1-Butyl-3-methylimidazolium 3,5-dinitro-1,2,4-triazolate: a novel ionic liquid containing a rigid, planar energetic anion†

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The novel ionic liquid, 1-butyl-3-methylimidazolium 3,5-dinitro-1,2,4-triazolate has been synthesized and exhibits an unexpectedly low melting point (35 °C) considering the size and shape of the rigid, planar anion; analogous tetraalkylammonium salts (methyl, ethyl and *n*-butyl) have also been prepared and the tetraethylammonium example was characterized by single crystal X-ray diffraction.

It is widely recognized that many combinations of cations and anions can support the formation of stable ionic liquids (IL) with low melting points.[1] While the effects of cation structural modification on the structural and chemical properties of the resultant ILs are reasonably predictable,[2] it is the nature of the anionic component which controls the gross characteristics of the systems.[3] The observation of IL formation in salts with anions as varied as simple mononuclear inorganic anions through to complex inorganic,[4] metallate or organic examples illustrates the diversity of IL systems available.

The need for new, safe, high performance propellants and deep-bore mining explosives, coupled with the desire to reduce environmental footprints and overall exposure to hazardous, and potentially toxic materials including hydrazine, metals, and perchlorates, has led to renewed efforts to explore new, advanced energetic salts.[5] It has been suggested that non-volatile, thermally stable IL systems might be desirable in the context of forming new liquid energetic materials.[6]

New insensitive energetic materials are needed and nitro- and/or amine functionalized triazoles[7] such as 5-amino-3-nitro-1,2,4-triazole (ANTA)[8] and 3,5-dinitro-1,2,4-triazole (DNT)[9] have been investigated. Ring substitution with electron-withdrawing groups tends to produce energetic materials with high energy, high density, low sensitivity and good heat resistance, enhancement of ring aromaticity can also lead to increased thermal stability—all desirable characteristics.

Drake and co-workers[6] have demonstrated how energetic ILs can be prepared by combining cations containing energetic functionality (in this case from 1*H*–1,2,4-triazole, 4-amino-1,2,4-triazole and 1*H*–1,2,3-triazole as the cation precursors) with relatively small inorganic energetic anions ([NO$_3$]$^-$, [ClO$_4$]$^-$, and [N(NO$_2$)$_2$]$^-$). Importantly, it was suggested that the ready formation of ionic liquids with these cations appeared to be due to topographical shape and charge distribution similarity with more conventional imidazolium cations. Ogihara *et al.*[10] have recently described two new 1-ethyl-3-methylimidazolium based ILs with simple triazolate and tetrazolate anions.

We were interested in determining whether IL forming salts could be prepared containing a wider range of azolate anions, particularly with examples containing electron-withdrawing substituents which might be anticipated to stabilize heterocyclic anion formation through inductive and mesomeric effects. Here, we describe how the energetic nitro-substituted heterocycle, 3,5-dinitro-1,2,4-triazole, can be utilized in the anionic form to prepare novel ILs. The crystalline, but low melting IL, 1-butyl-3-methylimidazolium 3,5-dinitro-1,2,4-triazolate (**I**, Fig. 1) described here illustrates how a wide range of potentially interesting new ILs with charge delocalized heterocyclic anions can be prepared.

1-Butyl-3-methylimidazolium 3,5-dinitro-1,2,4-triazolate (**I**) and analogous tetramethylammonium (**II**), tetraethylammonium (**III**) and tetrabutylammonium (**IV**) salts were prepared by metathesis from the corresponding organic halide salts with potassium 3,5-dinitro-1,2,4-triazolate[11–14] as pure, crystalline salts in 78–96% yields after removal of the inorganic halide following Scheme 1.†

The thermal behavior of the salts was investigated using DSC and TGA (Table 1). The imidazolium example **I**, melts sharply at 35–36 °C to form a moderately fluid ionic liquid. The tetraalkylammonium salts (**II–IV**) are higher melting, although in each case, as with **I**, the salts melted to form stable liquids which decomposed cleanly above 200 °C with a single exothermic mass loss event. In contrast, ammonium 3,5-dinitro-1,2,4-triazolate has been reported to melt with decomposition, liberating ammonia.[9] It is well known
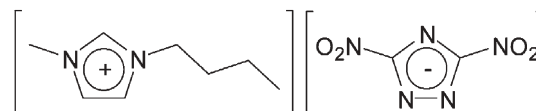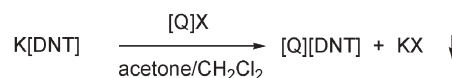

Fig. 1 Chemical structure of 1-butyl-3-methylimidazolium 3,5-dinitro-1,2,4-triazolate (**I**). Analogous salts with tetramethylammonium (**II**), tetraethylammonium (**III**), and tetrabutylammonium (**IV**) cations were also prepared.

Scheme 1 General procedure for the formation of organic 3,5-dinitro-1,2,4-triazolate salts.

	Cation	Mp/°C^a	Fp/°C^b	T_{dec}/°C^c
I	$[C_4mim]^+$	35–36 (32)	−8	239
II	$[N(CH_3)_4]^+$	219–221 (228)	137	235
III	$[N(C_2H_5)_4]^+$	104–106 (100)	99	205
IV	$[N(C_4H_9)_4]^+$	136–138 (139)	67	219
	$[NH_4]^+$	170 (dec)		

^{a} Visual from hot stage, peak from DSC in parenthesis. ^{b} Onset temperature for the exothermic crystallization transition determined by DSC, cooling rate 5 °C min^{-1}. ^{c} Onset temperature (determined to 5% mass fraction loss), heating at 5 °C min^{-1} under He.

that salts containing *N*-protonated cations tend to be significantly less thermally stable than corresponding examples with *N*-alkylated cations, and this observed increase in thermal stability was anticipated.

Crystals of **III** suitable for X-ray diffraction‡ were obtained by crystallization from dichloromethane–diethyl ether; the crystal structure is shown in Fig. 2. The triazolate anion is planar with the two nitro-groups in the plane of the ring. The cations and anions form an ordered alternating array held together primarily *via* Coulombic interactions. The three shortest and most significant cation–anion close contacts are C4–H···N3 (2.60 Å), C5–H···O2 (2.41 Å), and C7–H···O1 (2.54 Å). The cation has a flattened, oblate structure which presumably allows the ions to approach and pack more effectively in the crystal. However, the reduction in melting point compared to the methyl and butyl analogs indicates that the crystal packing is not optimal.

A preliminary *ab initio* geometry optimization of the isolated anion using GAMESS (6-311+G(d,p) basis set)[15] showed no significant changes in the anion geometry from that observed in the crystal structure and indicates that the negative charge is delocalized over the entire heterocycle ring, with the oxygen atoms of the two nitro groups having only negligible effective charge (Fig. 3).

One aspect of this study was to prepare functional ionic liquid materials; we are interested in the ability to prepare ionic liquids in which either the cation, anion, or both contain peripheral substituents, especially with nitro-groups. Nitro-substituted heterocycles are readily available and mono-nitro substituted imidazolium salts are known and can be prepared with relative ease. However, the electron-withdrawing effect of these functional groups reduces the pK_a of the heterocycles, addition of more than one nitro-substituent renders the *N*-atoms of the ring unreactive to
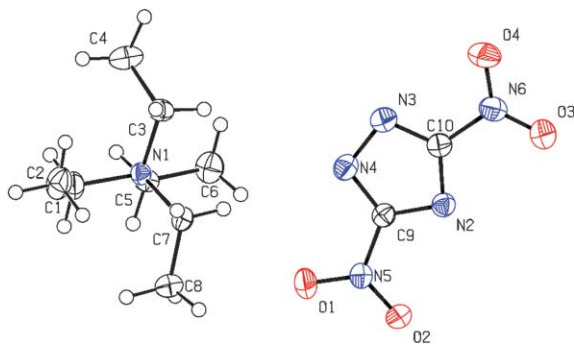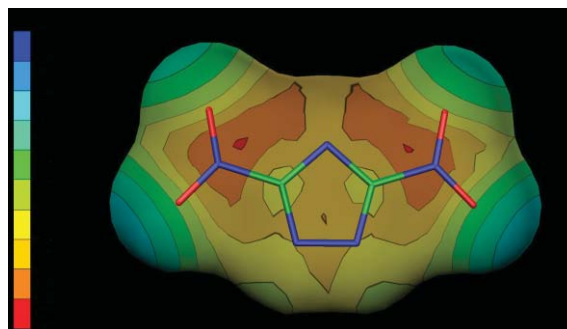

Fig. 3 Calculated electrostatic potential surface for the 3,5-dinitro-1,2,4-triazolate anion showing the extensive charge delocalization. Scale shows partial charge, ranging from −0.11 (*blue*) to −0.21 (*red*).

either alkylation or protonation reactions needed to synthesize organic salts even with strong alkylating agents (dimethyl sulfate or methyl triflate) or strong acids.[16]

The converse is that addition of electron-withdrawing substituents activates heterocycles to reduction and formation of azolate anions. Protonated ammonium 3,5-dinitro-1,2,4-triazolate acid–base pairs have been described as a method for the purification of 3,5-dinitro-1,2,4-triazole by solvent extraction. It is interesting to consider that, by choosing an appropriate, protonizable imidazole, ILs could also be formed, facilitating enhancements in the separation and purification of 3,5-dinitro-1,2,4-triazole along similar lines to that described recently for the BASIL (Biphasic Acid Scavenging utilizing Ionic Liquids) process from BASF.[17]

The ability to form ILs with simple triazolate and tetrazolates, as well as with 3,5-dinitro-1,2,4-triazolate as described here, indicates how one might prepare new IL materials where the ionic components have similar topologies to those of conventional ionic liquids, but for each ion shape, have opposite charges. The introduction of aromaticity into planar heterocyclic anions is one aspect of this, and may lead to interesting new IL systems which have significantly different solvent properties. For example, the azolate anions have hydrogen-bond acceptor characteristics in contrast to the hydrogen-bond donor characteristics of imidazolium cations.

In conclusion, low melting ionic liquid salts can be prepared with this relatively large, rigid heterocyclic anion. Addition of electron-withdrawing nitro-substituents to the triazole ring enhances the tendency to form stable aromatic charge delocalized anions, compared to unsubstituted triazoles, which interact only weakly through hydrogen-bonding with the cation. Further ongoing work will extend the range of similar anions, develop systems with higher density heterocyclic cations, and evaluate the properties of these materials.

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Fig. 2 ORTEP diagram showing the asymmetric unit of **III**.

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