Strategies toward the design of energetic ionic liquids: nitro- and nitrile-substituted *N*,*N*′-dialkylimidazolium salts†

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Twelve novel 1,3-dialkylimidazolium salts containing strongly electron-withdrawing nitro- and cyano-functionalities directly appended to the cationic heterocyclic rings have been synthesized; the influences of the substituents on both formation and thermal properties of the resultant ionic liquids have been determined by DSC, TGA, and single crystal X-ray diffraction, showing that an electron-withdrawing nitro-substituent can be successfully appended and has a similar influence on the melting behaviour as that of corresponding methyl group substitution. Synthesis of di-, or trinitro-substituted 1,3-dialkylimidazolium cations was unsuccessful due to the resistance of dinitro-substituted imidazoles to undergo either *N*-alkylation or protonation, while 1-alkyl-4,5-dicyanoimidazoles were successfully alkylated to obtain 1,3-dialkyl-4,5-dicyanoimidazolium salts. Five crystal structures (one of each cation type) show that, in the solid state, the NO_2-group has little significant effect, beyond the steric contribution, on the crystal packing.

Introduction

Ionic liquids (ILs; conventionally defined with a melting point of below 100 °C) have come under intense scrutiny in recent years. The intrinsic non-volatility, thermal stability, and large liquid ranges achievable with many ILs have proven to be important drivers[1–7] supporting many advances beyond the initial investigation of ILs as liquid electrolytes. Current topics include electrochemistry,[8–10] separation science,[11–14] chemical synthesis,[2,4,5,15–19] and catalysis.[4,5,17]

This interest in ILs and their applications has led synergistically to the development of an extensive, and diverse range of organic salts that can support low melting ionic liquid phases (with examples ranging from simple mononuclear[20] to complex[21–25] anions) and to the exploration of materials applications utilizing the novel characteristics of these ionic liquid phases, including thermal fluids, lubricants, photovoltaics, and fuel cell electrolytes.[26–28] One such example is in the effort to develop "energetic liquids" (non-volatile liquid high energy density materials)[29] for energy storage and propellant uses.

Drake and co-workers[30] have prepared energetic ILs by combining cations containing energetic functionality with relatively small inorganic energetic anions ($[NO_3]^-$, $[ClO_4]^-$, and $[N(NO_2)_2]^-$). In this, and related work by Shreeve and co-workers,[31,32] energetic low melting organic salts contained amine-functionalized triazoles and tetrazoles as cations. Importantly, it was suggested that the ready formation of ionic liquids with these cations appeared to be due to a similarity in topographical shape and charge conventional IL systems.

Although ILs with imidazolium cations have been widely studied, modification of the structure has been largely restricted to variations in ring-alkyl group substitution[33,34] or to the addition of hydroxy,[35] ether,[36,37] epoxy,[38] amine, or cyano[39] groups in the N-substituent sidechains, with the notable exceptions of quite complex substituents in "Task Specific Ionic Liquids".[40] Direct modification of functionality in the heterocyclic cation core has previously received only limited attention,[41–43] perhaps because of anticipation that the combination of size/shape effects with changes in the cation polarization and dipole moments might promote the formation of salts with relatively higher melting points.[42]

In the present work, the preparation and physical properties of imidazolium-based ILs containing strongly electron-withdrawing nitro- and nitrile-functionalities directly attached to the ring have been investigated. To this end, we have prepared a series of imidazolium salts bearing NO_2-functionalized heterocyclic cations to evaluate how the physical and thermodynamic properties (thermal stability, melting, and decomposition temperatures) of the resulting salts are related to the presence of electron-withdrawing substituents in the cation ring. The goal is to develop synthetic and predictive strategies

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† Electronic supplementary information (ESI) available: Cation···anion close contact geometries (Table S1), bond distances and angles in the imidazolium rings (Table S2), and crystallographic data for compounds **3a**, **5a**, **7b**, **10a**, **13b**. See DOI: 10.1039/b509260d.

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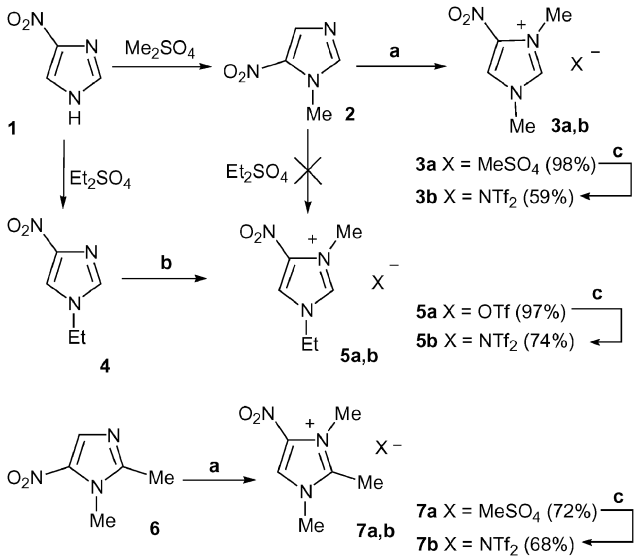
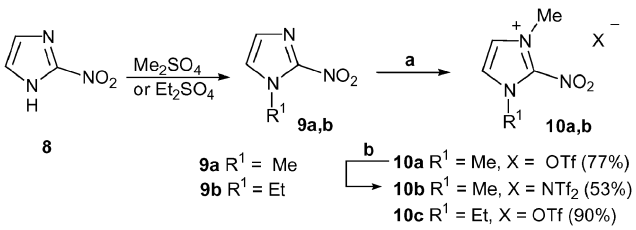


Scheme 1 Reaction conditions: (a) Me_2SO_4, toluene, 20 °C, 48 h; (b) MeOTf, toluene, 20 °C, 72 h; (c) $LiNTf_2$, water–dichloromethane, 20 °C.



Scheme 2 Reaction conditions: (a) MeOTf, toluene, 20 °C, 72 h for **10a** or 48 h for **10c**; (b) $LiNTf_2$, water–dichloromethane, 20 °C.

for the introduction of energetic functions and components into ionic liquid systems, as well as to understand how to engineer low melting or specific activity ILs.

We report here the synthesis and physical properties of 12 imidazolium-based ILs containing strongly electron-withdrawing nitro- and cyano-functionalities linked directly to the ring. The solid states of five examples have additionally been characterized by single crystal X-ray crystallography, identifying the principle cation–anion interactions.

Results and discussion

We have prepared 12 new *N*,*N*′-dialkylimidazolium salts containing $-NO_2$ and –CN substituents in the imidazolium ring and characterized these in terms of structural and thermal properties. The synthetic approach to the preparation of *N*,*N*′-dialkylimidazolium salts utilized key quaternization of weakly nucleophilic ring-substituted *N*-alkyl imidazoles.

Synthesis

A systematic strategy to prepare mono-, di-, and trinitro-substituted 1,3-dialkylimidazolium cations was limited by the resistance of dinitro-substituted imidazoles to undergo either *N*-alkylation or protonation. Thus, only mononitro-substituted, but no dinitro-substituted imidazolium salts could be isolated. In contrast, 1-alkyl-4,5-dicyanoimidazole was successfully alkylated to obtain 1,3-dialkyl-4,5-dicyanoimidazolium salts.

1-Methyl-5-nitroimidazole[44] **2** was prepared in 80% yield by the reaction of 4-nitroimidazole **1** with dimethyl sulfate in dioxane under reflux following a published procedure[44] (Scheme 1). The treatment of **2** with dimethyl sulfate in toluene[45] at room temperature for 48 h gave the corresponding quaternary 1,3-dimethyl-4-nitroimidazolium methyl sulfate **3a** in 98% yield. Similar reaction of 1,2-dimethyl-5-nitroimidazole **6** with dimethyl sulfate in toluene afforded the corresponding quaternary salt **7a** (72% yield).

Attempts to prepare unsymmetrical 1-ethyl-3-methyl-4-nitroimidazolium salt **5**, similarly, by quaternization of 1-methyl-5-nitroimidazole **2** with diethyl sulfate failed and resulted in recovery of compound **2** (Scheme 1). However, treatment of 1-ethyl-4-nitroimidazole **4**, available from 4-nitroimidazole **1** by alkylation with diethyl sulfate in aqueous media in the presence of sodium hydroxide at 45 °C,[46] with methyl triflate in toluene at 20 °C for 72 h gave the imidazolium salt **5a** in 97% yield (Scheme 1).

1-Methyl-2-nitroimidazole[47,48] **9a** and 1-ethyl-2-nitroimidazole[49] **9b** (Scheme 2) were prepared by alkylation of 2-nitroimidazole **8** with the appropriate dialkyl sulfate in aqueous media in the presence of sodium bicarbonate at 60–65 °C in 39% and 36% yields, respectively. Treatment of **9a** and **9b** with methyl triflate in toluene at 20 °C for 48 and 72 h gave quaternary salts **10a,c** in 77% and 90% yields, respectively.

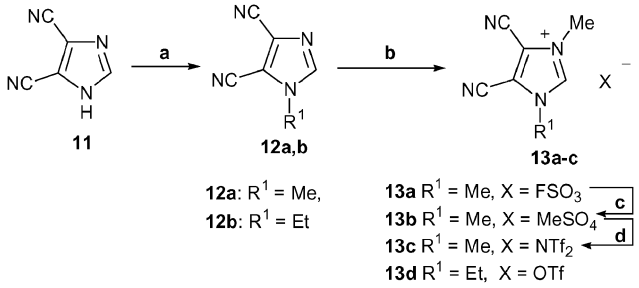
1-Methyl-4,5-dicyanoimidazole **12a** was prepared in 81% yield according to a published procedure[50] from 4,5-dicyanoimidazole **11** and dimethyl sulfate in an aqueous medium in the presence of sodium bicarbonate at 60–65 °C (Scheme 3).

Quaternization of **12a** with dimethyl sulfate in toluene at 20–25 °C for 72 h produced the corresponding quaternary salt **13b** in only 10% yield; reaction in chloroform under reflux for 24 h increased the yield to 25%. Treatment of compound **12a** with methyl fluorosulfonate in chloroform at room temperature for 48 h, followed by methanolysis of the intermediate fluorosulfonate **13a** (not isolated) from methanol afforded the methyl sulfate salt **13b** in 71% yield (Scheme 3). Attempts to convert **12a** into the asymmetric 1-ethyl-3-methyl-4,5-dicyanoimidazolium methyl sulfate (**13**, R^1 = Et, X = $MeSO_4$) by the reaction with diethyl sulfate failed and resulted in recovery of **12a**.

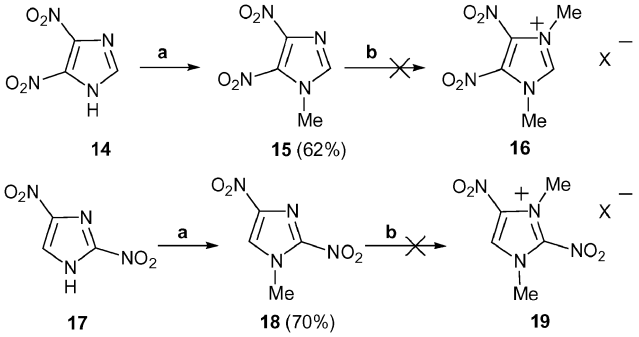
Unsymmetrical 1-ethyl-3-methyl-4,5-dicyanoimidazolium triflate **13d** was synthesized in 67% yield by quaternization of 1-ethyl-4,5-dicyanoimidazole **12b** (available from 4,5-dicyanoimidazole and triethyl orthoformate in 72% yield)[51] with methyl triflate in toluene at 20–25 °C for 72 h.

1-Methyl-4,5-dinitroimidazole[52] **15** and 1-methyl-2,4-dinitroimidazole[52] **18** (Scheme 4) were prepared from corresponding dinitroimidazoles **14** and **17**, and dimethyl sulfate according to previously published procedures.[52]

The presence of two nitro groups in the imidazole ring deactivated **15** and **18**, and attempted quaternizations of dinitroimidazoles **15** and **18** with dimethyl sulfate, methyl fluorosulfonate and methyl triflate were unsuccessful, resulting in either recovery or decomposition of the starting imidazoles.



Scheme 3 Reaction conditions: (a) for **12a**: Me_2SO_4, aqueous $NaHCO_3$, 65 °C, 2 h, 81%; for **12b**: $(EtO)_3CH$, 100 °C for 1 h, 150 °C for 1 h, 72%; (b) for **13a**: **12a**, $MeOSO_2F$, chloroform, 20 °C, 48 h; for **13b**: **12a**, Me_2SO_4, toluene, 20 °C, 72 h, 10%; or Me_2SO_4, chloroform, reflux, 24 h, 25%; for **13d**: **12b**, MeOTf, toluene, 20 °C, 72 h, 67%; (c) recrystallized from methanol–diethyl ether, 71% yield from **12a**; (d) $LiNTf_2$, water–dichloromethane, 20 °C, 71%.



Scheme 4 Reaction conditions: (a) Me_2SO_4, aqueous $NaHCO_3$, 20 °C, 12 h; (b) Me_2SO_4, $MeOSO_2F$, or MeOTf.

The structures of the salts **3a,b**, **5a,b**, **7a,b**, **10a–c**, and **13b–d** were supported by their ^1H and ^{13}C NMR spectra, and elemental analysis. The NMR spectra of **3a,b**, **5a,b**, **7a,b**, **10c**, and **13d** showed the appearance of new signals in the range 3.92–4.12 ppm (^1H-) and 36.0–39.8 ppm (^{13}C-spectra) corresponding to the *N*-methyl group. The NMR spectra of the salts **10a** and **13b** with symmetric cations showed a single signal of increased relative intensity corresponding to the *N*-methyl group and slight downfield shifts 4.09 → 4.13 and 3.92 → 4.06 ppm (in the ^1H-) and 37.4 → 39.7 and 33.9 → 36.9 ppm (in the ^{13}C-spectra) as compared with **9a** and **12a**, respectively. Interestingly, the two *N*,*N*′-methyl groups in the unsymmetric cation of **3a** showed equivalent shifts and a single signal in the ^{13}C NMR spectrum at 37.1 ppm, although the shifts of the hydrogens were differentiated as two signals at 3.93 and 4.09 ppm in the ^1H spectrum. The NMR spectra of **3b**, **5b**, **7b**, **10b**, and **13c** showed patterns of signals similar to those observed for the corresponding salts **3a**, **5a**, **7a**, **10a**, or **13b** used in their preparation.

Metathesis reactions

The functionalized imidazolium cations were initially prepared, isolated and characterized as either methyl sulfate or triflate salts, as shown in Table 1, through the direct alkylation procedures (Schemes 1–4). In order to obtain a homogenous set of anions for comparison with conventional ILs, the bis(triflyl)imide salts of each cation were prepared by metathesis of the water soluble triflate **5a**, **10a** or methyl sulfate **3a**, **7a**, **13b** salts with $LiNTf_2$ in water, yielding the insoluble bis(triflyl)imide salts (**3b**, **5b**, **7b**, **10b**, **13c**) which precipitated initially as colorless solids or, for **3b** and **5b**, as liquids and were then extracted with dichloromethane.

Thermal investigations

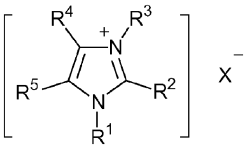
The bis(triflyl)imide salts, **3b** and **5b** with 1,3-dimethyl-4-nitroimidazolium and 1-ethyl-3-methyl-4-nitroimidazolium cations, formed room temperature ILs; all the other salts prepared were isolated as crystalline solids in good yields and high purity. The melting transition, measured visually

Table 1 Thermal data for the nitro- and nitrile-substituted 1,3-dialkylimidazolium salts[a]

	Cation	Anion	$T_{m(onset)}$ (±1 °C)	$T_{m(peak)}$ (±1 °C)	ΔH_{fus} (J g^{-1})	T_{dec}
3a	1,3-Dimethyl-4-nitroimidazolium	$MeSO_4^-$	95	104	84	166
3b		NTf_2^-	−41[b], 35[c]			258
5a	1-Ethyl-3-methyl-4-nitroimidazolium	OTf^-	120[f]	122[f]	88[f]	
			92	94	50	260
5b		NTf_2^-	−45[b], 18[c]			270
7a	1,2,3-Trimethyl-4-nitroimidazolium	$MeSO_4^-$	150	162	70	196, 285[g]
7b		NTf_2^-	110	113	97	269, 340[g]
10a	1,3-Dimethyl-2-nitroimidazolium	OTf^-	105	116	20	234, 298[g]
10b		NTf_2^-	72	77	40	248, 318[g]
10c	1-Ethyl-3-methyl-2-nitroimidazolium	OTf^-	105	107	75	230
13b	1,3-Dimethyl-4,5-dicyanoimidazolium	$MeSO_4^-$	130	143[d]	54	218
13c		NTf_2^-	84[e], 105[f]	111[f]	99[f]	
			84	97	36	264
13d	1-Ethyl-3-methyl-4,5-dicyanoimidazolium	OTf^-	75–80[e]			
			140	148	58	229

[a] Melting points (onset and peak positions) and heats of fusion were determined by DSC from the second heating cycle after initially melting the salts, then cooling to −110 °C. Decomposition temperatures (T_{dec}) were determined by TGA from onset to 5 wt% mass loss, heating at 5 °C min^{-1} under helium. [b] Glass transition temperature. [c] Two second order transitions observed. [d] Broad melting transition. [e] Solid transition. [f] Only during first heating. [g] Change in the slope of the decomposition.

Table 2 Melting points (°C) of selected quaternary imidazolium salts



Entry	R^1	R^2	R^3	R^4	R^5	$MeSO_4^-$	OTf^-	NTf_2^-
1	Et		Me			−65 (T_g)[45]	−9[33]	−3[33]
2	Et	Me	Me			73[45]	109[33]	20[33]
3	Et		Me		Me		6[33]	−3[33]
4	Me	NO_2	Me				105 (**10a**)	72 (**10b**)
5	Me		Me	NO_2		95 (**3a**)		−41 (T_g) (**3b**)
6	Et	NO_2	Me				105 (**10c**)	
7	Et		Me	NO_2			92 (**5a**)	−45 (T_g) (**5b**)
8	Me	Me	Me	NO_2		150 (**7a**)		110 (**7b**)
9	Me	Me	Me			116[45]		
10	Me		Me	CN	CN	130 (**13b**)		84 (**13c**)
11	Et		Me	CN	CN		140 (**13d**)	

and by DSC, and thermal decomposition data, determined by TGA from the onset of decomposition to 5 wt% mass loss, are shown in Table 1. Crystalline mononitro-substituted dimethyl- **3a**, **10a**, trimethyl- **7a**, ethylmethyl- **5a**, **10c** nitroimidazolium, and dimethyl- **13b** and ethylmethyl- **13d** dicyanoimidazolium salts, were obtained either as methyl sulfates or as triflates. For each salt, a sharp, first order melting transition in the temperature range 95–154 °C was observed on heating of the solids. By comparison, transition temperatures for the corresponding salts with bis(triflyl)imide anions were reduced by up to 40 °C for the crystalline salts compared to the respective methyl sulfate or triflate analogs, and for the 1,3-dimethyl-4-nitroimidazolium **3a,b** and 1-ethyl-3-methyl-4-nitroimidazolium **5a,b** examples, by up to 90 °C to the highest temperature transition observed which was a second order transition. Neither **3b** nor **5b** could be induced to crystallize on cooling, and in the DSC experiment were observed to undergo two first order transitions, at ~35 and −41 °C and at ~18 and −45 °C, respectively.

Comparison of **3** and **7** with the corresponding iodide, perchlorate, and nitrate salts recently reported by Shreeve and co-workers during the course of this work also clearly highlights the effects of anion replacement as a means of controlling the melting points and propensities of the salts to form ionic liquids.[32] The melting points of the salts of the two cations (**3** and **7**) with the five anions decrease in the order $I^- > [ClO_4]^- > [NO_3]^- > [CH_3SO_4]^- > [NTf_2]^-$ with values of 180, 172, 163, 104, 35 °C and 191, 186, 161, 150, 110 °C, respectively, for the 1,3-dimethyl-4-nitroimidazolium (**3**) and 1,2,3-trimethyl-4-nitroimidazolium (**7**) cations.

Upper thermal stabilities, measured by TGA for all the salts were in the range ~250–300 °C, measured from the initial onset of decomposition. Characteristic thermograms show a single mass-loss event. The decomposition temperatures reported here were determined from the onset to initial 5 wt% mass loss on isocratic heating, a measure which provides a more realistic representation of thermal stability at elevated temperatures, and based on this measure[53] are comparable to other ILs with equivalent anions. This indicates that the initial thermal decomposition mechanism of these salts (under normal, non-accelerated conditions) is that of conventional E_2 elimination of *N*-alkyl substituents from the cations.

The contribution that the single nitro-substituent on the imidazolium cations has on the melting points of these salts appears principally to be that of a single non-interacting functional group, with the variation in melting point contribution being somewhat equivalent to that of a methyl-substituent at the same position. Thus, for example, the change from 1-ethyl-3-methylimidazolium triflate (Table 2, Entry 1) to 1-ethyl-2,3-dimethylimidazolium triflate (Entry 2) results in an increase in melting point of approximately 120 °C on C(2)-methylation. Subsequent mutation of the C(2)–CH_3 group to C(2)–NO_2 (Entry 6, **10c**) results in a 4 °C drop in melting point. Comparisons of the group contributions are not so clear between other sets of examples, for example, between 1,3-dimethyl-2-nitroimidazolium (Entry 4, **10b**) and 1,3-dimethyl-4-nitroimidazolium (Entry 5, **3b**) bis(triflyl)imides, movement of the nitro-substituent destabilizes the crystalline state by at least 37 °C (perhaps due to asymmetry), whereas the equivalent transformation between 1-ethyl-3-methyl-2-nitroimidazolium (Entry 6, **10c**) and 1-ethyl-3-methyl-4-nitroimidazolium (Entry 7, **5a**) triflate leads to a net stabilization of 9 °C. However, despite these alternative transitional indications, it is clear that the introduction of an electron-withdrawing energetic function, in the shape of a nitro-group, onto the aromatic cation ring of an organic salt can still lead to the potential for IL formation.

X-Ray crystallography

Crystals suitable for single crystal X-ray structure determination were obtained for five of the twelve imidazolium salts (**3a**, **5a**, **7b**, **10a**, and **13b**) by crystallization at room temperature from methanol solution by trituration with diethyl ether (Table 3).¶ In each case, all non hydrogen atoms were fully refined anisotropically and all hydrogen atoms refined isotropically. The five structurally characterized salts are depicted in Fig. 1–5 with each asymmetric unit shown oriented

¶ CCDC reference numbers 272562–272566. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b509260d

Table 3 Crystal and structure refinement data

Compound	[1,3-Dimethyl-4-nitroimidazolium][$MeSO_4$] **3a**	[1-Ethyl-3-methyl-4-nitroimidazolium][OTf] **5a**	[1,2,3-Trimethyl-4-nitroimidazolium][NTf_2] **7b**	[1,3-Dimethyl-2-nitroimidazolium][OTf] **10a**	[1,3-Dimethyl-4,5-dicyanoimidazolium][$MeSO_4$] **13b**
Color/shape	Colorless/needles	Colorless/needles	Colorless/needles	Colorless/needles	Colorless/plates
Formula	$C_6H_{11}N_3O_6S$	$C_7H_{10}F_3N_3O_5S$	$C_8H_{10}F_6N_4O_6S_2$	$C_6H_8F_3N_3O_5S$	$C_8H_{10}N_4O_4S$
Formula weight	253.24	305.24	436.32	291.21	258.26
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1$
T (K)	173	173	173	173	173
a (Å)	8.366(3)	9.872(2)	8.113(2)	6.882(3)	8.4703(14)
b (Å)	11.036(4)	12.839(3)	12.596(4)	11.924(5)	7.9000(13)
c (Å)	11.379(4)	9.5949(19)	17.035(5)	13.324(6)	8.9145(15)
α (°)	90	90	70.065(5)	90	90
β (°)	100.580(6)	96.630 (4)	81.042(5)	96.911(6)	111.568(3)
γ (°)	90	90	77.570(5)	90	90
Z	4	4	4	4	2
V (Å^3)	1032.8(6)	1207.9(4)	1591.7(8)	1085.4(8)	554.75(16)
D_{calc} (g cm^{-3})	1.629	1.678	1.821	1.782	1.546
Independent/ Observed reflections	1490 (R_{int} = 0.0497)/ 1210 ([$I > 2\sigma(I)$])	1735 (R_{int} = 0.0152)/ 1639 ([$I > 2\sigma(I)$])	4389 (R_{int} = 0.0183)/ 3501 ([$I > 2\sigma(I)$])	1561 (R_{int} = 0.0265)/ 1466 ([$I > 2\sigma(I)$])	1552 (R_{int} = 0.0151)/ 1438 ([$I > 2\sigma(I)$])
GooF	1.029	1.061	1.040	1.141	1.088
R_1, wR_2 $> I > 2\sigma(I)$]	0.0385, 0.0928	0.0240, 0.0623	0.0355, 0.0839	0.0308, 0.0808	0.0340, 0.0965
R_1, wR_2 (all data)	0.0531, 0.0992	0.0253, 0.0631	0.0505, 0.0924	0.0328, 0.0822	0.0379, 0.0986

$R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $R_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma(w(|F_o|^2)^2]\}^{\frac{1}{2}}$

perpendicularly to the plane of the imidazolium ring with the shortest cation–anion hydrogen bonding contact displayed.

In only one case (**13b**) was any disorder observed. In this structure the methyl sulfate anion exhibited two conformations with the sulfur, carbon, and one oxygen atom [O(4)] fully occupied and three oxygen atoms [O(1)–O(3)] in half occupied positions. The disorder appears to be a result of the alternatives for weak hydrogen bonding interactions to the cation. When the anion is in the O(1)–O(3) conformation, the closest contact is from the C6 methyl hydrogen atom to O(2); while the alternate conformation [O(1A)–O(3A)] allows the closest contact to be between the ring C(2) hydrogen atom and O(2A).

Compound **7b** is the only one of the five salts characterized to have more than one cation–anion pair in the asymmetric unit. Here too, this can be attributed to alternatives in the weak intermolecular hydrogen bonding. Careful inspection of the ions reveals little difference in the two cations or in the conformations of the two anions. However, as shown in Fig. 3, the shortest hydrogen bonding interactions between cation and anion are subtly different, with the C(51) hydrogen atom making its close contact to O(31), while the C(52) hydrogen atom makes its closest contact to O(42). The resulting relative orientation in the two anions and cations is sufficient to break any higher symmetry. Interestingly, this is the only NTf_2^- salt of those prepared that does not fit the strict definition of an 'ionic liquid,' that is, with melting point <100 °C.

As the two above examples imply, the overall packing in each case is dominated by attractive Coulombic forces, augmented by hydrogen-bonding from imidazolium ring donor hydrogen or alkyl hydrogen positions to available anionic hydrogen-bond acceptor sites. All of the salts crystallized into relatively simple close-packed structures and the principal

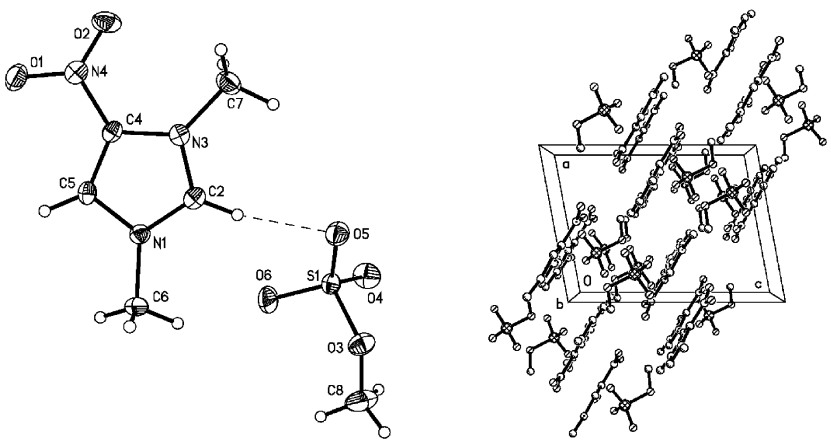


Fig. 1 ORTEP diagram showing connectivity, conformation, and the atom numbering scheme of the individual cations and anions present in the asymmetric unit and packing diagram of [1,3-dimethyl-4-nitroimidazolium][$MeSO_4$] (**3a**). The intermolecular contact with the largest negative difference from van der Waals separation is noted.

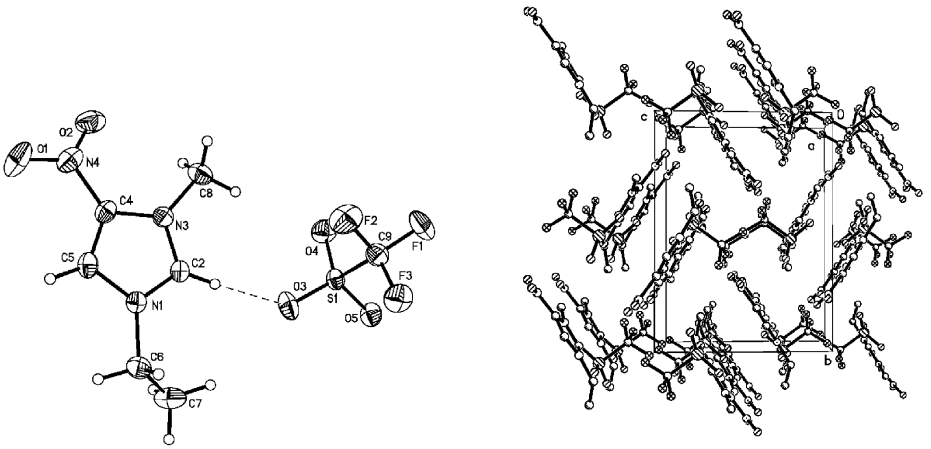


Fig. 2 ORTEP diagram showing connectivity, conformation, and the atom numbering scheme of the individual cations and anions present in the asymmetric unit and packing diagram of [1-ethyl-3-methyl-4-nitroimidazolium][OTf] (**5a**). The intermolecular contact with the largest negative difference from van der Waals separation is noted.

close-contacts and hydrogen-bonding interactions between the ions in each case are shown in Table S1.†

There is little effect of substitution on the bond lengths and angles within the imidazolium cations (Table S2).† In **7b** however, the methyl group in the C(2) position elongates the central N(1)–C(2) and C(2)–N(3) bonds.

The nitro-substituents in imidazolium salts **3a**, **5a**, **7b**, and **10a** are twisted slightly out of the plane of the heterocycle ring, reducing conjugation. The observed dihedral twist is, however, small ranging from 2.6° **10a** to 10.7° **5a** comparable to that in other nitroimidazolium and imidazolium structures. The nitro-groups do not have any significant hydrogen-bond donor

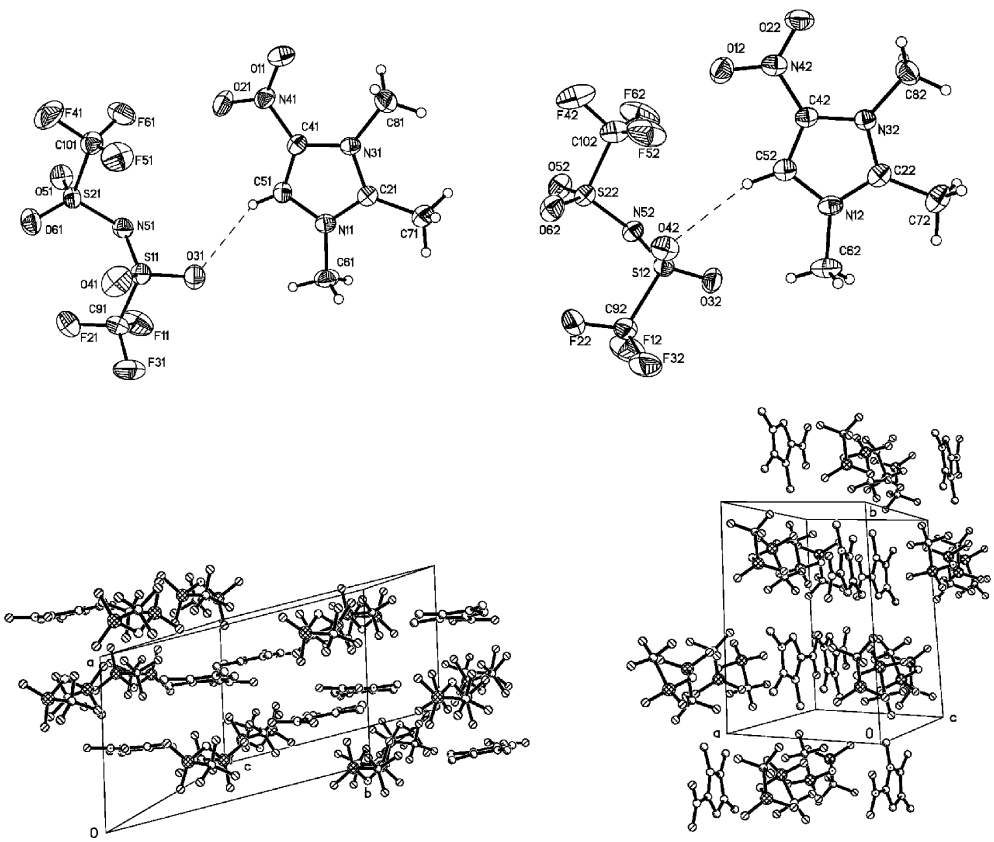


Fig. 3 ORTEP diagrams showing connectivity, conformation, and the atom numbering scheme of the individual cations and anions present in the asymmetric unit and packing diagrams of [1,2,3-trimethyl-4-nitroimidazolium][NTf_2] (**7b**). The intermolecular contact with the largest negative difference from van der Waals separation is noted.

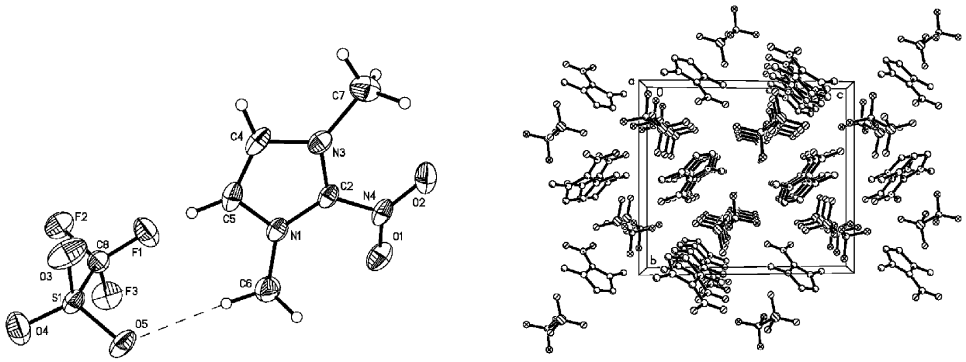


Fig. 4 ORTEP diagram showing connectivity, conformation, and the atom numbering scheme of the individual cations and anions present in the asymmetric unit and packing diagram of [1,3-dimethyl-2-nitroimidazolium][OTf] (**10a**). The intermolecular contact with the largest negative difference from van der Waals separation is noted.

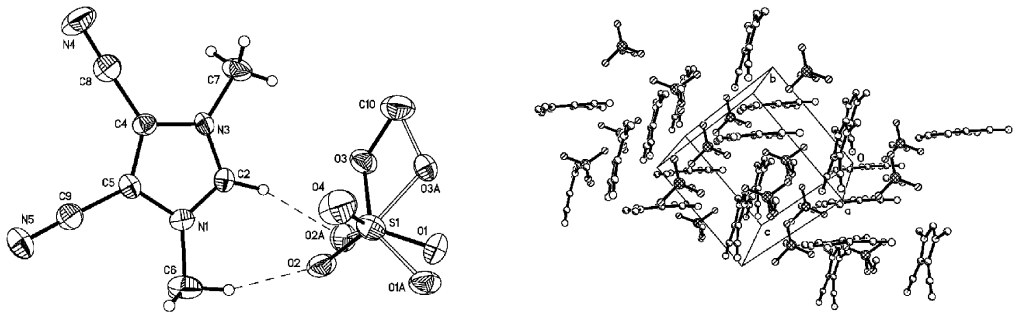


Fig. 5 ORTEP diagram showing connectivity, conformation, and the atom numbering scheme of the individual cations and anions present in the asymmetric unit and packing diagram of [1,3-dimethyl-4,5-dicyanoimidazolium][$MeSO_4$] (**13b**, disordered anion). The intermolecular contact with the largest negative difference from van der Waals separation is noted.

or acceptor interactions beyond simple close-packing in the crystal structures which could influence the lattice energies and melting points of these salts.

The packing diagrams for the five structurally characterized salts are also depicted in Fig. 1–5. The cations are all parallel in salts **3a** and **7b**, but not in the remaining salts. Zones of fluorine atoms are apparent in **5a**, but this is not the case for either **7b** or for **10a**.

Conclusion

In this work, the focus has been on establishing the influence of substituent type and position on the properties of nitro- and cyano-substituted imidazolium salts. Functionalization of heterocycles with electron-withdrawing substituents, such as these described here, results in a reduction in nucleophilicity of the heterocycle and thus reduced ability to form quaternary salts by S_N2 alkylation reactions. Mono-substituted crystalline quaternary salts (and some liquids with bis(triflyl)imide) could be isolated, but higher-substitution with electron-withdrawing groups resulted in the imidazoles failing to undergo quaternization even with strong alkylating agents (methyl triflate or fluorosulfonate) due to the reduced nucleophilicity of the azoles. Imidazolium salts with two nitrile substituents (**13b–d**) could be obtained. A computational investigation of proton and methylene-group affinities, and cation stability relative to the the parent azoles has recently been conducted.[61]

Substitution of hydrogens in the ring-carbon position of imidazolium cations tends, in general, to increase the melting points of the respective salts. For example, compare the transition temperatures for 1-ethyl-3-methylimidazolium, 1-ethyl-2,3-dimethylimidazolium and 1-ethyl-3,5-dimethylimidazolium salts in Table 2 (Entries 1–3) where it is clearly illustrated that relatively large variations in melting points can be achieved through changes in the cation substitution patterns.

The five crystal structures (one of each cation type) show that in the solid state the NO_2-group has little significant effect, beyond a steric contribution, to the crystal packing: no major hydrogen-bonding or directional close contacts are observed. This lends support to our initial analysis of the group contribution of the NO_2 function to IL properties as roughly equivalent to that of a methyl-function at the same ring-position.

Experimental section

Caution

Although no problems were encountered during this work, the introduction of energetic functionalities into heterocyclic compounds has inherent risks and appropriate procedures must be taken and all materials handled with extreme care.

General methods

NMR spectra were obtained in $CDCl_3$, DMSO-d_6 or CD_3OD with TMS as the internal standard for ^1H or the solvent as the internal standard for ^{13}C. *J* values are given in Hz. All of the chemicals were employed as supplied.

Lithium bis(triflyl)imide ($LiNTf_2$) was a gift from 3M (St Paul, MN).

Materials

2-Nitroimidazole **8** was prepared according to the published procedure by diazotization of 2-aminoimidazolium sulfate (available from aminoacetaldehyde diethyl acetal and *S*-methylisothiourea)[54] followed by substitution with nitrite anion in the presence of copper sulfate.[55] 2,4-Dinitroimidazole **17** was prepared by *N*-nitration[56,57] of 4-nitroimidazole **1** followed by isomerization of intermediate 1,4-dinitroimidazole in chlorobenzene at 115 °C.[58]

Procedure for the preparation of 4,5-dinitroimidazole (14)

To 4-nitroimidazole (2.0 g, 18 mmol) dissolved in a minimum quantity of concentrated sulfuric acid was added a mixture of concentrated sulfuric acid (10 cm^3) and fuming nitric acid (90%, 8 cm^3, 0.17 mol). The mixture was heated under reflux for 5 h. After cooling, the mixture was poured into ice, and the pH was adjusted to 2 with sodium bicarbonate. The product was extracted with ethyl acetate. The extract was concentrated to give 4,5-dinitroimidazole **14** as yellow crystals from water (1.55 g, 55%), mp 173–176 °C (lit.[57] 188–189 °C); δ_H (300 MHz, DMSO-d_6) 12.37 (1 H, br s, NH), 8.06 (1 H, s); δ_C (75 MHz, DMSO-d_6) 135.5, 134.9.

General procedure for the preparation of imidazolium methyl sulfates (3a and 7a)

Dimethyl sulfate (7 mmol, 0.88 g, 0.66 cm^3) was added to a solution of 1-alkylimidazole **2** or **6** (7 mmol) at 20–25 °C under nitrogen. The reaction mixture was stirred at 20–25 °C for 48 h. The solvent was removed and the residue was recrystallized from methanol–diethyl ether to give imidazolium methyl sulfate **3a**, **7a**.

1,3-Dimethyl-4-nitroimidazolium methyl sulfate (3a). Yellowish crystals (98%), mp 101–103 °C (from methanol–diethyl ether); δ_H (300 MHz, DMSO-d_6) 9.38 (1 H, s), 9.02 (1 H, s), 4.09 (3 H, s, CH_3), 3.93 (3 H, s, CH_3), 3.37 (3 H, s, CH_3); δ_C (75 MHz, DMSO-d_6) 139.9, 137.8, 125.7, 52.8, 37.1. Found: C, 28.64; H, 4.27; N, 16.35. Calc. for $C_6H_{11}N_3O_6S$: C, 28.46; H, 4.38; N, 16.59%.

1,2,3-Trimethyl-4-nitroimidazolium methyl sulfate (7a). Yellowish microcrystals (72%), mp 153–154 °C (from methanol–diethyl ether); δ_H (300 MHz, CD_3OD) 8.74 (1 H, br s), 4.09 (3 H, s), 3.92 (3 H, s), 3.65 (3 H, s), 2.74 (3 H, s); δ_C (75 MHz, CD_3OD) 150.4, 126.2, 55.1, 36.8, 36.0, 10.8. Found: C, 31.48; H, 4.87; N, 15.32. Calc. for $C_7H_{13}N_3O_6S$: C, 31.46; H, 4.90; N, 15.72%.

General procedure for the preparation of imidazolium triflates (5a, 10a, 10c, and 13d)

To a solution of appropriate 1-alkylimidazole **4**, **9a**, **9b**, or **12b** (5 mmol) in toluene (3 cm^3) was added methyl triflate (5 mmol, 0.57 cm^3) at 20–25 °C under nitrogen. The reaction mixture was stirred at 20–25 °C for 72 hours (48 h for **10c**). The precipitate was filtered and recrystallized from methanol–diethyl ether to give 1,3-dialkylimidazolium triflate **5a**, **10a**, **10c**, **13d**.

1-Ethyl-3-methyl-4-nitroimidazolium triflate (5a). White needles (97%), mp 114–117 °C (from methanol–diethyl ether); δ_H (300 MHz, DMSO-d_6) 9.49 (1 H, s), 9.16 (1H, s), 4.31 (2 H, q, *J* 7.3, CH_2CH_3), 4.11 (3 H, s, CH_3), 1.50 (3 H, t, *J* 7.3, CH_2CH_3); δ_C (75 MHz, DMSO-d_6) 139.2, 138.1, 124.5, 120.7 (q, *J* 320.5, CF_3), 46.0, 37.2, 14.6. Found: C, 27.87; H, 3.24; N, 13.46. Calc. for $C_7H_{10}F_3N_3O_5S$: C, 27.55; H, 3.30; N, 13.77%.

1,3-Dimethyl-2-nitroimidazolium triflate (10a). White needles (77%), mp 112–114 °C (from methanol–diethyl ether); δ_H (300 MHz, DMSO-d_6) 8.10 (2 H, s), 4.13 (6 H, s, 2 × CH_3); δ_C (75 MHz, DMSO-d_6) 139.5, 125.3, 120.7 (q, *J* 319.9, CF_3), 39.7. Found: C, 24.63; H, 2.69; N, 14.00. Calc. for $C_6H_8F_3N_3O_5S$: C, 24.75; H, 2.77; N, 14.43%.

1-Ethyl-3-methyl-2-nitroimidazolium triflate (10c). White microcrystals (90%), mp 105–106 °C (from methanol–diethyl ether); δ_H (300 MHz, DMSO-d_6) 8.17 (1 H, d, *J* 1.9), 8.13 (1 H, d, *J* 1.9), 4.54 (2 H, q, *J* 7.2, CH_2CH_3), 4.12 (3 H, s, CH_3), 1.47 (3 H, t, *J* 7.2, CH_2CH_3); δ_C (75 MHz, DMSO-d_6) 139.1, 125.7, 123.9, 120.7 (q, *J* 319.9, CF_3), 48.2, 39.8, 14.6. Found: C, 27.75; H, 3.21; N, 13.54. Calc. for $C_7H_{10}F_3N_3O_5S$: C, 27.55; H, 3.30; N, 13.77%.

1-Ethyl-3-methyl-4,5-dicyanoimidazolium triflate (13d). White microcrystals (67%), mp 147–148 °C (from methanol–diethyl ether); δ_H (300 MHz, DMSO-d_6) 9.79 (1 H, s), 4.44 (2 H, q, *J* 7.1, CH_2CH_3), 4.05 (3 H, s, CH_3), 1.49 (3 H, t, *J* 7.1, CH_2CH_3); δ_C (75 MHz, DMSO-d_6) 142.0, 120.6 (q, *J* 319.9, CF_3), 115.9, 114.5, 106.1, 106.0, 46.5, 36.9, 13.9. Found: C, 34.84; H, 2.78; N, 17.55. Calc. for $C_8H_{10}N_4O_4S$: C, 34.84; H, 2.92; N, 18.06%.

Procedure for the preparation of 1,3-dimethyl-4,5-dicyanoimidazolium methyl sulfate (13b)

To a solution of 1-methyl-4,5-dicyanoimidazole **12a** (1.8 g, 13.6 mmol) in chloroform (25 cm^3) was added methyl fluorosulfonate (13.6 mmol, 1.07 cm^3) at 20–25 °C under nitrogen. The mixture was stirred at 20–25 °C for 48 h. The precipitate of 1,3-dimethyl-4,5-dicyanoimidazolium fluorosulfonate **13a** was collected by filtration. Dissolution of **13a** in methanol resulted in methanolysis of the anion to methyl sulfate. 1,3-Dimethyl-4,5-dicyanoimidazolium methyl sulfate **13b** was isolated by precipitation with diethyl ether and was recrystallized from methanol–diethyl ether as white microcrystals (2.5 g, 71%), mp 134–139 °C (from methanol–diethyl ether); δ_H (300 MHz, DMSO-d_6) 9.69 (1 H, s), 4.06 (6 H, s, 2 × CH_3), 3.37 (3 H, s, CH_3SO_4); δ_C (75 MHz, DMSO-d_6) 142.6, 115.6, 106.1, 52.9, 36.9. Found: C, 37.13; H, 3.80; N, 21.64. Calc. for $C_8H_{10}N_4O_4S$: C, 37.21; H, 3.90; N, 21.69%.

General procedure for the preparation of imidazolium bis(triflyl)imides (3b, 5b, 7b, 10b, and 13c)

An aqueous solution of $LiNTf_2$ (0.29 g, 1 mmol, in 15 cm^3 of water) was added to an aqueous solution of the appropriate salt **3a**, **5a**, **7a**, **10a**, or **13b** (1 mmol in 15 cm^3 of water) at 20–25 °C. The reaction mixture was stirred either at 20–25 °C for 1 h (**3b** or **7b**) or at 30 °C for 3 h (**5b**, **10b** and **13c**). Then dichloromethane (25 cm^3) was added and the mixture was stirred for an additional 20 min to extract the product and the organic phase was separated. The product was twice extracted with dichloromethane in the same manner. The combined extracts were dried over sodium sulfate and the solvent was removed under reduced pressure using a rotary evaporator over 5 h to give the corresponding bis(triflyl)imides in 50–75% isolated yields.

1,3-Dimethyl-4-nitroimidazolium bis(triflyl)imide (3b). Colorless liquid (59%), T_g −41 °C (from dichloromethane); δ_H (360 MHz, DMSO-d_6) 9.37 (1 H, s), 9.02 (1 H, d, J 1.8), 4.08 (3 H, s, CH_3), 3.92 (3 H, s, CH_3); δ_C (90 MHz, DMSO-d_6) 139.8, 125.60, 119.4 (q, J 320.0, CF_3), 37.0 (N–CH_3), 36.99 (N–CH_3).

1-Ethyl-3-methyl-4-nitroimidazolium bis(triflyl)imide (5b). Colorless liquid (74%), T_g −45 °C (from dichloromethane); δ_H (360 MHz, DMSO-d_6) 9.46 (1 H, d, J 1.6), 9.14 (1 H, d, J 1.6), 4.28 (2 H, q, J 7.3, CH_2CH_3), 4.08 (3 H, s, CH_3), 1.46 (3 H, t, J 7.3, CH_2CH_3); δ_C (90 MHz, DMSO-d_6) 139.0, 124.4, 119.4 (q, J 319.8, CF_3), 45.9 (N–CH_2), 37.0 (N–CH_3), 14.5 (CH_2CH_3).

1,2,3-Trimethyl-4-nitroimidazolium bis(triflyl)imide (7b). Colorless needles (68%), mp 111–112 °C (from dichloromethane); δ_H (360 MHz, DMSO-d_6) 9.00 (1H, s), 4.00 (3 H, s), 3.85 (3 H, s), 2.72 (3 H, s); δ_C (90 MHz, DMSO-d_6) 148.8, 125.2, 119.4 (q, J 319.6 CF_3), 35.8 (N(3)–CH_3), 35.0 (N(1)–CH_3), 10.2 (C(2)–CH_3).

1,3-Dimethyl-2-nitroimidazolium bis(triflyl)imide (10b). White microcrystals (53%), mp 74–75 °C (from dichloromethane); δ_H (360 MHz, DMSO-d_6) 8.10 (2 H, s), 4.13 (6 H, s, 2 × CH_3); δ_C (90 MHz, DMSO-d_6) 139.4, 125.1, 119.7 (q, J 257.4, CF_3), 39.6 (N–CH_3).

1,3-Dimethyl-4,5-dicyanoimidazolium bis(triflyl)imide (13c). White microcrystals (71%), mp 107–108 °C (from dichloromethane); δ_H (360 MHz, DMSO-d_6) 9.67 (1 H, s), 4.06 (6 H, s, 2 × CH_3); δ_C (90 MHz, DMSO-d_6) 142.5, 119.4 (q, J 319.7, CF_3), 115.5, 106.0, 36.9 (N–CH_3).

Analyses

Melting points of the isolated salts were determined by differential scanning calorimetry (DSC) using a TA Instruments model 2920 Modulated DSC (New Castle, DE) cooled with a liquid nitrogen cryostat. The calorimeter was calibrated for temperature and cell constants using indium (melting point 156.61 °C, ΔH 28.71 J g^{-1}). Data were collected at constant atmospheric pressure, using samples between 10–40 mg in aluminium sample pans. Experiments were performed heating at 5 °C min^{-1}. The DSC was adjusted so that zero heat flow was between 0 and −0.5 mW, and the baseline drift was less than 0.1 mW over the temperature range 0–180 °C. An empty sample pan was used as reference.

Thermal decomposition temperatures were measured in the dynamic heating regime using a TGA 2950 TA Instrument under a helium atmosphere. Samples between 2–10 mg were heated from 40–500 °C under constant heating at 5 °C min^{-1}.

X-Ray crystallographic studies

Samples were recrystallized from methanol by trituration with diethyl ether at 25 °C. Single crystals were collected in air, mounted on fibers and transferred to the goniometer. The crystals were cooled to −100 °C with a stream of nitrogen gas and data were collected on a Siemens SMART diffractometer with a CCD area detector, using graphite monochromated MoKα radiation. The SHELXTL software, version 5, was used for solutions and refinements.[59] Absorption corrections were made with SADABS.[60] Each structure was refined by full-matrix least-squares on F^2.

In each structure, the atoms were readily located and the positions of all non-hydrogen atoms were refined anisotropically. The hydrogen atoms (except for those associated with the disordered anion in **13b**) were added in approximated positions and allowed to refine unconstrained in order to obtain proper close contact interactions.

Disorder was observed for the methyl sulfate anion in **13b** with two positions each at 50% occupancy resolved for O1, O2, and O3. These three atoms were refined in alternate least-squares cycles from their disordered counterparts (O1A, O2A, and O3A). The remaining atoms in the anion (S1, O4, and C10) were refined at full occupancy. No attempt was made to include the methyl hydrogen atoms associated with C10 in the refinement.

Acknowledgements

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