Looking at the glass transition temperature, the order of ionic liquids is: imidazolium **4** < pyrrolidinium **112** < pyridinium **73** ≈ oxazolidinium **169** < piperidinium **138** < triazolium **183** < morpholinium **151**. The decomposition temperatures of the ionic liquids are in the order: morpholinium **151** < oxazolidinium **169** < triazolium **183** < piperidinium **138** < pyridinium **73**. For the density, the order is pyrrolidinium **112** ≈ pyrazolium **174** < piperidinium **138** < imidazolium **4** < pyridinium **73** ≈ oxazolidinium **169** < triazolium **183** < morpholinium **151**. This suggests that the triazolium cation has a higher packing efficiency than the other heterocycles except for morpholinium cations. Along with the highest density, the triazolium ionic liquid **183** has the highest viscosity with the order being imidazolium **4**

[xxii] With caveats on ambiguity as before.

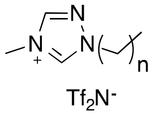
< pyridinium **73** < pyrazolium **174** < pyrrolidinium **112** < piperidinium **138** < oxazolidinium **169** < triazolium **183**. This suggests that it is the addition of the extra nitrogen (when compared with imidazolium case **4**) that changes the intermolecular forces.

Looking at the ionic liquids **180** and **182-185**, the glass transition temperature and decomposition temperatures do not follow a trend. This is consistent with the series of ionic liquids containing imidazolium heterocyclic cations that have been discussed above (Table 1). The density of ionic liquids **182** and **183** are very similar, whilst increasing the length of the *N*-alkyl substituent further results in a decrease in the density of the ionic liquids. The latter is consistent with that seen for previous series (imidazolium, pyridinium, pyrrolidinium, piperidinium, morpholinium and pyrazolium); the similarity between the first two values may give an indication of the uncertainties in the data, which are not reported. When considering viscosity of ionic liquids **180** and **182-185** with increasing alkyl chain length, the value for the ionic liquid **183** with a butyl chain is significantly higher than that of the other ionic liquids (which increase in a systematic fashion, as has been seen for other ionic liquids previously and is readily rationalised). The origin for this anomaly is not clear.

Comparing ionic liquid **180** containing a cation with an *n*-propyl substituent with ionic liquid **181** containing a cation with an *i*-propyl substituent shows that ionic liquid **181** with the branched alkyl chain has a higher glass transition temperature than ionic liquid **180** and this might arise from a change in the structure to one with fewer degrees of freedom. The ionic liquid **181** also has a lower decomposition temperature than the ionic liquid **180**, suggesting that the branched nature of the cation of the ionic liquid **181** helps facilitate decomposition. In the case of density, the values are not sufficiently different such that, without valid uncertainties, further discussion is not warranted. For the viscosity data, the ionic liquid **181** containing cation with the *i*-propyl group has a higher value than the ionic liquid **180**. This would be consistent with there being less ion mobility due to the bulkier side chain. These trends are the same as those observed for that of branched alkyl chains in ionic liquids containing other heterocyclic cations (Tables 5 and 20).

The next series of ionic liquids is isomeric to that described above with the larger substituent being at the 1-position of the heterocyclic ring in this case. The study[105] originally reporting these properties did not tabulate the data (either in the manuscript or supporting information), so some of the discussion presented below is based on data presented graphically and in text. The glass transition temperature and decomposition temperatures are presented in Table 42.

Looking at the glass transition temperature and decomposition temperature for ionic liquids **186-192**, no clear trend is observed. This is consistent with glass transition temperatures of ionic liquids containing other heterocyclic cations described above. The density values for ionic liquids **186-192** were presented in a graph and it could be observed that as the alkyl chain length increases, the density decreases. This is consistent with what as been observed previously for series ionic liquids containing one of a range of heterocyclic cations. The viscosity values were presented graphically and it could be observed that as the length of the alkyl chain on the nitrogen centre increases in the ionic liquids **186-192**, the viscosity increases. The authors describe this as analogous to imidazolium-based ionic liquids and attribute it to increased van der Waals forces between the alkyl chains as the chain length increases;[105] this is consistent with the explanations put forward above for previous systems. The molar conductivity was also investigated and with increasing alkyl chain length of ionic liquids **186-192** the conductivity decreased, consistent with the viscosity data.



186, n = 1
187, n = 2
188, n = 3
189, n = 5
190, n = 7
191, n = 9
192, n = 11

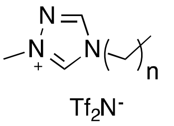
Table 42. The glass transition (T_g) and decomposition temperature (T_d) of the ionic liquids **186-192**.[105]

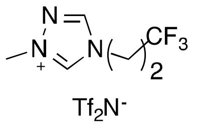
	Ionic liquid	T_g / K [a]	T_d / K [a]
1	[1emtz][Tf_2N] **186**	200.2	628
2	[1pmtz][Tf_2N] **187**	201.4	638
3	[1bmtz][Tf_2N] **188**	202.8	623
4	[1hmtz][Tf_2N] **189**	201.7	618
5	[1omtz][Tf_2N] **190**	200.8	619
6	[1dmtz][Tf_2N] **191**	-	630
7	[1dodmtz][Tf_2N] **192**	-	627

[a] Uncertainties in the glass transition and decomposition temperatures are reported as ± 0.2 K.

Fluorinated triazolium ionic liquids have also been studied. The properties for ionic liquids **193**, **194** and the corresponding protiated ionic liquids **182** and **185** are presented in Table 43. The first comparison is between ionic liquid **193** which contains a trifluorinated cation and the corresponding ionic liquid **182** with a protiated cation. Ionic liquid **193** containing the fluorine atoms has the higher glass transition temperature. This is not surprising and has been observed for the pyrrolidinium ionic liquids described above (Table 23), with likely the same origin (change in intermolecular forces). The decomposition temperature of ionic liquid **193** containing fluorine atoms is higher than that of the ionic liquid **182**, suggesting this level of fluorination does not facilitate, rather it inhibits decomposition; this effect has also been observed for ionic liquids containing pyrrolidinium cations (Table 23) and those containing piperidinium cations (Table 29). The temperature at which the density of ionic liquid **193** was measured was not reported, although based upon the value of ionic liquid **193** (1.66 g cm^{-3}) it can reasonably be said that its value is significantly higher than that of the parent ionic liquid **182**. This is expected, as the introduction of fluorine to the cation increases the molar mass of the cation and changes the intermolecular forces; this has been discussed previously for ionic liquids containing imidazolium, pyrrolidinium, piperidinium, morpholinium and oxazolidinium cations (Tables 10, 23, 29, 35 and 36).

The only comparison that can be made between ionic liquids **194** and **185** is for the decomposition temperature data. The decomposition temperature for ionic liquid **194** containing the fluorous chain is higher than that for the corresponding octyl chain ionic liquid **185**. This is consistent with the data presented immediately above for related systems. The next series of ionic liquids although not simply related through the extension of an alkyl chain or addition of a particular functional group, allows the effects of variously substituted aryl groups on the *N*-alkyl chain of triazolium cations on the properties of the corresponding ionic liquids to be assessed. The properties of the ionic liquids **195-199** are presented in Table 44.


182, n = 2
185, n = 7


193

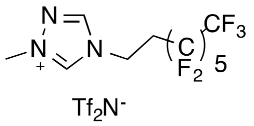
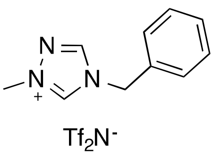

194

Table 43. The glass transition temperature (T_g), decomposition temperature (T_d) and density (ρ) of the ionic liquids **182**, **185**, **193** and **194** at 298.15 K (unless otherwise specified).

	Ionic liquid	T_g / K	T_d / K	ρ / g cm^{-3}
1	[4pmtz][Tf_2N] **182**[a]	201.9	624	1.485
2	[4omtz][Tf_2N] **185**[a]	201.8	611	1.314
3	[4(F_3p)mtz][Tf_2N] **193**[b]	215	649	1.66
4	[4($CF_3(CF_2)_5$e)mtz][Tf_2N] **194**[b]	-	654	-

[a]From Hillesheim *et al.*[107] [b]From Mirzaei *et al.*,[108] no temperature was reported.

The first comparison to make is that between ionic liquid **195** containing a benzyl group and the ionic liquids **196** and **197** containing a trifluoromethoxy substituent at either the *para* or *ortho* position on the phenyl ring. Looking at the glass transition temperatures for the three ionic liquids **195-197** the values are not significantly different so no conclusions can be drawn. The decomposition temperatures of ionic liquids **196** and **197** containing the trifluoromethoxy substituents are higher than the corresponding ionic liquid **195**. This suggests that the trifluoromethoxy substituent is causing the ionic liquid to be more thermally stable, irrespective of the site of substitution and is consistent with previous cases where fluorine has been added to the cation of an ionic liquid (see the ionic liquids containing either pyrrolidinium or piperidinium cations, Tables 23 and 29). It is difficult to differentiate between the decomposition temperatures of ionic liquids **196** and **197** due to no uncertainties being presented.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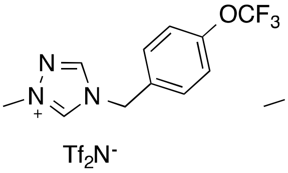
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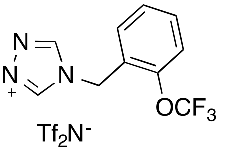
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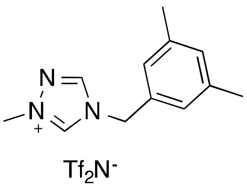
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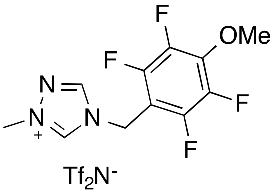
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Table 44. The glass transition temperature (T_g), decomposition temperature (T_d) density (ρ) and dynamic viscosity (η) of the ionic liquids **195-199** at 298.15 K.[107]

	Ionic liquid	T_g / K	T_d / K	ρ / g cm^{-3}	η / mPa s
1	[(Ph)mmtz][Tf_2N] **195**	227.2	544	1.488	317 ± 10
2	[(4-CF_3OPh)mmtz][Tf_2N] **196**	228.6	561	1.590	530 ± 33
3	[(2-CF_3OPh)mmtz][Tf_2N] **197**	227.5	567	1.598	573 ± 23
4	[(35m_2Ph)mmtz][Tf_2N] **198**	235.9	526	1.420	839 ± 34
5	[(4-MeOFPh)mmtz][Tf_2N] **199**	238.8	563	-	2048 ± 51

Ionic liquids **196** and **197** have higher densities than the unsubstituted ionic liquid **195**. This suggests that the ionic liquids **196** and **197** have a better packing efficiency than ionic liquid **195**, which may be the result of introducing these substituents and increasing the interactions between the components of the ionic liquid. Looking at the difference between ionic liquids **196** and **197** with different positions of the trifluoromethoxy group, the ionic liquid **197** with an *ortho* substituent has a higher density than ionic liquid **196** with *para* substitution; the origin of this difference is unknown. The viscosity values for ionic liquids **196** and **197** are higher than for ionic liquid **195** without substitution on the phenyl ring of the cation. This is consistent with reduced ionic mobility due to differences in the intermolecular forces caused by addition of an electron-withdrawing group to the phenyl ring. The uncertainties for the viscosity values are quite large, so no differentiation between ionic liquids **196** and **197** can be made. The next comparison is between ionic liquid **198** containing methyl substituents at both *meta*-positions of the phenyl ring and the ionic liquid **195**. For the glass transition temperature, the methylated ionic liquid **198** has a higher temperature than the parent ionic liquid **195**. The opposite is observed for the decomposition temperature, with ionic liquid **198** decomposing at a lower temperature than the ionic liquid **195**. This suggests that addition of methyl groups to the phenyl ring helps facilitate decomposition. The density of ionic liquid **198** is lower than the corresponding ionic liquid **195**; this isn't surprising as addition of bulky methyl groups would increase the molar volume resulting in a decreased packing efficiency. This is observed for addition of methyl substituents in ionic liquids containing either imidazolium or pyridinium cations (see Tables 11 and 14). The viscosity of ionic liquid **198** is significantly higher than the corresponding unsubstituted case **195**. Again this suggests that the methyl groups are causing reduced ion mobility for ionic liquid **198**, likely due to differenced in the intermolecular forces, and is consistent with previously.

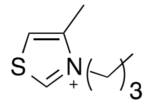
The last comparison made here is between ionic liquid **199** containing a *para*-methoxy substituent and fluorine atoms around the remainder of the phenyl ring and the parent ionic liquid **195**. The glass transition temperature is higher in ionic liquid **199** than for ionic liquid **195**, which is due to the number of additional fluorine atoms. This is not surprising as fluorine atoms appear to increase both the glass transition and melting temperatures of ionic liquids (Tables 23 and 29). The decomposition temperature for ionic liquid **199** is also higher than the unsubstituted ionic liquid **195**, consistent with fluorination results previously and the effects of trifluoromethoxy groups noted above. The density of case **199** is unable to be compared with the other system **195** due to data not being available for ionic liquid **199**. Ionic liquid **199** has a signifcantly higher viscosity than ionic liquid **195**, suggesting that ionic liquid **199** has very limited ion mobility, likely due to the differences in intermolecular forces and weight of the molecule. This may be the result of either the addition of four fluorine atoms, the introduction of the methoxy group at the *para* position or a combination of both; previous data suggests the latter.

2.9. Thiazolium cations

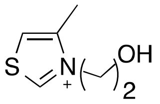
Thiazolium-based cations are similar to imidazolium cations with one of the nitrogen atoms replaced by a sulphur atom. Ionic liquids based on this type of cation are rare in the literature, however a recent study has determined the physicochemical properties of a few thiazolium ionic liquids with a range of *N*-substituents.[109] These ionic liquids can be readily synthesised through the alkylation of thiazole and subsequent anion metathesis to give the desired ionic liquids.[109] The abbreviation convention used here for the thiazolium-based ionic liquids is [*x*th][Tf_2N], where *x* is the first letter of the name of the alkyl chain on the nitrogen centre.[xxiii] Currently there is no study on the physicochemical properties of a series of these salts in which the length of the *N*-alkyl substituent is varied, nor any studies on systems which are not substituted at the C4 position.

Hydroxy, phenyl and ester substituents are added to the *N*-substituent in the series of thiazolium ionic liquids below; the properties of ionic liquids **200-203** are presented in Table 45. It is worth noting that only ionic liquids containing 4-methylated thiazolium cations have been prepared in literature.

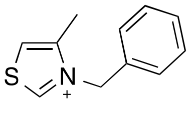
On comparing the properties of the ionic liquids **200** and **201**, which have similar molecular weights, a few trends are observed. The glass transition temperature of the ionic liquid **201** containing a cation bearing a hydroxyl group is higher than that of the ionic liquid **200**. This can be rationalised in that introduction of a group capable of hydrogen bonding increases intermolecular forces and the energy required for the transition.



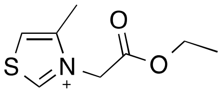
Tf$_2$N$^-$ **200**



Tf$_2$N$^-$ **201**



Tf$_2$N$^-$ **202**



Tf$_2$N$^-$ **203**

Table 45. The melting temperature (T_m), decomposition temperature (T_d), density (ρ) and dynamic viscosity (η) of the ionic liquids **189-192** at 298.15 K.[109]

	Ionic liquid	T_g **/ K**	T_d **/ K**	ρ **/ g cm**$^{-3\,a}$	η **/ mPa s**
1	[b4mth][Tf$_2$N] **200**	205.1	627.6	1.505	129 ± 2
2	[(HOe)4mth][Tf$_2$N] **201**	208.8	618.0	1.626	216 ± 6
3	[(Ph)m4mth][Tf$_2$N] **202**	226.7	544.2	1.548	443 ± 5
	[(eCOOm)4mth][Tf$_2$N] **203**	226.3	582.8	1.562	613 ± 9

[a]Density values are not experimental values; they were calculated using COSMOtherm.

Ionic liquid **201** with the hydroxyl group has a lower decomposition temperature than the corresponding alkyl ionic liquid **200**.In terms of density, the ionic liquid **201** containing the hydroxyl group has a higher value than the corresponding ionic liquid **200**. This isn't surprising as the substituent capable of hydrogen bonding will increase the forces between the components of the ionic liquid, reducing the molar volume. The viscosity of ionic liquid **201** is higher than the corresponding alkylated ionic liquid **200** and, again, this is consistent with the introduction of a group capable of hydrogen bonding and the resultant increase in the intermolecular forces. All of the above trends have been observed with the other ionic liquids based on hydroxyl-containing cations, demonstrating that these occur irrespective of the nature of the heterocyclic cation used.

The ionic liquid **202** with a phenyl group on the cation has a higher glass transition temperature than the butylated ionic liquid **200**, which is reasonable given the increase in molecular mass and the increase in forces between components based on the introduction of the additional aromatic component. Ionic liquid **202** has a lower decomposition temperature than the case **200**, suggesting the more reactive phenyl group facilitates decomposition. The phenyl-containing ionic liquid **202** has a higher density that the butylated ionic liquid **200**, suggesting greater packing efficiency, again likely due to increased interactions between

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[xxiii] With caveats on ambiguity as before.

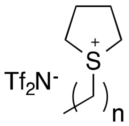
the components of the ionic liquid. The viscosity is also higher in ionic liquid **202** than in ionic liquid **200**, this is expected as bulkier *N*-substituents, with increased interactions, decrease ion mobility in ionic liquids.

The ionic liquid **203** containing the ester group has a higher glass transition temperature than ionic liquid **200** containing the simple alkyl chain. Ionic liquid **203** also has a lower decomposition temperature than **200**, which perhaps is reasonable given the introduction of a reactive ester group. The ionic liquid **203** containing the ester group has a higher density than the butylated ionic liquid **200**. The ester group is increasing the packing efficiency, likely due to fewer degrees of freedom and an increase in intermolecular forces. The viscosity of ionic liquid **203** is higher than ionic liquid **200** containing the butyl chain. This is readily rationalised since the differences in intermolecular forces are likely causing a decrease in the ion mobility. These trends are reasonable and have been observed previously for other ionic liquid based on cations containing ester functionalities (see Tables 18 and 26).

2.10. Thiolanium cations

Just as cyclic ammonium cations are described in the literature, a few studies have addressed the physicochemical properties of cyclic sulfonium cations, particularly the *S*-alkylthiolanium cation (also known as the tetrahydrothiophenium cation). This cation type appears to be rare in the ionic liquid literature, however a couple of studies of varying the alkyl chain length of the cation on the properties of the corresponding ionic liquids have been undertaken. These ionic liquids are synthesised through the alkylation of thiolane and then subsequent anion metathesis to the desired anion.[110] The abbreviated naming used here for these type of ionic liquids is [*x*tl][Tf$_2$N], where where *x* is the first letter of the name of the alkyl chain on the sulfur centre.[xxiv]

The series of ionic liquids discussed contain cations in which the length of the *S*-alkyl chain is varied. The properties of the ionic liquids **204-206** are presented in Table 46.



204, n = 2
205, n = 3
206, n = 4

Table 46. The melting point (T_m), decomposition temperature (T_d), density (ρ), dynamic viscosity (η) and electrical conductivity (κ) of the ionic liquids **204-206** at 298.15 K (unless otherwise specified).

	Ionic liquid	T_m / K	T_d / K	ρ / g cm^{-3}	η / mPa s	κ / mS cm^{-1}
1	[ptl][Tf$_2$N] **204**	299^a	313.2^a	1.52^b	50.5^{a,c} / 52.00^b	3.76^{a,c} / 4.10^b
2	[btl][Tf$_2$N] **205**	<213^a	280.0^a	1.30^a / 1.46^b / 1.456^c	80.4^a / 53.60^b	2.10^a / 2.43^b
3	[p$_e$tl][Tf$_2$N] **206**	<213^a	310.3^a	1.31^a / 1.40^b	91.1^a / 53.60^b	1.46^a / 1.91^b

^{a}From Zhang *et al.*[110] ^{b}From Guo *et al.*[111] ^{c}Measured at 333.15 K.

The first comparison to make is that between ionic liquid **205** containing a butyl chain and all the other ionic liquids containing heterocyclic cations of similar molecular weights **4**, **73**, **112**, **138**, **151**, **169**, **174** and **183**. The decomposition temperatures of the ionic liquids are in the order morpholinium **151** < thiolanium **205** < oxazolidinium **169** < triazolium **183** < piperidinium **138** < pyridinium **73**. This means that the

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[xxiv] With caveats on ambiguity as before.

thiolanium ionic liquid cation readily decomposes. For the density, the order is pyrrolidinium **112** ≈ pyrazolium **174** < piperidinium **138** < imidazolium **4** < pyridinium **73** ≈ thiolanium **205** ≈ oxazolidinium **169** < triazolium **183** < morpholinium **151**. This suggests that the thiolanium cation has a relatively high packing efficiency similar to that of the oxazolidinium **169** which has a similar structure. For the viscosity, the order is as follows imidazolium **4** < pyridinium **73** < pyrazolium **174** < pyrrolidinium **112** ≈ thiolanium **205** < piperidinium **138** < oxazolidinium **169** < triazolium **183**. For the conductivity, the order for the ionic liquids is piperidinium **138** < oxazolidinium **169** < thiolanium **205** ≈ pyridinium **73** < pyrrolidinium **112** < pyrazolium **174** < imidazolium **4**.

For the melting temperature of ionic liquids **204-206**, the ionic liquid with the smallest cation **204** has a higher melting temperature than the other ionic liquids **205** and **206**, suggesting more efficient packing due to the decreased degrees of freedom in that case. No trend is apparent in the decomposition temperature data. For the density data, it is a little difficult to ascertain a trend as the values reported for the ionic liquids **205** and **206** each cover a large range. Based upon previous data, it would be expected that as the alkyl chain length increases, the density values would decrease. This is observed for the data presented by Guo *et al.*[111] however not for the data presented by Zhang *et al.*[110]. The reason behind this discrepancy is unclear and without uncertainties it is difficult to make any conclusions. Similarly for the viscosity data, it would be expected that as the alkyl chain length of ionic liquids **204-206** increased, so would the viscosity. This is observed for the data presented by Zhang *et al.*,[110] however not for the data presented by Guo *et al.*[111] Again, the reason behind this discrepancy is unknown. The conductivity from both studies[110,111] follows the expected trend observed with increasing alkyl chain length of ionic liquids **204-206** resulting in a decrease in the conductivity.

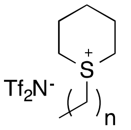
2.11. Thianium cations

Thianium (also known as tetrahydrothiopyranium) cations are clearly related to both the thiolanium cations and the piperidinium cations. This cation type is rare in the ionic liquid literature, however a study that considers the properties of thianium-based ionic liquid and the effect on such of varying the alkyl chain length has been undertaken.[111] These ionic liquids are synthesised through the alkylation of thiane (tetrahydrothiopyran) and then subsequent anion metathesis to the desired anion.[111] The abbreviation used here for this type of ionic liquids is [*x*tn][Tf_2N], where *x* is the first letter of the name of the alkyl chain on the sulphur atom.[xxv] The series considered is made up of ionic liquids where the length of the *S*-alkyl chain has been varied; the properties of the ionic liquids **207-209** are presented in Table 47.

The first comparison is that between ionic liquid **207** containing a propyl chain and all the other hetrocycles **4**, **73**, **112**, **138**, **151**, **169**, **174**, **183** and **205** of similar molecular weights. For melting temperature, the thianium cation has the highest melting temperature with the ionic liquids in the order of pyrrolidinium **112** < imidazolium **4** < oxazolidinium **169** ≈ piperidinium **138** < pyridinium **73** < thianium **207**. For the density, the order is pyrrolidinium **112** ≈ pyrazolium **174** < piperidinium **138** < imidazolium **4** < pyridinium **73** ≈ thiolanium **205** ≈ oxazolidinium **169** ≈ thianium **207** < triazolium **183** < morpholinium **151**. The high density for the thianium cation suggests that there is good packing efficiency. For the viscosity, the order is: thianium **207** < imidazolium **4** < pyridinium **73** < pyrazolium **174** < pyrrolidinium **112** ≈

[xxv] With caveats on ambiguity as before.

thiolanium **205** < piperidinium **138** < oxazolidinium **169** < triazolium **183**. The low viscosity for the thianium ionic liquid **207** suggests increased ion mobility for the system. For the conductivity, the order for the ionic liquids is piperidinium **138** < oxazolidinium **169** < thiolanium **205** ≈ pyridinium **73** < thianium **207** < pyrrolidinium **112** < pyrazolium **174** < imidazolium **4**.



207, n = 2
208, n = 3
209, n = 4

Table 47. The melting point (T_m), density (ρ), dynamic viscosity (η) and conductivity (κ) of the ionic liquids **207-209** at 298.15 K.[111]

	Ionic liquid	T_m / K	ρ / g cm^{-3}	η / mPa s	κ / mS cm^{-1}
1	[ptn][Tf$_2$N] **207**	303	1.46	48.70	2.57
2	[btn][Tf$_2$N] **208**	263	1.48	68.00	2.07
3	[p$_e$tn][Tf$_2$N] **209**	<213	1.41	56.50	1.50

Looking at the melting points of ionic liquids **207-209** the temperature decreases as the alkyl chain length increases, consistent with decreased packing efficiency due to the increased degrees of freedom on increasing alkyl chain length. A similar argument, which has been used above for other systems, would suggest that the density of the ionic liquid should decrease on increasing the alkyl chain length. For the density of ionic liquids **207-209** the expected trend is not observed with ionic liquid **208** containing a butyl chain having a higher value than the ionic liquids **207** and **209**. It is not clear if that value is incorrect, or if the trend does not hold for thianium ionic liquids. The fact that the butyl case **208** may be anomalous is supported by the viscosity data. It might be expected on previous results that viscosity of a thianium-based ionic liquid would increase with increasing alkyl chain length on the cation; this is not observed, with the ionic liquid **208** with the butyl chain having a much higher value than the other ionic liquids **207** and **209**. Note that the conductivity changes with cation do not parallel viscosity changes either. The reasons for these anomalous results are unknown.

2.12. Summary

The above sections have extensively covered the effect of the structure of the cation of an ionic liquid on its properties. Whilst comparison of the effects of changing the heterocyclic core of the ionic liquids has been described in each section above, it is of use to consider the effects of modification of the cation that are consistent across all the different types of heterocycles and may allow rational choice of modification of an ionic liquid. These general trends are summarised in Table 48 below, with any exceptions noted.

3. The effect of varying the cation of an ionic liquid on reaction outcome

As has been discussed above, varying the structure of an ionic liquid cation will change the physicochemical properties of that ionic liquid. It is also known that this can change how ionic liquids behave as solvents, particularly in how they affect reaction outcome.[xxvi]

[xxvi] Note that the only solvent effects will be discussed in this sections, not cases where reactivity of the solvent (such as being protic) causes a change in the reaction outcome.

Table 48. Trends in ionic liquid properties on variation of the cation. Substituents on the heteroatom refers to changes to the alkyl chain on the heteroatom(s) of the cation, substituents on the heterocycle refers to substituents on the carbon skeleton of the heterocycle of the cation.

Property	**General Trend**
Glass transition temperature	*Increases with:* Substituents on the heteroatom: cycloalkyl, aromatic, hydroxyl, nitrile moieties and incorporation of fluorine atoms.
Melting temperature	*Increases with:* Substituents on the heteroatom: branched and incorporation of fluorine atoms. *Decreases with:* Substituents on the heteroatom: aromatic and ether functionality.
Decomposition temperature	*Increases with:* Substituents on the heteroatom: increasing alkyl chain length, inclusion of nitrile moieties and incorporation of fluorine atoms.[a] *Decreases with:* Substituents on the heteroatom: ether functionality.
Density	*Increases with:* Substituents on the heteroatom: cycloalkyl, aromatic, allyl, branching of substituents, incorporation of hydroxyl, nitrile, ester, ether and incorporation of fluorine atoms. Substituents on the heterocycle: nitrile and halogen. *Decreases with:* Substituents on the heteroatom: increasing alkyl chain length and incorporation of silicon atoms. Substituents on the heterocycle: methylation.[b]
Viscosity	*Increases with:* Substituents on the heteroatom: increasing alkyl chain length, cycloalkyl, branching of substituents,[c] incorporation of hydroxyl, nitrile, ester and incorporation of fluorine atoms. Substituents on the heterocycle: nitrile, halogens and methyl groups.[d] *Decreases with:* Substituents on the heteroatom: aromatic, allyl, inclusion of ether functionality and incorporation of silicon atoms.
Conductivity	*Increases with:* Substituents on the heteroatom: allyl and inclusion of ether functionality.[e] *Decreases with:* Substituents on the heteroatom: increasing alkyl chain length, incorporation of hydroxyl and nitrile moieties and incorporation of fluorine atoms. Substituents on the heterocycle: methyl groups.
Surface Tension	*Increases with:* Substituents on the heteroatom: aromatic substituents and inclusion of nitrile functionality. *Decreases with:* Substituents on the heteroatom: increasing alkyl chain length.

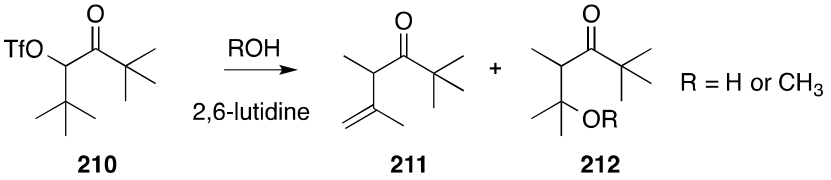
[a] Except oxazolidinium cations, see Table 36. [b] Except for pyridinium cations, where the methyl substituent is at the 2-position, see Table 14. [c] Except for triazolium cations, see Table 41. [d] Except for pyridinium cations, where the methyl substituent is at the 4-position, see Table 14. [e] Except oxazolidinium cations, see Table 37.

A number of studies examining ionic liquids as solvents have been undertaken and many of these attempt to determine the origin of these changes. The effect of ionic liquids on reaction outcomes has been considered extensively in previous work;[3,8,16,17,112,113] herein the focus is on how varying the cation of an ionic liquid can change the reaction outcome for a series of reactions grouped by reaction type.

Before discussing ionic liquid effects on reaction outcome it is important to highlight the importance of the fraction of the ionic liquid in the reaction mixture; to allow convenient comparison of different ionic liquids, this is best measured using the mole fraction of ionic liquid in the reaction mixture. Along with the intrinsic interest of what the reaction solvent really is (an ionic liquid or a dilute salt solution), reaction outcomes have been found to vary significantly with the mole fraction of ionic liquid in the reaction mixture and this variation is not consistent between reaction types.[114] As such, knowing the mole fraction of ionic liquid in the reaction mixture is important in understanding reaction outcome yet it is often not reported in the literature; the mole fractions of ionic liquid used in the reactions considered below will be mentioned where it is reported.

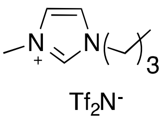
3.1. Rearrangement proceeding through a carbocationic intermediate

The reaction of the α-keto triflate **210** initiated by 2,5-lutidine proceeds through an ionisation mechanism to form a carbocation intermediate. This intermediate can rearrange and subsequently react to give the elimination product **211** and the alcohol **212** (Scheme 1). Given the extent of charge delocalisation in the transition state, and interactions seen in related systems,[115] it is not unreasonable to consider that the nature of the cation would be important.



Scheme 1. The reaction of triflate **210**, initiated by lutidine, which was examined in the ionic liquids **4**, **73** and **213**.[116,117]

This reaction was examined in a number of ionic liquids, including [bmim][Tf$_2$N] **4**, [bpy][Tf$_2$N] **73** and [b$_3$mN][Tf$_2$N] **213**.[117][xxviii] It was found that the relative rate constants for the reaction in each of the ionic liquids were as follows: 1.00 for the imidazolium salt **4**, 1.21 for the ionic liquid **73** and 0.49 for the ionic liquid **213**, which confirms that in this reaction, variation of the ionic liquid cation can change the rate of reaction. Unfortunately, unlike related systems[115] no activation parameter data are available and the authors[117] do not explain this trend but rather just simply compare the ionic liquids to molecular solvents. Given the difference in charge localisation of the cations used, it may be that interaction of species along the reaction coordinate with the charged centre is significant in this case.



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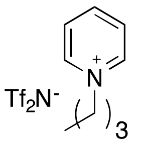

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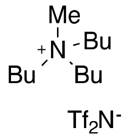

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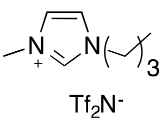
The same reaction has also been subsequently examined in ionic liquids **4**, **37**, **73** and **112**,[116] though it is important to note that the mole fraction of ionic liquid present for these reactions varied



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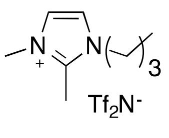

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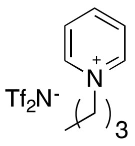

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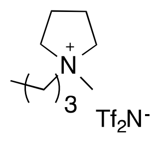


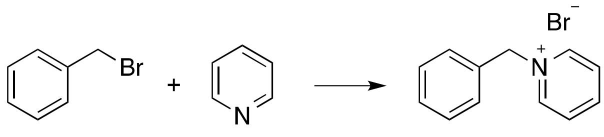
112

[xxviii] Whilst not introduced previously as they are not cyclic, quaternary ammonium cations are typically abbreviated to the form [*wxyz*N]$^+$, where *w*, *x*, *y* and *z* are the first letters of the names of the alkyl chains on the nitrogen atom (with any subscripts indicating the multiple occurrence of that length alkyl chain).

from near 0 up to 0.5. Given that such variation in mole fraction has been shown to dramatically alter the reaction outcome for related systems,[118] any ordering of rate constants must take this into account. However, the trend in the rate constants were as follows **37** > **112** > **73** > **4**, which has a good correlation with the hydrogen bond donor ability suggesting that increased hydrogen bond donor ability of the ionic liquids caused a decrease in the rate of reaction. This may be due to an unfavourable interaction with, say, the lutidine but this was not discussed.

3.2. Bimolecular nucleophilic substitution (S_N2) reactions

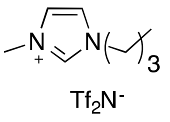
Another reaction type that has been examined in ionic liquids is the Menschutkin reaction between benzyl bromide **214** and pyridine **215** (Scheme 2),[119–122] which proceeds *via* an S_N2 reaction mechanism; compared to the case above, the extent of charge delocalisation in the transition state is considerably smaller. This reaction has been thoroughly investigated with ionic liquids containing nine different cations, with most being imidazolium, however pyrrolidinium and ammonium cations have also been considered. In all cases, the mole fraction of ionic liquid present was reported and was typically *ca.* 0.9; this has been shown to correspond to the maximum effect of ionic liquids on these types of systems.[119,121]



214 **215** **216**

Scheme 2. The Menschutkin reaction between benzyl bromide **214** and pyridine **215** which was examined in the ionic liquids **4**, **37**, **67-71**, **112** and **217**.[119–121]

It has been shown that the rate constant enhancement for this reaction in an ionic liquid was entropically driven[119] and the key interaction in solution was between the ionic liquid cation and lone pair of the pyridine **215**.[120] On changing the nature of the cation, the rate constants were in the order of **4** ≈ **37** ≈ **68-70** ≈ **112** > **67** > **71** > **217**. This is consistent with access to the nitrogen charged centre and the extent of charge localisation being important in determining the rate constant enhancements observed for the ionic liquids; the greater the accessibility to the charge and charge localisation, the greater the interaction with the nucleophile **215** and the greater the rate constant enhancements.



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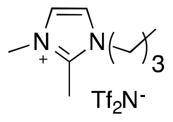

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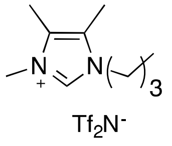

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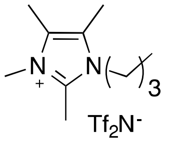

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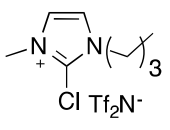
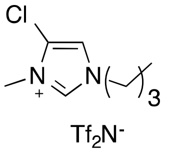


68



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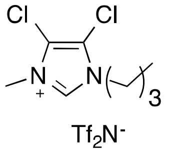

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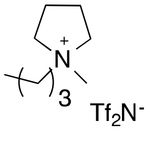

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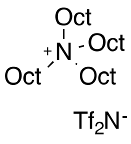
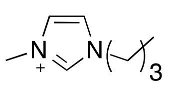


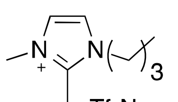
217

Direct comparison of specific systems allows deconvolution of the effects. When comparing the reaction outcomes in the ammonium ionic liquids **112** and **217**, a clear difference in rate constant is observed, where the tetraoctylammonium ionic liquid **217** case is significantly slower than the cyclic ammonium **112** case. This is likely due to the large differences in access to the charged centre with the cation of ionic liquid **217** being severely sterically hindered.

Also, it is interesting to note the differences in reaction outcome given the differences in charge localisation on the cation of the imidazolium **4** and pyrrolidinium **112** salts. The imidazolium ionic liquid **4** has a delocalised net charge, while the pyrrolidinium **112** has a localised net charge; this does not seem to affect the rate constant with both ionic liquids having similar values. The ionic liquids **67** and **70**, with methyl substitution as opposed to chlorine substitution on the cation, show different rate constants; the reaction in ionic liquid **70** (containing the chlorine atoms on the cation) has a greater rate constant than the case in ionic liquid **67**. This suggests the electron withdrawing nature of the chlorine substituents increases the magnitude of the charge on the nitrogen centre, allowing for a greater cation-nucleophile interaction, which enhances the beneficial entropic effects on reaction outcome.



4



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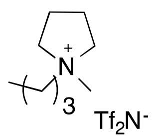
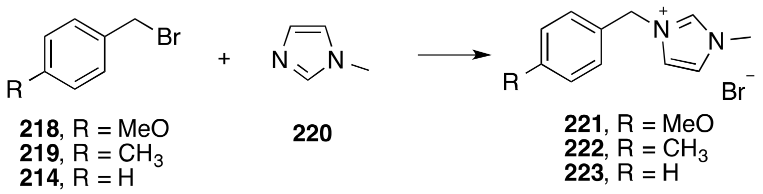
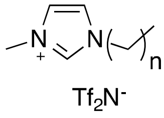


112

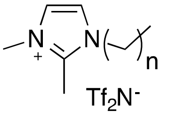
Similar Menschutkin reactions between a number of substituted benzyl bromides **214**, **218** and **219** with *N*-methyl imidazole **220** (Scheme 3) have been examined in a variety of ionic liquids.[123] The ionic liquids examined as solvents for this reaction were salts **4**, **37** and **112**. For all the benzylbromides (except **214**), the order of rate constants was **4** > **37** > **112**; this order can be rationalized through correlation with the hydrogen-bond acidity parameter. In the case of the unsubstituted bromide **214**, the order of the rate constants was **112** > **4** > **37**; the authors[123] could not correlate these data with any one of the solvent parameters. It was stated though that an increase in both the polarisability/polarity and the hydrogen-bond donating ability causes an increase in the rate of reaction and an increase in the hydrogen-bond basicity and cohesive pressure will reduce the reactivity.[123] No activation parameter data was presented, nor was any mole fraction dependence data.



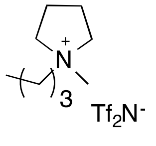
Scheme 3. The Menschutkin reaction between benzyl bromides **214**, **218**, **219** and methylimidazole **220.**[123]



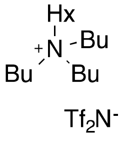
4, n = 3
8, n = 7



37, n = 3
224, n = 7

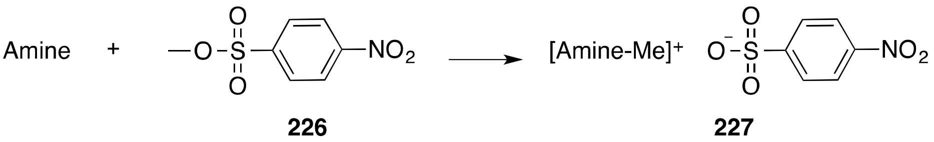


112



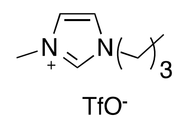
225

A similar reaction between benzyl bromide **214** and 1,2-dimethylimidazole has also been considered in ionic liquids containing different cations.[124] The ionic liquids examined in this reaction included imidazolium salts **4**, **8**, **37** and **224**, the pyrrolidinium salt **112** and ammonium salt **225**. The rate constants for all the ionic liquids investigated were the same within error. The reaction between a range of butylamines (primary, secondary and tertiary) and methyl *p*-nitrobenzenesulfonate **226** (Scheme 4) also proceeds *via* an S_N2 mechanism[125] and has been investigated in a range of ionic liquids.



Scheme 4. The reaction between a butylamine (Amine) and methyl *p*-nitrobenzenesulfonate **226**.[125]

Whilst considered in a range of ionic liquids, relevant to the topic discussed here the reaction was examined in two trifluoromethanesulfonate ($[TfO]^-$) ionic liquids with different cations; the imidazolium salt **228** and the pyrrolidinium salt **229**. For all three amine types, the rate constants for the reaction in the pyrrolidinium ionic liquid **229** were higher than those in the imidazolium salt **228**; for the tributylamine case, the rate constant in ionic liquid **229** is higher than in the imidazolium case **228** by an order of magnitude. The authors suggest[125] that high polarizability values the reaction rate would increase. Once again, the localisation of charge may be significant but activation parameters for this reaction in each of the ionic liquids were found to be the same (within uncertainty). No mole fraction dependence data was reported.



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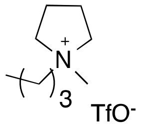
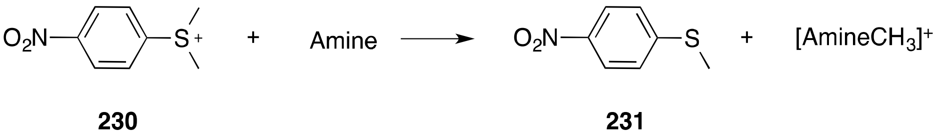


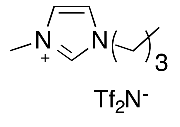
229

Another related S_N2 reaction that has been examined in a range of ionic liquids is that between dimethyl-4-nitro-phenylsulfonium *bis*(trifluoromethanesulfonyl)imide **230** and one of a range of butylamines (primary, secondary and tertiary; Scheme 5); this case involves a charged electrophile.[126]

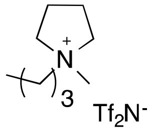


Scheme 5. The reaction between the dimethyl-4-nitro-phenylsulfonium **230** with the amine, which was examined in the ionic liquids **4** and **112**.[126]

The ionic liquids used as solvents in this reaction were ionic liquids **4** and **112**. For all the amines examined, the pyrrolidinium ionic liquid **112** had a higher rate constant than the imidazolium **4**. This was explained through ionic liquid **4** having a higher Kamlett-Taft α value (higher acidity) than ionic liquid **112**. The nucleophilic attack is slowed by solvents with higher α values, as there is deactivation of the amine through hydrogen bond donation by the solvent to the lone pair on the amine.[126] This is in contrast to the argument presented for the reaction of benzyl bromide **214** with pyridine **215** (Scheme 2). No activation parameters were presented. The same reaction was also examined in ionic liquids **4**, **37** and **112** with a chloride rather than an amine nucleophile.[127] The rate constants were in the order of **112** > **37** > **4**, although the differences were not rationalised.[127]

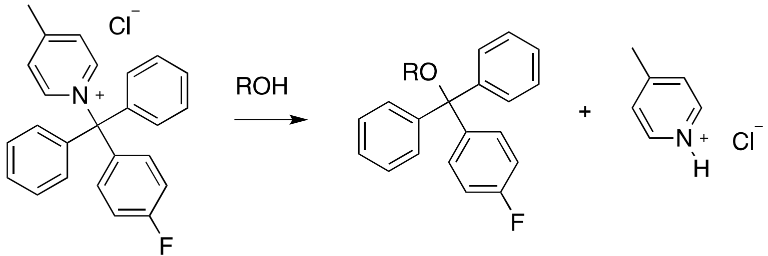


4



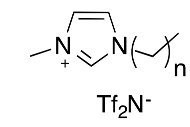
112

The reaction between the picolinium salt **232** and a range of alcohols (and water) has also been examined in a range of imidazolium ionic liquids.[128,129] The reaction proceeds through attack of a nucleophile onto the intimate ion pair formed through the dissociation of the starting material and, as such, exhibits bimolecular kinetics and is included in this section.



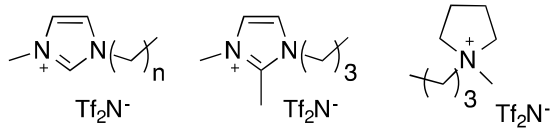
232 **233** **234**

Scheme 6. The reaction between picolinium salt **232** and a range of hydroxyl-containing nucleophiles.[128,129]



2, n = 1
4, n = 3
6, n = 5
8, n = 7
10, n = 9

The ionic liquids examined in this reaction were the imidazolium salts **2**, **4**, **6**, **8** and **10**, which vary the *N*-alkyl substituent length. The nucleophiles used were water, methanol, ethanol, propanol, butanol and benzyl alcohol. For each of the nucleophiles examined, a significant rate enhancement was observed when the length of the alkyl side chain of the ionic liquid cation increased.[128] The extent of rate enhancement between the ionic liquids is larger for water than for the alcohols. The authors state[128] that as the variation of the alkyl side chain length is unlikely to affect any solvent-transition state interactions and that the rate enhancement must come from a structural effect within the ionic liquid; the rate enhancement arises from the nanoscale heterogeneity of the solvent. The reactants are concentrating in the polar domains, which are smaller in volume as the *N*-alkyl substituent of the ionic liquid cation increases resulting in an increase in the rate constant. Mole fraction data for this reaction was not reported.

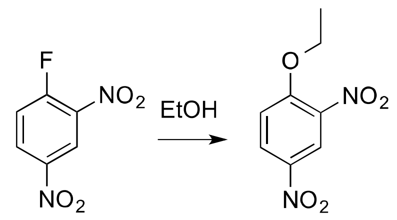


2, n = 1
4, n = 3
37
112

The same group has also varied the cation of the ionic liquids **2**, **4**, **37** and **112** in the same reaction with the same types of nucleophiles (including the additional alcohol phenol in these cases).[129] The rate constants for all the nucleophiles examined (with the exception of phenol), were in the order of **2** < **4** < **112** ≈ **37**. It was stated that the reduction of the hydrogen-bond acidity of the solvent, gave an increase in the rate constant,[129] though no further explanation was given.

3.3. Nucleophilic aromatic substitution (S_NAr) reactions

Along with substitution at alkyl centres, nucleophilic aromatic substitution reactions have also been examined in ionic liquids including the ethanolysis of 1-fluoro-2,4-dinitrobenzene **235** (Scheme 7).[130,131]

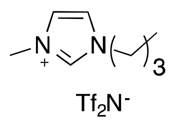


235 **236**

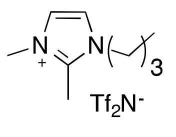
Scheme 7. The reaction between 1-fluoro-2,4-dinitrobenzene **235** and ethanol which was examined in the ionic liquids **4**, **37**, **67**, **69**, **70**, **71**, **112** and **217**.[130,131]

This reaction has also been examined in a large range of ionic liquids including those containing imidazolium, pyrrolidinium and tetraalkylammonium cations, at a consistent mole fraction of *ca.* 0.5.

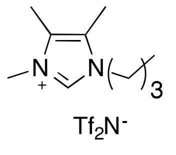
It has been reported[130] that the rate enhancement of this reaction was entropically driven and that the key interaction was that between the ionic liquid anion and the π-system of the starting material. This reaction was examined in the ionic liquids **4**, **37**, **67**, **69**, **70**, **71**, **112** and **217** and it was found that there was a general ionic liquid effect;[131] in all cases where an ionic liquid was used as a solvent, the reaction proceeds faster than in the molecular solvent, ethanol. The outcome is consistent with the key interaction being between the anion of the ionic liquid and the starting material **235**, which is clearly not substantially affected by changing the cation of the solvent.



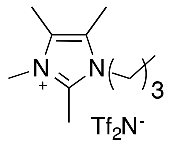
4



37



67



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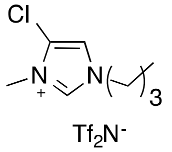

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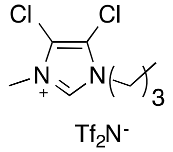

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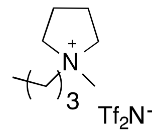

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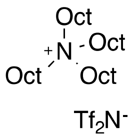
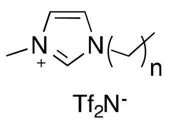


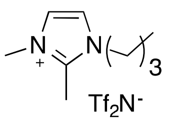
217

3.4. Electrophilic addition reactions

The electrophilic addition reaction between the alkynes **237** and **238** with the tribromide ion (Scheme 8) has been examined in ionic liquids containing a variety of imidazolium cations.[132] The ionic liquids used as solvents for this reaction were the imidazolium ionic liquids **2**, **4**, **6** and **37**. For both the alkynes, the order of the rate constants was **2** > **4** > **6** > **37**. The authors mention that as the viscosity of each of the ionic liquids decrease, the rate of reaction increases. For the phenylacetylene **237**, activation parameters were determined for ionic liquids **2**, **4** and **37**. The enthalpy of activation was in the order of **37** > **4** > **2**, whereas the entropy of activation was in the order of **4** ≈ **37** > **2**. The authors mentioned that the activation parameters for each of the ionic liquids were similar (though outside uncertainty) and no conclusions were drawn. Mole fraction data for this reaction was not reported.

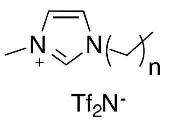


2, n = 1
4, n = 3
6, n = 5

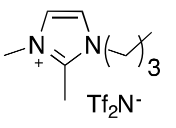


37

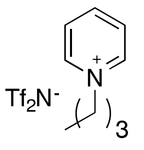
Similarly, the reaction between pent-2-ene **241** and iodine dichloride (Scheme 9) was examined in the ionic liquids **2**, **4**, **37** and **73**. The rate constants for this reaction were in the order of ionic liquids **2** > **73** > **4** > **6**, which does not correspond to viscosity, in contrast to the argument presented for the above reaction (Scheme 8). The activation parameter data for this reaction show a greater dependence on the ionic liquid structure than that previous case,[132] the enthalpy of activation is in the order of **4** > **73** > **2** > **37** and the entropy of activation shows the opposite trend.



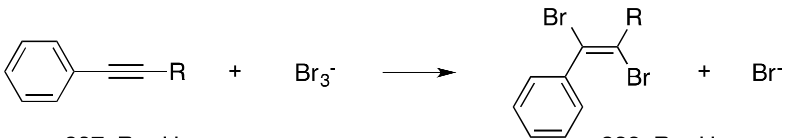
2, n = 1
4, n = 3



37



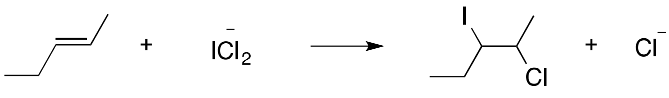
73



237, R = H
238, R = CH_3
239, R = H
240, R = CH_3

Scheme 8. The reaction between the alkynes **237** and **238** and the tribromide ion, which has been examined in the ionic liquids **2**, **4**, **6** and **37**.[132]

The values of $\Delta G^{\ddagger}$ are very similar for all the ionic liquids, which is consistent with enthalpy-entropy compensation.[114,119,133] The authors suggested[132] that the hydrogen bond donating ability of the ionic liquid is the main factor affecting reactivity in ionic liquids **2**, **4** and **73**, however for ionic liquid **37**, viscosity is also a contributor, as the viscosity of **37** is significantly different and higher than the other ionic liquids. It is interesting to note the differences in activation parameters of ionic liquids **2** and **4**. With similar structures and Kamlett-Taft α and β parameters, the enthalpies of activations are markedly different; 30.8 kJ mol^{-1} in ionic liquid **2** and 15.3 kJ mol^{-1} in salt **4**. Similarly for the entropy of activation, large differences are observed (-178 J K^{-1} mol^{-1} in ionic liquid **2** and -238 J K^{-1} mol^{-1} in ionic liquid **4**). These values are not readily rationalised and do not match the proposed arguments.

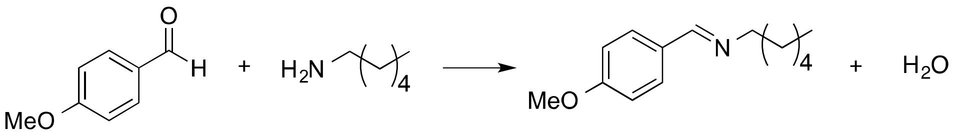


241 **242**

Scheme 9. The reaction between pent-2-ene **241** and iodine dichloride that was examined in the ionic liquids **2**, **4**, **37** and **73**.[132]

3.5. Condensation reactions

A condensation reaction between anisaldehyde **243** and hexylamine **244** (Scheme 10) has also been investigated with ionic liquids as solvents.[133,134] The ionic liquids used included those involving imidazolium, pyrrolidinium and ammonium cations and studies were carried out across a range of proportions of the salts in the reaction mixture at a mole fraction of *ca.* 0.9.

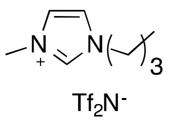


243 **244** **245**

Scheme 10. The condensation reaction between anisaldehyde **243** and hexylamine **244** which was examined in the ionic liquids **4**, **37**, **71**, **112** and **217**.[133,134]

The ionic liquids examined as solvents for the condensation reaction above were the imidazolium salts **4**, **37** and **71**, the pyrrolidinium salt **112** and the ammonium salt **217**.[133] It has been shown that the key interaction responsible for the rate enhancement was between the lone pair on the amine **244** and the ionic liquid cation, similar to that described above for the bimolecular substitution case (Scheme 2).[120]

The activation parameters observed for this reaction showed that the enthalpy of activation varied with the solvent in the order **112** > **4** > **37** > **71** > **217**. This is consistent with less interaction of the cation with the nucleophile **244** as the charged centre of the cation becomes more sterically hindered. The more marked changes observed compared to the bimolecular case above are likely the result of the reduced size of the nucleophile **244** compared to pyridine.



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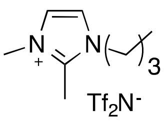

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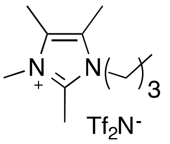
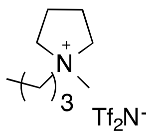
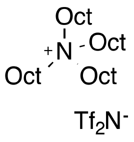


71



112

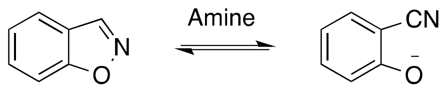


217

The Michael addition of ethyl acetoacetate and 2-ethylhexylacrylate has also been examined in two ionic liquids [p$_e$mim][Tf$_2$N] **5** and trihexyltetradecylphosphonium ([d$_3$h$_4$P]) [Tf$_2$N] however comparison between the ionic liquids was not presented.[135]

3.6. E2 reactions

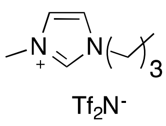
The amine induced elimination reaction (a Kemp elimination) of benzisoxazole **246** to the cyanophenolate **247** (Scheme 11) has been studied in ionic liquids.[136] The ionic liquids examined in this reaction were the imidazolium salts **4**, **37** and the pyrrolidinium salt **112** while the amines used for this reaction were pyrrolidine and piperidine. It was shown that for both of the amines, the elimination process occurs faster in the ionic liquids than in methanol.



246 **247**

Scheme 11. The Kemp elimination reaction of benzisoxazole **246** to the cyanophenolate **247** which was examined in the ionic liquids **4**, **37** and **112**.[136]

Variation of the ionic liquid cation showed differences in the rate constant in the order of **112** > **37** > **4**; the ionic liquids with less acidic protons favoured the elimination. This order of reactivity could not be explained using either solvent or polarity parameters. It was suggested by the authors[136] that the ionic liquid could be stabilising the transition state through either interaction of the anion and the hydrogen atom on the ammonium nitrogen, or the cation and the oxygen atom on the isoxazole unit. The activation parameters in all cases did not provided any further insight and no dependence on the proportion of the ionic liquid was reported.



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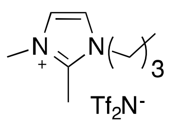

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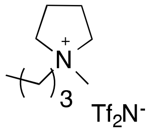
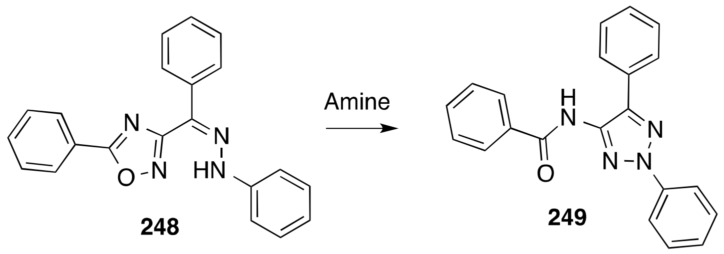


112

3.7. Rearrangement reactions

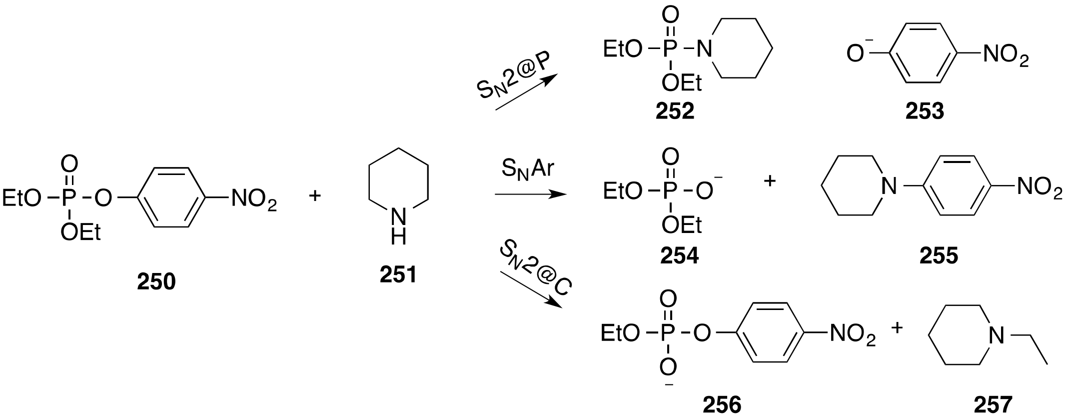
The amine-catalysed rearrangement reaction of 3-benzoyl-5-phenyl-1,2,4-oxadiazole **248** (Scheme 12) has also been examined in ionic liquids.[137,138] This reaction was investigated using three types of amines; butylamine, piperidine and triethylamine.[138] The ionic liquids examined as solvents for this reaction were the imidazolium salts **4**, **37** and the pyrrolidinium salt **112**. The rate constants for this reaction for all the different amines varied with the ionic liquid in the order **4** > **37** > **112**. The authors[138] explain this reactivity in terms of the cation's ability to stabilise the transition state through π–π interactions. The activation parameters determined for this reaction show enthalpy of activation values in the order **37** > **4** > **112**, with the opposite trend being observed for the entropy of activation values. It was suggested that the cation’s abilities to hydrogen bond and have π–π interactions significantly affect the activation parameters.[138] The ionic liquids **4** and **37** with the aromatic cations are more effective at stabilising the transition state, and the resultant system is more ordered, than when the pyrrolidinium ionic liquid **112** is used as a solvent. No data on the importance or otherwise of the mole fraction of the ionic liquid used was reported.



Scheme 12. The rearrangement reaction of phenylhydrazone **248** which has been examined in ionic liquids **4**, **37** and **112**.[137,138]

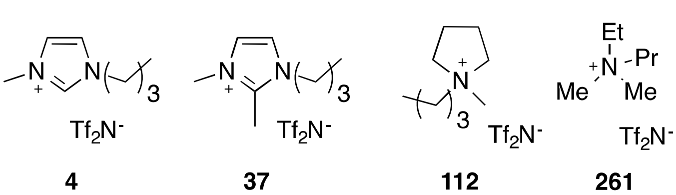
3.8. Competition reactions involving phosphorus species

It is not just reaction outcomes involving organic species that can be affected by ionic liquids. The reaction with paraoxon **250** and piperidine **251** (Scheme 13) can proceed through three competing mechanisms; nucleophilic substitution can occur at either the phosphorus centre (S_N2@P) or at a carbon centre (S_N2@C[xxix]), and nucleophilic aromatic substitution (S_NAr) can occur. This reaction has been examined in a number of ionic liquids.[139]



Scheme 13. The degradation of paraoxon **250** by piperidine **251**, which can proceed through three different mechanisms and has been studied in a range of ionic liquids.[139]

The ionic liquids examined in this reaction were the imidazolium salts **4** and **37**, the pyrrolidinium salt **112** and the ammonium salt **261**.



The reaction proceeded through each of the three mechanisms described above in each of the ionic liquids. In all of the ionic liquids the S_N2@C mechanism was dominant, with product distributions indicating this pathway accounted for 50-57% of the reaction. For each of the mechanisms, the reactions rate constants varied with the ionic liquid in the order **4** > **37** > **261** > **112**; the highest rate constants were observed in liquids containing an aromatic cation. The authors suggest[139] that this is due to a π–staking interaction between aromatic cation of the ionic liquid and the transition state of the reaction, rather than interaction with the reactants.[139] It is also suggested that the comparison between ionic liquids **4** and **37** can be explained by the differences in the hydrogen bond donor ability of the cations. This means that the aromaticity and hydrogen bond donor ability needs to be taken

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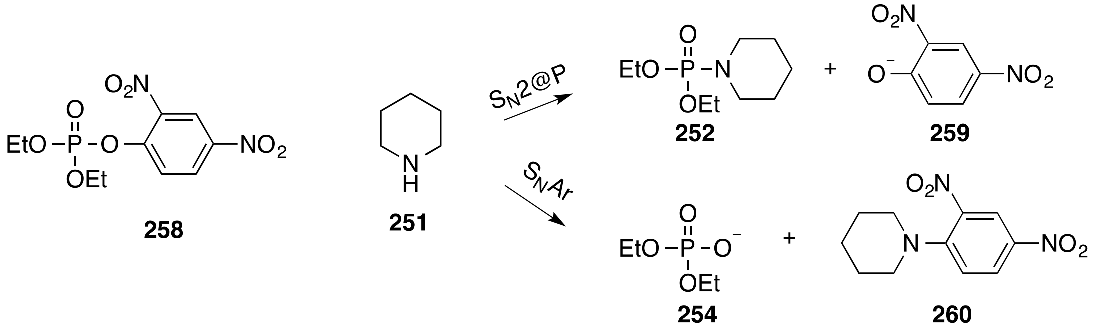
[xxix] Specified here, though not previously, to delineate from the equivalent reaction at phosphorus.

into account when considering ionic liquid cations for this reaction. No mole fraction data was reported for this study.

The same group[140] has considered similar processes involving *O*,*O*-diethyl-*O*-(2,4-dinitrophenyl) phosphate **258** as the electrophile (Scheme 14). This reaction proceeds *via* two of the three mechanisms described above, S_N2@P and S_NAr; no evidence for the equivalent S_N2@C process was observed. The ionic liquids examined in this reaction are the same as described above; salts **4**, **37**, **112** and **261**.

For this reaction, all of the ionic liquids favoured the S_NAr mechanism, with the product distribution indicating it accounts for 86-92% of the reaction. The rate constants for both reaction mechanisms varied in the order of **261** > **37** > **112** > **4**. The authors do not comment[140] on the differences in rate constants, concluding they are all similar and suggesting that both the S_N2 and S_NAr mechanisms are mostly affected by the anion.



Scheme 14. The reaction of *O*,*O*-diethyl-*O*-(2,4-dinitrophenyl) phosphate **258** with piperidine **251** which has been examined in the ionic liquids **4**, **37**, **112** and **261**.[140]

From what has been discussed above, ionic liquids are useful as solvents in organic reactions. Variation of the ionic liquid cation can change the reaction outcome, which can lead to greater control of reactivity. Taking into account the traditional solvent measures (polarity, hydrogen bond donor and acceptor ability) is not always useful in predicting the behaviour of ionic liquids; the cases that are best understood consider the ionic liquid's interactions with components along the reaction coordinate. With a better understanding of ionic liquids and how they affect a given reaction, solvent controlled reactivity could become a reality.

4. Conclusions

There are a wealth of options in terms of cations for ionic liquids, which means there is almost an unlimited number of potential ionic liquids available for use as solvents. Through variation of the ionic liquid cation, changes in a range of properties can be observed and rationalised, which means that these properties can be tailored in a logical fashion by selective modification of the cation. Further, there is also the opportunity to use the structure of ionic liquid cations to control the reaction outcome of a given reaction.

Acknowledgments

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