Supplementary Information

Appendix 1. Derivation of formulae for C^+A^- and $C^{2+}2A^-$ type ILs

Here we show how an expression may be derived for the enthalpy of vaporisation of an IL comprising a Coulombic contribution and van der Waals contributions from the anion and the cation. In deriving the Coulombic contribution, we use Kapustinskii's equation [1]. This equation, which provides a value for the energy necessary to completely separate all the ions in an ionic solid (the lattice energy) has been used previously to estimate the solubility parameter, δ, of ionic liquids [2,3]. In the derivation below we need to consider the formation of gas phase ion pairs from the liquid, not separate ions, to make the necessary link with the enthalpy of vaporisation.

Monocationic ILs of type C^+A^-.

For a system at zero Kelvin, i.e. with no kinetic energy, we can use the thermodynamic cycle in figure A1 to relate the lattice energy of the ionic liquid, $U_{lattice}$, the internal energy of the gaseous ion pair, U_{r12}, and the internal energy of vaporisation $\Delta_{vap}U_0$, where

$$\Delta_{vap}U_0 = U_{lattice} + U_{r12} \qquad \text{(A1)},$$

and r_{12} is the equilibrium distance between the two ions in the gas phase ion pair.

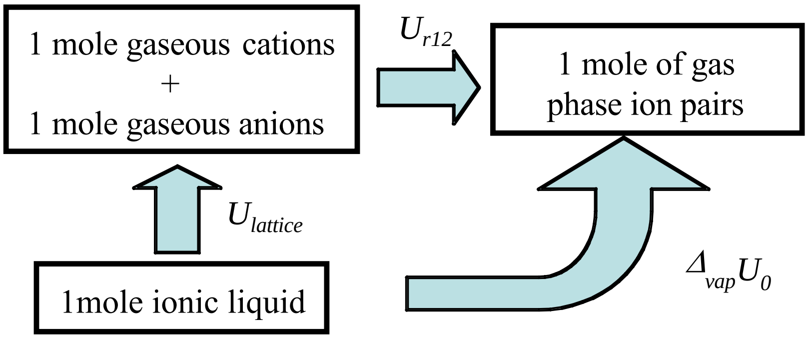

Figure A1. Thermodynamic cycle for evaporation of an ionic liquid at zero Kelvin.

The value of $U_{lattice}$ (in kJ mol^{-1}) for a wide range of crystalline ionic solids can be approximated to U_K, the lattice energy given by the Kapustinskii equation [1]

$$U_K = \frac{1.214x10^5 V|Z_+||Z_-|}{(r_+ + r_-)}\left[1 - \frac{\rho}{(r_+ + r_-)}\right] = \frac{|Z_+||Z_-|e^2 N_A\left(\frac{A_{NaCl}}{2}\right)V\ 10^9}{4\pi\varepsilon_0 (r_+ + r_-)}\left[1 - \frac{\rho}{(r_+ + r_-)}\right] \quad \text{(A2)}$$

where $|Z_+|$ and $|Z_-|$ are the modulii of the oxidation states of the ions (1 and 1 for C^+A^-), V is the number of ions in the molecular formula (2 for C^+A^-), ρ is a constant normally taken as 34.5 pm [4] and $(r_+ + r_-)$ is the nearest neighbour separation of the charges in the ionic solid in pm. It should be pointed out here that as the Kapustinskii equation is a sum of potentials over the entire three dimensional crystal, the distance $(r_+ + r_-)$ represents the *average* nearest neighbour distance between the positive and negative ions. For simple ions, this average separation is simply the sum of the ionic radii, but for more complex, non spherical ions in solids, and for the ions in ILs considered here, it is the average distance between the oppositely charged ions. (The numerical value $1.214x10^5 = 10^9\ e^2 N_A(A_{NaCl}/2)/4\pi\varepsilon_0$ where e is the electronic charge, N_A is Avogadro's number, ε_0 is the permittivity of free space, $A_{NaCl}=1.748$ is the Madelung constant for rock salt [4] and the 10^9 is because $(r_+ + r_-)$ and U_K are in units of nm and kJ mol^{-1} respectively). As this equation remains remarkably accurate over a range of crystal structures [4], we reason that it can be successfully applied to the partially ordered structures to be found in ionic liquids [2,3,5]. However, whereas for simple ionic solids the effect of attractive van der Waals forces between the ions is only about 1% of the lattice energy [4], for the much larger ions found in ILs, we would expect the van der Waals forces to be greater. We include the change in internal energy on evaporation due to van der Waals bonding, $\Delta U_{vdw,lattice}$, as in equation (A3). Note that here we use van der Waals bonding to encompass all bonding, including hydrogen bonding, which is neither covalent nor Coulombic in nature.

$$U_{lattice} = U_K + \Delta U_{vdw,lattice} = \frac{|Z_+||Z_-|e^2 N_A\left(\frac{A_{NaCl}}{2}\right)V\,10^9}{4\pi\varepsilon_0(r_+ + r_-)}\left[1 - \frac{\rho}{(r_+ + r_-)}\right] + \Delta U_{vdw,lattice}$$

(A3)

Turning to the energy of the gas phase ion pair, U_{r12} (in kJ mol^{-1}) is given by the Born-Mayer equation for a single ion pair [4] plus the van der Waals energy for the gas phase neutral ion pair, $\Delta U_{vdw,r12}$,

$$U_{r12} = -\frac{|Z_+||Z_-|e^2 N_A A_{eff}}{4\pi\varepsilon_0 r_{12}}10^9\left[1 - \frac{\rho}{(r_{12})}\right] - \Delta U_{vdw,\,r12} \quad \text{(A4).}$$

r_{12} is the classical separation in pm of the charges in the gas phase ion pair, while A_{eff} is the effective Madelung constant which, for a neutral ion pair for which there is only a single Coulombic attraction, is equal to 1, see appendix 2 . r_{12} is the separation of the charges in the ion pair for the particular geometry adopted in the gas phase and is not the same as the average value, $(r_+ + r_-)$, defined for the condensed liquid phase. Combining equations (A1), (A3) and (A4) we obtain

$$\Delta_{vap}U_0 = \frac{|Z_+||Z_-|e^2 N_A 10^9}{4\pi\varepsilon_0}\left(\frac{\left(\frac{A_{NaCl}}{2}\right)V}{(r_+ + r_-)}\left[1 - \frac{\rho}{(r_+ + r_-)}\right] - \frac{A_{eff}}{r_{12}}\left[1 - \frac{\rho}{r_{12}}\right]\right) + \left(\Delta U_{vdw,lattice} - \Delta U_{vdw,r12}\right)$$

(A5).

$\Delta U_{vdw,lattice}$ involves the breaking of all the van der Waals bonds around each ion in the liquid phase, whereas $\Delta U_{vdw,r12}$ involves the making of just one van der Waals bond between the two ions in the gas phase. So we can assume that $\Delta U_{vdw,lattice}$ is substantially larger than $\Delta U_{vdw,r12,}$ and replace the term in brackets on the right with just ΔU_{vdw} which is slightly smaller than $\Delta U_{vdw,lattice}$, giving

$$\Delta_{vap}U_0 = \Delta U_{Cou} + \Delta U_{vdw} = \frac{|Z_+||Z_-|e^2 N_A 10^9}{4\pi\varepsilon_0}\left(\frac{\left(\frac{A_{NaCl}}{2}\right)V}{\left(r_+ + r_-\right)}\left[1-\frac{\rho}{\left(r_+ + r_-\right)}\right]-\frac{A_{eff}}{r_{12}}\left[1-\frac{\rho}{r_{12}}\right]\right)+\Delta U_{vdw}$$

(A6),

where ΔU_{Cou} is the Coulomb energy involved in breaking the lattice ($U_{lattice}$) and then forming the ion pair in the gas phase (U_{r12}).

As discussed at greater length by Jones et al [5], one would expect the average distance between ions in the liquid state, $(r_+ + r_-)$, to be greater than the distance between charges in the gas phase neutral ion pair (NIP), r_{12}. We therefore introduce the ratio R_r as

$R_r = r_{12} / (r_+ + r_-)$ (A7).

We can also relate the value of $(r_+ + r_-)$ (in pm) to the molar volume of the IL, V_m (in cm^3) using

$(r_+ + r_-) = 10^{10}\ {}_3\surd\ (V_m/V\mathrm{N_A})$ (A8) where $V = 2$ for ILs of type C^+A^-, and N_A is Avogadro's number. On substituting (A7) and (A8) into (A6) we obtain

$$\Delta_{vap}U_0 = \Delta U_{Cou} + \Delta U_{vdw} = \frac{|Z_+||Z_-|e^2 N_A^{\frac{4}{3}}}{40\pi\varepsilon_0}\sqrt[3]{\frac{V}{V_M}}\left(\left(\frac{A_{NaCl}}{2}\right)V\left[1-\frac{\rho}{10^{10}\sqrt[3]{\frac{V_m}{VN_A}}}\right]-\frac{A_{eff}}{R_r}\left[1-\frac{\rho}{10^{10}R_r\sqrt[3]{\frac{V_m}{VN_A}}}\right]\right)+\Delta U_{vdw}$$

(A9).

On substituting in values for $|Z_+|=|Z_-|=1$, e, N_A π, ε_0, $V=2$, $A_{NaCl}=1.748$, $A_{eff}=1$ and $\rho=34.5$ pm we obtain

$$\Delta_{vap}U_0 = \Delta U_{Cou} + \Delta U_{vdw} = \frac{1478}{\sqrt[3]{V_M}}\left(1.748\left[1-\frac{0.3671}{\sqrt[3]{V_M}}\right]-\frac{1}{R_r}\left[1-\frac{0.3671}{R_r\sqrt[3]{V_M}}\right]\right)+\Delta U_{vdw} \quad \text{(A10)}$$

which is a function of only V_m, R_r and ΔU_{vdw}.

Equation (A10) pertains to a system at zero Kelvin, with no kinetic energy, whereas the internal energy, $\Delta_{vap}U_T$, and enthalpy, $\Delta_{vap}H_T$, at temperature T are the experimentally determined values. $\Delta_{vap}U_0$ must therefore be related to these values; to do this we follow the procedure described in ref [6].

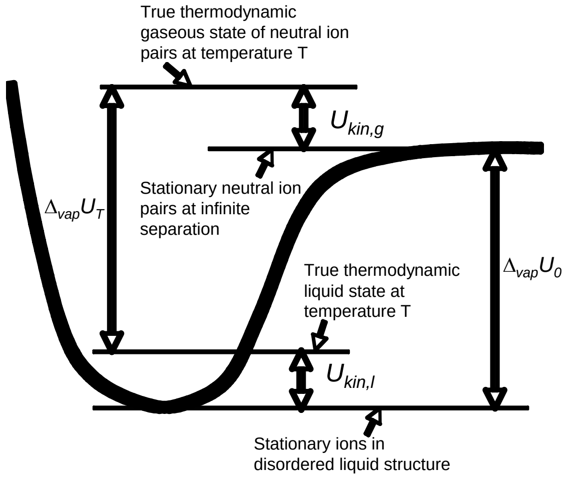

Figure A2. Potential energy curve representing the evaporation of liquid C^+A^- to gaseous ion pairs at zero Kelvin. Superimposed are the internal energies involved for evaporation at temperature T K.

Figure A2 shows a classical representation of the potential energy curve for the evaporation of an ionic liquid of type C^+A^-. $\Delta_{vap}U_0$ is the internal energy difference between stationary ions in the disordered liquid structure and stationary neutral ion pairs at infinite separation in the gas phase. (Note that this is *not* a lattice energy, which would involve separate ions in the gas phase). At a finite temperature T the liquid phase will have a kinetic energy of $U_{kin,l}$ while the neutral ion pairs in the gas phase will have a kinetic energy of $U_{kin,g}$. From fig.2A it can be seen that

$\Delta_{vap}U_T = \Delta_{vap}U_0 + U_{kin,g} - U_{kin,l}$ (A11).

Classically, for the gas phase, the translational energy is 3RT/2, the rotational energy is 3RT/2 and each vibration is RT. As the gas phase comprises C^+A^- neutral ion pairs, we can assign to $U_{kin,g}$ the above translational and rotational energies, plus RT for the single vibrational mode between the two ions, plus U_{int}, the internal energy of all the other vibrational and internal rotational modes within both ions, giving

$U_{kin,g} = 3RT/2+3RT/2 + RT + U_{int} = 4RT + U_{int}$ (A12).

Classically, for the condensed liquid phase, we assume that the ionic liquid behaves similarly to an ionic solid. For a solid, each ion has a kinetic energy of 3RT per mol about its average position. As we have two ions, C^+ and A^- in the IL, this amounts to 6RT per mol of IL. Each ion within the liquid phase will also have internal kinetic energy modes, which we assume will be the same as those in the gas phase species, U_{int}. We can then write for the liquid

$U_{kin,l} = 6RT+U_{int}$ (A13).

Substituting (A12) and(A13) into (A11) gives

$\Delta_{vap}U_T = \Delta_{vap}U_0 - 2RT$ (A14).

For vaporisation from a condensed phase (small volume) to a gaseous phase (large volume), the relationship between ΔH and ΔU is

$\Delta H = \Delta U + \Delta n \mathrm{R} T$ (A15)

where Δn is the number of moles evolved in the gas phase. For C^+A^- ionic liquids, neutral ion pairs are formed in the gas phase, and hence Δn=1. (Note, if we were relating ΔH and ΔU for a *lattice* energy, then $\Delta n=2$ because the gas phase would then contain separate C^+ and A^- ions amounting to two moles of gas, see ref [6] for this situation). Combining (A14) and A(15) with Δn = 1 we get

$\Delta_{vap}H_T = \Delta_{vap}U_0 - 2\mathrm{R}T + \mathrm{R}T = \Delta_{vap}U_0 - \mathrm{R}T$ (A16)

and combining this with (A10) we get

$\Delta_{vap}H_T = \Delta U_{Cou} + \Delta U_{vdw} - \mathrm{R}T$ (A17)

As RT is small (= 2.5 kJ mol^{-1} for T=298 K) compared to the other three terms in the equation, we write $\Delta H_{vdw} = \Delta U_{vdw} - \mathrm{R}T$, giving

$$\Delta_{vap}H_{298} \approx \Delta U_{Cou} + \Delta H_{vdw} = \frac{1478}{\sqrt[3]{V_M}}\left(1.748\left[1-\frac{0.3671}{\sqrt[3]{V_M}}\right]-\frac{1}{R_r}\left[1-\frac{0.3671}{R_r\sqrt[3]{V_M}}\right]\right)+\Delta H_{vdw}$$

(A18)

To use this equation we need a value for R_r which applies to all ILs (at least approximately) and values for ΔU_{vdw} for each IL. This is dealt with in the main part of the paper.

Di- and polycationic ILs $C^{m+}mA^-$

These ILs are composed of two or more singly charged cations (imidazoliums in the case of compound **12**) which are joined by flexible alkyl chains, each cation having a balancing singly charged anion in the molecular formula, figure A3.

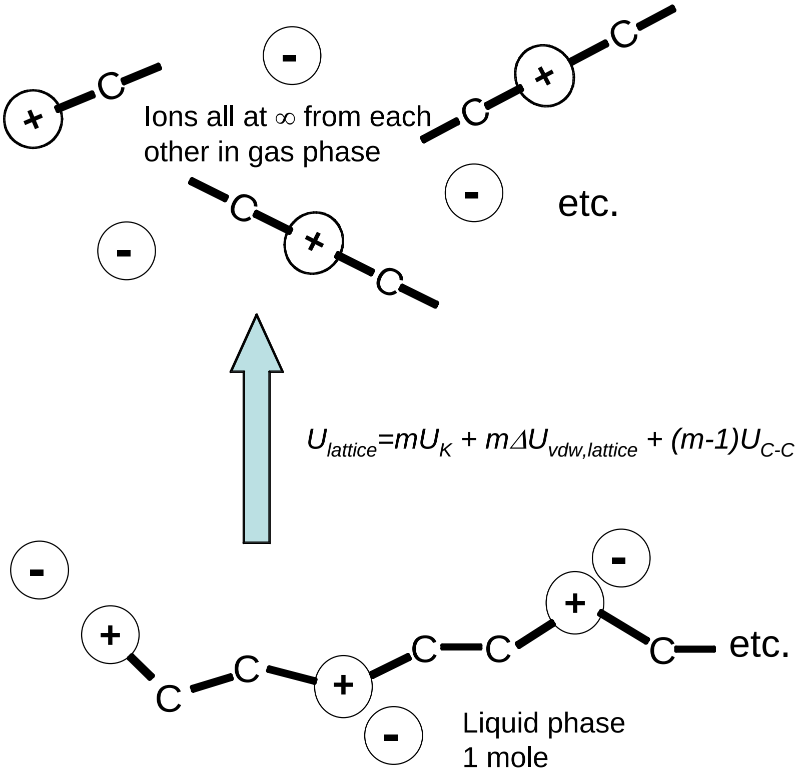

Figure A3. Lattice energy, $U_{lattice}$, of a polycatioinic IL containing *m* singly charged cations linked by alkyl chains with m associated singly charge anions, showing complete separation of the charged species with concomitant C-C bond scission.

We assume that for such polycationic ILs in the liquid state the singly charged cation groups are sufficiently distant from each other, and have sufficient freedom of movement, that each one will have a nearest neighbour shell of anions which will be similar to that of an equivalent monocationic IL (C^+A^-). If we define the lattice energy for the polycationic IL as the energy required to form *m* singly charged cations (i.e. $|Z_+| = 1$) and *m* singly charged anions (i.e. $|Z_-| = 1$) in the gas phase, figure A3, then we have to break *m*-1 C-C bond in the alkyl chain linkages to produce these ions. The Coulombic energy necessary to separate the *m* cations and *m* anions, will then be *m* times the Kapustinskii energy, U_K (equation (A2), required to separate the singly charged anions and cations in one mole of monocationic IL. Similarly, the van der Waals contribution to the lattice energy of the polycationic IL will be *m* times $\Delta U_{vdw,\,lattice}$, the contribution to the monocationic C^+A^- equivalent IL. The lattice energy is therefore given by

$$U_{lattice} = mU_K + m\Delta U_{vdw,lattice} + (m-1)U_{C-C} = m\frac{|Z_+||Z_-|e^2 N_A\left(\frac{A_{NaCl}}{2}\right)V\,10^9}{4\pi\varepsilon_0(r_+ + r_-)}\left[1 - \frac{\rho}{(r_+ + r_-)}\right] + m\Delta U_{vdw,lattice} + (m-1)U_{C-C} \quad \text{(A19)}$$

which is the polycationic equivalent of equation (A3) for the monocationic ILs, (note that $|Z_+|$ and $|Z_-|$ are both 1).

We now turn to the gas phase polycationic species. Given that C^+A^- ILs produce C^+A^- NIPs in the gas phase, and $C^{2+}2A^-$ ILs (compound **12**) produces $C^{2+}2A^-$ neutral ionic triplets (NITs) in the gas phase[7], we expect $C^{m+}mA^-$ ILs to produce $C^{m+}mA^-$ neutral ionic multiplets (NIMs). As can be seen from equation (A9) for C^+A^- species, the effective Madelung constant of the gas phase NIM, A_{eff}, quantitatively affects the internal energy of vaporisation, and the effective Magelung constant depends on the structure of the vapour phase species which is not known, at present. We therefore restrict ourselves to $C^{2+}2A^-$ ILs (compound **12**) where a reasonably generalised structure can be formulated which relates directly to the simple C^+A^- gas phase structure of monocationic ILs.

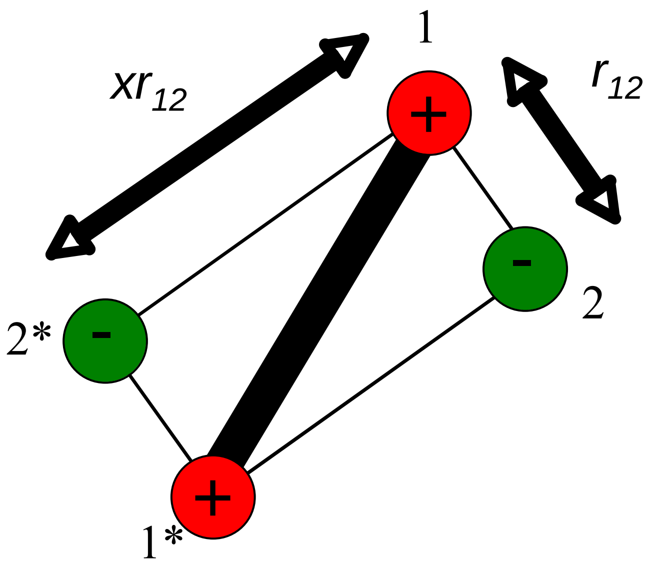

Figure A4. Rectangular geometry of a dication NIT. The dication has positive charges at 1 and 1*, which are associated with anions 2 and 2* to form two dipoles 1-2 and 1*-2*.

Figure A4 shows a simple structure for the dication NIT. The two positive charges on the dication are shown separated, but connected by an alkyl linkage. Each positive charge has an associated negative charge at a distance of r_{12}, forming two dipoles at opposite ends of the molecule. The two dipoles are anti-aligned as this is the minimum energy configuration for a dipole pair. For simplicity, the four ions are arranged at the corners of a rectangle, though in reality van der Waals forces will be expected to distort this geometry. The distance between the dipoles, xr_{12} is given in units of the dipole distance, r_{12}. The internal energy involved in bringing these four ions together from infinite separation (with an appropriate carbon radical on each cation, fig. A4) is given by

$$U_{r12} = -\frac{|Z_+||Z_-|e^2 N_A\left(2+\frac{2}{x}-\frac{2}{\sqrt{1+x^2}}\right)}{4\pi\varepsilon_0 r_{12}} 10^9\left[1-\frac{\rho}{(r_{12})}\right] - 2\Delta U_{vdw,\,r12} - U_{C-C} \qquad \text{(A20)}$$

where A_{eff} in equation (A4) is now equal to $2+2/x - 2/\sqrt{(1+x^2)}$ for the four attractive interactions along the edges of the rectangle and the two repulsive interactions across the diagonals, see appendix 2. We now make the simplifying assumption that the van der Waals interaction within this $C^{2+}2A^-$ species will be twice that of the C^+A^- IL. Clearly this ignores the van der Waals interaction between what are effectively two adjacent C^+A^- molecules in fig.A4, but we assume this would be relatively small as the two halves of the NIT are separated by the alkyl chain. The U_{C-C} accounts for the C-C bond which is re-made.

We now combine equations (A1), A(19) (with m=2) and A(20) to obtain the internal energy of vaporisation for the rectangular NIT in the gas phase

$$\Delta_{vap}U_0 = \Delta U_{Cou} + 2\Delta U_{vdw} = \frac{|Z_+||Z_-|e^2 N_A 10^9}{4\pi\varepsilon_0}\left(2\frac{\left(\frac{A_{NaCl}}{2}\right)V}{(r_+ + r_-)}\left[1-\frac{\rho}{(r_+ + r_-)}\right] - \frac{A_{eff}}{r_{12}}\left[1-\frac{\rho}{r_{12}}\right]\right) + 2\Delta U_{vdw}$$

(A21)

where the U_{C-C} in (A20) and (A19) have cancelled out and $2\Delta U_{vdw}$ has replaced $2(\Delta U_{vdw,lattice}-\Delta U_{vdw,r12})$ as for C^+A^- ILs, above. In equation (A21) $|Z^+|$ is 1 and V is still 2 as we have dealt with the dication as a linked pair of C^+A^- ILs. Equations (A6) (for C^+A^-) and (A21) (for $C^{2+}2A^-$) are the same except for two factors of 2. We can again determine the value of $(r_+ + r_-)$ from V_m, but as we consider the dication as behaving like two moles of C^+A^- type ILs, we use V_m/m where m=2.

$(r_+ + r_-) = 10^{10}\ {}_3\surd\ (V_m/mVN_A)$ (A22)

Combining (A21), A(22) (with m=2) and (A7) which relates r_{12} to $(r_+ + r_-)$, we obtain

$$\Delta_{vap}U_0 = \Delta U_{Cou} + 2\Delta U_{vdw} = \frac{|Z_+||Z_-|e^2 N_A^{\frac{4}{3}}}{40\pi\varepsilon_0}\sqrt[3]{\frac{2V}{V_M}}\left(2\left(\frac{A_{NaCl}}{2}\right)V\left[1-\frac{\rho}{10^{10}\sqrt[3]{\frac{V_m}{2VN_A}}}\right]-\frac{A_{eff}}{R_r}\left[1-\frac{\rho}{10^{10}R_r\sqrt[3]{\frac{V_m}{2VN_A}}}\right]\right)+2\Delta U_{vdw}$$

(A23)

which is the dicationic IL version of (A9).

The $2\Delta U_{vdw}$ in equation (A23) refers to ΔU_{vdw} for the single monocationic species used in the derivation. We will replace $2\Delta U_{vdw}$ with $\Delta U_{vdw,C2+2A-}$., the total van der Waals contribution for the $C^{2+}2A^-$ IL, and on substituting in values for $|Z_+| = |Z_-| = 1$, e, N_A π, ε_0, V=2, A_{NaCl}=1.748, ρ=34.5 pm, $A_{eff} = 2 + 2/x - 2\sqrt{(1-x^2)}$) and x=1.43 (see main text), we obtain

$$\Delta_{vap}U_0 = \frac{1862}{\sqrt[3]{V_m}}\left(3.496\left[1-\frac{0.4625}{\sqrt[3]{V_m}}\right]-\frac{A_{eff}}{R_r}\left[1-\frac{0.4625}{R_r\sqrt[3]{V_m}}\right]\right)+\Delta U_{vdw,C2+2A-}$$

(A24)

for one mole of $C^{2+}2A^-$ type IL, which is equivalent to (A10) for one mole of C^+A^- type IL.

Equation (A24) pertains to the dicationic system at zero Kelvin. We now follow the same procedure for $C^{2+}2A^-$ to relate $\Delta_{vap}U_0$ to $\Delta_{vap}H_{298}$, as has been described for C^+A^- ILs above. For $C^{2+}2A^-$ we have neutral ion triplets in the gas phase. These will have translational (3RT/2) and rotational (3RT/2) contributions to $U_{kin,g}$, plus three vibrational modes of RT each between the ions (N=3 in 3N-6 assuming non-linear geometry) and internal modes within the ions, U_{int},

$U_{kin,g} = 3\mathrm{R}T/2 + 3\mathrm{R}T/2 + 3\mathrm{R}T + U_{int} = 6\mathrm{R}T + U_{int}$ (A25)

In the condensed liquid phase we have three ions, each contributing 3RT per mole of vibrational energy, plus the internal modes within the ions, U_{int}.

$U_{kin,l} = 9\mathrm{R}T + U_{int}$ (A26)

Combining (A11), (A25) and (A26), with (A15) (where $\Delta n=1$ because one one of neutral ion triplets are evolved during evaporation), we get

$\Delta_{vap}H_T = \Delta_{vap}U_0 - 2\mathrm{R}T$ (A27)

which combined with (A24) gives

$\Delta_{vap}H_T = \Delta U_{Cou} + \Delta U_{vdw,C2+2A-} - 2\mathrm{R}T$ (A28)

2RT (= 5 kJ mol^{-1} for T=298 K) is small compared to the other terms in the equation, so we write $\Delta H_{vdw,C2+2A-} = \Delta U_{vdw,C2+2A-} - 2\mathrm{R}T$, to give

$$\Delta_{vap}H_{298} \approx \Delta U_{Cou} + \Delta H_{vdw,C2+2A-} = \frac{1862}{\sqrt[3]{V_m}}\left(3.496\left[1-\frac{0.4625}{\sqrt[3]{V_m}}\right]-\frac{A_{eff}}{R_r}\left[1-\frac{0.4625}{R_r\sqrt[3]{V_m}}\right]\right)+\Delta H_{vdw,C2+2A-}$$

(A29)

which is the equivalent of (A18) for C$^+$A$^-$ ILs.

Appendix 2. Formulae for effective Madelung constants in gas phase species

The lattice energy per mole of a ionic crystalline solid is given by the Born-Mayer equation [4]

$$U_{lattice} = -\frac{|Z_+||Z_-|e^2 N_A A_{struc}}{4\pi\varepsilon_0(r_+ + r_-)}\left[1 - \frac{\rho}{(r_+ + r_-)}\right] \qquad \text{(A30)}$$

where A_{struc} is the Magdelung constant for the particular structure; 1.748 (rock salt), 1.763 (CsCl) etc. and $(r_+ + r_-)$ is the nearest distance between pairs of oppositely charged ions in the ionic solid (all terms are in SI units). This is the same as the Kapustinskii equation, (A2), where A_{struc} has been replaced by $V(A_{NaCl}/2)$ and the 10^9 accommodates the particular units used in (A2).

For an Avogadro number of ion pairs (1and 2) in a C^+A^- type IL, charges $|Z^+|$ and $|Z^-|$, separation r, in the gas phase, the internal energy due to Coulomb attraction is

$$U = -\frac{|Z_+||Z_-|e^2 N_A 1}{4\pi\varepsilon_0 r} + N_A B\exp\left(-\frac{r}{\rho}\right) \qquad \text{(A31)}$$

where there is just one Coulombic interaction, represented by the 1 in the equation. If we differentiate this equation with respect to r, dU/dr, then for the ions at their equilibrium distance from each other, r_{12}, one can set $dU/dr = 0$ and solve for B. On inserting this solution for B back into (A31), the equation can be simplified to give the Coulombic energy for a mole of gas phase ion pairs, U_{12},

$$U_{12} = -\frac{|Z_+||Z_-|e^2 N_A 1}{4\pi\varepsilon_0 r_{12}} + \left(1 - \frac{\rho}{r_{12}}\right) \qquad \text{(A32).}$$

Clearly this is the same as the Born-Meyer equation except for an effective Madelung constant, A_{eff}, = 1 for gas phase neutral ion pairs.

For the rectangular dicationic IL, $C^{2+}2A^{-}$ shown in fig. A4, the Coulombic energy of the entire structure at any distance r (defined as the distance between 1 & 2 and 1* & 2* in the rectangular geometry) is given by

$$U = -\frac{|Z_+||Z_-|e^2 N_A\left(2+\frac{x}{2}-\frac{2}{\sqrt{1+x^2}}\right)}{4\pi\varepsilon_0 r} + N_A B\exp\left(-\frac{r}{\rho}\right) \tag{A33}$$

where the 2, $x/2$ and $-2/\sqrt{(1+x^2)}$ originate from the two attractive interactions along the short edges, the two attractive interactions along the long edges, and the two repulsive interactions across the diagonals of the rectangle, respectively. On eliminating B at the equilibrium separation r_{12} for the rectangular neutral ion triplet, this becomes

$$U_{12} = -\frac{|Z_+||Z_-|e^2 N_A\left(2+\frac{2}{x}-\frac{2}{\sqrt{1+x^2}}\right)}{4\pi\varepsilon_0 r_{12}} + \left(1-\frac{\rho}{r_{12}}\right) \tag{A34}$$

where it is clear that the effective Madelung constant is now $A_{eff} = (2+2/x - 2/\sqrt{(1+x^2)})$.

Similar equations can be constructed to give the Coulombic interactions for other gas phase IL geometries.

Appendix 3. Syntheses carried out in Nottingham

1-methyl-1-butylpyrrolidinium bromide [C_4C_1Pyrr]Br [8]

To a solution of 92 g (1.08 moles) of 1-methylpyrrolidine in 300 mL of ethyl acetate, under argon at room temperature, was added dropwise 123 g (1.27 mol) of 1-bromobutane. The reaction mixture was stirred for 24 hours at 50 °C. The solvent and remaining reactants were removed by vacuum filtration, rotary evaporation and heating at 70 °C under vacuum for 24 hours to give 181.45 g (91 %) of **[C_4C_1Pyrr]Br** as a white, crystalline solid.

^{1}H NMR, δ_H (300 MHz, $CDCl_3$), 1.00 (3H, t), 1.47 (2H, m), 1.77 (2H, m), 2.31 (4H, m), 3.32 (3H, s), 3.70 (2H, m), 3.87 (4H, m)

^{13}C NMR, δ_C (300 MHz, $CDCl_3$), 14.13, 20.18, 22.06, 26.37, 31.33, 64.85

1-methyl-1-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide (compound 7) [C_4C_1Pyrr][NTf_2] [9]

To a solution of 30 g (0.135 mol) of [C_4C_1Pyrr]Br in 100 mL de-ionised water was added dropwise a concentrated aqueous solution of 43 g (0.150 mol) lithium bis(trifluoromethanesulfonyl)imide. The reaction mixture was stirred overnight at 70 °C. The biphasic mixture was transferred to a separating funnel and the ionic liquid phase was washed three times with ice-cold deionised water. The extracted ionic liquid fraction was placed on the rotary evaporator for one hours and then heated under vacuum at 70 °C overnight to yield 51.28 g (90 %) of [C_4C_1Pyrr][NTf_2] as a clear, colourless liquid.

^{1}H NMR, δ_H (300 MHz, CD_3OD), 1.03 (3H, t), 1.45 (2H, m), 1.79 (2H, m), 2.24 (4H, m), 3.06 (3H, s), 3.35 (2H, m), 3.53 (4H, m)

^{13}C NMR, δ_C (300 MHz, $CDCl_3$), 12.83, 19.77, 21.53, 25.68, 64.42

1-methyl-1-hexylpyrrolidinium bis(trifluoromethanesulfonyl)imide (compound 8)

$[C_6C_1Pyrr][NTf_2]$

The synthesis of **8** was analogous to compound **7**, all spectroscopic data was consistent with the structure and indeed previously published data.[10]

1-methyl-1-octylpyrrolidinium bis(trifluoromethanesulfonyl)imide (compound 9)

$[C_8C_1Pyrr][NTf_2]$

The synthesis of **9** was analogous to compound **7**, all spectroscopic data was consistent with the structure and indeed previously published data.[10]

Synthesis of 1-methyl-3-ethylimidazolium bromide $[C_2C_1Im]Br$ [11]

To 86 g (1.05 mol) of 1-methylimidazole, under argon at room temperature, was added dropwise 189 g (1.73mol) of ethylbromide. After 90 minutes the mixture had crystallized into a brownish-white solid and unreacted liquid reagents were decanted off. Excess 1-methylimidazole was removed by flask distillation at 150 °C under vacuum. Once cooled, the solid was recrystallised in a 2:1 mixture of acetonitrile and ethyl acetate to give a white crystalline solid. The solvent was removed by rotary evaporation and heating at 70 °C under vacuum for 24 hours.

^{1}H NMR, δ_H (300 MHz, $CDCl_3$), 1.56 (3H, t), 4.08 (3H, s), 4.36 (2H, q), 7.56 (2H, s), 10.24 (1H, s)

^{13}C NMR, δ_C (300 MHz, $CDCl_3$), 15.76, 36.78, 45.35, 121.97, 123.73, 137.07

1-methyl-3-octylimidazolium chloride, [C_8C_1Im]Cl

The procedure was adapted from that for [C_2MIm]Br. 21 g (0.26 mol) of 1-methylimidazole was reacted under solventless conditions with 43 g (0.29 mol) of 1-chlorooctane. After stirring for 3 days at 70 °C under argon, unreacted 1-methylimidazole and 1-chlorooctane was removed by flash distillation at 150 °C under moderate vacuum (5 x 10^{-2} torr) to yield the product 54.31 g (91 %) as a viscous, yellow liquid.

^{1}H NMR, δ_H (300 MHz, $CDCl_3$), 0.86 (3H, t), 1.24-1.32 (10H, m), 1.90 (2H, m), 4.13 (3H, s), 4.31 (2H, t), 7.28 (1H, d), 7.40 (1H, d), 10.89 (1H, s)

^{13}C NMR, δ_C (300 MHz, $CDCl_3$), 14.08, 22.59, 26.28, 28.97, 29.03, 30.35, 31.68, 36.61, 50.10, 121.87, 123.71, 137.88

1-methyl-3-ethylimidazolium tetrafluoroborate [C_2C_1Im][BF_4] [12] (compound 1)

To a solution of 115 g (0.60 mol) of [C_2MIm][Br] in 300 mL dichloromethane was added 80 g (0.72 mol) of $NaBF_4$. The mixture was stirred for 3 days at room temperature. The solid NaBr by-product was removed by vacuum filtration. The dichloromethane was removed by rotary evaporation and heating at 50 °C under moderate vacuum (5 x 10^{-2} torr) for 24 hours to yield 112.76 g (94%) of [C_2MIm][BF_4] as a clear, pale yellow liquid.

^{1}H NMR, δ_H (300 MHz, CD_3OD), 1.54 (3H, t), 3.95 (3H, s), 4.29 (2H, quad), 7.57 (1H, s), 7.65 (1H, s), 8.90 (1H, s)

^{13}C NMR, δ_C (300 MHz, CD_3OD),14.25, 35.14, 44.70, 121.97, 123.61, 136.79

1-methyl-3-octylimidazolium dicyanamide $[C_8C_1Im][N(CN)_2]$ [13] (compound 4)

A similar procedure was followed as for $[C_2MIm][BF_4]$. 15 g (0.07 mol) of $[C_8MIm][Cl]$ and 7 g (0.08 mol) of $Na[N(CN)_2]$ in acetonitrile yielded 13.32 g (73 %) of $[C_8MIm][N(CN)_2]$ as a clear, yellow liquid.

^{1}H NMR, δ_H (300 MHz, DMSO-d_6), 0.87 (3H, t), 1.10-1.40 (10H, m), 1.79 (2H, quin), 3.87 (3H, s), 4.17 (2H, t), 7.71 (1H, s), 7.77 (1H, s), 9.11 (1H, s)

^{13C} NMR, δ_C (300 MHz, $CDCl_3$), 14.47, 22.62, 26.06, 28.89, 29.02, 29.94, 31.72, 36.31, 49.37, 119.02, 122.81, 124.16, 137.05

1,3-bis(3-methylimidazolium-1-yl) propane dibromide, $[C_3(C_1Im)_2]Br_2$,

1,3-dibromopropane, 26.3 g (0.13 mol) was added dropwise to a stirred solution of 1-methylimidazole, (30.8 g (0.26 mol), in 100 ml of ethyl acetate under an inert N_2 atmosphere. After 18 hours the white precipitate formed was filtered under vacuum and washed several times with ethyl acetate to remove unreacted starting materials. Excess solvent was removed *in vacuo* to yield the product as a white waxy solid, 44.5 g (78 %).

1,3-bis(3-methylimidazolium-1-yl) propane bis[(trifluoromethyl)sulfonyl]imide, $[C_3(C_1Im)_2][Tf_2N]_2$, (compound 12)

$Li[Tf_2N]$, 25 g in 90 ml of deionised water was added to a stirred solution of $[C_3(C_1Im)_2]Br_2$, 16 g in 100 ml of deionised water (2:1 mole ratio). The $[C_3(C_1Im)_2][Tf_2N]_2$, was recovered as an waxy solid which was washed with deionised water and dried *in vacuo*, yielding a white crystalline solid (70 %) Mpt_{DSC} 50.5°C.

^1H NMR (270 MHz, Methanol): δ_H(ppm) no peak deuterium exchange (2H), 7.63 (s, 4H), 4.33 (t, 4H), 3.94 (s, 6H), 2.50-2.55 (m,2H).

^1H NMR (270 MHz, DMSO): δ_H(ppm) 9.10 (s, 2H), 7.76 (s, 4H), 4.22 (t,4H), 3.88 (s 6H), 2.30-2.50 (m,2H).

References for appendices 1 to 3

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Appendix IV. Syntheses of ILs in Moscow

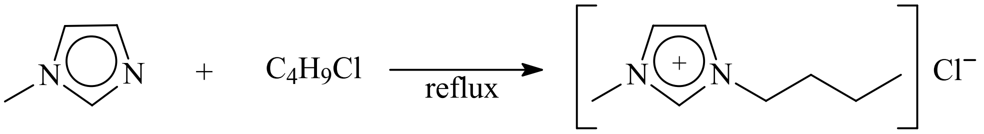
(references for this appendix are at the end of the appendix).

Experimental

Materials. Ionic liquids were prepared using standard procedures. All reagents and solvents were pure analytical grade materials purchased from commercial sources (Aldrich, Acros Organics) and were used without further purification, if not stated otherwise. 1-Methylimidazole, 1-chlorobutane, 1-chlorohexane, toluene, dichloromethane were distilled from CaH_2 prior to use. Acetonitrile and acetone were purified by distillation after standing 24 hr over molecular sieves (3A°). Lithum tris(pentafluoroethyl)trifluorophosphate was prepared according to a literature method[i].

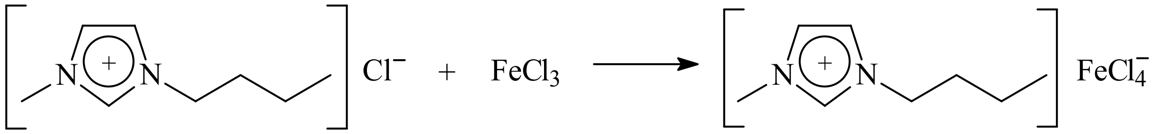
Methods. FT-IR spectra were recorded with a Nicolet Protégé 460 spectrometer in the region 4000-400 cm^{-1}, liquid film. ^1H, ^{13}C NMR spectra were recorded on a Bruker AM300 instrument at 300 and 75 MHz, respectively, in DMSO-d_6 with TMS as internal standard.

1-Butyl-3-methylimidazolium chloride ($[C_4C_1Im][Cl]$)[ii]



A 2-L, three-necked, round-bottomed flask was equipped with a heating bath, an argon inlet adapter, an internal thermometer adapter, an overhead mechanical stirrer and a reflux condenser. The flask was flushed with argon and charged with 328.8 g (4.01 mol, 1 equiv) of freshly distilled 1-methylimidazole, 556.6 g (6.01 mol, 1.5 equiv) of 1-chlorobutane and, 300 mL of dry toluene and brought to a gentle reflux (75-80°C internal temperature). The solution was heated under reflux for 48 hr and then cooled to room temperature. The remaining light-yellow oil was washed with dry toluene and the volatile material was removed under reduced pressure. The resulting light-yellow ionic liquid was dissolved in 500 mL dry dichloromethane, stirred with activated charcoal for 12 hr and filtered. The dichloromethane was removed from solution under reduced pressure (0.5 mmHg) at 70°C for 3 hr. After cooling to room temperature the imidazolium salt begins to crystallize to obtain a white solid. Yield 645 g (92%).

1-Butyl-3-methylimidazolium tetrachloroferrate (III) ($[C_4C_1Im][FeCl_4]$)[iii] (Compound 3)



A 250-mL, two-necked, round-bottomed flask was equipped with an argon inlet adapter and a magnetic stirrer. The flask was flushed with argon and charged with 31.1 g (0.18 mol) of 1-butyl-3-methylimidazolium chloride and 28.9 g (0.18 mol) of anhydrous iron(III) chloride. A dark brown liquid was obtained as a result of an exothermic solid-state reaction. Yield 60 g (100 %).

Analysis, found: C 28.70%, H 4.47%, N 8.29%, Cl 41.97 %, Fe 16.29%; calculated for $C_8H_{15}Cl_4N_2Fe$: C 28.52%, H 4.49 %, N 8.31%, Cl 42.10%, Fe 16.58%.

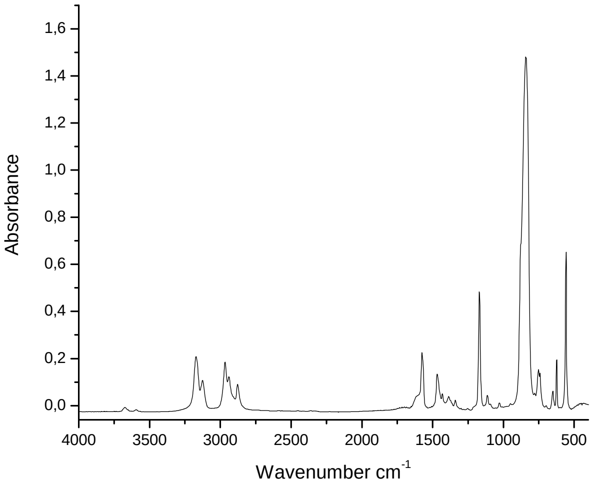
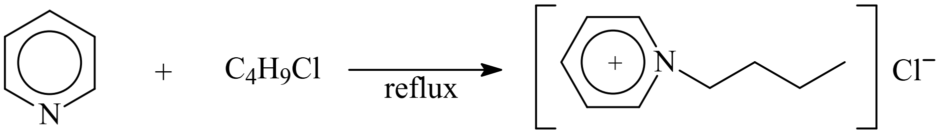


Fig.1. FT-IR-spectra of 1-butyl-3-methylimidazolium tetrachloroferrate.

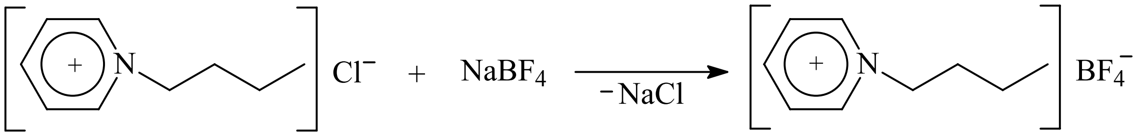
1-butyl-3-methylimidazolium tetrachloroferrate FT-IRS (neat, ν): 3675, 3694, 3172, 3126, 2965, 2938, 2879, 1575, 1467, 1430, 1386, 1340, 1170, 1112, 1030, 843, 752, 651, 622, 557 cm^{-1}.

N-Butylpyridinium chloride ([C$_4$Py][Cl])[iv]



A 500-mL, three-necked, round-bottomed flask was equipped with a heating bath, an argon inlet adapter, an internal thermometer adapter, a magnetic stirrer and a reflux condenser. The flask was flushed with argon and charged with 98.9 g (1.25 mol) of freshly distilled pyridine, 138.9 g (1.50 mol, 1.2 equiv) of 1-chlorobutane and, 100 mL of dry acetonitrile. The mixture was heated under reflux for 72 hr and then cooled to room temperature. The product was recrystallized from acetonitrile/ethyl acetate (9:1, v/v) twice, filtered and dried under reduced pressure at 70-80°C for 12 hr. Yield 137 g (80 %).

N-Butylpyridinium tetrafluoroborate ([C$_4$Py][BF$_4$]) (Compound 10)



A 500-mL, one-necked, round-bottomed flask was equipped with a magnetic stirrer and charged with 130 g (0.76 mol, 1 equiv) of N-butylpyridnium chloride in 200 mL of distilled water. Sodium tetrafluoroborate (83.4 g, 0.76 mol, 1 equiv) was added in portions to a rapidly stirred solution of N-butylpyridnium chloride in water. The reaction mixture was stirred at room temperature for 2 hr and extracted with dichloromethane (3 × 200 mL). The organic layer was collected and washed with water (7 × 10 mL) until the aqueous fraction observed to be free of chloride ($AgNO_3$). The dichloromethane solution was mixed with activated charcoal, stirred for 2 hr, filtered and dried over anhydrous magnesium sulfate. After 1 hr of standing the suspension was filtered and dichloromethane was removed by rotary evaporation. The resulting colourless or light-yellow viscous liquid was dried under reduced pressure (0.5 mmHg) at 70°C for 24 hr. Yield 189.5 g (85 %).

N-butylpyridinium tetrafluorborate; ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm relative to TMS): 0.90 (t, 3H, CH_3); 1.30 (m, 2H, CH_2); 1.90 (m, 2H, CH_2); 4.59 (t, 2H, NCH_2); 8.14 (m, 2H, aromatic proton); 8.59(m, 1H, aromatic proton); 9.04 (m, 2H, aromatic protons). **^{13}C NMR** (75 MHz, DMSO-d_6, δ/ppm): 13.23 (CH_3); 18.88 (CH_2); 32.72 (CH_2); 61.07 (NCH_2); 128.26 (2 CH aromatic); 144.69 (1 CH aromatic); 145.64 (2 NCH aromatic). **FT-IRS** (neat, ν): 3636, 3564, 3141, 3098, 3077, 2965, 2942, 2880, 1636, 1584, 1557, 1541, 1503, 1491, 1468, 1387, 1325, 1285, 1252, 1223, 1169, 1063, 961, 869, 813, 773, 740, 687,648, 523 cm^{-1}.). **Analysis**, found: C 48.36%, H 6.40%, B 4.81%, F 33.89%, N 6.15; calculated for $C_9H_{14}BF_4N$: C 48.47%, H 6.33 %, B 4.85%, F 34.07%, N 6.28%.

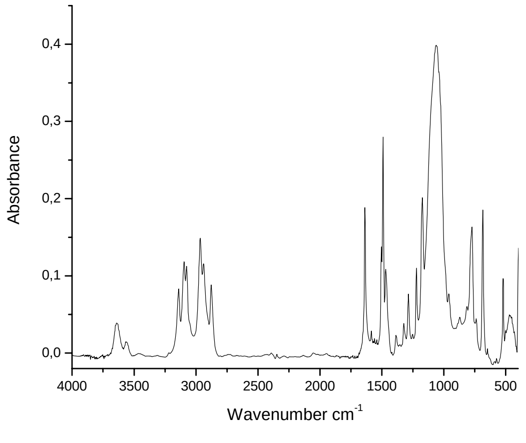


Fig. 2. FT-IR-spectra of N-butylpyridinium tetrafluorborate.

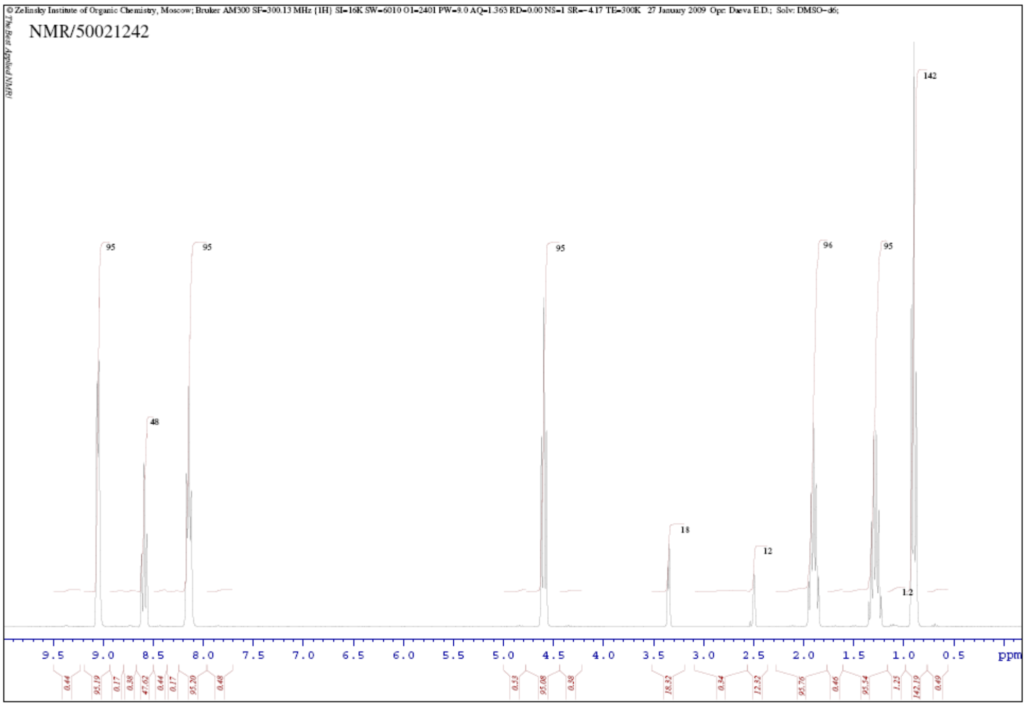
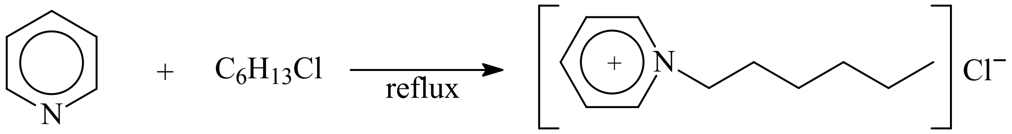


Fig. 3. ^{1}H NMR spectra of N-butylpyridinium tetrafluorborate.

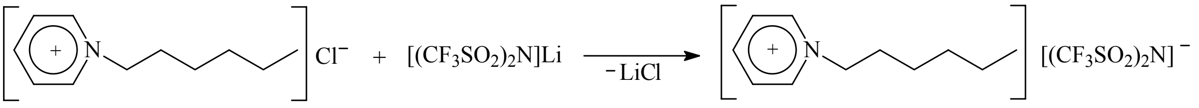
Fig. 4. ^{13}C NMR spectra of N-butylpyridinium tetrafluorborate.

N-Hexylpyridinium cloride ([C_6Py][Cl])



The same procedure was used as for [C_4Py][Cl]. From 50 g (0.63 mol) of pyridine and 91.2 g (0.76 mol, 1.2 equiv) of 1-chlorohexane, there was obtained 93 g of [C_6Py][Cl] (74%), as a white solid.

N-Hexylpyridinium bis(trifluoromethylsulfonyl)imide ([C_6Py][$(CF_3SO_2)_2N$])[v] (Compound 11)



A 200-mL, one-necked, round-bottomed flask was equipped with a magnetic stirrer and charged with 43.1 g (0.15 mol, 1 equiv) of lithim bis(trifluoromethylsulfonyl)imide, and 30.0 g (0.15 mol, 1 equiv) of N-hexylpyridinium chloride dissolved in 70 mL of distilled water. The reaction mixture was stirred at room temperature for 2 hr affording a two-phase system. Then 100 mL of dichloromethane was added. The lower organic layer was separated and washed with water (5 × 10 mL) until the aqueous fraction observed to be free of chloride ($AgNO_3$). The dichloromethane solution was mixed with activated charcoal, stirred for 2 hr, filtered and dried over anhydrous magnesium sulfate. After 1 hr, the suspension was filtered and the volatile material was removed by rotary evaporation. The resulting colourless viscous liquid was dried under reduced pressure (0.5 mmHg) at 70°C for 12 hr. Yield 62.5 g (94 %).

N-hexylpyridinium bis(trifluormethylsulfonyl)imide: ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm relative to TMS): 0.85 (t, 3H, CH_3); 1.28 (m, 6H, 3 CH_2); 1.92 (m, 2H, CH_2); 4.60 (t, 2H, NCH_2); 8.15 (t, 2H, aromatic proton); 8.59(t, 1H, aromatic proton); 9.09 (d, 2H, aromatic protons). **^{13}C NMR** (75 MHz, DMSO-d_6, δ/ppm): 13.38 (CH_3), 21.79 (CH_2), 25.09 (CH_2), 30.53 (CH_2), 30.79 (CH_2), 61.21 (NCH_2), 113.22 (CF_3), 117.48(CF_3), 121.74(CF_3), 126.01(CF_3), 128.0866 (2 CH aromatic), 144.66 (1 CH aromatic), 145.39 (2 NCH aromatic). **FT-IRS** (neat, ν): 3134, 3093, 3067, 2960, 2939, 2863, 1846, 1794, 1636, 1582, 1505, 1489, 1465, 1352, 1333, 1271, 1193, 1137, 1056, 957, 789, 772, 743, 685, 655, 617, 602, 571, 410 cm^{-1}. **Analysis**, found: C 35.02%, H 4.15%, F 25.66%, N 6.20%, S 14.58 %; calculated for $C_{13}H_{18}F_6N_2O_4S_2$: C 35.14%, H 4.08 %, F 25.65%, N 6.30%, S 14.43%.

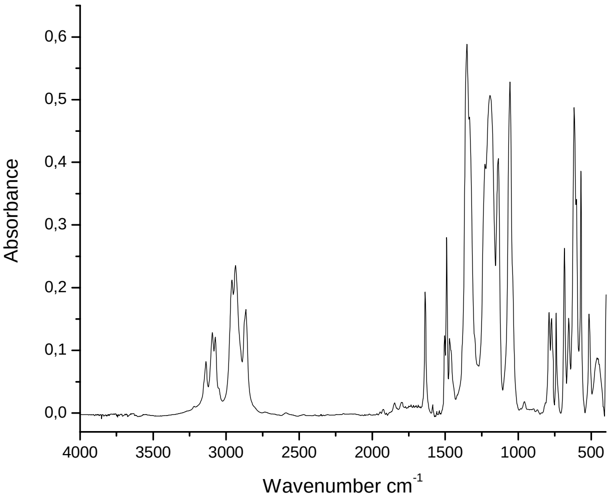


Fig. 5. FT-IR-spectra of N-hexylpyridinium bis(trifluormethylsulfonyl)imide.

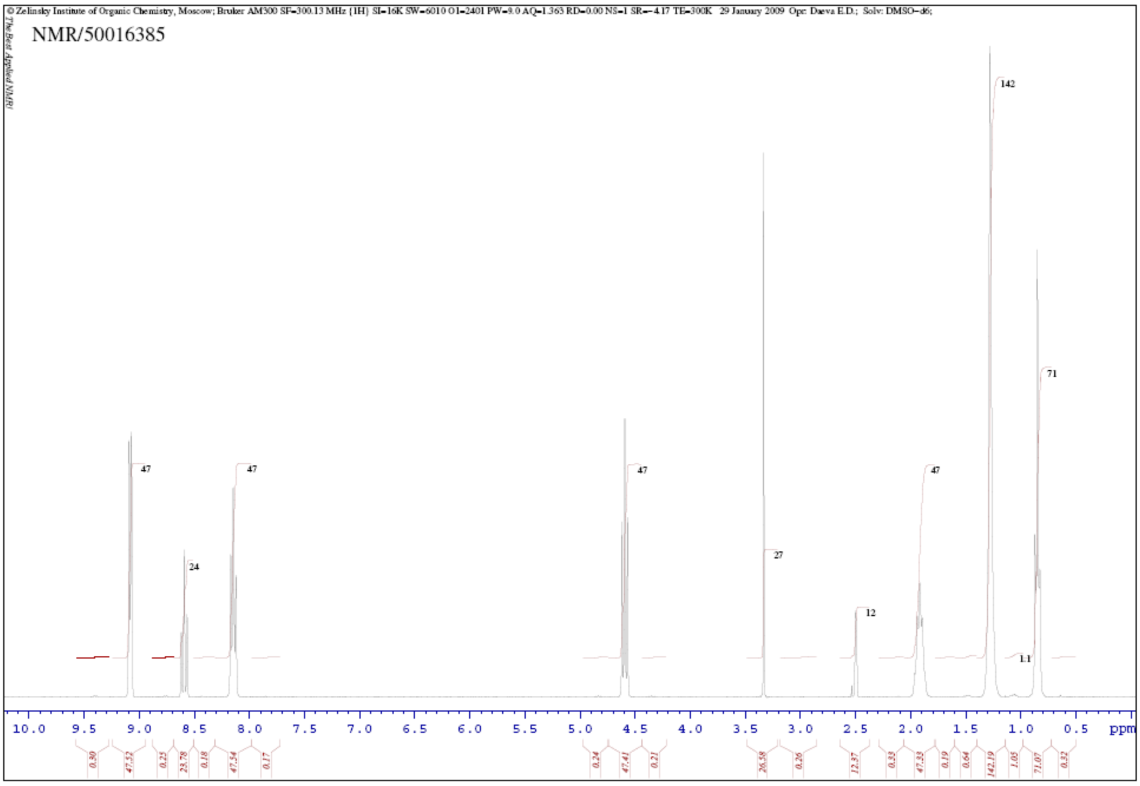


Fig. 6. ^{1}H NMR spectra of N-hexylpyridinium bis(trifluormethylsulfonyl)imide.

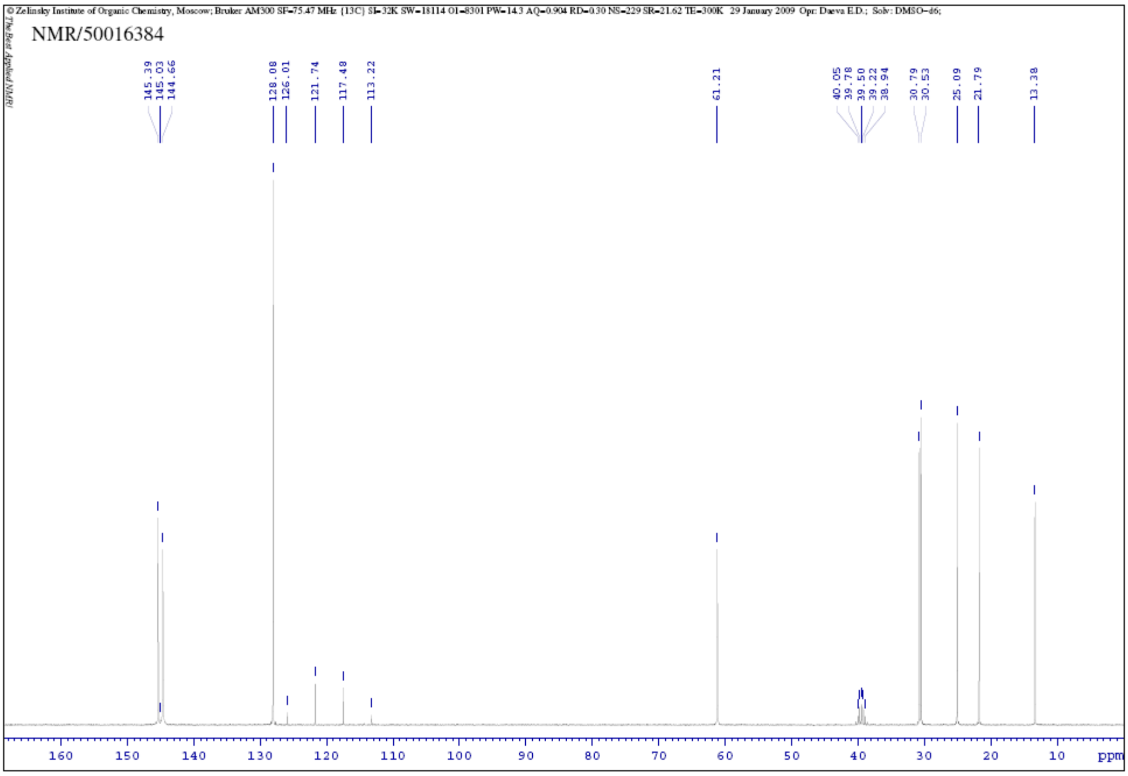
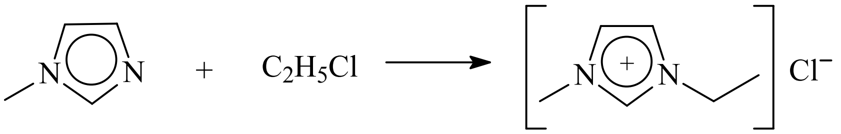


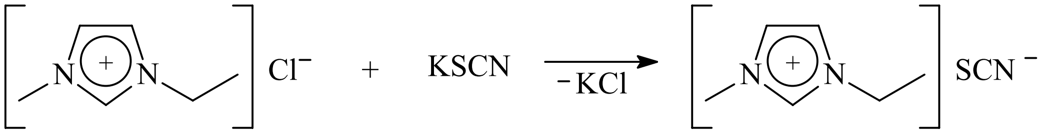
Fig. 7. ^{13}C NMR spectra of N-hexylpyridinium bis(trifluormethylsulfonyl)imide.

1-Ethyl-3-methylimidazolium chloride ($[C_2C_1Im][Cl]$)[vi]



An 250-mL autoclave was charged with 103 g of 1-methylimidazole (1.26 mol, freshly distilled from KOH) and cooled to 0°C under an argon atmosphere. 1-Chloroethane (100 g, 1.55 mol) was condensed into a partially evacuated 200-ml Schlenk tube and transferred to the autoclave, which was then sealed and pressurised to 5 bar with argon. The autoclave was heated at 75°C for 48 hr. The reactor contents were transferred to a round-bottomed flask under argon and the excess of 1-chloroethane was removed with heating at 70°C under reduced pressure. The resulting colourless viscous liquid was dried *in vacuo* at 50°C for 12 hr and cooled to give a white solid. Yield 181.5 g (99%)

1-Ethyl-3-methylimidazolium thiocyanate ($[C_2C_1Im][SCN]$)[vii](Compound 2)



A 200-mL, two-necked, round-bottomed flask was equipped with a magnetic stirrer, an argon inlet adapter and charged with 29.0 g (0.30 mol, 2 equiv) of potassium thiocyanate, and 22.0 g (0.15 mol, 1 equiv) of 1-ethyl-3-methylimidazolium chloride dissolved in 100 mL of acetone. The reaction mixture was stirred at room temperature for 48 hr. The resulting suspension was filtered and the filtrate was subjected to a vacuum to remove volatile material. The residue was dissolved in dichloromethane (300 mL) and again filtered. The filtrate was mixed with activated charcoal, stirred for 2 hr, filtered and dried over anhydrous magnesium sulfate. After 1 hr, the suspension was filtered and the volatile material was removed by rotary evaporation. The resulting colourless viscous liquid was dried under reduced pressure (0.5 mmHg) at 70°C for 12 hr. Yield 20.6 g (81 %)

1-Ethyl-3-methylimidazolium thiocyanate ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm relative to TMS): 1.42 (t, 3H, CH_3); 3.86 (s, 3H, N-CH_3); 4.19 (m, 2H, NCH_2); 7.70 (t, 1H, CH aromatic proton); 7.78 (t, 1H, CH aromatic proton); 9.11 (s, 1H, NCHN aromatic protons). **^{13}C NMR** of 1-ethyl-3-methylimidazolium thiocyanate (75 MHz, DMSO-d_6, δ/ppm): 15.09 (CH_3), 35.82 (CH_3N), 44.40 (CH_2N), 121.83 (C**H**NCH aromatic), 123.41 (C**H**NCH_3 aromatic), 129.92 (SCN), 136.23 (NCHN). **FT-IRS** (neat, ν): 3146, 3094, 2981, 2796, 2057, 1570, 1459, 1426, 1387, 1337, 1173, 1090, 1026, 954, 837,750, 700, 646, 623 cm^{-1}. **Analysis**, found: C 49.61%, H 6.60%, S 18.75%, N 24.67%; calculated for $C_7H_{11}SN_3$: C 49.68%, H 6.55 %, S 18.94%, N 24.83%.

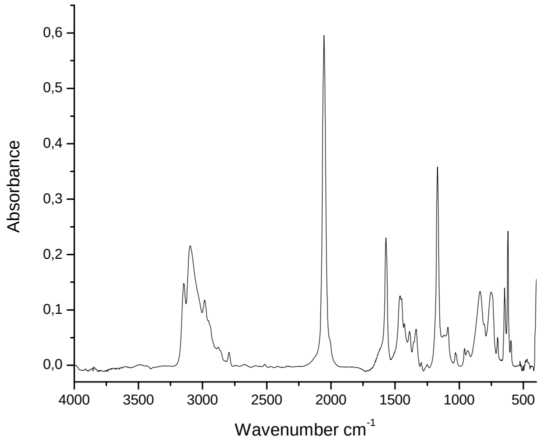


Fig. 8. FT-IR-spectra of 1-ethyl-3-methylimidazolium thiocyanate.

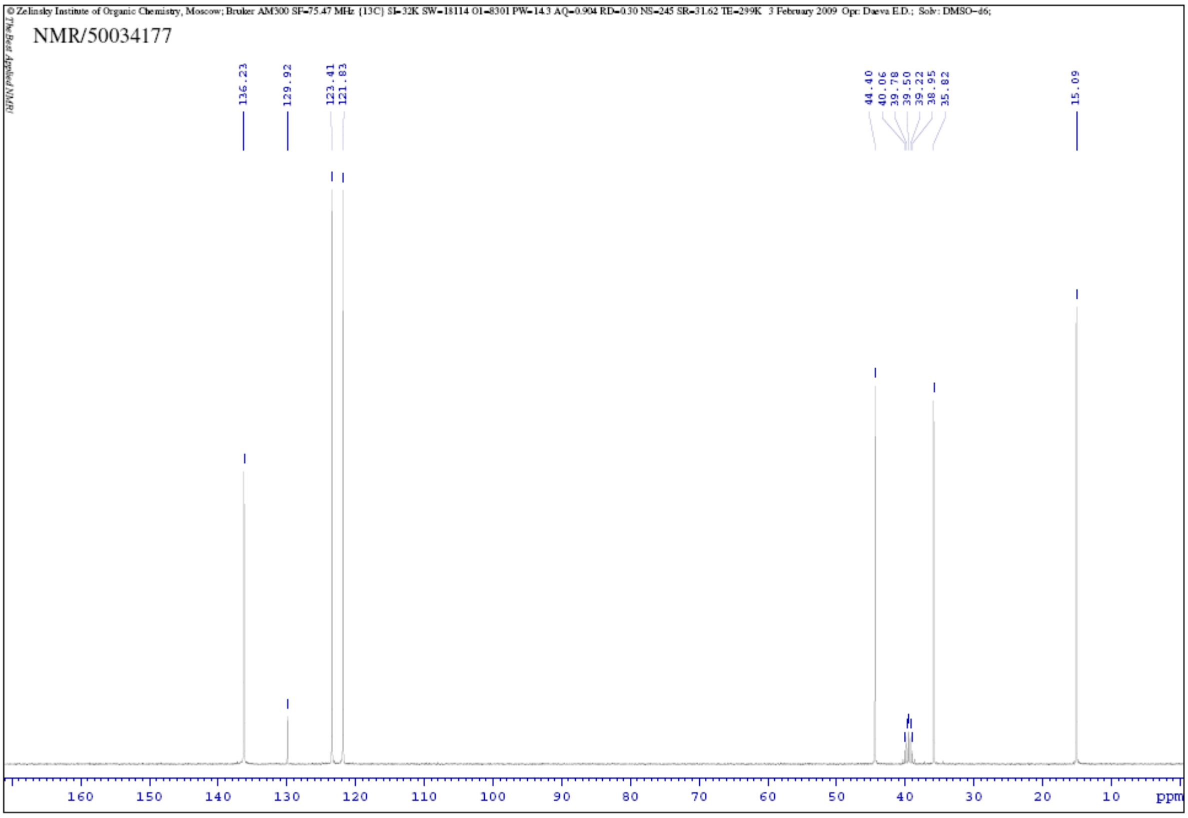


Fig. 9. ^{13}C NMR spectra of 1-ethyl-3-methylimidazolium thiocyanate.

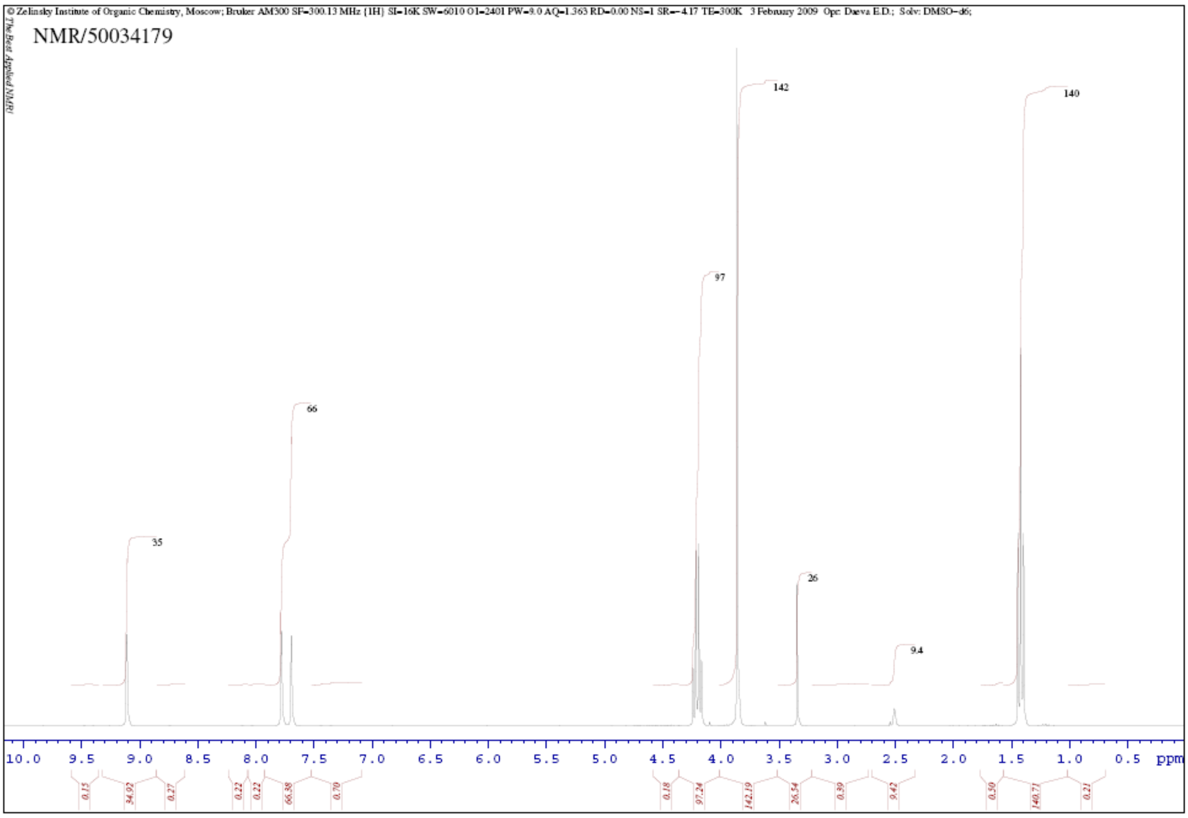
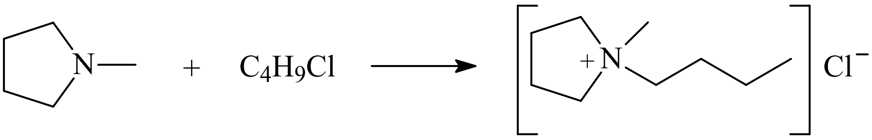


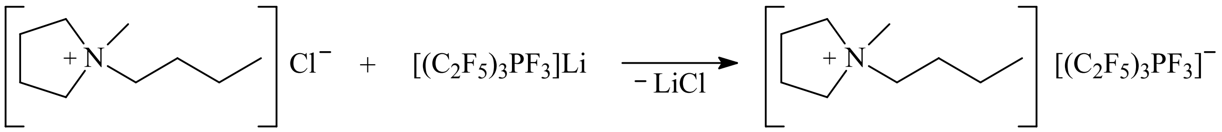
Fig. 10. ^{1}H NMR spectra of 1-ethyl-3-methylimidazolium thiocyanate.

1-Butyl-1-methylpyrrolidinium chloride ($[C_4C_1Pyrr][Cl]$)[viii]



A 2-L, three-necked, round-bottomed flask was equipped with a heating bath, an argon inlet adapter, an internal thermometer adapter, an overhead mechanical stirrer and a reflux condenser. The flask was flushed with argon and charged with 298 g (3.5 mol, 1 equiv) of freshly distilled 1-methylpyrrolidine, 485.6 g (5.25 mol, 1.5 equiv) of 1-chlorobutane and, 300 mL of dry toluene and brought to a gentle reflux (70°C internal temperature). The solution was heated under reflux for 50 hr and then cooled to room temperature. The remaining light-yellow oil was washed with dry toluene and the volatile material was removed under reduced pressure. The resulting light-yellow ionic liquid was dissolved in 500 mL dry dichloromethane, stirred with activated charcoal for 12 hr and filtered. The dichloromethane was removed from solution under reduced pressure (0.5 mmHg) at 70°C for 3 hr. After cooling to room temperature the pyrrolidinium salt begins to crystallize to obtain a white solid. Yield 560 g (90%).

1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ($[C_4C_1Pyrr][(C_2F_5)_3PF_3]$) (Compound 6)



A 500-mL, one-necked, round-bottomed flask was equipped with a magnetic stirrer and charged with 126.5 g (0.28 mol, 1 equiv) of lithim tris(pentafluoroethyl)trifluorophosphate, and 50.0 g (0.28 mol, 1 equiv) of 1-butyl-1-methylpyrrolidinium chloride dissolved in 100 mL of distilled water. The reaction mixture was stirred at room temperature for 1 hr affording a two-phase system. Then 100 mL of dichloromethane was added. The lower organic layer was separated and washed with water (5 × 10 mL) until the aqueous fraction observed to be free of chloride ($AgNO_3$). The dichloromethane solution was mixed with activated charcoal, stirred for 2 hr, filtered and dried over anhydrous magnesium sulfate. After 1 hr, the suspension was filtered and the volatile material was removed by rotary evaporation. The resulting colourless viscous liquid was dried under reduced pressure (0.5 mmHg) at 70°C for 12 hr. Yield 151.5 g (92 %)

1-butyl-1-methylpyrrolidinium tris(pentafluorethyl)trifluorphosphate: ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm relative to TMS): 0.93 (t, 3H, CH_3); 1.30 (m, 2H, CH_2); 1.68 (m, 2H, CH_2); 2.08 (m, 4H, 2CH_2 cycle); 2.98 (s, 3H, NCH_3); 3.28 (m, 2H, NCH_2); 3.45 (m, 4H, 2NCH_2 cycle). **^{13}C NMR** (75 MHz, DMSO-d_6, δ/ppm): 12.95 (CH_3), 19.30 (CH_2), 21.10 (2CH_2, cycle), 25.08 (CH_2), 47.61 (CH_3N), 63.65 (CH_2N), 63.69 (2 CH_2N, cycle), 114.45-126.18 (C_2F_5). **FT-IRS** (neat, ν): 2974, 2946, 2907, 2887, 1480, 1467, 1436, 1311, 1297, 1216, 1191, 1134, 1099, 1069, 1023, 1002, 974, 928, 813, 762, 743, 724, 640, 620, 581, 534, 496 cm^{-1}. **Analysis**, found: C 30.61%, H 3.55%, F 58.35%, N 2.47%, P 5.12%; calculated for $C_{15}H_{20}F_{18}NP$: C 30.68%, H 3.43 %, F 58.23%, N 2.39%, P 5.27%.

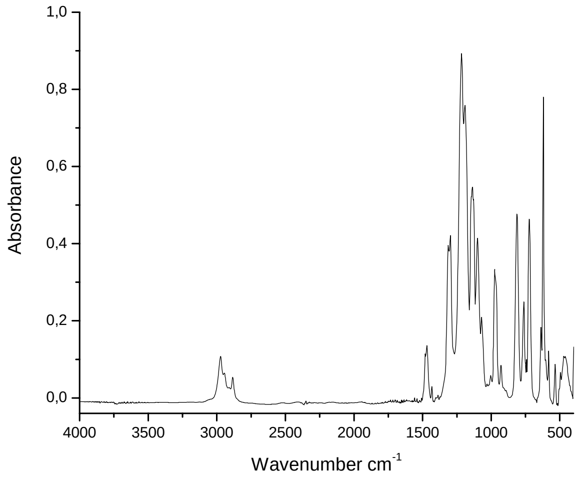


Fig. 11. FT-IR-spectra of 1-butyl-1-methylpyrrolidinium tris(pentafluorethyl)trifluorphosphate.

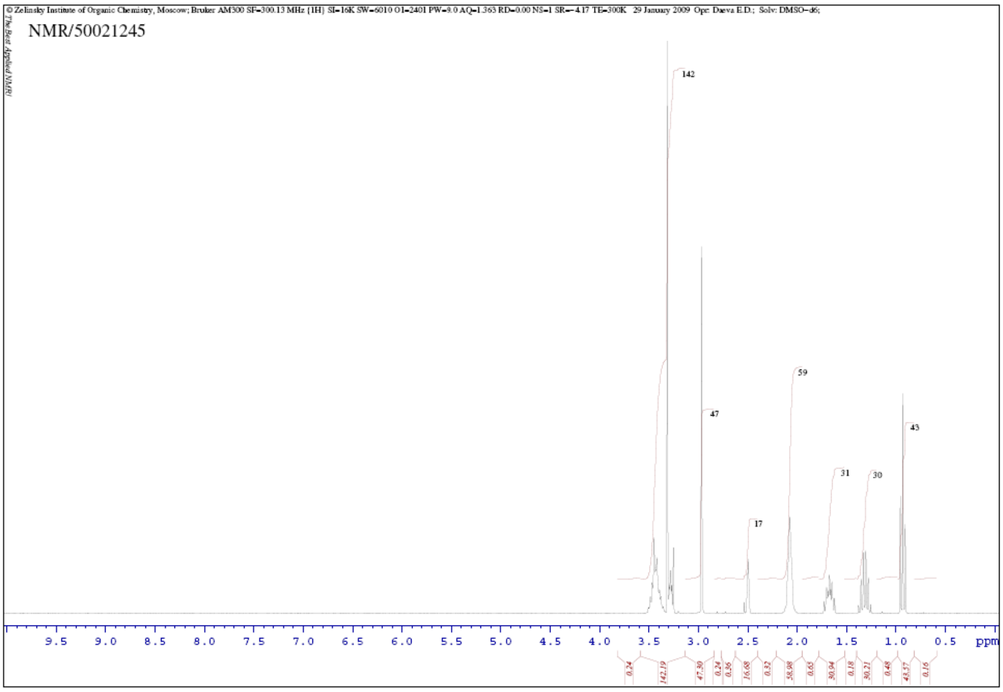


Fig. 12. ^{1}H NMR spectra of 1-butyl-1-methylpyrrolidinium tris(pentafluorethyl)trifluorphosphate.

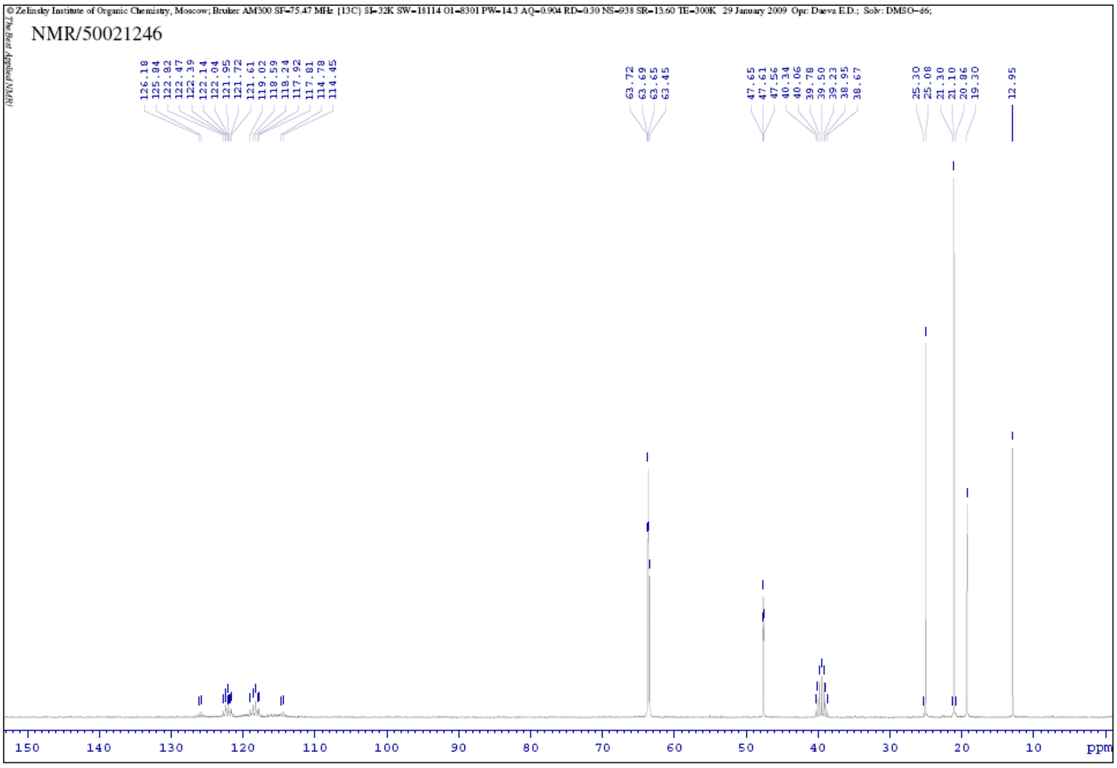


Fig. 13. ^{13}C NMR spectra of 1-butyl-1-methylpyrrolidinium tris(pentafluorethyl)trifluorphosphate.

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