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Quaternary ammonium ionic liquids containing fluorous ponytails: Competitive alkylation and elimination reactions of $I(CH_2)_nR_f$ ($n = 2, 3$) with tertiary amines

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ABSTRACT

The formation of quaternary ammonium iodides possessing a fluorine-containing chain has been investigated. Reactions of tertiary amines, such as *i*-$PrMe_2N$ and *n*-$BuMe_2N$ with $I(CH_2)_n(CF_2)_m(CF_3)$, ($n = 2$, $m = 5$ and 7) do not cleanly yield the anticipated quaternary ammonium halide salt, instead elimination occurs and $[RMe_2NH]I$ (R = *i*-Pr, *n*-Bu) and $CH_2{=}CH(CF_2)_m(CF_3)$ are formed. This is confirmed by the crystallographic characterisation of [*n*-$BuMe_2NH$]I which is found to adopt a micellar-type arrangement in the solid state. Increasing the spacer chain-length to $n = 3$ does result in the desired quaternary ammonium halide salts, $[RMe_2N(CH_2)_3(CF_2)_m(CF_3)]I$, ($m = 3$, 7). Quaternisation of $MeBuN((CH_2)_3C_8F_{17})$ with 1-iodooctane gave the asymmetric quaternary ammonium salt possessing a fluorinated alkyl chain, [*n*-$BuMeOctN((CH_2)_3C_8F_{17})$]I. Unlike in previously studied perprotio systems, low symmetry ammonium systems possessing long fluorinated chains do not result in room temperature ionic liquids.

1. Introduction

Ionic liquids (ILs) are defined as salts with low melting points, whilst those which melt at temperatures below 25 °C are commonly referred to as room temperature ionic liquids (RTILs) [1]. Because these liquids are composed entirely of ions they inherently possess low volatilities, they also exhibit good solvency properties and many of their physical properties may be tuned by modification of the ions, so these liquids have been variously described as “designer” or “green” solvents. Ionic liquids have been used, or studied, for a wide number of applications in both academia and industry, including BASF’s BASIL process [2].

A wide range of different cation:anion pairs have been investigated for their potential as ionic liquids, with the most commonly used RTILs being composed of imidizolium or ammonium cations coupled with fluorine-containing anions, such as tetrafluoroborate $[BF_4]^-$ or derivatives, triflate $[(CF_3SO_3]^-$ or trifluoromethylsulfonylamide (TFSI), $[(CF_3SO_2)_2N]^-$, and a number of these are commercially available. Interestingly, there are relatively few reports of systems based on organofluorine-containing cations in the literature, despite the potential they have to significantly modify the solvency properties and miscibility of such ionic liquids.

In 1970 Bohme and Hilp described the synthesis of *mono*-fluoromethyldialkylamines of the type $R_2N\text{-}CH_2F$ [$R_2{=}(CH_2)_2O(CH_2)_2$, $(CH_2)_4$, $(CH_2)_5$, R = Me, Et, $(CH_2)_3CH_3$] [3]. One of these, Me_2NCH_2F, was subsequently reacted with methylhalides to form hydroscopic trimethyl-fluoromethyl-ammonium halides. A number of routes to *di*fluoromethyltrialkylammonium salts have been reported, including the reaction of a tertiary amine with $Bi(CF_3)_3$ in the presence of $AlCl_3$ [4], or with *S*-(difluoromethyl)-diarylsulfonium tetrafluoroborate [5]. While in 2007 Nawrot and Jonczyk reported a series of *di*fluoromethyltrialkylammonium salts prepared from the reaction of an amine with:CF_2H derived from chlorodifluoromethane to give good yields of $[R^1R^2R^3NCHF_2]^+X^-$, however the melting points of these salts were not reported [6].

The first report of trifluoromethyl-containing ammonium salts came following the work of Yagupolskii et al., in 1980, who described the formation of Me_2NCF_3 from the reaction of Me_2NCCl_3 with antimony trifluoride. This, and other related, hydrolytically sensitive R_2NCF_3 compounds were treated with methyl iodide in the presence of silver tetrafluoroborate to give $[MeR_2N(CF_3)]^+(BF_4)^-$. These salts are thermally stable with melting points in the range 265 °C (R = Me) to 53 °C for dimethyltrifluoromethyl-*p*-chlorophenylammonium tetrafluoroborate. [7]

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A limited number of perfluoroalkyl amines are known, some, such as tris(perfluorobutyl)amine are commercially available, but these show no appreciable basic properties and so do not form a useful basis for preparing quaternary ammonium salts. In 1989, Nogami et al. reported that the reaction between 1,4-diazabicyclo [2.2.2.] octane (DABCO) with $CF_3(CF_2)_9CH_2Br$ and $CF_3(CF_2)_7I$ gave solid compounds which they formulated as $[R_f\text{-DABCO-}R_f]X_2$ and $[R_f\text{-DABCO-R}]X_2$ [8]. However, more recent work suggests that these might instead be halogen bonded $R_fX\ldots DABCO\ldots XR_f$ adducts [9].

There are a number of reports of amines and quaternary ammonium salts containing fluorous chains possessing spacer units of the type $R_f{-}(CH_2)_n{-}$ ($n = 2, 3, 5$). Thus, the quaternisation of R_3N (R = Bu, Oct) with $I(CH_2)_2(CF_2)_nCF_3$, ($n = 3, 7, 9$) is reported to give the quaternary ammonium iodides $[R_3N(CH_2)_2(CF_2)_nCF_3]I$ in ca. 80% yield. [10] Surprisingly, the authors report that there is relatively little effect on the physical properties of the ammonium salt on changing the fluorine-containing alkyl chain, instead the properties appear to be controlled by the identity of the non-fluorinated groups. For example, the salts $[Oct_3N(CH_2)_2(CF_2)_mCF_3]I$ ($m = 3, 7, 9$) were all reported to be room temperature ionic liquids which possess melting points within the range 18–22 °C, whilst replacing the octyl groups with n-C_4H_9 gave solids which all melt at temperatures between 82–91 °C. More recently the formation of fluorous quaternary ammonium salts for phase transfer catalysis applications have been described, including $[\{CF_3(CF_2)_7(CH_2)_5\}_3N(CH_2)_2(CF_2)_7CF_3]I$ which contains both $-(CH_2)_2-$ and $-(CH_2)_5-$ spacer units as a solid which is stable to ca. 160 °C. [11]

A number of quaternary ammonium systems containing a $-CH_2CH_2CH_2{-}R_f$ group have been reported previously; these include the synthesis of $[C_8F_{17}(CH_2)_3NBu_3]F$, a fluorous analogue of TBAF [12], fluoroalkyl-containing amines such as $[CF_3(CF_2)_7(CH_2)_3NR_3]I$ (R = Me, Et) with biological activity [13], phase-transfer catalysts such as $[Me_2N((CH_2)_3(CF_2)_3CF_3)_2]Cl$ [14], and solvents for electrochemical deposition [15]. We, and others, have published work suggesting that by reducing the symmetry of the constituent ions the melting point of an ionic liquid is generally lowered [16,17]. This is, in part, because of the influence that the size and shape of the ions have on the packing arrangement and hence lattice energy [18]. Since some of the fluorous ammonium iodides described above are claimed to possess remarkably low melting points we were interested in reducing the degree of symmetry around the nitrogen centre in related systems by studying the quaternisation of low symmetry tertiary amines with some long-chain fluorous iodides, in doing so we have identified some inconsistencies with some of the previously reported studies.

2. Results and discussion

The reaction between the mixed-alkyl group amine Me_2BuN and long-chained alkyl-halides, $C_ZH_{2Z+1}X$, has previously provided a reliable route to the formation of ionic liquids of the type $N_{114Z}X$, where the subscript numbers refer to the chain lengths of the four substituents attached to the nitrogen centre [16]. However, this does not appear to be the case when reacting tertiary amines with fluoroalkyl iodides possessing $-CH_2CH_2-$ spacers.

As series of reactions were carried out between Me_2BuN and $ICH_2CH_2R_f$ ($R_f = C_6F_{13}$, C_8F_{17}) without the use of a solvent by heating each fluoroalkyliodide with the amine in a sealed Schlenk tube at 80 °C for 24 h. After this time, on cooling, in both cases a white solid was formed. The ^1H NMR spectra of the solid showed signals for the butyl (1.0, 1.46, 1.89 and 3.06 ppm) and methyl groups (2.81 ppm) shifted from those of the starting amine (0.85, 1.25, 1.37 and 2.14 ppm) suggesting that quaternisation has occurred, but no signals were observed for the $-CH_2CH_2-$ spacer of the fluorinated chain. The fluorine NMR spectra did not show any significant signals due to the presence of a fluoroalkyl chain, also suggesting that the $CH_2CH_2R_f$ group had not been incorporated. Interestingly, the proton NMR spectra showed a broad signal at 10.5 ppm, which integrated to a single proton. Furthermore the solid produced in both reactions gave similar elemental analysis figures, Table 1. These figures were inconsistent with

Table 1
Characterising and physical data for quaternary ammonium systems studied.

System	%C	%H	%N	m.p./°C
$BuMe_2N + I(CH_2)_2(CF_2)_5CF_3$	31.95	6.10	5.01	116–118
$[BuMe_2N(CH_2)_2(CF_2)_5CF_3]I$	(29.22)	(3.33)	(2.44)	
$[BuMe_2NH]I$	(31.44)	(7.04)	(6.11)	
$BuMe_2N + I(CH_2)_2(CF_2)_7CF_3$	30.63	5.16	4.31	116–117
$[BuMe_2N(CH_2)_2(CF_2)_7CF_3]I$	(28.44)	(2.84)	(2.07)	
$[BuMe_2NH]I$	(31.44)	(7.04)	(6.11)	
$Bu_3N + I(CH_2)_2(CF_2)_7CF_3$	46.0	9.3	4.4	97
$[Bu_3N(CH_2)_2(CF_2)_7CF_3]I$	(34.78)	(4.12)	(1.84)	
$[Bu_3NH]I$	(45.99)	(9.01)	(4.47)	103 [27]
$BuMe_2N + CH_3CHICH_2CF_3$	31.86	7.14	6.02	111–114
$[BuMe_2NCH(CH_3)CH_2CF_3]I$	(35.39)	(6.24)	(4.13)	
$[BuMe_2NH]I$	(31.44)	(7.04)	(6.11)	
$BuMe_2N + I(CH_2)_3(CF_2)_7CF_3$	30.13	2.88	2.08	167(dec)
$[BuMe_2N(CH_2)_3(CF_2)_7CF_3]I$	(29.61)	(3.07)	(2.03)	
i-$PrMe_2N + I(CH_2)_3(CF_2)_7CF_3$	28.75	3.12	2.50	183 (dec)
$[i$-$PrMe_2N(CH_2)_3(CF_2)_7CF_3]I$	(28.44)	(2.84)	(2.07)	
$Bu_3N + I(CH_2)_3(CF_2)_7CF_3$	36.03	4.41	1.91	83–86
$[Bu_3N(CH_2)_3(CF_2)_7CF_3]I$	(35.70)	(4.30)	(1.81)	
$BuMe_2N + I(CH_2)_3(CF_2)_3CF_3$	32.31	4.38	3.13	140–142
$[BuMe_2N(CH_2)_3(CF_2)_3CF_3]I$	(31.90)	(4.33)	(2.86)	
i-$PrMe_2N + I(CH_2)_3(CF_2)_3CF_3$	30.54	3.87	3.29	>190 (dec)
$[i$-$PrMe_2N(CH_2)_3(CF_2)_3CF_3]I$	(30.31)	(4.03)	(2.95)	
$BuMeN(CH_2)_3(CF_2)_7CF_3 + OctI$	38.13	4.70	1.86	97–99
$[BuMeOctN(CH_2)_3(CF_2)_7CF_3]I$	(36.59)	(4.48)	(1.78)	

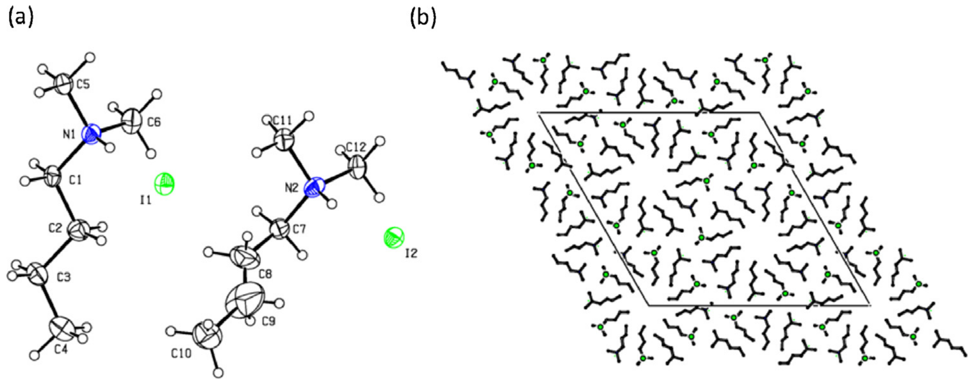


Fig. 1. (a) Molecular structure of $[Me_2BuNH]I$. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: N(1)-C(1) = 1.51(2), N(1)-C(5) = 1.50(3), N(1)-C(6) = 1.51(2), N(2)-C(7) = 1.50(2), N(2)-C(11) = 1.52(3), N(2)-C(12) = 1.52(2); C(1)-N(1)-C(5) = 111.5(13), C(1)-N(1)-C(6) = 111.7(15), C(5)-N(1)-C(6) = 110.4(14), C(7)-N(2)-C(11) = 114.0(13), C(7)-N(2)-C(12) = 112.0(14), C(11)-N(2)-C(12) = 109.4(13). (b) Packing diagram viewed down the c-axis, with hydrogens removed for clarity.

$[n\text{-}BuMe_2NCH_2CH_2R_f]I$ (calculated: 28.44% C, 2.84% H, $R_f = C_8F_{17}$; 29.22% C, 3.33% H, $R_f = C_6F_{13}$), but were a better match for $[n\text{-}BuMe_2NH]I$ (31.44% C, 7.04% H). The elemental analysis figures and the NMR data taken together suggested that in both cases $[n\text{-}BuMe_2NH]I$ had been formed instead of the expected quaternary ammonium product via the Menshutkin reaction. Confirmation that this was indeed the case came from an X-ray diffraction study of single crystals grown from the solid in a dichloromethane/hexane layered solution. From the X-ray data the structure represented in Fig. 1(a) was obtained.

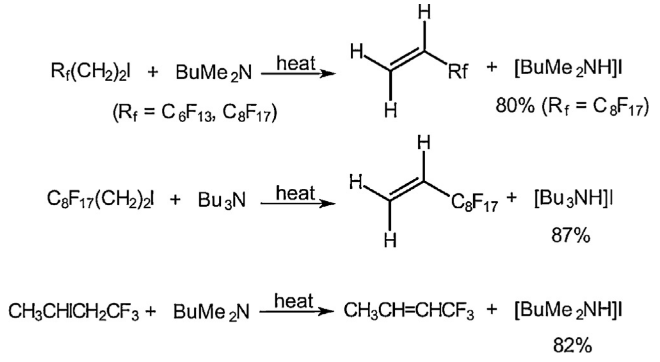
As shown in Fig. 1, there are two unique molecules contained within the unit cell, in one molecule some disorder is observed in the butyl chain, the atomic displacement ellipsoids for C8 and, in particular, C9 are elongated, leading to an apparent shortening of bond C8–C9. This has been interpreted as a vibrational effect in this case, but could also be the consequence of static disorder in which atoms C8 and C9 are each split over two partially occupied sites. Both of the $[n\text{-}BuMe_2NH]I$ molecules exhibit similar features around the nitrogen centre; the C–N bond lengths lie between 1.50(2) and 1.52(3) Å, whilst the C–N–C bond angles range from 109.4(13) to 114.0(13)°. Classical hydrogen bonds are formed between each N–H unit and an iodide with N…I distances of 3.458(15) and 3.463(15) Å.

The packing diagram, Fig. 1(b), viewed down the *c*-axis shows that a micellar-like structure is adopted, in that all the butyl chains point towards each other such that at the four corners of the unit cell micelles are generated, with two more contained within the cell. This is composed of six sets of alternating residues 1 and 2, with the iodides sitting above and below the quaternary nitrogen centre. In this way channels are generated parallel to the *c*-direction which in total constitute ca. 7.5% of the cell volume according to Platon [31]. Interestingly, a search of the crystallographic database shows that there are no crystal structures of other dimethylalkylammonium halides with which to make a direct comparison. However, for well-known cationic surfactants, such as hexadecyltrimethylammonium bromide [19] the longer alkyl chains lie parallel to each other, rather than forming a micellar-like arrangement, as observed here.

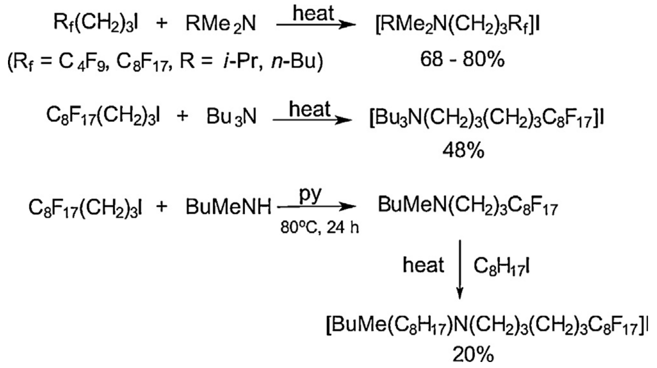
In addition to solid $[n\text{-}BuMe_2NH]I$ being generated in these reactions, a liquid product was also formed, the ^{19}F NMR spectrum of which showed the presence of a CF_3 group and seven CF_2 signals. The ^1H NMR spectrum of this liquid displayed two apparent second-order signals in the ratio 1:2 at 5.75 and 5.91 ppm. These data are assigned to heptadecafluoro-1-decene by comparison with previously published NMR data [20]. Thus, the reaction between neat Me_2BuN and $ICH_2CH_2C_6F_{13}$ or $ICH_2CH_2C_8F_{17}$ at 80 °C in our hands results in $[n\text{-}BuMe_2NH]I$ and $CH_2{=}CHC_6F_{13}$ or $CH_2{=}CHC_8F_{17}$.

These findings are at variance with the behaviour previously reported for the reaction of $n\text{-}Bu_3N$ with $CF_3(CF_2)_7CH_2CH_2I$ carried out in refluxing acetonitrile, for which $[n\text{-}Bu_3NCH_2CH_2(CF_2)_7CF_3]I$ was reported in 80% yield as a solid with a melting point of 91 °C. [10] In order to see whether the products formed are dependent on the presence, or otherwise, of the solvent and the temperature used we modified our experimental procedure such that Me_2BuN was reacted with $CF_3(CF_2)_7CH_2CH_2I$ in refluxing acetonitrile. Once again after cooling, evaporating the solvent and separating the solid we obtained the same products, $[Me_2BuNH]I$ and $CH_2{=}CHC_8F_{17}$. Being concerned that the differences in basicity (pK_a for Me_2BuNH^+ is 10.02 and for Bu_3NH^+ 10.89 [21]) might be influencing the outcome we also undertook the reaction of Bu_3N with $CF_3(CF_2)_7CH_2CH_2I$ in acetonitrile, as had been reported previously. After heating the reaction mixture for 24 h, a solid material was obtained, the ^1H NMR spectrum of which showed resonances due to the butyl groups at 0.92, 1.34, 1.77 and 2.97 ppm and a broad singlet at ca. 10 ppm which is assigned to an N–H proton. No resonances for the CH_2–spacers of the fluoroalkyl group were detected, and this was consistent with a lack of any signals in the ^{19}F NMR spectrum of the solid. Similarly, we found that the elemental analysis figures (C: 46.0%, H: 9.3%, N: 4.4%) were inconsistent with that calculated for $[Bu_3NCH_2CH_2(CF_2)_7CF_3]I$ (C: 34.78%, H: 4.12%, N: 1.84%), but remarkably close to the figures for $[Bu_3NH]I$ (C: 45.99%, H: 9.01%, N: 4.47%). It therefore appears that the outcome of the reaction is similar for both Bu_3N and Me_2BuN, that is quaternisation does not occur as readily as was previously reported, but instead HI is eliminated from $CF_3(CF_2)_7CH_2CH_2I$ resulting in the formation of $CH_2{=}CHC_8F_{17}$ and the ammonium iodide salt, $N_{114H}I$ (Scheme 1).

This behaviour is consistent with the previously observed propensity for fluoroalkyl iodides with a $-CH_2CH_2-$ spacer to undergo elimination reactions in the presence of potassium hydroxide [22] and other bases [23]. Indeed Feiring et al. reported that reaction of $CF_3(CF_2)_5CH_2CH_2I$ with Me_2NH ($pK_a = 10.64$) in diethylether at 25 °C, undergoes elimination, rather than S_N2 substitution, to generate $CF_3(CF_2)_5CH{=}CH_2$, which in the presence of an excess of amine ultimately yields $CF_3(CF_2)_4CF{=}CHCH_2N(CH_3)_2$ [24]. However, in the case of softer bases, such as phosphines (Bu_3P, $pK_a = 8.43$ [25]), quaternisation is possible, and in this way salts of the type $[R_3P(CH_2)_2R_f]I$ (R = Me, Bu, Oct; $R_f = C_4F_9, C_6F_{13}, C_{10}F_{21}$) have been prepared [26]. We also note that Riess et al., obtained Zwitterionic salts of the type $Me_2N(CH_2COO)(CH_2CH_2R_f)$ ($R_f = C_4F_9, C_6F_{13}, C_8F_{17}$) by first forming the fluoroalkyl-containing amine, $Me_2NCH_2CH_2R_f$, via a three-step



Scheme 1. The reaction of amines with perfluoroalkyliodides containing a $-CH_2CH_2-$ spacer unit, for conditions see text.



Scheme 2. The reaction of amines perfluoroalkyliodides containing a $-CH_2CH_2CH_2-$ spacer unit, to generate quaternary ammonium systems containing a fluorous ponytail.

route starting with R_fCH_2COOH or R_fCH_2I, followed by quaternisation with a non-fluorinated reagent, rather than the other way around [13].

On changing to a secondary fluorinated alkyl halide we observed a similar reaction. Thus, when following work-up after the reaction of 3-iodo-1,1,1-trifluorobutane, $CH_3CHICH_2CF_3$, with n-$BuMe_2N$ a white solid was obtained which showed ^1H NMR data and elemental analysis figures consistent with the formation of [n-$BuMe_2NH$]I.

Unlike the elimination reactions observed for fluorous iodides possessing a $-CH_2CH_2-$ spacer, we were able to successfully quaternise analogues with a $-CH_2CH_2CH_2-$ spacer. Previously a number of quaternary ammonium systems containing a $-CH_2CH_2CH_2-R_f$ group have been reported; [11–15] however, in those cases the degree of symmetry at the nitrogen centre is relatively high, with only two different substituents being present giving ions of generic formula $[RNR'_3]^+$ and $[R_2NR'_2]^+$. We therefore investigated the reaction of $I(CH_2)_3(CF_2)_nCF_3$ ($n = 3, 7$) with less symmetric amines, such as n-$BuMe_2N$ and i-$PrMe_2N$ to give salts of the type $[R_2NR'R_f]I$ and with an asymmetric amine to generate $[RNR'R''R_f]I$.

Treatment of dimethylisopropylamine with 1-iodo-1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-heptadecafluoroundecane in acetonitrile in a sealed Schlenk tube over 24 h yielded, after removal of the solvent, a solid, for which elemental analysis figures were obtained which were consistent with [i-$PrMe_2N(CH_2)_3(CF_2)_7CF_3$]I. In this case the proton NMR spectrum showed the presence of peaks due to the alkyl groups on the starting amine, shifted to higher frequency, and resonances for the three CH_2 spacer groups were observed at 2.10, 2.33 and 3.83 ppm, also shifted to higher frequencies compared with the starting iodide (2.02, 2.23 and 3.18 ppm). These data, and those obtained from similar reactions between Bu_3N and i-$PrMe_2N$ with $I(CH_2)_3(CF_2)_7CF_3$ and n-$BuMe_2N$ and i-$PrMe_2N$ with $I(CH_2)_3(CF_2)_3CF_3$ are summarised in Table 1 and confirm that in this case quaternisation, rather than HI elimination has occurred.

Reaction of MeBuNH with $C_8F_{17}(CH_2)_3I$ in the presence of pyridine at 80 °C resulted, after work-up, in the isolation of an oily liquid, which analysed satisfactorily as the asymmetric amine containing a fluorous chain, $BuMeN((CH_2)_3C_8F_{17})$ and had similar NMR data to those previously reported for $MeNH((CH_2)_3C_8F_{17})$ [28]. This amine was reacted with 1-iodooctane to give a 20% yield of a yellow solid with a melting point of 97 °C. Confirmation of this material as [n-$BuMeOctN((CH_2)_3C_8F_{17})$]I was obtained from NMR spectroscopy and elemental analysis. This is, to the best of our knowledge, the first report of a completely asymmetric quaternary ammonium system in which one of the groups is fluorinated, Scheme 2.

Table 1 lists the melting points of the prepared quaternary ammonium iodides possessing fluoroalkyl chains. Firstly, we note that changing the length of the fluorinated chain, in these systems, does result in different melting points, $[BuMe_2N(CH_2)_3(CF_2)_3CF_3]I$ (140–142 °C) and $[BuMe_2N(CH_2)_3(CF_2)_7CF_3]I$ (167 °C). Comparison with similar non-fluorinated systems shows that the fluoroalkyl-containing quaternary ammonium iodides possess considerably higher melting points than those of similar non-fluorinated systems. For example, the melting points of $[BuMe_2N(octyl)]I$, $[BuMe_2N(decyl)]I$ and $[BuMe_2N(tetradecyl)]I$ are 92, 55 and 11 °C respectively, [29] all of which are lower than those of $[BuMe_2N(CH_2)_3R_f]I$ ($R_f = (CF_2)_3CF_3$, 140–142 °C and $R_f = (CF_2)_7CF_3$, 167 °C). A further difference between the perprotio-quaternary ammonium salts and their partially fluorinated analogues is that on decreasing the symmetry around the nitrogen centre in the hydrocarbon series $[Me_3NOct]I$, $[Me_2BuNOct]I$, [MeBuOctN(tetradecyl)]I a decrease in the melting points is observed from 145, 92 to 11 °C respectively. While the melting point of the least symmetric system studied here, $[MeBuOctN(CH_2)_3(CF_2)_7CF_3]I$, (97 °C) is higher than that of the more symmetric $[Bu_3N(CH_2)_3(CF_2)_7CF_3]I$ (83–86 °C) salt, but lower than that of $[Me_2BuN(CH_2)_3(CF_2)_7CF_3]I$ which did not melt below its decomposition temperature of 167 °C.

3. Conclusions

An investigation into the synthesis of quaternary ammonium halide salts with a fluoroalkyl chain and two or three other distinct groups on the nitrogen has shown that reactions of $R_fCH_2CH_2I$ with $R_2R'N$ do not always yield the anticipated quaternary ammonium systems via the Menshutkin reaction, instead a competitive elimination reaction results in the formation of a non-fluorinated ammonium salt of the type $[R_2R'NH]I$ and $R_fCH{=}CH_2$. However, when similar reactions are carried out using iodides possessing a longer $-CH_2CH_2CH_2-$ spacer compounds of the type $[R_2R'N(CH_2)_3R_f]I$ do result, all of which possess relatively high melting points. Interestingly, unlike for the analogous perprotio-iodides, there is little correlation between the lowering of the symmetry around the nitrogen centre and the lowering of the observed melting point of the salts. Indeed, the quaternary ammonium salts possessing a fluorinated chain generally exhibit higher melting points than their non-fluorinated analogues, so while they may form suitable ions for fluorous systems, they are unlikely to be useful ionic liquids. It is considered that hydrogen bonding involving the fluorinated chain is most likely to contribute to the increase in melting points.

4. Experimental

All reagents were obtained from standard chemical suppliers and were used as supplied.

Table 2
Crystallographic data for [Me_2BuNH]I.

	[Me_2BuNH]I
Empirical formula	C6 H16 I1 N1
fw	228.97
Colour, habit	Colourless, plate
Crystal system	Trigonal
Space group	R-3 (No.148)
Crystal size	$0.03 \times 0.06 \times 0.18\,mm^3$
Unit cell dimensions	$a = 36.558(8)$ Å, $\alpha = 90^\circ$ $b = 36.558(8)$ Å, $\beta = 90^\circ$ $c = 7.828(8)$ Å, $\gamma = 120^\circ$
Volume	9060(12) Å^3
T	100(2) K
Z	36
$D_{calcd.}$	1.512 mg/m^3
λ	Å
μ	3.111 mm^{-1}
$F(000)$	4032
2θ range	3.1–25.5°
No. of reflections and parameters	2323 (2323 unique) 146
R/wR_2	0.0907/0.2139
S	1.44
Largest diff. peak and hole	1.49 and −1.07 eÅ^{-3}

^{1}H NMR spectra were recorded on either Bruker DPX 300 or Bruker Avance (III) spectrometers operating at 300.13 and 399.99 MHz respectively, and internally referenced to $SiMe_4$. ^{19}F NMR spectra were recorded on a Bruker Avance (III) spectrometer operating at 376.49 MHz and chemical shifts are quoted relative to $CFCl_3$ using the high frequency positive convention. C, H, N elemental analyses were performed by the School of Chemistry microanalysis lab using a Thermo Scientific Flass 2000 organic elemental analyser.

4.1. Crystallographic details

Details of the structure analysis carried out on [Me2BuNH] + I$^-$ are summarised in Table 2. Measurements were made on crystals prepared by slow solvent evaporation of a CH_2Cl_2/hexane solution on a Nonius MAC3 CAD4 diffractometer. All the data obtained were corrected for Lorentz-polarisation factors and subsequently for absorption using the psi-scan method. X-ray structural data solution was by direct methods and refined against F2 using SHELXTL [30] or SHELX-97 [31] with H-atoms in idealised positions. All non-H atoms were modelled with anisotropic displacement parameters. The figures were produced using Platon [32]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre CCDC 953367. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or deposit@ccdc.cam.ac.uk).

4.2. Preparation of [i-$PrMe_2N(CH_2)_3(CF_2)_7CF_3$]I.

Dimethylisopropylheptadecafluoroundecyl ammonium iodide was prepared by mixing equimolar quantities of dimethylisopropyl amine (0.286 g, 3.3 mmol) and 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl iodide (1.80 g, 3.0 mmol) in a sealed Schlenk tube with acetonitrile (30 ml). The reaction mixture was heated and stirred at 150 °C for 24 h. After cooling to room temperature, the solvent was removed under vacuum and the crude material was washed with hexane to afford dimethylisopropylheptadecafluoroundecyl ammonium iodide as a beige solid (1.5 g, 68%) M.P 183 °C (dec). ^{19}F NMR ($CDCl_3$): δ-80.75(t, 3F, J = 10 Hz), −113.70(br, 2F), −121.79(bs, 6F), −123.09(bs, 4F), −126.13(bs, 2F). ^{1}H NMR ($CDCl_3$): δ 1.43(d, 6H), 2.10(bm, 2H), 2.33(bm, 2H), 3.28(s, 6H), 3.83(m, 2H), 3.90(m, 1H). Elemental analysis calc. for $C_{16}H_{19}F_{17}IN$ (675.03 gmol^{-1}) C 28.44, H 2.84, N 2.07% Found C 28.75, H 3.12, N 2.50%.

4.3. Preparation of [n-$BuMe_2N(CH_2)_3(CF_2)_7CF_3$]I.

Dimethylbutylheptadecafluoroundecyl ammonium iodide was prepared by mixing equimolar quantities of dimethylbutyl amine (0.330 g, 3.3 mmol) and 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl iodide (1.80 g, 3.0 mmol) in acetonitrile (30 ml).The reaction mixture was stirred at 150 °C for 24 h in a sealed Schlenk tube. The solvent was removed under vacuum and the crude material was washed with hexane resulting in dimethylbutylheptadecafluoroundecyl ammonium iodide as a white solid (1.8 g, 80%) M.P 167 °C (dec). ^{19}F NMR ($CDCl_3$) δ −80.77(t, J = 9.9 Hz, 3F), −113.68(m, 2F), −121.8(bs, 2F), −121.90(bs, 4F), −122.76(bs, 2F), −123.16 (bs, 2F), −126.16(bs, 2F). ^{1}H NMR ($CDCl_3$) δ 1.04(t, 3H), 1.48(sep, 2H), 1.78(m, 2H), 2.15(m, 2H), 2.36(m, 2H), 3.44(s, 6H), 3.60(m, 2H), 3.89(m, 2H). Elemental analysis calc. for $C_{17}H_{21}F_{17}IN$ (689.04 gmol^{-1}) C 29.61,H 3.07, N 2.03% Found C 30.13, H 2.88, N 2.08%.

4.4. Preparation of [n-$Bu_3N(CH_2)_3(CF_2)_7CF_3$]I.

Following the same procedure as above the reaction of n-tributylamine (0.79 ml, 3.3 mmol) with 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl iodide (1.80 g, 3.0 mmol) resulted in tributylheptadecafluoroundecyl ammonium iodide (1.2 g, 48% yield) as an off-white solid M.P 83–86 °C. ^{19}F NMR ($CDCl_3$) δ −80.87 (t, 3F, J = 10 Hz), −113.43 (br, 2F), −121.70 (br, 2F), −122.00 (br, 4F), −122.80 (br, 2F), −123.2 (br, 2F), −126.20 (bs,2F). ^{1}H NMR ($CDCl_3$) δ 0.96 (t, 9H, J = 7.3 Hz), 1.41 (sextet, 6H), 1.66 (br, 6H), 2.08 (br, 2H), 2.36 (m, 2H), 3.33 (m, 6H), 3.63(m, 2H). Elemental analysis, calc. for $C_{23}H_{33}F_{17}NI$ (773.14 gmol^{-1}) C 35.70, H 4.30, N 1.81% Found C 36.03, H 4.41, N 1.91%.

4.5. Preparation of [i-$PrMe_2N(CH_2)_3(CF_2)_3CF_3$]I.

Following the procedure above, dimethylisopropylamine (0.286 g, 3.3 mmol), 4,4,5,5,6,6,7,7,7-perfluoroheptyl iodide (0.64 ml, 3.0 mmol) was stirred in acetonitrile (30 ml) at 150 °C for 24 h in a sealed Schlenk tube resulting in a yellow solid (1.18 g, 76%) M.P > 190 °C (dec). ^{19}F NMR ($CDCl_3$) δ −80.97 (t, 3F), −113.70 (m, 2F), −124.10 (m, 2F), −125.96 (t, 2F). ^{1}H NMR ($CDCl_3$) δ 1.43(d, J = 6.6 Hz, 6H), 2.11(bm, 2H), 2.33(bm, 2H), 3.27(s, 6H), 3.81(m, 2H), 3.90(sep, J = 6.6 Hz, 1H). Elemental analysis, calc. for $C_{12}H_{19}F_9NI$ (475.04 gmol^{-1}) C 30.31, H, 4.03, N 2.95%. Found C 30.54, H 3.87, N 3.29%.

4.6. Preparation of [n-$BuMe_2N(CH_2)_3(CF_2)_3CF_3$]I.

Following the procedure described above, dimethylbutylamine (0.33 g, 3.3 mmol), 4,4,5,5,6,6,7,7,7-perfluoroheptyl iodide (0.64 ml, 3.0 mmol) and acetonitile (30 ml) were stirred at 150 °C for 24 h in a sealed Schlenk tube resulting in a yellow solid (1.23 g, 77%) M.P 140–142 °C. ^{19}F NMR ($CDCl_3$) δ −80.90 (t, 3F), −113.80 (m, 2F), −124.15 (m,2F), −125.94 (t, 2F). ^{1}H NMR ($CDCl_3$) δ 0.96 (t, 3H), 1.41 (sextet, 2H), 1.69 (m, 2H), 2.07 (m, 2H), 2.28 (m, 2H), 3.38 (s, 6H), 3.50 (m, 2H), 3.82 (m, 2H). Elemental analysis, calc. for $C_{13}H_{21}F_9NI$ (489.06 gmol^{-1}) C 31.90, H, 4.33, N 2.86%. Found C 32.31, H 4.38, N 3.13%.

4.7. Preparation of $MeBuN(CH_2)_3(CF_2)_7CF_3$.

MeBuNH (30.73 mmol, 3.63 ml) was added drop-wise to a mixture of $C_{11}H_6F_{17}I$ (4.016 g, 6.83 mmol) and pyridine (6.6 ml) the reaction mixture was stirred at 80 °C for 4 h. Addition of NaOH

(10 ml, 10% solution) followed by separation and drying with $MgSO_4$ resulted in isolation of a clear yellow oily liquid (1.71 g, 11% yield). ^1H NMR ($CDCl_3$) δ 0.84 (t, 3H, CH_3), 1.25 (sextet, 2H, CH_2), 1.36 (m, 2H, CH_2), 1.68 (quintet,2H, CH_2), 2.03 (bm,2H, CH_2), 2.12 (s, 3H, CH_3), 2.24 (t, 2H, NCH_2), 2.31 (t, 2H, NCH_2). ^{19}F NMR ($CDCl_3$) δ −80.75 (t,3F, CF_3), −114.14 (bm,2F,CF_2), −121.7 (bm, 2F, CF_2), −121.92 (bm, 4F, $2CF_2$), −122.7 (bm, 2F, CF_2), −123.4 (bm, 2F, CF_2), −126.1 (bm, 2F, CF_2). Elemental analysis calc for $C_{16}H_{18}F_{17}N$, C 35.09, H 3.32, N 2.56% Found C 35.71, H 3.08, N 2.98%.

4.8. Preparation of [MeBuOctN$(CH_2)_3(CF_2)_7CF_3$]I

A neat reaction was performed using equimolar quantities of $MeBuN(CH_2)_3(CF_2)_7CF_3$ (1.71 g, 3.0 mmol) and 1-iodooctane (0.54 ml, 3.0 mmol) in a sealed Schlenk tube at 90 °C for 24 h, a yellow solid was isolated and washed with hexane (0.5 g, 20%) M.P 97–99 °C. ^1H NMR ($CDCl_3$) δ 0.81(t, 3H, CH_3), 0.96(t, 3H, CH_3), 1.2–1.4 (bs, 12H, $(CH_2)_6$), 1.64 (bm, 4H, β-CH_2), 2.05 (bm, 2H, R_f-CH_2), 2.30 (bm, 2H, $RfCH_2CH_2$), 3.31(s, 3H, CH_3), 3.38 (bm, 4H, βCH_2), 3.76 (m, 2H, αCH_2). ^{19}F NMR ($CDCl_3$) δ −80.74 (t, 3F, CF_3), −113.48 (bm, 2F, CF_2), −121.60 (bm, 2F, CF_2), −121.94 (bm, 4F, $2CF_2$), −122.70 (bm, 2F, CF_2), −123.09 (bm, 2F, CF_2), −126.14 (bm, 2F, CF_2). Elemental analysis calc for $C_{24}H_{35}F_{17}IN$ (787.15 $gmol^{-1}$) C 36.59, H 4.48, N 1.78% Found C 38.13, H 4.70, N 1.86%.

4.9. Reaction of Me_2BuN with $I(CH_2)_2(CF_2)_5CF_3$ to give [Me_2BuNH]I

Equimolar quantities of *N*,*N*-dimethylbutylamine (2.023 g, 20.0 mmol) and 1*H*, 1*H*, 2*H*, 2*H*-perfluorooctyliodide (9.48 g, 20.0 mmol) are placed in a Schlenk tube which was sealed and stirred at 90 °C for 24 h. After cooling to room temperature a clear liquid and an off-white solid were obtained. The solid was separated by filtration, washed with hexane and dried to yield a white powder (yield 3.69 g, 80%) M.P 116–118 °C. ^1H NMR ($CDCl_3$): δ 0.91(t, 3H), 1.37(sextet, 2H), 1.80(m, 2H), 2.80(s, 6H), 3.07(m, 2H). ^{19}F NMR ($CDCl_3$): no signals. Elemental analysis calc for $C_{14}H_{19}F_{13}NI$ (575.03 $gmol^{-1}$), C 29.22 H 3.33, N 2.44% Found C 31.95, H 6.10, N 5.01%, calc for [Me_2BuNH]I C 31.44, H 7.04, N 6.11%. The liquid layer was separated, washed with acidified water and dried to yield $CH_2CH(CF_2)_5CF_3$ which was identified by comparison with its previously reported ^1H and ^{19}F NMR data [20].

4.10. Reaction of Me_2BuN with $I(CH_2)_2(CF_2)_7CF_3$ to give [Me_2BuNH]I

In a similar fashion to that described above *N*,*N*-dimethylbutylamine (2.023 g, 20.0 mmol) and 1*H*,1*H*,2*H*,2*H*-perfluorodecyliodide (11.47 g, 20.0 mmol) were mixed in a Schlenk tube which was sealed and heated with stirring at 90 °C for 24 h resulting in a beige solid (yield 0.55 g, 12%) M.P 116–117 °C. ^1H NMR ($CDCl_3$) δ 1.0(t, 3H), 1.46 (sextet, 2H), 1.89 (m, 2H), 2.81 (s, 6H), 3.06 (m, 2H). Elemental analysis calc for $C_{16}H_{19}F_{17}NI$ (675.03 $gmol^{-1}$), C 28.44, H 2.84, N 2.07% Found C 30.63, H 5.16, N 4.31% calc. for [Me_2BuNH]I C 31.44, H 7.04, N 6.11%.

4.11. Reaction of Bu_3N with $I(CH_2)_2(CF_2)_7CF_3$ to give [Bu_3NH]I

Tri-*n*-butylamine (0.79 ml, 3.3 mmol) was added to 1*H*, 1*H*, 2*H*, 2*H*-perfluorodecyliodide (1.89 g, 3.3 mmol) in 30 ml acetonitrile and heated at 150 °C for 24 h in a sealed Schlenk tube. The solvent was removed under vacuum and washed with hexane to yield a beige solid (0.9 g, 87%) M.P 97 °C. ^1H NMR ($CDCl_3$) δ 0.92 (t, 9H), 1.34 (sextet, 6H), 1.77 (m, 6H), 2.97 (m, 6H). Elemental analysis calc for $C_{22}H_{31}F_{17}NI$ (313.13 $gmol^{-1}$) C 34.78, H 4.12, N 1.84% Found C 46.00, H 9.30, N 4.44% calc for [Bu_3NH]I C 45.99, H 9.01, N 4.47%.

4.12. Reaction of Me_2BuN with $CH_3CHICH_2CF_3$ to give [Me_2BuNH]I

The reaction between equimolar quantities of *N*,*N*-dimethylbutylamine (1.019 g, 10.0 mmol) and 3-iodo-1,1,1-trifluorobutane (2.379 g, 10.0 mmol) was carried out in a sealed Schlenk tube at 90 °C for 24 h. A white solid was isolated, which was washed with hexane (yield 1.88 g, 82%) M.P 111–114 °C. ^1H NMR ($CDCl_3$) δ 0.91 (t, 3H), 1.37 (m, 2H), 1.81 (m, 2H), 2.78 (s, 6H), 3.06 (m, 2H). Elemental analysis calc. for $C_{10}H_{21}F_3NI$ (339.07 $gmol^{-1}$) C 35.39, H 6.24, N 4.13% Found C 31.86, H 7.14, N 6.02% calc. for [Me_2BuNH]I C 31.44, H 7.04, N 6.11%.

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References

[1] P. Wasserscheid, T. Walton, Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, New York, 2002.
[2] K.R. Seddon, Nat. Mater. 2 (2003) 363–365.
[3] H. Bohme, M. Hilp, Chem. Ber. 103 (1970) 104–111.
[4] S.V. Pasenok, N.V. Kirij, Yu.L. Yagupolskii, D. Naumann, W. Tyrra, A. Fitzner, Z. Anorg, Allg. Chem. 625 (1999) 834.
[5] G.K.S. Prakash, C. Weber, S. Chacko, G.A. Olah, Org. Lett. 9 (2007) 1863.
[6] E. Nawrot, A. Jonczyk, J. Org. Chem. 72 (2007) 10258–10260.
[7] L.M. Yagupol'skii, N.V. Kondratenko, G.N. Timofeeva, M.I. Dronkina, Yu.L. Yagupol'skii, J. Org. Chem. USSR 16 (1980) 2139–2143.
[8] T. Terada, T. Nogami, Y. Shirota, Bull. Chem. Soc. Jpn. 62 (1989) 2793–2797.
[9] S. Dordonne, B. Crousse, D. Bonnet-Delpon, J. Legros, Chem. Commun. 47 (2011) 5855–5857.
[10] O.D. Gupta, P.D. Armstrong, J.M. Shreeve, Tetrahedron Lett. 44 (2003) 9367–9370.
[11] D. Mandal, J.A. Gladysz, Tetrahedron Lett. 66 (2010) 1070–1077.
[12] S. Fustero, A.G. Sancho, J.L. Acena, J.F. Sanz-Cervera, J. Org. Chem. 74 (2009) 6398–6401.
[13] J.B. Nivet, R. Bernelin, M. Le Blanc, J.G. Riess, Eur. J. Med. Chem. 27 (1992) 891–898.
[14] Q. Weiming, US Patent US6054615 (2000) assigned to Du Pont.
[15] P.N. Bartlett, D.C. Cook, M.W. George, J. Ke, W. Levason, G. Reid, W. Su, W. Zhang, Phys. Chem. Chem. Phys. 12 (2010) 492–501.
[16] A.D. Ballantyne, A.K. Brisdon, R.A.W. Dryfe, Chem. Commun. (2008) 4980–4982.
[17] H. Matsumoto, N. Terasawa, T. Umecky, S. Tsuzuki, H. Sakaebe, K. Asaka, K. Tatsumi, Chem. Lett. 37 (2008) 1020–1021.
[18] J.M. Slattery, C. Daguenet, P.J. Dyson, T.J.S. Schubert, I. Krossing, Angew. Chem. Int. Ed. 46 (2007) 5384–5388.
[19] A.R. Campanelli, L. Scaramuzza, Acta. Crystallogr. C 42 (1986) 1380.
[20] C.J. Pouchert, J. Behrike, The Aldrich Library of 13C and 1H FT NMR Spectra 1, 1993 spectrum 149C;
B. Ameduri, B. Boutevin, M. Nouiri, M. Talbi, J. Fluorine Chem. 74 (1995) 191–198.
[21] H.K. Hall Jr., J. Am. Chem. Soc. 79 (1957) 5441–5444.
[22] N.O. Brace, L.W. Marshall, C.J. Pinson, G. van Wingerden, J. Org. Chem. 49 (1984) 2361–2368.
[23] C.S. Rondestvedt Jr., J. Org. Chem. 42 (1977) 1985–1990.
[24] A.E. Feiring, M.C. Hovey, S.D. Arthur, J. Fluorine Chem. 24 (1984) 125–132.
[25] W.A. Henderson Jr., C.A. Streuli, J. Am. Chem. Soc. 82 (1960) 5791–5794.
[26] J.J. Tindale, C. Na, M.J. Jennings, P.J. Ragogna, Can. J. Chem. 85 (2007) 660–667.
[27] K. Witschonke, C.A. Kraus, J. Am. Chem. Soc. 69 (1947) 2472.
[28] Z. Szlávik, G. Tárkányi, Á. Gömöry, G. Tarczay, J. Rábai, J. Fluorine Chem. 108 (2001) 7–14.
[29] H. Alhanash, PhD Thesis, The University of Manchester, 2012.
[30] G.M. Sheldrick, SHELXTL, Siemans Analytical X-ray Instruments, Madison, WI, 1995.
[31] G.M. Sheldrick, SHELX-97, Institut fur Anorganische Chemie der Universitat Göttingen, Göttingen, Germany, 1998.
[32] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utreht, The Netherlands, 2005.