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14. ABSTRACT
Our work on the topic of Energetic Ionic Liquids has focused on (i) fundamental understanding of ILs (azolium cation based and azolate anion based salts), (ii) the effect of different (energetic) substitution patterns on the overall properties of the developed systems (nitro, amino, cyano substituted molecules), (iii) compartmentalized molecular level design of a wide range of new energetic materials (through analysis of homological series of salts), as well as, (iv) novel performance enhancement and delivery options (formation of eutectic mixtures or halide free synthesis). Additionally, from a strictly energetic material application point of view, the discovered flexibility and modularity of ILs may, for example, allow for a unique delivery system for energetic fluids: one ion can be fine tuned for its energy content, while the second ion can be independently fine tuned to provide oxygen balance, and the optimal physical properties, or vice-versa. IL strategies can also take advantage of the dual nature of ILs to realize property enhancement, safe delivery options, increased handling safety due to its liquid form and no vapor pressure, and possibility of on-site, on-demand formation.

15. SUBJECT TERMS
Energetic Ionic Liquids, Energetic materials, Thermal properties

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FINAL REPORT

Project Title:
Energetic Ionic Liquids: Fundamental Studies Relating
Target Structures and Key Physical Properties

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I. OBJECTIVES

Synthesis, using existing, and developed procedures, as well as, investigation of physical and chemical properties is directed toward development of an understanding of the criteria needed to model and predict Ionic Liquid (IL) materials incorporating energetic and complementary properties. Using a matrix/systematic screening approach, a fundamental understanding of model compounds provides core information about key component interactions that will lead to the design of new energetic ILs.

1. The key objectives and experimental approach include:
   i. **Synthesis.** Synthetic efforts were not directed *a priori* to the preparation of energetic fluids, but rather to synthesizing new materials (in particular incorporating energetic functions) that will enable the links between chemical functionality and physical and thermodynamic properties to be developed. We are taking advantage of the opportunity to introduce independent design control of the IL properties through modification of the cation, the anion, or both. This design approach can be used as a platform strategy to deliver different functional attributes, in the corresponding cationic and anionic components of an IL, while retaining the core desirable features of the IL state of matter, and has applicability in many different materials areas.
   ii. **Evaluation.** The relationship of structural contributions to the fluid properties of the materials produced are being evaluated using DSC and TGA techniques. The use of computational methods are increasing our understanding of the structural contributions through modeling of the fundamental properties of the energetic ILs.
   iii. **Codification**
   Accurate Thermochemical Properties for Energetic Materials Applications.
   A computational approach for the prediction of the heats of formation ($\Delta H_f°$s) of solid-state energetic salts from electronic structure and volume-based thermodynamics (VBT) calculations will be developed

2. The research is directed toward answering the following key questions:
   i. What is the effect of incorporating 'energetic components' on the IL properties of the salts?
   ii. What makes an 'IL' more energetic?
   iii. Can energetic, thermodynamic, and IL-sustaining requirements all be combined in a single material?

II. STATUS OF EFFORT

Synthesis and Characterization. Synthesis of candidate ILs with energetic cationic or anionic components has been undertaken. IL salts of protonated, quaternized, nitro- and nitrile-substituted imidazolium cations have been prepared and isolated with methylsulfate, bis(trifluoromethylsulfonyl)imide, triflate, nitrate, and picrate anions. In addition, the group of energetic azolate anion-based energetic ILs has been prepared in combination with tetraalkylammonium and 1-butyl-3-methylimidazolium cations. Thermophysical investigations of these salts using DSC and TGA were performed to identify and quantify melting points, upper liquid limit, and decomposition profiles.

Examples from all the series of prepared salts, protonated, alkylated, and nitro-functionalized imidazolium alkylsulfate, nitrate, and picrates, as well as, azolate based ILs have been characterized by single crystal X-ray diffraction.

Preparation of imidazolium salts containing multiple nitro-substituents to a central imidazole ring has been shown to be limited and resulted in a set of new definitions concerning IL synthesis protocols. The concept of nitro-substituted, stable azolate anions as an alternative for unstable nitro-substituted imidazolium cations has been explored and proven. We have shown that multiple nitro-substitutions can activate heterocyclic rings to electron-addition and formation of energetic *anionic* species. Synthesis protocols, as well as, product characterization has been performed resulting in a set of new definitions relating structure of the salt to its thermal properties.

III. ACCOMPLISHMENTS

Synthesis and Investigation of Energetic ILs. As our approach has broadened (energetic cations, common energetic anions, azolate-based energetic anions, etc.) and we moved from commercially available to newly synthesized components (e.g., anions and cations or cation forming bases), we have been able to identify and prepare a large set of IL materials for further evaluation. Physical characteristics of the ILs and organic salts (melting point, thermal stability, decomposition temperature, etc.) have been investigated using Differential Scanning Calorimetry and Thermogravimetric Analysis. A number of solid salts have been isolated as crystalline materials and the single crystal X-ray structures of these have been determined. Analysis of the changes in ion-ion interactions in the solid state and comparison with relative changes in melting point characteristics is providing significant insight into the liquid behavior of the samples. Additionally, we have developed a computational approach to (i) predict the thermodynamics for forming a variety of imidazolium-based salts and Ionic Liquids and (ii) predict the heats of formation ($\Delta H_f°$s) of solid-state energetic salts from electronic structure and volume-based thermodynamics (VBT) calculations.

IV. BACKGROUND

Our approach was directed toward fostering development of new EILs from our modular design perspective to select and synthesize target compounds that separately implement each specific property needed for an ideal composition of ions. Thus, we are trying to take advantage of the dual-functional nature of ILs, which in concept and in practice, allows for the modular, interchangeable use of ions to achieve desired chemical and physical properties (Table 1). Additionally, we have envisioned that due to the ionic composition of those salts, each ion component of the product can be tuned separately and brought to the final product in the last step of synthesis. Thus, each component, anion and cation, may be independently modified towards the desired final material, through incorporation and modification of functional groups (Figure 1).

Table 1. Performance requirements for EILs.

Physical Properties		**Thermal stability**	
Melting point	< -40 °C	TGA (75 °C, isothermal)	< 1% loss of material over 24 h
Surface tension	< 100 dyne cm^{-1}	TGA (rate 10 °C/min)	> 120 °C for T_{decomp}
Density	> 1.4 g cm^{-3}	**Thermodynamic properties**	
Viscosity	As low as possible	Heat of formation	as positive as possible
Hazard Sensitivity		Heat of combustion	> 6 kcal g^{-1}
Impact	> 50 kg cm	**Toxicology**	
Friction	> 120 N	LD_{50}	> 0.5 g kg^{-1}
Detonation Electrostatic discharge	> 5000 V at 0.25 J	AMES	Negative

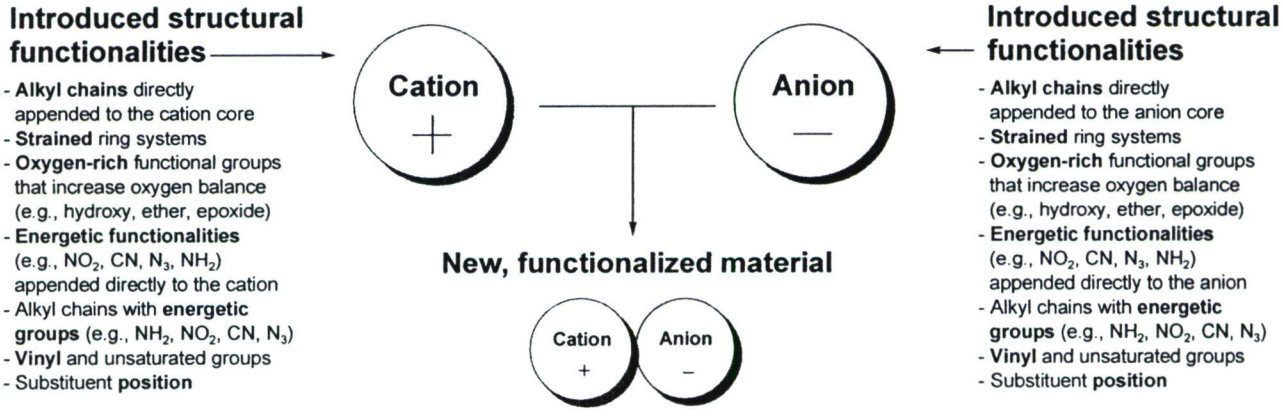


Figure 1. Independent design of components in multifunctional EILs.

We have directed our approach toward understanding how EILs might be designed from a modular design perspective. That is, each targeted property (e.g., melting point, density, viscosity, long term thermal stability, etc.) is investigated separately to allow for a better understanding of how structural modification in *either ion* affects the IL properties as a whole. This knowledge allows us to develop an 'IL toolbar', from which a variety of IL design options can be brought to bear on any synthetic scheme based on the desired set of final IL properties.

V. TECHNICAL SUMMARY OF THE WORK ACCOMPLISHED.

Synthesis and extensive experimental, and crystallographic analysis of the properties of protonated ILs, including nitro substituted 1-alkyl-3-H-imidazolium and 1-alkyl-2-methyl-3-H-imidazolium nitrate and picrate salts

1. **Stability and thermal decomposition of quaternary and protonated imidazolium nitrate and picrate salts.** Holbrey, J. D.; Reichert, W. M.; Smiglak, M.; Spear, S. K.; Yang, H.; Manju, K.; Kirichenko, K.; Katritzky, A. R.; Thrasher, J. S.; Sun, L. Y.; Rogers, R. D.; *Proceedings - Electrochemical Society*, 2004-24 (Molten Salts XIV), 2006, 396-406.

For our first research goal, we selected the most straightforward, fast, and simple synthetic approach for the formation of ILs via acid-base neutralization reaction to form protonated azolium-based salts. The hypothesis behind this choice was that the easier the product can be synthesized (manufactured), the more likely it could find an application as energetic material.

Utilizing the cation module, a variety of imidazole-based compounds (Figure 2) were initially selected based on their substitution patterns and homological differences in the imidazole ring structure. Supported by the expertise provided by the heterocyclic chemistry group of Prof. A. R. Katritzky, systematic changes were implemented in the substitution patterns of N-alkyl imidazole cores, ranging from C-alkylsubstituted, to energetically substituted cations (NO_2 and CN groups directly appended to the imidazolium core) (synthesis of azolium cores described in Appendix A1). This approach allowed us to screen a large range of products and to evaluate their properties in terms of usefulness to EILs. Protonated picrate and nitrate salts of imidazole based cores were prepared using defined synthetic protocol (See Appendix A1) and characterized for their thermal properties.

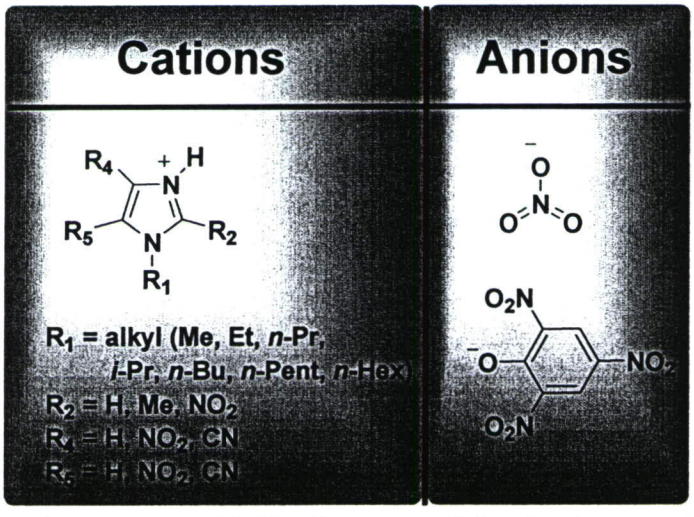


Figure 2. Investigated protonated imidazolium cores with functional groups appended to the heterocyclic core.

The initial melting point analysis revealed that generally, due to the size and shape of the anion, the nitrate salts exhibit significantly lower melting points than their picrate equivalents (Table 2) (See Appendix B1). Thermogravimetric analyses (TGA) of nitro-substituted and non-substituted protonated imidazolium salts revealed that thermal stabilities range from ~70 - 200 °C, with picrate salts exhibiting higher stabilities (by ~40 °C) than nitrate salts (See Appendix B1). Disappointingly, however, the thermal stabilities of these protonated salts were significantly lower then those of alkylated derivatives (Figure 3).

Overall, the melting points of the protonated ILs we studied were in acceptable ranges, and the overall structure/property trends were satisfactory. However, the relatively narrow liquidus ranges, and especially the low temperatures of decomposition are problematic. In order for this class of compounds to be considered further, new design options are needed to overcome these limitations.

Obtained and analyzed crystal structures are disclosed in Appendix C1.

Table 2. Influence of substitution patterns on the melting point of protonated EILs (representative data).

Cation	Picrate (mp °C)	Nitrate (mp °C)
1-methyl-3-H-imidazolium	159	59
1-hexyl-3-H-imidazolium	40	1
1,2-dimethyl-3-H-imidazolium	181	79

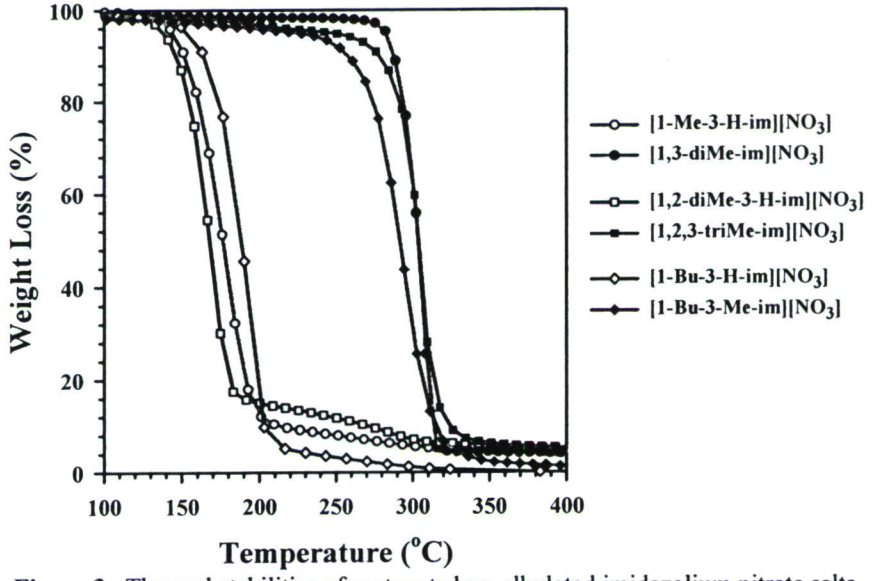


Figure 3. Thermal stabilities of protonated vs. alkylated imidazolium nitrate salts.

In general:

- Picrate protonated, not nitro substituted imidazolium salts are more thermally stable than their nitrate equivalents
- C(2)-Me substituted picrate salts tend to be more stable than those not substituted

- By changing the position of NO_2 group from C(2) to C(4) the increase of the stability is observed for both nitrates and picrates, while the melting points for those pairs don't change significantly (difference below 20 °C)
- Generally the decomposition temperatures for the nitrates and picrate salts substituted with a NO_2 group seems to be ~20-50 °C lower than those of not nitro substituted cations
- From the group of over 30 compounds investigated, more than half of them (also with NO_2 substituents) melt below 100 °C, and among them 9 are liquid at room temperature or below

Characterization of energetic ILs in terms of their ability to combust

1. **Combustible ionic liquids by design: Is laboratory safety another ionic liquid myth?** Smiglak, M.; Reichert, W. M.; Holbrey, J. D.; Wilkes, J. S.; Sun, L.; Thrasher, J. S.; Kirichenko, K.; Singh, S.; Katritzky, A. R.; Rogers, R. D.; *Chemical Communications* **2006**, *24*, 2554-2556.
2. **Combustible ionic liquids by design: Destroying another ionic liquid myth.** Smiglak, M.; Reichert, W. M.; Holbrey, J. D.; Wilkes, J. S.; Sun, L.; Thrasher, J. S.; Rogers, R. D., Abstracts of Papers, 231st ACS National Meeting, Atlanta, GA, United States, March 26-30, 2006, IEC-103.

In collaboration with Dr. John Wilkes, from the U.S. Air Force Academy, we tested a wide variety of salts for their ability to ignite, and found them to readily combust (and thus destroyed another myth regarding the overgeneralized safety of ILs) (Figure 4). Our preliminary results suggest that the analyzed ILs are not flammable *per se*, but rather a potential hazard may source form they gaseous decomposition products.

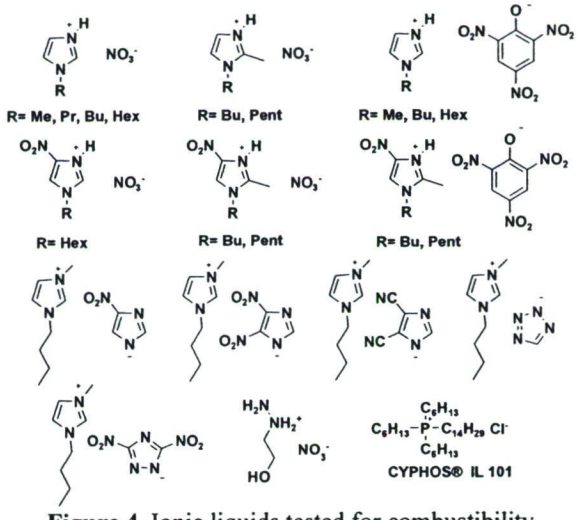


Figure 4. Ionic liquids tested for combustibility

To better understand this decomposition and the energetic character of the ILs, we studied these salts using TGA and accelerating rate calorimetry (ARC) in collaboration with Dr. Joseph S. Thrasher from The University of Alabama. The results suggest vigorous exothermic decomposition reactions occur in protonated EILs, which results in large amounts of thermal energy and highly flammable (combustible) gases, which can easily ignite upon contact with a flame source. Additionally, it was observed that in comparison with Cl^- salts of the same cations, nitrate and picrate anions have an additional positive influence on the rapid exothermic decomposition processes, thereby making these anions suitable candidates for future design of other EILs.

Investigation of thermal properties and stability behavior, as well as, influence of the energetic substituents on the properties of alkylated energetic imidazolium cations: Nitro- and Nitrile-substituted N,N'-dialkylimidazolium salts

1. **Strategies toward the design of energetic ionic liquids: nitro- and nitrile-substituted N,N'-dialkylimidazolium salts.** Katritzky, A. R.; Yang, H.; Zhang, D.; Kirichenko, K.; Smiglak, M.; Holbrey, J. D.; Reichert, W. M.; Rogers, R. D.; *New Journal of Chemistry* **2006,** *30*, 349-358.

In comparison with the work on the protonated imidazolium based EILs, we next focused on the use of permanent cations (e.g., N,N'-dialkylimidazolium), and addition of energetic $-NO_2$ or -CN modifications to the cation core in order to increase the thermal stability of the salts over the protonated analogs. To simplify the systems, we initially focused on using commonly known IL-forming anions such as methylsulfate, triflate, and bistriflimide (Figure 5).

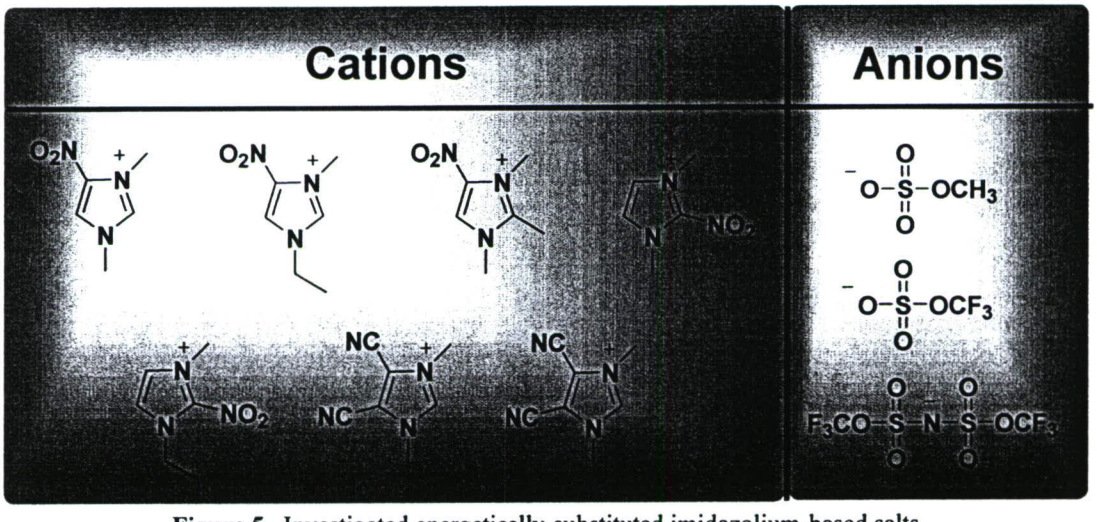


Figure 5. Investigated energetically-substituted imidazolium-based salts.

In general, the methylsulfate and triflate salts exhibited melting points in the range of 70 °C to 140 °C. We thus paired the cations with the bistriflimide (NTf_2^-) anion, known to result in lower melting, less viscous ILs. Salts of 1,3-dimethyl-4-nitroimidazolium and 1-ethyl-3-methyl-4-nitroimidazolium with this anion were indeed found to be low melting, with melting points close to room temperature (18 - 35 °C). Comparing our results with those reported by Shreeve and co-workers, for iodide, perchlorate, and nitrate salts, further indicates how anions affect melting points. Additionally, comparing those results with data for 1,2,3-trimethyl-4-nitroimidazolium salts, the effect of a methyl group attached to the C2 position of the imidazolium ring can be clearly seen in this set (increase in the melting point when the C2 position in the imidazolium ring is alkylated) (Table 3).

Table 3. Influence of anion type and C2 methyl group substitution on the melting points of resulted salts.

Cation / Anion	I^-	ClO_4^-	NO_3^-	$CH_3SO_4^-$	NTf_2^-
1,3-dimethyl-4-nitroimidazolium	180	172	163	104	34
1,2,3-trimethyl-4-nitroimidazolium	191	182	161	150	110

Using crystalline analogs, we have also analyzed the effect of nitro substitution on crystal packing of five nitro-appended imidazolium salts. No major hydrogen-bonding or directional close contacts were observed, suggesting that in the solid state, the nitro group has a very limited effect, beyond its steric contribution, in the crystal packing. This indeed suggests that the nitro substituents can be added without major increases of the resulting salt melting points.

Also importantly, TGA analyses of these alkylated imidazolium-based salts revealed substantial improvement of the thermal stability compared to the protonated cation analogs. In most of the analyzed salts, the decomposition temperatures exceeded 220 °C, allowing consideration of this class of cations in the future design of EILs.

The synthesis of dinitro- and dicyano-substituted, alkylated and protonated alkylimidazolium salts, was attempted with limited success. Only the dicyano derivatives were isolated. The functionalization of these heterocycles with electron-withdrawing substituents such as NO_2 or CN, results in a reduction in nucleophilicity of the heterocycle, and thus a reduced ability to form quaternary salts by S_N2 alkylation, even with strong alkylating agents (e.g., methyltriflate or fluorosulfonate), or acids (e.g., nitric acid, picric acid). Indeed, the isolation of a co-crystal of 1-methyl-2,4-dinitroimidazole and picric acid (Figure 6 and Appendix C1) revealed, that due to the high electron density of the nitro groups attached to the imidazole core the nitrogen atom of the imidazole ring fails to undergo protonation and thus salt formation. Imidazolium salts with two nitrile substituents could be obtained only via the reaction of 1-methyl-4,5-dicyano-imidazole with the strong alkylating agents $MeOSO_2F$ and $(MeO)_2SO_2$.

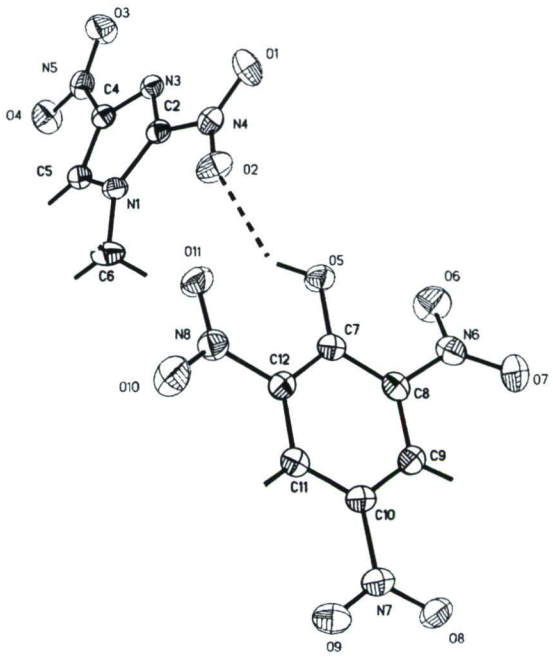


Figure 6. Cocrystal of unreacted 1-methyl-2,4-dinitroimidazole and picric acid; Yellow needles; $C_9H_5N_7O_{11}$; MW 387.20; Monoclinic; $P2_1$; a = 6.287(1) Å; b = 11.646(2) Å; c = 10.307(2) Å; β = 93.367(3)°; V = 753.3(2) Å^3; D_{calc} = 1.707 g cm^{-3}; R_1, wR_2 [$I > 2\sigma(I)$] = 0.0234, 0.0548; R_1, wR_2 (all data) = 0.0254, 0.0558.

Computational investigation of the properties of protonated and alkylated ILs, including nitro substituted 1-alkyl-3-H-imidazolium and 1-alkyl-2-methyl-3-H-imidazolium nitrate and picrate salts

1. **Prediction of the Formation and Stabilities of Energetic Salts and Ionic Liquids Based on ab Initio Electronic Structure Calculations.** Gutowski, K. E.; Holbrey, J. D.; Rogers, R. D.; Dixon, D. A.; *Journal of Physical Chemistry B* **2005**, *109*, 23196-23208.

We have developed a computational approach to predict the thermodynamics for forming a variety of imidazolium-based salts and Ionic Liquids. The gas-phase proton and methyl cation acidities of several protonating and methylating agents, as well as the proton and methyl cation affinities of methyl-, nitro-, and cyano-substituted imidazoles, have been calculated using DFT (B3LYP) and MP2 methods. These accurate values are used in conjunction with an empirical approach based on molecular volumes to estimate the lattice enthalpies and entropies of Ionic Liquids, organic solids, and organic liquids. A thermodynamic cycle was constructed (Figure 7) for salt formation to predict the ability to synthesize salts including ones with potentially high energetic densities.

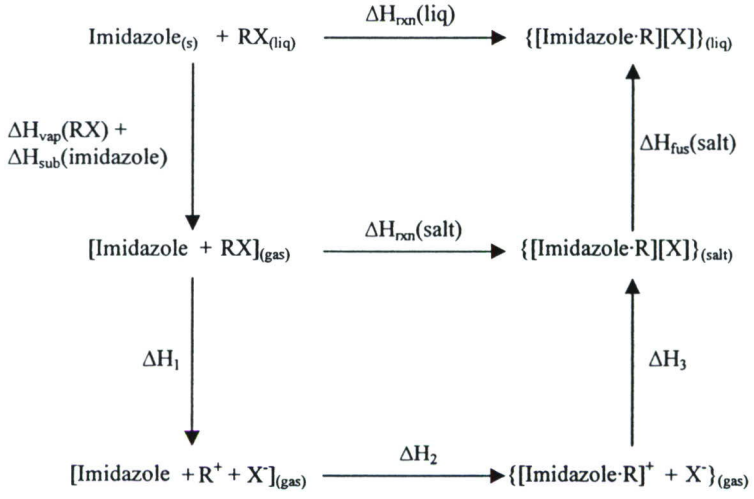


Figure 7. Thermodynamic cycle for salt formation.

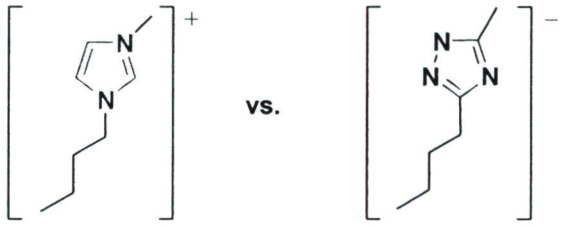
An adjustment of the gas phase thermodynamic cycle to account for condensed phase chemistries provides the best overall assessment. As substitution of the cation with electron-withdrawing groups increases, the triflate reagents appear to be the best protonating and methylating agents. Stronger alkylating agents should be considered to enhance the chances of synthetic success. When using the enthalpies of reaction for the gas phase reactants to form a salt, a cut-off value of -13 kcal mol^{-1} or lower (more negative) should be used as the minimum value for predicting whether or not a salt can be synthesized.

Synthesis and investigation of stability and thermal properties of azolate based ILs, along with crystal structure investigation of formed products

1. **1-Butyl-3-methylimidazolium 3,5-dinitro-1,2,4-triazolate: a novel ionic liquid containing a rigid, planar energetic anion.** Katritzky, A. R.; Singh, S.; Kirichenko, K.; Holbrey, J. D.; Smiglak, M.; Reichert, W. M.; Rogers, R. D.; *Chemical Communications.* **2005**, 868-870.
2. **In search of ionic liquids incorporating azolate anions.** Katritzky, A. R.; Singh, S.; Kirichenko, K.; Smiglak, M.; Holbrey, J. D.; Reichert, W. M.; Spear, S. K.; Rogers, R. D.; *Chemistry - A European Journal* **2006**, *12*, 4630-4641.

Unfortunately, even though the designed property (thermal stability) was greatly improved by changing from protonated cations to their alkylated analogs, the synthetic limitations for introducing energetic groups directly to the heterocyclic ring narrowed the range of available, reactive precursors suitable for cation formation. Nonetheless, these results led us to speculate that the addition of electron withdrawing groups to the neutral

imidazole will allow for the formation of stable azolate anions, where the tunability inherent in azolium cations could also be implemented in azolate anions (Figure 9).



1-butyl-3-methylimidazolium cation **3-butyl-5-methyltriazolate anion**

Figure 9. Similarity in the structural platforms for cation and anion tunability.

In collaboration with the Katritzky group, we thus synthesized a variety of energetically substituted azolate-anions that were later paired with common IL-forming cations (Figure 10) (See Appendix A2 for unpublished results). The resulting products were analyzed for their thermal behavior and initially assessed to be a very promising group of compounds that should be further studied (See Appendix B2). Obtained and analyzed crystal structures are disclosed in Appendix C2.

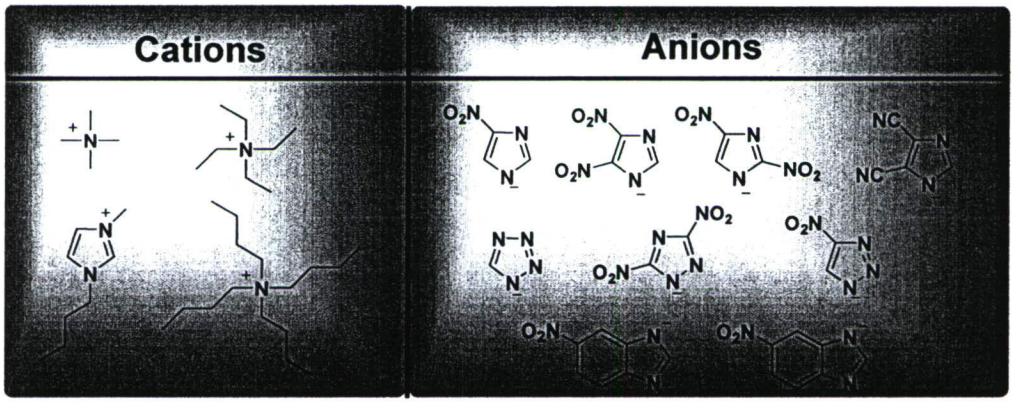


Figure 10. Investigated energetically substituted azolate based salts.

As expected, the melting points of the symmetric quaternary ammonium salts were insufficiently low and only in a few cases (e.g., tetraethylammonium and tetrabutylammonium azolates) recorded below 100 °C (See Appendix B2). We thus shifted our focus to the modification/tuning of the melting point and began introducing common IL-forming cations such as $[1\text{-Bu-3-Me-im}]^+$. As expected, pairing the dialkylimidazolium cations with energetically substituted azolate anions, often resulted in the formation of salts with very low melting points, reaching -82 °C in the case of [1-Bu-3-Me-im][tetrazolate] (Figure 11). In fact, all combinations of the $[1\text{-Bu-3-Me-im}]^+$ cation with the 9 azolate anions our group has studied resulted in the formation of room temperature ionic liquids.

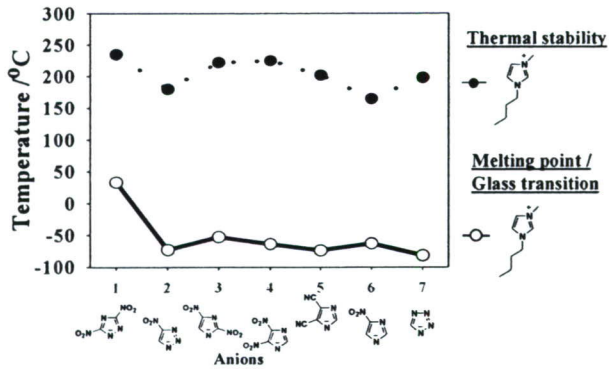


Figure 11. Liquid range and thermal stability of new azolium azolate ILs.

Nitrile-functionalized imidazolium-based ILs

In conjunction with the work described previously for the nitrile functionalization of the heterocyclic cores of azole-based IL-forming precursors, a related effort is underway to explore the physical and chemical properties that result from the energetic functionalization of N-alkyl side-chains of imidazolium-based cations. How do physical and chemical properties of an IL fluctuate with respect to changes in size and shape of the appended alkyl chain bearing an energetic function as well as with respect to the regiochemistry of the energetic function? The search for information to address this question remains a high goal, as an understanding of how modifications of the IL structure affect the resultant properties of synthetic targets may contribute to the overall knowledge of IL chemistry that will lend in its utility for a wide range of applications – such as energetic materials in this case.

From previous investigations, the cyano substituent has been noted to decrease melting points and increase density when incorporated into the structure of ILs. As these properties trends are congruent with the performance needs of the AFOSR, initially the cyano (-CN) group was introduced as an energetic function appended to N-ethyl chains by S_N2 alkylation reaction with bromopropionitriles. Variation in the position of the cyano group, as well as the length of N-alkyl chain length of 1-methyl and 1-butylimidazole starting materials (Appendix A3), are features modulated for the design of targeted energetic salts. Of related interest is the current effort for the synthesis of N-cyanomethyl-substituted methyl- and butylimidazolium cations; where a shortening of the appended N-alkyl chain from one to two carbons in length may be compared. Future work utilizes these IL salts as precursors for anion exchange, whereby the chloride and bromide innocuous anion may be exchanged with a common energetic anion (e.g., nitrate) (Figure 8). The analysis of these products should permit a comparison, then, of structural changes made in the imidazolium-based cations (change in nitrile position, change in alkyl chain length) and the resultant energetic properties in the nitrate salts while holding the anion structure constant.

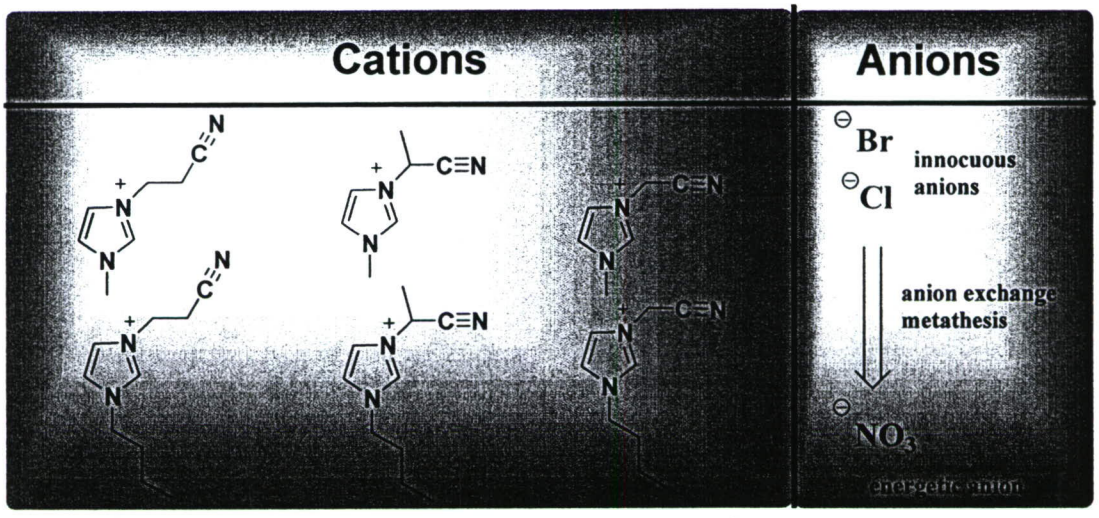


Figure 8. Targeted nitrile-substituted dialkylimidazolium salts.

TGA and DSC analyses have been obtained for both N-methyl and N-butyl derivatives of the N-(2-cyanoethyl) and N-(1-cyanoethyl) imidazolium bromide salts for comparison of thermal decomposition temperatures and melting point/glass transitions, respectively (Appendix for Thermal Analysis). Additionally, crystal structures have been obtained for both 1-(2-cyanoethyl)-3-methylimidazolium and 1-(1-cyanoethyl)-3-methylimidazolium bromide salts (Appendix for XRD). Additional work to obtain the N-cyanomethyl-substituted species as well as exchanging the halide anions of isolated ILs for the nitrate anion in all synthesized targets is underway.

Chemistry of the 1,3-dimethylimidazolium-2-carboxylate system in the reactions with different acids (e.g., HNO_3, HCl, H_2SO_4, HPF_6, etc.) and the behavior of isomers under different thermal and chemical conditions

1. **Ionic liquids via reaction of the zwitterionic 1,3-dimethylimidazolium-2-carboxylate with protic acids. Overcoming synthetic limitations and establishing new halide free protocols for the formation of ILs.** Smiglak, M.; Holbrey, J. D.; Griffin, S. T.; Reichert, W. M.; Swatloski, R. P.; Katritzky, A. R.; Yang, H.; Zhang, D.; Kirichenko, K.; Rogers, R. D.; *Green Chemistry,* **2007**, *9*, 90-98.

Our early EIL research has primarily focused on the investigation of the influence of cation and anion structures on the resulting physical and chemical properties of novel EILs. However, realizing the growing need for improved synthetic methodologies for the formation of new ILs, we have initiated a research program aimed at synthetic and delivery systems based on the IL platform. For example, by considering the dual-component nature of ILs, and the ability to independently design and introduce desired physical and chemical properties to both cationic and anionic components of the salts,

formation of the desired products can be achieved via separate synthesis of innocuous components of the final product (neutral or charged species), that can be later combined on-site and on-demand, resulting in the formation of targeted material and easy to remove byproducts.

Utilizing some of our previous work, we developed a synthetic methodology for halide- and metal-free, time- and cost-efficient, environmentally-sound synthesis of azolium salts, including azolium azolates, via reaction of azolium-2-carboxylate zwitterions with virtually any acid. This protocol allows for the formation of pure ILs without the need for elaborate purification, since the only byproduct present after complete reaction is CO_2, which can be removed under vacuum with moderate heating.

We have proven this concept with the reaction of 1,3-dimethylimidazolium-2-carboxylate with both inorganic and organic acids and found that this protocol generally works for all strong acids ($pK_a < 1$) without the need of a catalyst; and for weaker acids ($pK_a \sim 1$-10), with the addition of the Krapcho reaction catalyst DMSO (Figure 12). Moreover, this protocol can also be easily adapted to the synthesis of energetic azolium azolate salts. In addition, our recent work on the synthesis of the first imidazolium hydrogencarbonate salt, using carbonic acid in the decarboxylation reaction of zwitterionic dialkylimidazolium-2-carboxylates, opens more avenues for the halide-free formation of imidazolium salts.

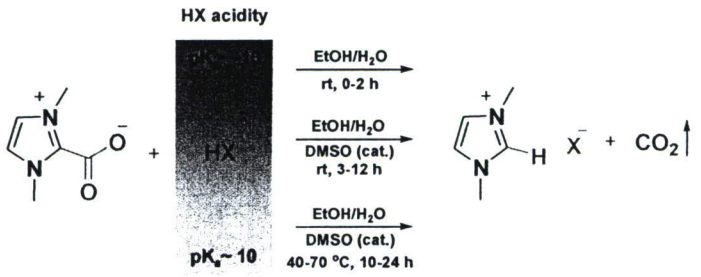


Figure 12. New, byproduct-free synthetic methodology toward the formation of ionic liquids.

Synthesis of hydrogen carbonate ionic liquids through the Krapcho reaction

1. **An Intermediate for the Clean Synthesis of Ionic Liquids: Isolation and Crystal Structure of 1,3-Dimethylimidazolium Hydrogen Carbonate Monohydrate** Bridges, N. J.; Hines, C. C.; Smiglak, M.; Rogers, R. D.; *Chemistry - A European Journal* **2007**, DOI: 10.1002/chem.200601792

Currently, the greatest problem that the IL field faces for fundamental studies is ion purity. Most non-halide ILs are synthesized through halide intermediates that are later metathesized to the desired IL. One of the proposed routes around halide contamination is to have a stable yet reactive anion that can easily be removed through a reaction yielding volatile byproducts (e.g., CO_2, H_2O, CH_3OH, etc.). An alternative route to yield a large variety of ion-pure ILs through the synthesis of a stable intermediate was described above.

In the past few years it has been recognized that to achieve the goal of ultra-pure ILs, the effort can no longer be focused on improvement of currently used purification techniques; rather focus should be on the design of synthetic routes for formation of ILs in processes that assure contaminant-free products. Thus, highly desirable, clean, contaminate-free intermediates for a variety of ILs could come from a class of anions which can easily be used by further metathesis reactions, leaving no by-products or original anions, even in trace amounts. One approach was to have a reactive anion which could react to the desired product or into an inert by-product. The carbonate anion, due to its clean decomposition to gaseous CO_2 and H_2O in the presence of stronger acids, would be an ideal candidate.

The synthesis of the stable [1,3-diMIM][HCO_3] was made possible through the manipulation of H_2O, CO_2, pressure, and temperature, proceeding through the Krapcho mechanism (Figure 13).

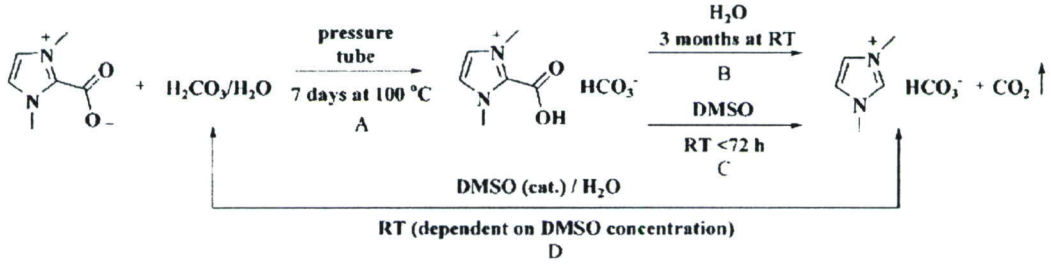


Figure 13. Synthesis routes to 1,3-dimethylimidazolium hydrogen carbonate salt

The isolation of a single crystal confirmed the synthesis route as NMR spectroscopy was not sufficient in this case. The [1,3-diMIM][HCO_3] is not thermodynamically stable in the presence of some common organic solvents (i.e., DMSO or CH_3OH) but it shows sufficient kinetic stability that allows for reactions to be conducted in a timely manner with no adverse effects.

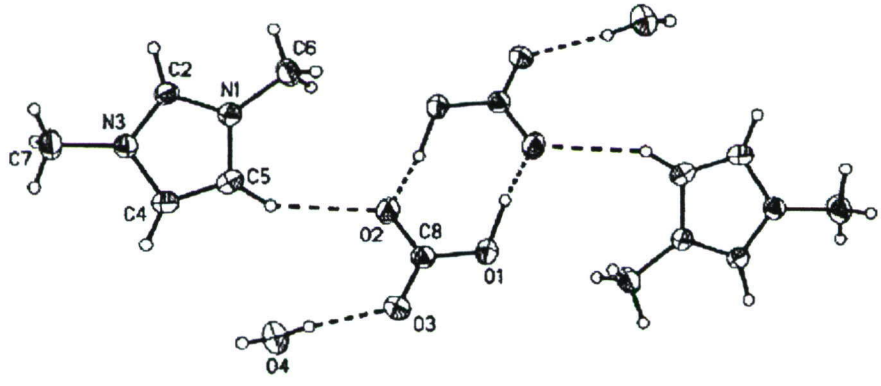


Figure 14. Crystal structure of 1,3-dimethylimidazolium hydrogen carbonate (hydride)

Azolium Azolates via the 1,3-dimethylimidazolium-2-carboxylate system

1. **Halide free synthesis of energetic azolium azolate salts.** Smiglak, M.; Drab, D. M.; Hines, C. C.; Reichert, W. M.; Rogers, R. D.; Kirichenko, K.; Vincek, A., Abstracts of Papers, 232nd ACS National Meeting, San Francisco, CA, United States, Sept. 10-14, 2006, PHYS-522.

Analyzing all of the thermal behavior for the azolium azolate salts we studied, we concluded that this platform is valuable for the development of novel energetic materials. Additionally, analysis of current research progress in this field suggests a range of possible target ions (Figure 15) that could be considered, after slight structural modifications if necessary, as valuable precursors for the formation of other energetic azolium azolate salts.

Until very recently, formation of azolium azolates was only obtainable through ion exchange metathesis reactions, or in limited cases (when differences in the pKa values of the substrates permitted), via Brønsted acid-base neutralization reactions. Our current efforts toward the development of a new synthetic route for obtaining azolium azolates allow for the formation of energetic salts through one-pot synthesis with easy to remove byproducts (methanol and CO_2) – avoiding halide and metal impurities.

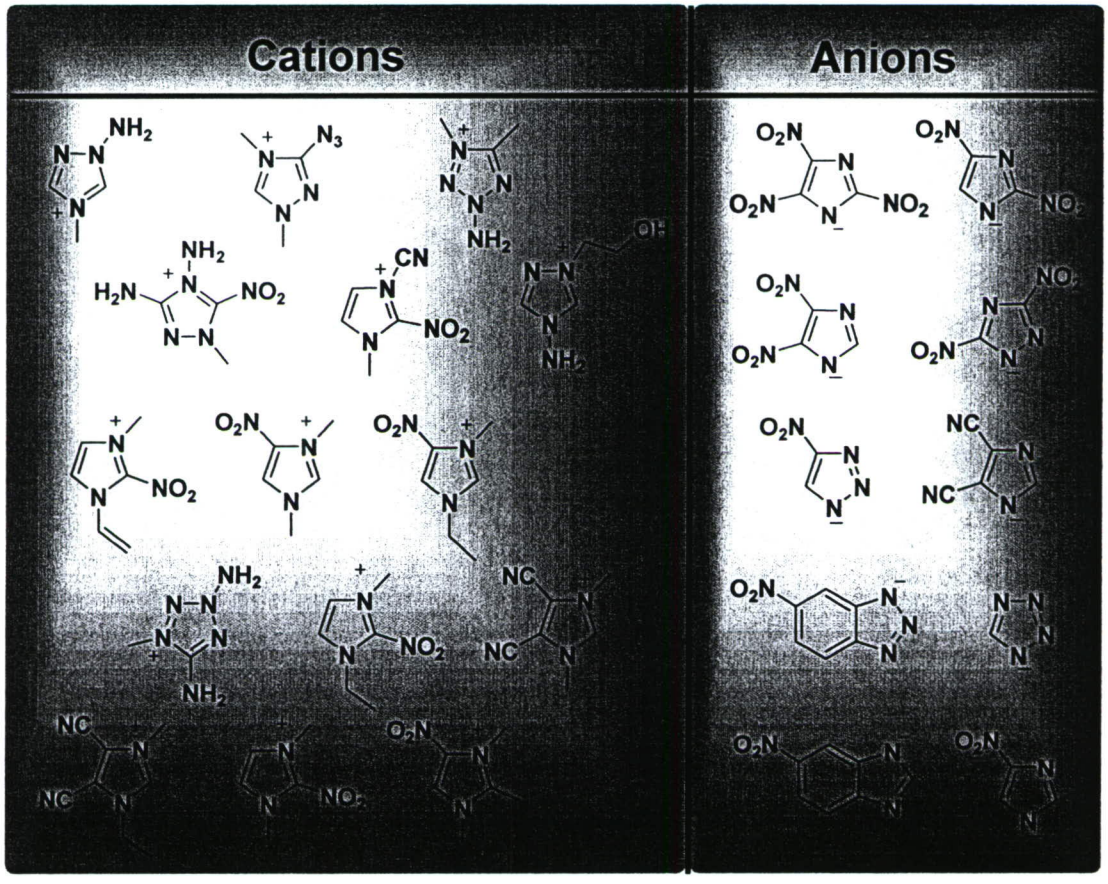


Figure 15. Examples of possible ions leading to azolium azolate EILs.

Previously reported routes to produce 1,3-dimethylimidazolium salts via the reaction of the 1,3-dialkylimidazolium-2-carboxylate zwitterion with protic acids (**H**-B) were reinvestigated in detail in order to determine and overcome the limitations and difficulties associated with this synthesis. This allows for wider utilization of this protocol for the preparation of ILs including azolium azolates via halide-free routes as shown in Figure 16 (See Appendixes A4, B4, and C3). By application of the new protocols to more sophisticated systems, the formation of azolium azolates is easily accessible when certain requirements are fulfilled: (i) the precursor of the cation must incorporate 2-COO^- species appended directly to the azolium ring, and (ii) the acidic proton of the neutral azole (**H**-Az) must have a lower pKa value than that of the proton at the C-2 position in the decarboxylated azolium cation.

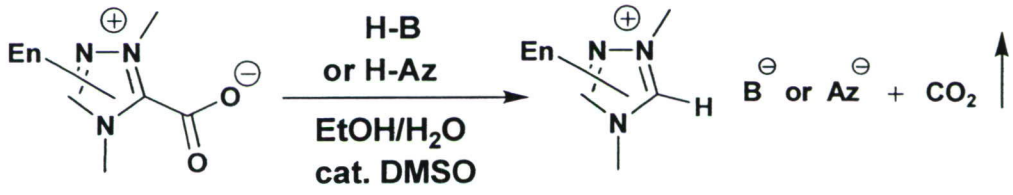


Figure 16. One-pot, halide free synthesis of azolium salts including azolate anion species.

Computational analysis of H_f of EILs

1. **Accurate Thermochemical Properties for Energetic Materials Applications. I. Heats of Formation of Nitrogen-Containing Heterocycles and Energetic Precursor Molecules from Electronic Structure Theory**. Gutowski, K. E.; Rogers, R. D.; Dixon, D. A.; *Journal of Physical Chemistry A* **2006**, *110*, 11890-11897.
2. **Accurate Thermochemical Properties for Energetic Materials Applications. II. Heats of Formation of Imidazolium-, 1,2,4-Triazolium-, and Tetrazolium-Based Energetic Salts from Isodesmic and Lattice Energy Calculations.** Gutowski, K. E.; Rogers, R. D.; Dixon, D. A.; *Journal of Physical Chemistry* ACS ASAP.

The heats of formation of 1H-imidazole, 1H-1,2,4-trizazole, 1H-tetrazole, CH_3NO_2, CH_3N_3, CH_3NH_2, CH_2CHNO_2, $HClO_4$, and phenol, as well as, cations and anions derived from some of these molecules have been calculated using ab initio molecular orbital theory methods (Figure 17). These molecules are important as models for compounds used for energetic materials synthesis. The predicted heats of formation of the heterocycle-based compounds are in excellent agreement with available experimental values (within <1 kcal/mol). The heats of formation of the nitro and amino molecules, as well as, phenol/phenolate, also are in good agreement with the experimental values (<1.5 kcal/mol). The heat of formation of CH_3N_3 is predicted to be 72.8 kcal/mol at 298 K with an estimated error bar of ± 1 kcal/mol on the basis of the agreement between the calculated and experimental values for $\Delta H_f(HN_3)$. The heat of formation at 298 K of $HClO_4$ is -0.4 kcal/mol, in very good agreement with the experimental value, as well as, a

W2 literature study. An extrapolation of the CCSD(T)/aug-cc-pV(Q,5) energies was required to obtain this agreement. These results are currently used for the prediction of the heats of formation of energetic salts using isodesmic and lattice energy calculations.

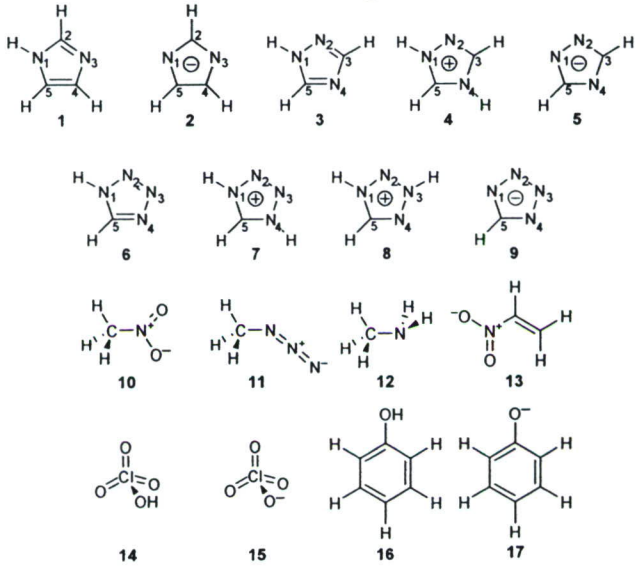


Figure 17. Model molecules used for calculations of ΔH_f of energetic materials.

In the later article, a computational approach for the prediction of the heats of formation ($\Delta H_f°$s) of solid-state energetic salts from electronic structure and volume-based thermodynamics (VBT) calculations has been developed. The method uses as its starting point $\Delta H_f°$s for energetic precursor molecules and ions as described above. The $\Delta H_f°$s of more complex energetic species such as substituted imidazole-, 1,2,4-triazole-, and tetrazole molecules and ions containing amino, azido, and nitro (including methyl) substituents, are calculated using an isodesmic approach at the MP2/complete basis set (CBS) level. This isodesmic approach is accurate to <3 kcal/mol for the predicted cation and anion $\Delta H_f°$s on the basis of comparisons to experimental data. The $\Delta H_f°$s of the energetic salts in the solid state are derived from lattice energy (U_L) calculations using a VBT approach. Improved values for the α and β parameters of 19.9 (kcal·nm)/mol and 37.6 kcal/mol for the U_L equation were obtained on the basis of comparisons to experimental U_Ls for a series of 23 salts containing ammonium, alkylammonium, and hydrazinium cations. The total volumes are adjusted to account for differences between predicted and experimental total volumes due to different shapes of the ions (flat vs. spherical). The predicted $\Delta H_f°$s of the energetic salts are estimated to have error bars of 6 to 7 kcal/mol, on the basis of comparisons to established experimental $\Delta H_f°$s of a subset of the salts studied. Energetic salts with the highest positive $\Delta H_f°$s are predicted for azido-containing cations, coupled with heterocyclic anions containing nitro substituents. The substitution of functional groups on carbon versus nitrogen atoms of the heterocyclic cations has interesting stabilization and destabilization effects, respectively. The use of revised U_Ls was also shown to improve the agreement between predictions and experimental observations for our previous study on the formation and stabilities of energetic salts and ILs

VI. PERSONNEL SUPPORTED:

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The University of Florida

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Dr. Kavita Manju (Postdoctoral Researcher)
Hongfang Yang (Graduate Student)
Dazhi Zhang (Graduate Student)
Shailendra Singh (Graduate Student)
Adam S. Vincek (Graduate Student)

VII. PUBLICATIONS (BETWEEN JUNE 1, 2003 – DEC 31, 2006)

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2. Gutowski, K. E.; Holbrey, J. D.; Rogers, R. D.; Dixon, D. A. "Prediction of the Formation and Stabilities of Energetic Salts and Ionic Liquids Based on ab Initio Electronic Structure Calculations" *J. Phys. Chem. B,* **2005**, *109*, 23196-23208.
3. Holbrey, J. D.; Reichert, W. M.; Smiglak, M.; Spear, S. K.; Yang, H.; Manju, K.; Kirichenko, K.; Katritzky, A. R.; Thrasher, J. S.; Sun, L. Y.; Rogers, R. D. "Stability and Thermal Decomposition of Quaternary and Protonated Imidazolium Nitrate and Picrate Salts" In Molten Salts XIV: Proceedings of the International Symposium, Trulove, P. C.; De long, H. C.; Mantz, R. A.; Stafford, G. R.; Matsunaga, M., Eds.; The Electrochemical Society: Pennington, NJ, **2006**, *2004-24*, 396-406.
4. Katritzky, A. R.; Yang, H.; Zhang, D.; Kirichenko, K.; Smiglak, M.; Holbrey, J. D.; Reichert, W. M.; Rogers, R. D. "Strategies toward the design of energetic ionic liquids: nitro- and nitrile-substituted N,N'-dialkylimidazolium salts" *New J. Chem.* **2006**, *30*, 349-358.
5. Katritzky, A. R.; Singh, S.; Kirichenko, K.; Smiglak, M.; Holbrey, J. D.; Reichert, W. M.; Spear, S. K.; Rogers, R. D. "In search of ionic liquids incorporating azolate anions" *Chem. Eur. J.,* **2006**, *12*, 4630-4641.
6. Smiglak, M.; Reichert, W. M.; Holbrey, J. D.; Wilkes, J. S.; Sun, L.; Thrasher, J. S.; Kirichenko, K.; Singh, S.; Katritzky, A. R.; Rogers, R. D. "Combustible ionic liquids

by design: Is laboratory safety another ionic liquid myth?" *Chem. Commun.* **2006**, 2554-2556; (Highlighted as a Hot Article by *Chem. Commun.* June 5, 2006). (Highlighted by M. Hölscher, *Green Chem.* **2006**, *8,* 675)
7. Drab, D. M.; Smiglak, M.; Rogers, R. D. "Should the Concepts of Green Chemistry be Restrictive or Prescriptive? The Greener Synthesis of High-Performance, Energetic Ionic Liquid Materials" *Chim. Oggi* **2006**, *24*, 27-30.
8. Gutowski, K. E.; Rogers, R. D.; Dixon, D. A. "Accurate Thermochemical Properties for Energetic Materials Applications. I. Heats of Formation of Nitrogen-Containing Heterocycles and Energetic Precursor Molecules from Electronic Structure Theory" J. *Phys. Chem. A* **2006**, 110, 11890-11897.
9. Smiglak, M.; Holbrey, J. D.; Griffin, S. T.; Reichert, W. M.; Swatloski, R. P.; Katritzky, A. R.; Yang, H.; Zhang, D.; Kirichenko, K.; Rogers, R. D. "Ionic liquids via reaction of the zwitterionic 1,3-dimethylimidazolium-2-carboxylate with protic acids. Overcoming synthetic limitations and establishing new halide free protocols for the formation of ILs" *Green Chem.* **2007**, *9,* 90-98.
10. Bridges, N. J.; Hines, C. C.; Smiglak, M.; Rogers, R. D. "An intermediate for the clean synthesis of ionic liquids: Isolation and crystal structure of 1,3-dimethylimidazolium hydrogen carbonate monohydrate" *Chem. Eur. J.* **2007**, DOI: 10.1002/chem.200700055.
11. Gutowski, K. E.; Rogers, R. D.; Dixon, D. A. "Accurate Thermochemical Properties for Energetic Materials Applications. II. Heats of Formation of Imidazolium-, 1,2,4-Triazolium-, and Tetrazolium-Based Energetic Salts from Isodesmic and Lattice Energy Calculations" *J. Phys. Chem. B* , **2007**, DOI: 10.1021/jp066420d.
12. Smiglak, M.; Metlen, A.; Rogers, R. D. "The Second Evolution of Ionic Liquids - From Solvents and Separations to Advanced Materials: Energetic Examples from the Ionic Liquid Cookbook" *Acc. Chem. Res.,* **2007**, submitted

VIII. PRESENTATIONS

1. R. D Rogers, J. D Holbrey, S. K Spear, W. M. Reichert, M. R Smiglac, H. Yang, K. Manju, and A. R Katritzky, "Energetic ionic liquids: Fundamental studies relating target structures and key physical properties," Presented by R. D. Rogers to the AFOSR Contractor's Review on Ionic Liquids Research (2004), Tampa, FL.
2. R. D. Rogers, "The Past, Present, and Future of Ionic Liquids: From Designer Solvents for Crystal Engineering to Advanced New Materials," Presented by R. D. Rogers to The University of Tokyo, Tokyo, Japan on 7/20/05.
3. R. D. Rogers, "Ionic Liquids: Applications are Coming; Get Ready Now!," Presented by R. D. Rogers to NIEHS, Raleigh, NC, on 5/4/05.
4. R. D. Rogers, "Green Chemistry, Ionic Liquids, Advanced Materials, and Everything in Between" Presented by R. D. Rogers to the Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China on 5/26/05.
5. R. D. Rogers, "Energetic Ionic Liquids: Fundamental Studies Relating Target Structures and Key Physical Properties," Presented by R. D. Rogers to the Air Force Research Laboratory, Edwards Air Force Base, CA on 8/11/05.
6. R. D. Rogers, "Energetic Ionic Liquids: Fundamental Studies Relating Target Structures and Key Physical Properties," Presented by R. D. Rogers to the American

Pacific/Georgia Tech. Roundtable, Atlanta, GA on 10/6/05; (also Panel Member for the Energetic Materials Panel Discussion).

7. R. D. Rogers, "Strategies Toward the Design of Energetic Materials," Presented by R. D. Rogers at the Institute Le Bel, Université Louis Pasteur, Strasbourg, France on 6/16/06 (Visiting Professor Lecture).
8. R. D. Rogers, M. Smiglak, D. W. Drab, W. M. Reichert, K. E. Gutowski, T. Wilson, A Vincek, D. Zhang, H. Fang, K. Kirischenko, S. Singh, and A. R. Katritzky, "Energetic Ionic Liquids: Fundamental Studies Relating Target Structures and Key Physical Properties," Presented by R. D. Rogers before Air Force Office of Scientific Research Ionic Liquids Research Workshop (2006), Tuscaloosa, AL.
9. A Vincek, D. Zhang, H. Fang, K. Kirischenko, S. Singh, A. R. Katritzky, J. D. Holbrey, , M. Smiglak, W. M. Reichert, S. K. Spear, and R. D. Rogers, "In search of Energetic Ionic Liquids," Presented by K. Kirischenko before Air Force Office of Scientific Research Ionic Liquids Research Workshop (2006), Tuscaloosa, AL M. Smiglak, D. M. Drab, T. Wilson, W. M. Reichert, R. D. Rogers, H. Yang, D. Zhang, K. Kirichenko, and A. R. Katritzky, "Strategies Toward the Design of Energetic Ionic Liquids: Nitro- and Nitrile Substituted Imidazolium Salts," Presented by M. Smiglak before the Ionic Liquids Workshop: Background, State-of-the-Art, and Academic/Industrial Applications (2006), Tuscaloosa, AL.
10. M. Smiglak, D. M. Drab, T. Wilson, W. M. Reichert, R. D. Rogers, H. Yang, D. Zhang, K. Kirichenko, and A. R. Katritzky, "Strategies Toward the Design of Energetic Ionic Liquids: Azolate-Based Salts," Presented by M. Smiglak before the Ionic Liquids Workshop: Background, State-of-the-Art, and Academic/Industrial Applications (2006), Tuscaloosa, AL.
11. M. Smiglak, W. M. Reichert, S. T. Griffin, J. D. Holbrey, R. D. Rogers, K. Kirichenko, D. Zhang, and A. R. Katritzky, "Ionic liquids via reaction of the zwitterion 1,3-dimethylimidazolium-2-carboxylate with protic acids," Presented by M. Smiglak before the Ionic Liquids Workshop: Background, State-of-the-Art, and Academic/Industrial Applications (2006), Tuscaloosa, AL.
12. M. Smiglak, W. M. Reichert, J. D. Holbrey, L. Sun, J. S. Thrasher, R. D. Rogers, and J. S. Wilkes, "Combustible ionic liquids by design: Destroying another ionic liquid myth," Presented by M. Smiglak before the Ionic Liquids Workshop: Background, State-of-the-Art, and Academic/Industrial Applications (2006), Tuscaloosa, AL.
13. K. E. Gutowski, J. D. Holbrey, D. A. Dixon, and R. D. Rogers, "Prediction of the Formation and Stabilities of Energetic Salts and Ionic Liquids Based on Ab Initio Electronic Structure Calculations," Presented by K. E. Gutowski before the Ionic Liquids Workshop: Background, State-of-the-Art, and Academic/Industrial Applications (2006), Tuscaloosa, AL.
14. M. Smiglak, W. M. Reichert, J. D. Holbrey, J. S. Wilkes, L. Sun, J. S. Thrasher, and R. D. Rogers, "Combustible ionic liquids by design: Destroying another ionic liquid myth," Presented by M. Smiglak before the 231st ACS National Meeting (2006), Atlanta, GA, Abstract I&EC 103.
15. R. D. Rogers, "Separations and Energetic Materials," Presented before the Ionic Liquids Workshop: Background, State-of-the-Art, and Academic/Industrial Applications (2006), Tuscaloosa, AL. (Organizer).

16. M. Smiglak, W. M. Reichert, S. T. Griffin, J. D. Holbrey, R. D. Rogers, K. Kirichenko, D. Zhang, and A. R. Katritzky, "Ionic liquids via reaction of the zwitterion 1,3-dimethylimidazolium-2-carboxylate with protic acids," Presented by M. Smiglak before the 231st ACS National Meeting (2006), Atlanta, GA, Abstract I&EC 104.
17. M. Smiglak, D. M. Drab., C. C. Hines, W. M. Reichert, R. D. Rogers, K. Kirichenko, and A. Vincek, "Halide free synthesis of energetic azolium azolate salts," Presented by M. Smiglak before the 232nd ACS National Meeting (2006), San Francisco, CA, Abstract PHYS 522.
18. M. Smiglak, C. C. Hines, T. Wilson, W. M. Reichert, S. T. Griffin, R. D. Rogers, K. Kirichenko, S. Singh, and A. Vincek, "Ionic liquids based on azole anions," Presented by M. Smiglak before the 232nd ACS National Meeting (2006), San Francisco, CA, Abstract PHYS 555.
19. N. J. Bridges, M. Smiglak, and R.D. Rogers "Synthesis of hydrogen carbonate ionic liquids through the Krapcho reaction," Presented by N. J. Bridges before the 232nd ACS National Meeting (2006), San Francisco, CA, Abstract I&EC 82.
20. M. Smiglak, M. Dilip, N. J. Bridges, W. M. Reichert, and R. D. Rogers, "Formation of ionic liquid eutectic mixtures as a tool for melting point depression." Poster presented by M. Smiglak before the 15th International Symposium on Molten Salts part of the 2006 Joint International Meeting (210th Meeting of the Electrochemical Society Meeting/XXI Congreso de la Sociedad Mexicana de Electroquímica (2006), Cancun, Mexico, Abstract 70 and 2022.
21. R. D. Rogers, D. M. Drab, and M. Smiglak, "Ionic Liquids as a Unique and Versitile Platform for the Synthesis and Delivery of Energetic Materials," Presented by R. D. Rogers before the 54th Joint Army-Navy-NASA_Air Force (JANNAF) Propulsion Meeting (2007), Denver, CO, Program Booklet page 62.

IX. DISSERTATIONS

1. Yang, Hongfang, Benzotriazole intermediates in organic chemistry, PhD Dissertation, University of Florida, Gainesville, FL, 2004; http://etd.fcla.edu/UF/UFE0005743/yang_h.pdf

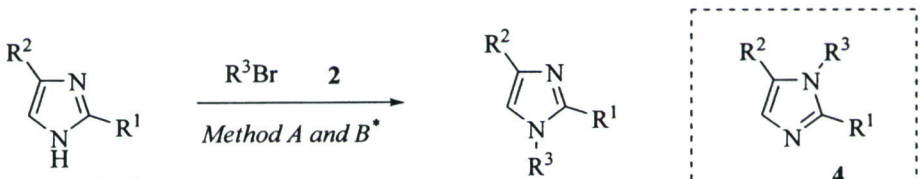
Appendix A
Synthesis of EILs

Appendix A1

Synthesis and extensive experimental and crystallographic analysis of the properties of protonated ILs, including nitro substituted 1-alkyl-3-H-imidazolium and 1-alkyl-2-methyl-3-H-imidazolium nitrate and picrate salts

The preparation of *N*-alkylimidazoles

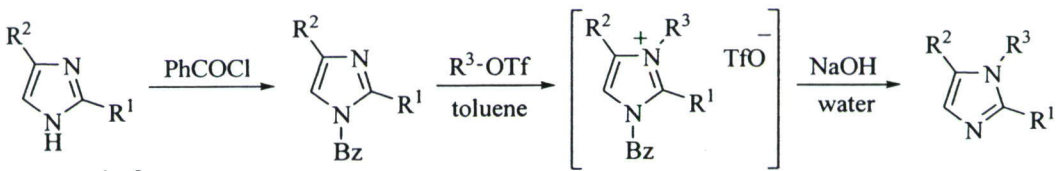
1-Alkyl imidazoles **3a-e,g** were prepared in 12–84% yields by the alkylation of corresponding imidazoles **1a–e,g** with alkyl bromides in organic solvents in the presence of potassium carbonate under reflux (Figure A1.1, Table A1.1, *Method A*).



1a (R^1,R^2 = H)
b (R^1 = CH_3, R^2 = NO_2)
c (R^2 = NO_2)
d (R^1 = CH_3)
e (R^1, R^2 = CH_3)

3a-j

Figure A1.1. Methods *A* and *B* for preparation of 1-alkylimidazoles **3a–j**.
**Method A*: K_2CO_3, Bu_4NBr, acetonitrile, reflux; *Method B*: KOBu^t, DMF, 20–25 °C.



1 e (R^1,R^2 = CH_3)
f (R^2 = CH_3)

5a,b

6a-d

4a-d

Figure A1.2. Method *C* for preparation of 1-alkylimidazoles **4a–d**.

Unfortunately, this procedure gave unsatisfactory 12–44% yields on alkylation of either unsubstituted or 2-(or 4-)alkyl imidazoles. Assuming that the low yields were caused by low acidity of imidazoles and/or low boiling point of propyl and *i*-propyl bromides, we used the strong base potassium *tert*-butoxide in DMF at 20–25 °C (*Method B*) for the preparation of compounds **3a–c**, which were obtained in yields of 60–82%. This procedure was also successfully employed for the preparation of 1-alkylimidazoles **3f,h–j** in yields of 73–92%.

Compounds **3a,c,e–i** were purified via column chromatography. Compound **3b** was isolated as its nitrate and compound **3j** as its hydrochloride by the treatment of residue with nitric acid and hydrochloric acid, respectively.

However, reactions of alkyl bromides with 4-methylimidazole (**1**, $R^2 = CH_3$) and 2,4-dimethylimidazole (**1**, R^1, $R^2 = CH_3$) in DMF in the presence of potassium *tert*-butoxide gave mixtures of isomeric products **3** and **4**, which could not be separated by crystallization or column chromatography due to similar physical properties.

4-Methylimidazole (**1e**, $R^1 = H$, $R^2 = CH_3$) and 2,4-dimethylimidazole (**1f**, R^1, $R^2 = CH_3$) were successfully converted regiospecifically into alkylimidazoles **4a–d** (*Method C*) via a reaction sequence involving initial benzoylation of imidazole **1** followed by quaternization with alkyl triflate and hydrolysis (Figure A1.2, Table A1.1).

1-Benzoyl-2,4-dimethyl- (**5a**, $R^1 = CH_3$) and 1-benzoyl-4-methyl- (**5b**, $R^1 = H$) imidazoles were prepared in 96% and 70% yields, respectively, from benzoyl chloride with two fold excess of corresponding imidazole **1e,f** in THF at 20–25 °C. Attempted treatment of benzoyl derivatives **5a,b** with alkyl bromides gave no reaction (quaternization). In contrast, reactions of **5a,b** with propyl and hexyl triflates in toluene at 20–25 °C for 48 h gave the corresponding quaternary salts **6a–d**, which were separated from the solvent and hydrolyzed in aqueous sodium hydroxide / diethyl ether at 20–25 °C to give alkylimidazoles **4a–d** in 63–94% yields. Unfortunately, no quaternization reaction was observed on the treatment of **5a,b** with *i*-propyl triflate under the same reaction conditions (probably due to detriflation of *i*-propyl triflate) and starting imidazoles **5a,b** were recovered.

Structures of the compounds **3a–j**, and **4a–d** were supported by their ^1H and ^{13}C NMR spectra, and elemental analysis.

Table A1.1. Preparation of *N*-alkylimidazoles **3a–j** and **4a–d**.

Product	R^1	R^2	R^3	Yield (%)		
				Method A	Method B	Method C
3a	H	H	Pr	14	82	
3b	H	H	*i*-Pr	12	60[a]	
3c	H	H	*n*-C_6H_{13}	44	72	
3d	CH_3	NO_2	*n*-Bu	84		
3e	CH_3	NO_2	*n*-C_5H_{11}	65		
3f	H	NO_2	*i*-Pr		78	
3g	H	NO_2	*n*-C_6H_{13}	62		
3h	CH_3	H	*n*-Bu		87	
3i	CH_3	H	*n*-C_5H_{11}		92	
3j	CH_3	CH_3	*n*-C_6H_{13}		73[b]	
4a	CH_3	CH_3	Pr			94
4b	CH_3	CH_3	*n*-C_6H_{13}			79
4c	H	CH_3	Pr			63
4d	H	CH_3	*n*-C_6H_{13}			89

[a] isolated as nitrate; [b] isolated as hydrochloride.

The protonated salts (Figure A1.3) (picrates and nitrates) of above precursors were obtained on neutralization of the appropriate azole with 1 equivalent of either ethanolic nitric or picric acid, and the salts isolated by slow evaporation in a dry atmosphere. All salts were obtained in high yields (>98%) and analyzed by NMR, DSC and TGA.

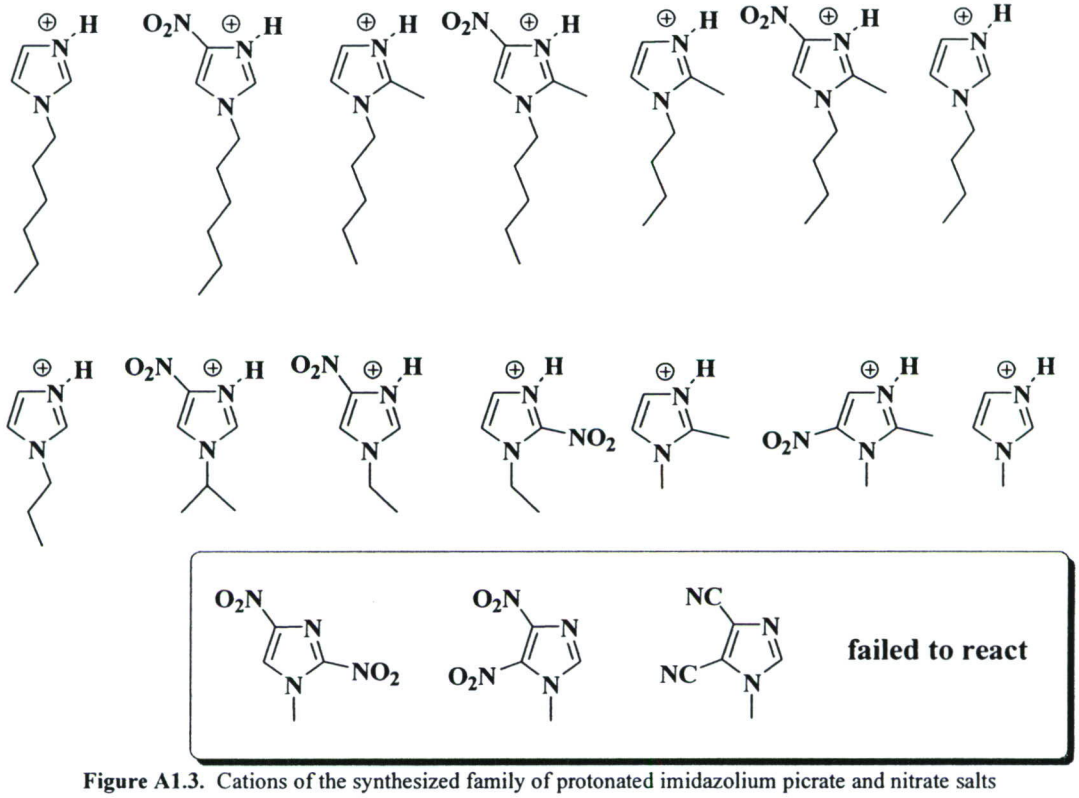


Figure A1.3. Cations of the synthesized family of protonated imidazolium picrate and nitrate salts

Appendix A2

Synthesis and investigation of stability and thermal properties of azolate based ILs, along with crystal structure investigation of formed products

Diverse organic salts, combinations of cations **(Q)** and anions **(Az)** from Figure A2.1, were prepared by metathesis of the corresponding potassium azolates with the corresponding ammonium or phosphonium halides in a solvent mixture of acetone:methylene chloride (1:1), at 20–25 °C (Figure A2.2). The cations used were tetraphenylphosphonium ($[Ph_4P]^+$) **3**, ethyltriphenylphosphonium ($[EtPh_3P]^+$) **4**, *N*-phenylpyridinium ($[N\text{-PhPyr}]^+$) **5**, 1-butyl-3-methylimidazolium ($[1\text{-Bu-3-Me-im}]^+$) **6** (commonly known as $[C_4mim]^+$), tetrabutylammonium ($[Bu_4N]^+$) **7**, tetraethylammonium ($[Et_4N]^+$) **8**, and tetramethylammonium ($[Me_4N]^+$) **9**. The anions used were 5-nitrobenzotriazolate ($[5\text{-}NO_2\text{-benztri}]^-$) **a**, 5-nitrobenzimidazolate ($[5\text{-}NO_2\text{-benzim}]^-$) **b**, 4-nitro-1,2,3-triazolate ($[4\text{-}NO_2\text{-}1,2,3\text{-tri}]^-$) **c**, 4-nitroimidazolate ($[4\text{-}NO_2\text{-im}]^-$) **d**, 3,5-dinitro-1,2,4-triazolate ($[3,5\text{-di}NO_2\text{-tri}]^-$) **e**, 2,4-dinitroimidazolate ($[2,4\text{-di}NO_2\text{-im}]^-$) **f**,

4,5-dinitroimidazolate ([4,5-diNO$_2$-im]$^-$) **g**, 4,5-dicyanoimidazolate ([4,5-diCN-im]$^-$) **h**, and tetrazolate ([tetr]$^-$) **i**.

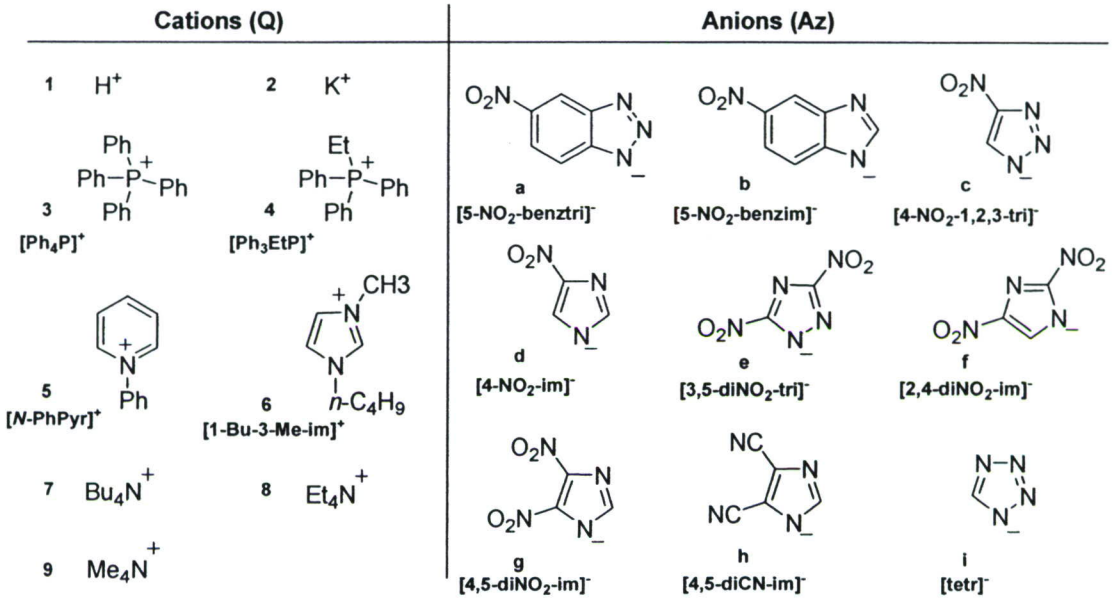


Figure A2.1. Cation and anion combinations explored in this work, with used ion names abbreviations in brackets.

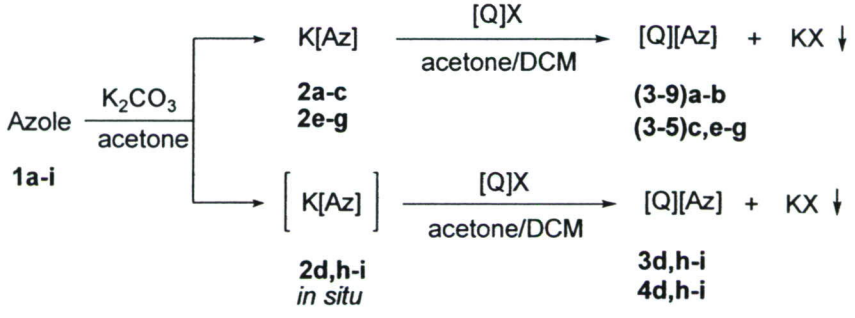


Figure A2.1. Synthetic routes to analyzed azolate-based salts.

The potassium azolate salts **2a–c, 2e-g** were initially prepared by treatment of the corresponding azoles **1a–c, 1e-g** with potassium carbonate in acetone. The potassium azolates **2a–c, 2e-g** were reacted with equimolar amounts of tetraphenylphosphonium, ethyltriphenylphosphonium, *N*-phenylpyridinium, 1-butyl-3-methylimidazolium or tetraalkylammonium halides, which allowed filtration of precipitated potassium halide. Isolation of the corresponding tetraphenylphosphonium, ethyltriphenylphosphonium, *N*-phenylpyridinium, 1-methyl-3-butylimidazolium, and tetraalkylammonium azolates **(3–9)a–b** and **(3–5)c,e–g** was performed, *in vacuo* from the filtrate, in 88–99% yields. The difficult isolation of pure potassium 4-nitroimidazolate **2d**, potassium 4,5-dicyanoimidazolate **2h**, and potassium tetrazolate **2i** was bypassed, by *in situ* generation with potassium carbonate, for the synthesis of 4-nitroimidazolates **3–4d**, 4,5-dicyanoimidazolates **3–4h**, and tetrazolates **3–4i** . Azoles **1d,h–i** were treated with *in situ*

potassium carbonate and with tetraphenylphosphonium, ethyltriphenylphosphonium, or *N*-phenylpyridinium halides to give good yields of salts **(3–4)d,h–i** after removal of inorganic salts.

Appendix A3

Nitrile-functionalized imidazolium-based ILs

The synthesis of 1-(2-cyanoethyl)-3-methylimidazolium and 1-butyl-3-(2-cyanoethyl)imidazolium bromides were synthesized by S_N2 quaternization reactions of 1-methyl or 1-butylimidazole, respectively, with a slight excess of 3-bromopropionitrile (1.1 equivalents) under conditions of either (i) reflux in acetonitrile for 48 hours or (ii) solvent-free conditions, where the starting materials were sealed in a high pressure vial and stored in a furnace at 70 °C for 48 hours (Figure A3.1). Similar procedures were followed for the synthesis of 1-(1-cyanoethyl)-3-methylimidazolium and 1-butyl-3-(1-cyanomethyl)imidazolium bromide salts from the reaction of the same 1-alkylimidazoles as above with 2-bromopropionitrile. All materials were used as received. For product purification, the reaction mixtures had solvent and excess starting materials removed by rotoevaporation followed by high vacuum drying, and the conversion to products was confirmed utilizing multinuclear NMR analysis.

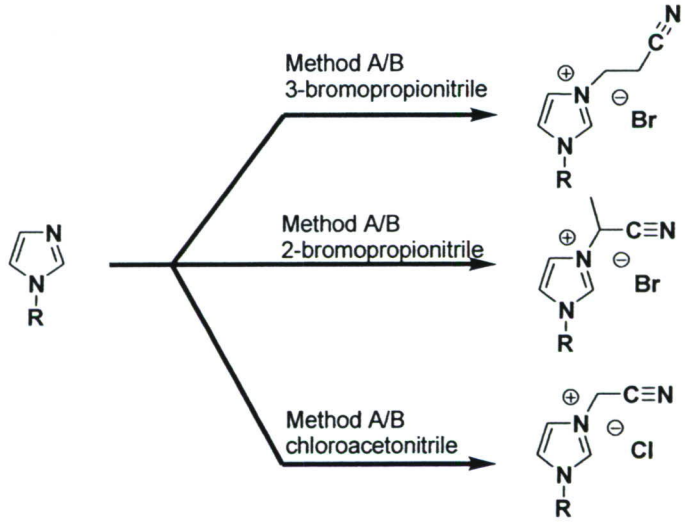


Figure A3.1. Synthesis of N-cyanoalkylated imidazolium cations; R = Me, Bu; Method A: acetonitrile, 48 h reflux; Method B: 70 °C furnace, solvent-free, 48 h.

Currently, a similar synthetic protocol is utilized for the synthesis of 1-(cyanomethyl)-3-methylimidazolium and 1-butyl-3-(cyanomethyl)imidazolium chlorides utilizing chloroacetonitrile as the alkylating agent under both solvent and solvent-free conditions. Additionally, all chloride and bromide salt products are to undergo anion exchange resulting in the formation of nitrate salts that may be compared with regards to how well their physical and chemical properties (e.g., melting point, thermal stability) compare with the needs set forth by the AFOSR.

Appendix A4

Azolium Azolates via 1,3-dimethylimidazolium-2-carboxyalte system

Utilizing the previously described protocol for the reaction of 1,3-dimethyl-2-carboxylate precursor with inorganic acids [i] we have paired 1,3-dimethylimidazolium-2-carboxylate with 7 examples of neutral azoles, which in present conditions are considered organic acids. The protocol for the synthesis of the family of 1,3-dimethylimidazolium azolate salts allows for their formation in the 100% impurity free route (Figure A3.1). The only byproducts of the reaction are gaseous CO_2 and the solvent used during the reaction (DMSO, acetone, or EtOH), which can be easily removed from the product by simple distillation.

Formation of azolium azolates is easily accessible when certain requirements are fulfilled: (i) the precursor of the cation must incorporate a 2-COO- species appended directly to the azolium ring, and (ii) the acidic proton of the neutral azole (H-Az) must have a lower pKa value than that of the proton at the C2 position in the decarboxylated azolium cation.

Obtained examples include:

1,3-dimethylimidazolium 4-nitro-1,2,3-triazolate
1,3-dimethylimidazolium 4-nitroimidazolate
1,3-dimethylimidazolium 2-methyl-5-nitroimidazolate
1,3-dimethylimidazolium 3,5-dinitro-1,2,4-triazolate
1,3-dimethylimidazolium 4,5-dinitroimidazolate
1,3-dimethylimidazolium 3-amino-1,2,4-triazolate
1,3-dimethylimidazolium 5-amino-tetrazolate
1,3-dimethylimidazolium 4,5-dicyanoimidazolate

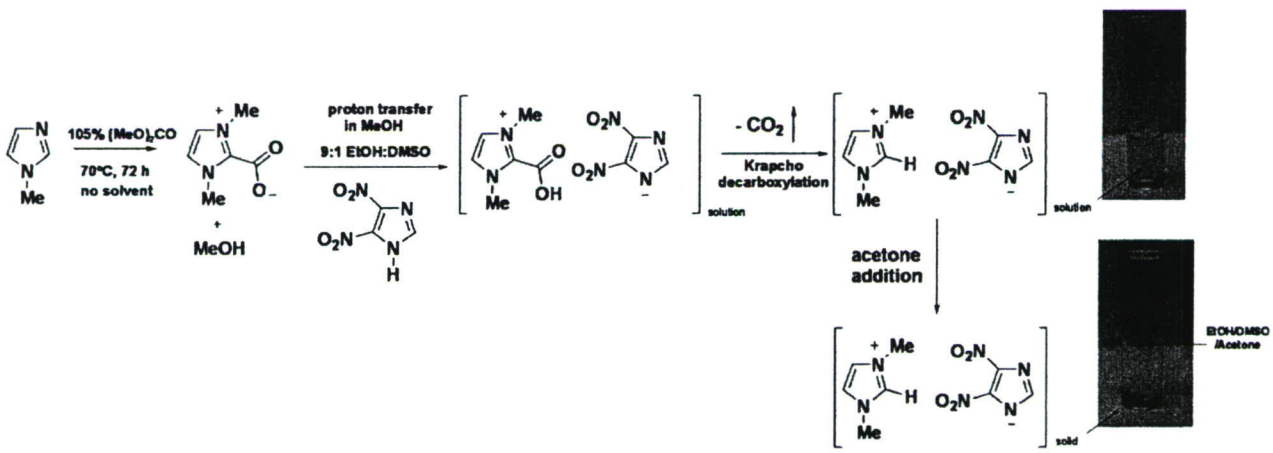


Figure A4.1. Halide free, synthetic protocol for the formation of azolium azolate salts.

[i] Smiglak, M.; Holbrey, J. D.; Griffin, S. T.; Reichert, W. M.; Swatloski, R. P.; Katritzky, A. R.; Yang, H.; Zhang, D.; Kirichenko, K.; Rogers, R. D. "Ionic liquids via reaction of the zwitterionic 1,3-dimethylimidazolium-2-carboxylate with protic acids. Overcoming synthetic limitations and establishing new halide free protocols for the formation of ILs" *Green Chem.* **2007**, *9*, 90-98.

Appendix B
Thermal data for EILs (DSC, TGA, ARC)

Appendix B1

Synthesis and extensive experimental and crystallographic analysis of the properties of protonated ILs, including nitro substituted 1-alkyl-3-H-imidazolium and 1-alkyl-2-methyl-3-H-imidazolium nitrate and picrate salts

Table B1.1 Thermal stabilities (onset to 5% decomposition), and melting/glass transitions of synthesized substituted imidazolium picrate and nitrate salts.

	Compound	TGA	DSC		Compound	TGA	DSC
		$T_{onset\ 5\%}$ (°C)	T_m (°C)			$T_{onset\ 5\%}$ (°C)	T_m (°C)
1	[1-M-3-H-IM][Pic]	184.2	159.4	21	[1-M-3-H-IM][NO_3]	137.2	59.9
2	[1,2-diM-3-H-IM][Pic]	203.8	181.6	22	[1,2-diM-3-H-IM][NO_3]	133.3	78.5
3	[1-Pr-3-H-IM][Pic]	177.2	96.7 (one time melt) T_g -23.7	23	[1-Pr-3-H-IM][NO_3]	143.3	-16.57 (one time melt) T_g -80.5 T_{l-l} 63.8
4	[1-Bu-3-H-IM][Pic]	198.4	Tg -38.4 T_{l-l} 33.9	24	[1-Bu-3-H-IM][NO_3]	149.6	Tg -76.4 m.p. 5.5
5	[1-Bu-2-M-3-H-IM][Pic]	223.9	T_m(first cycle) 75.2 T_m(next cycles) 103.6	25	[1-Bu-2-M-3-H-IM][NO_3]	121.4 but T_{ons} 167	T_g -76.4 T_m 20.1 T_{l-l} 65.8
6	[1-Pent-2-M-3-H-IM][Pic]	225.9	127.1	26	[1-Pent-2-M-3-H-IM][NO_3]	137.2 but T_{ons} 166.1	T_g -67.6
7	[1-Hex-3-H-IM][Pic]	150.9 but T_{ons} 240.8	T_g -44.1 T_m 40.6	27	[1-Hex-3-H-IM][NO_3]	137.7 but T_{ons} 173.0	T_g -72.3 T_m 0.9 T_{l-l} 78.7
8	[1-M-3-H-2-NO_2-IM][Pic]	112.0	41.8 (one time melt) Tg -24.5	28	[1-M-3-H-2-NO_2-IM][NO_3]	82.3	98.3
9	[1,2-diM-3-H-5-NO_2-IM][Pic]	144.7	165.2	29	[1,2-diM-3-H-5-NO_2-IM][NO_3]	122.5	87.5
10	[1-Et-3-H-2-NO_2-IM][Pic]	107.0	Tg -32.5 2nd Tg ~50.8	30	[1-Et-3-H-2-NO_2-IM][NO_3]	68.9	Tg -59.5 2nd T_g ~38.4
11	[1-Et-3-H-4-NO_2-IM][Pic]	161.4	Tg -26.2 2nd Tg ~42.1	31	[1-Et-3-H-4-NO_2-IM][NO_3]	82.7	T_g-51.3 T_{l-l} 40.3
12	[1-iPr-3-H-4-NO_2][Pic]	137.1 T_{ons} 181.3	56.7 (one time melt) T_g -28.0	32	[1-iPr-3-H-4-NO_2][NO_3]	86.8 but two slopes T_{ons1} 98.0 T_{ons2} 192.4	T_g -50.9 T_{l-l} 63.1
13	[1-Bu-2-M-3-H-4-NO_2][Pic]	187.8	T_g -28.4 Secund trans T_{l-l} 71.1	33	[1-Bu-2-M-3-H-4-NO_2][NO_3]	102.0 but two slopes T_{ons1} 115.4 T_{ons2} 212.6	Small tran ~52 T_m 67.1
14	[1-Pent-2-M-3-H-4-NO_2][Pic]	175.9	T_g -30.1	34	[1-Pent-2-M-3-H-4-NO_2][NO_3]	104.2 but two slopes T_{ons1} 115.4 T_{ons2} 202.5	Crystallization repeatable at -31.1
15	[1-Hex-3-H-4-NO_2][Pic]	174.8	T_g-32.8 T_m 78.8	35	[1-Hex-2-M-3-H-4-NO_2][NO_3]	102.1 but two slopes T_{ons1} 108.3 T_{ons2} 230.7	T_g -62.5 T_m 11.1
16	[1-M-3-H-2,4-diNO_2-IM][Pic] cocrystal	No rxn product. Mixture of Substrates.		36	[1-M-3-H-2,4-diNO_2-IM][NO_3]	No rxn product. Mixture of Substrates.	
17	[1-M-3-H-4,5-diNO_2-IM][Pic]			37	[1-M-3-H-4,5-diNO_2-IM][NO_3]		
18	[1-M-3-H-4,5-diCN-IM][Pic] cocrystal			38	[1-M-3-H-4,5-diCN-IM][NO_3]		

Melting (T_m), glass transition (T_g) and liquid-liquid transition (T_{l-l}) points (°C) were measured from the transition onset temperature and determined by DSC from the 2nd heating cycle at 5 °C min^{-1}, after initially melting and then cooling samples to –100 °C.

Decomposition temperatures shown were determined by TGA, heating at 5 °C min^{-1} under dried air atmosphere and are reported as (i) onset to 5 wt% mass loss ($T_{onset\ 5\%}$) and (ii) onset to total mass loss (T_{ons}).

The compounds abbreviations follow the key: [1-X-2-X-3-X-4-X-5-X-IM][An], where:

- 1, 2, 3, 4, 5 refer to the substituted positions around the imidazole ring.

- X after the number refers to the particular functional group substituted at that position (M–methyl; Et-ethyl, iPr-isopropyl; Bu-butyl; Pent-pentyl; Hex-hexyl; H-hydrogen; NO_2-nitro; CN-cyano).
- if the number for particular position is not indicated, it means that the position is substituted with a hydrogen atom.
- IM refers to the imidazole ring
- An refers to an anion (NO_3-nitrate; Pic-picrate)

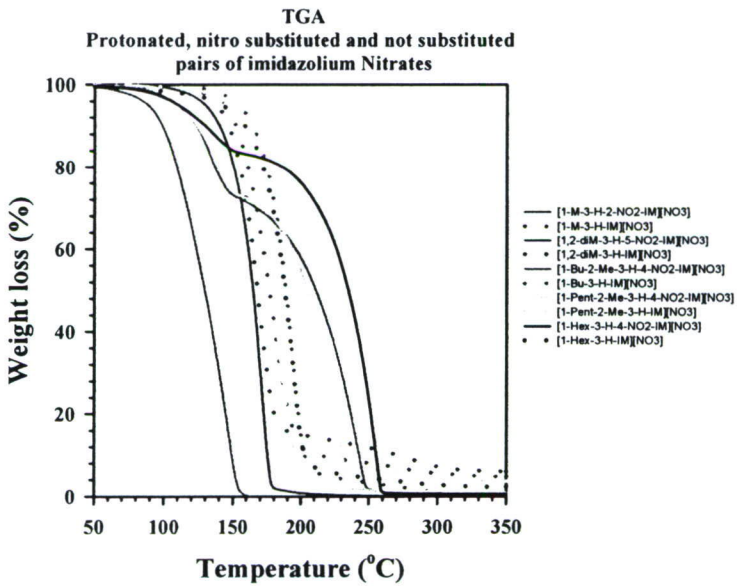


Figure B1.1 Thermogravimetric analysis of protonated, nitro substituted and not substituted pairs of imidazolium nitrate salts.

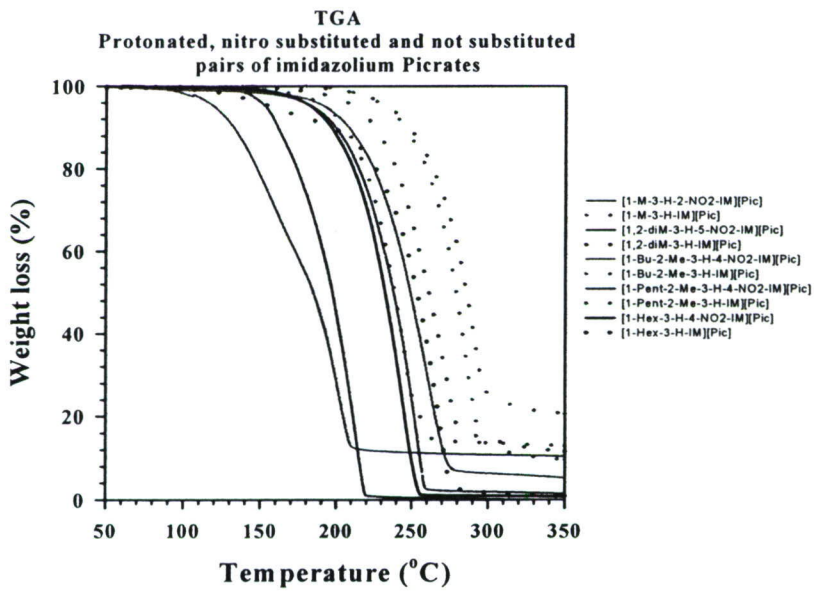


Figure B1.1 Thermogravimetric analysis of protonated, nitro substituted and not substituted pairs of imidazolium picrate salts.

Appendix B2

Synthesis and investigation of stability and thermal properties of azolate based ILs, along with crystal structure investigation of formed products

Table B2.1. Melting point and glass transitions for 3-9(a-i)[§].

Cation/ Anion		3 / $[Ph_4P]^+$	4 / $[EtPh_3P]^+$	5 / [*N*-PhPyr]$^+$	6 / [1-Bu-3-Me-im]$^+$	7 / $[Bu_4N]^+$	8 / $[Et_4N]^+$	9 / $[Me_4N]^+$
		mp (°C)	mp (°C)	mp (°C)	mp (°C)	mp (°C)	mp (°C)	mp (°C)
a	**[5-NO_2-benztri]$^-$**	145 [a,b]	131 [a]	**75** [a]	**-41** [c]	**60** [a,b]	**64** [a]	192 (at T_{dec})
b	**[5-NO_2-benzim]$^-$**	**55** [a]	**88** [a]	---	**-34** [c]	**81** [a]	101 [a,b]	119 [a,b]
c	**[4-NO_2-1,2,3-tri]$^-$**	155	**97** [a]	135 [a,b]	**-73** [c,d]	**87** [d]	**82** [d]	157 [d]
d	**[4-NO_2-im]$^-$**	171	**100** [b]	---	**-63** [c,d]	106 [d]	124 [d]	185 [d] (at T_{dec})
e	**[3,5-diNO_2-1,2,4-tri]$^-$**	171	127 [a]	167	**33** [d]	139 [d]	114 [d]	214 [d] (at T_{dec})
f	**[2,4-diNO_2-im]$^-$**	195	**70** [a]	143	**-53** [c,d]	**81** [d]	**86** [d]	181 [d]
g	**[4,5-diNO_2-im]$^-$**	145 [a,b]	**97** [a]	140	**-64** [c,d]	**85** [d]	**84** [d]	215 [d] (at T_{dec})
h	**[4,5-diCN-im]$^-$**	149 [b]	**-29** [c]	---	**-74** [c,d]	**79** [d]	118 [d]	197 [d] (at T_{dec})
i	**[tetr]$^-$**	290 (at T_{dec})	**51** [a,b]	---	**-82** [c,d]	**-66** [c,d]	114 [d]	216 [d] (at T_{dec})

[§]Melting (mp) or glass transition (T_g) points (°C) were measured from the transition onset temperature and determined by DSC from the 2nd heating cycle at 5 °C min^{-1}, after initially melting and then cooling samples to –100 °C unless otherwise indicated. Salts meeting the definition of ionic liquids (mp < 100 °C) are in **bold**.

[a] Glass transition temperatures (°C) of supercooled liquids (i) with consecutive crystallization and melting on heating; **3a**, 30; **3b**, 22; **3g**, 15; **4a**, 9; **4c**, -8; **4e**, -5; **5c**, -19; **7a**, -32; **7b**, -21; **8a**, -38; **8b**, -30; **9b**, 22; (ii) with no crystallization and melting under experimental conditions: **4b**, 15; **4f**, -4; **4g**, -11; **4i**, 2; **5a**, 7.

[b] Irreversible transition, from first heating; **3a**, 133; **3g**, 151; **3h**, 159; **4d**, 71, **4h**, 159; **4i**, 94; **5c**, 114;**7a**, 92; **8b**, 37; **9b**, 66.

[c] Glass transitions on heating.

[d] Katritzky, A. R.; Singh, S.; Kirichenko, K.; Smiglak, M.; Holbrey, J. D.; Reichert, W. M.; Spear, S. K.; Rogers, R. D. "In search of ionic liquids incorporating azolate anions" *Chem. Eur. J.* **2006**, *12*, 4630-4641.

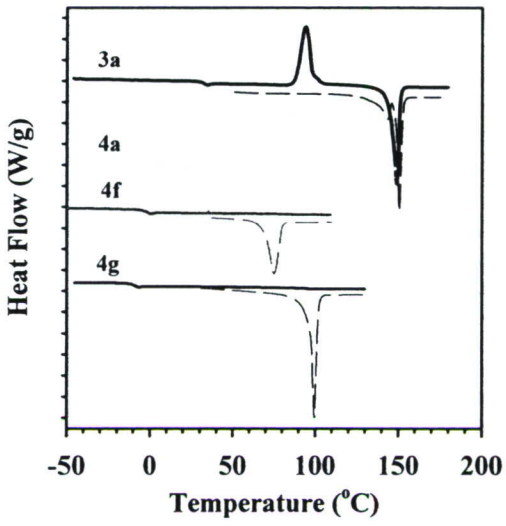


Figure B2.1. Examples of supercooled liquid behavior. The 1st heating cycle is shown as a dashed line and the 2nd heating cycle is shown as a solid line. Samples **3a** and **4a** after initial melting did not crystallize on cooling, but formed supercooled phases, which upon the 2nd heating cycle undergo a consecutive glass transition, crystallization, and melting. Samples **4f** and **4g** after initial melting did not crystallize, but formed supercooled phases, which upon heating exhibited glass transitions with no further thermal phase transitions.

Table B2.2. Thermal stabilities for 3-9(a-i)[§].

Cation/ Anion		3 $[Ph_4P]^+$	4 $[EtPh_3P]^+$	5 $[N\text{-}PhPyr]^+$	6 [1-Bu-3-Me-im]$^+$	7 $[Bu_4N]^+$	8 $[Et_4N]^+$	9 $[Me_4N]^+$
		$T_{5\%\,dec}$ (T_{dec})	$T_{5\%\,dec}$ (T_{dec})	$T_{5\%\,dec}$ (T_{dec})	$T_{5\%\,dec}$ (T_{dec})	$T_{5\%\,dec}$ (T_{dec})	$T_{5\%\,dec}$ (T_{dec})	$T_{5\%\,dec}$ (T_{dec})
a	[5-NO_2-benztri]$^-$	273 (305) [a]	247 (279) [a]	158 (162) [a]	186 (209) [a]	174 (202)	178 (205)	177 (197)
b	[5-NO_2-benzim]$^-$	223 (256)	220 (270) [a]	---	177 (189) [a]	169 (194)	169 (193)	141 (161) [a]
c	[4-NO_2-1,2,3-tri]$^-$	273 (308) [a]	241 (284) [a]	192 (201) [a]	219 [b]	192 [b]	194 [b]	180 [b]
d	[4-NO_2-im]$^-$	232 (283) [a]	220 (253) [a]	---	200 [b]	193 [b]	188 [b]	165 [b]
e	[3,5-diNO_2-1,2,4-tri]$^-$	368 (402) [a]	284 (321) [a]	277 (296) [a]	239 [b]	219 [b]	205 [b]	235 [b]
f	[2,4-diNO_2-im]$^-$	339 (379) [a]	281 (317) [a]	258 (281) [a]	254 [b]	221 [b]	216 [b]	222 [b]
g	[4,5-diNO_2-im]$^-$	279 (322)	248 (289)	204 (224) [a]	241 [b]	222 [b]	215 [b]	225 [b]
h	[4,5-diCN-im]$^-$	361 (399) [a]	291 (330) [a]	---	230 [b]	215 [b]	212 [b]	202 [b]
i	[tetr]$^-$	291 (311) [a]	248 (285) [a]	---	208 [b]	180 [b]	184 [b]	198 [b]

[§] Decomposition temperatures shown were determined by TGA, heating at 5 °C min^{-1} under dried air atmosphere and are reported as (i) onset to 5 wt% mass loss ($T_{5\%\,dec}$) and (ii) onset to total mass loss (T_{dec}) (in parentheses).

[a] T_{onset} for second decomposition step x °C @ (y %): **3a**, 495 (35%), **3c**, 487 (12%); **3d**, 490 (18%); **3e**, 509, (20%); **3f**, 509 (13%),**3h**, 528 (14%); **3i**, 501 (10%), **4a**, 466 (35%); **4b**, 497 (17%); **4c**, 471 (12%); **4d**, 480 (16%); **4e**, 535 (8%); **4f**, 482 (11%); **4h**, 486 (9%); **4i**, 500 (10%); **5a**, 441 (65%); **5c**, 454 (61%); **5e**, 486 (59%); **5f**, 499 (62%); **5g**, 440 (60%); **6a**, 499 (36%); **6b**, 511 (45%); **9b**, 328 (31%).

[b] Katritzky, A. R.; Singh, S.; Kirichenko, K.; Smiglak, M.; Holbrey, J. D.; Reichert, W. M.; Spear, S. K.; Rogers, R. D. "In search of ionic liquids incorporating azolate anions" *Chem. Eur. J.* **2006**, *12*, 4630-4641.

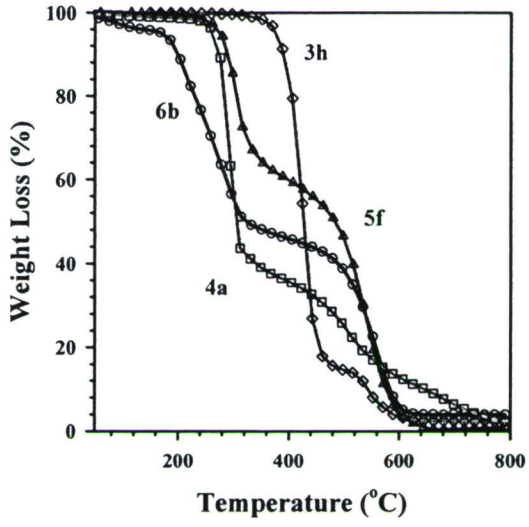


Figure B2.2. Examples of the observed thermal decomposition with distinguishable two step degradation: $[Ph_4P][4,5\text{-diCN-im}]$ **3h** (-◊-), $[Ph_3EtP][5\text{-}NO_2\text{-benztri}]$ **4a** (-□-), [*N*-PhPyr][2,4-diNO_2-im] **5f** (-Δ-), and [1-Bu-3-Me-im][5-NO_2-benzim] **6b** (-○-).

Appendix B3

Nitrile-functionalized imidazolium-based ILs

	Compound	TGA	DSC
		$T_{onset\ 5\%}$ (°C)	T_m (°C)
1	**[1-(2-CN-Et)-3-M-IM][Br]**	203.2	
2	**[1-Bu-3-(2-CN-Et)-IM][Br]**	191.1	
3	**[1-(1-CN-Et)-3-M-IM][Br]**	210.6	116.7 (T_g = -18.5)
4	**[1-Bu-3-(1-CN-Et)-IM][Br]**	207.1	T_g = -32.3
5	**[1-(CN-Me)-3-M-IM][Cl]**	TBD	TBD
6	**[1-Bu-3-(CN-Me)-IM][Cl]**	TBD	TBD

Melting (T_m), glass transition (T_g) and liquid-liquid transition ($T_{l\text{-}l}$) points (°C) were measured from the transition onset temperature and determined by DSC from the 2nd heating cycle at 5 °C min^{-1}, after initially melting and then cooling samples to –100 °C

Decomposition temperatures shown were determined by TGA, heating at 5 °C min^{-1} under dried air atmosphere and are reported as (i) onset to 5 wt% mass loss ($T_{onset\ 5\%}$) and (ii) onset to total mass loss (T_{ons}).

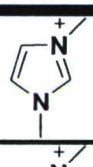
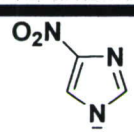
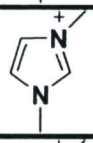
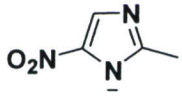
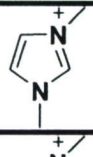
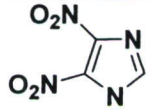
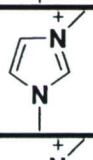
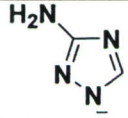
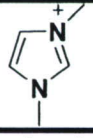
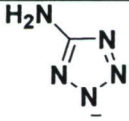
The compounds abbreviations follow the key: [1-X-2-X-3-X-4-X-5-X-IM][An], where:

- 1, 2, 3, 4, 5 refer to the substituted positions around the imidazole ring.
- X after the number refers to the particular functional group substituted at that position (M–methyl; Et-ethyl, iPr-isopropyl; Bu-butyl; Pent-pentyl; Hex-hexyl; H-hydrogen; NO_2-nitro; CN-cyano).

- if the number for a particular position is not indicated it means that the position is substituted with a hydrogen atom.
- IM refers to the imidazole ring

Appendix B4

Azolium Azolates via 1,3-dimethylimidazolium-2-carboxylate system

Ex	Cation	Anion	Temp (°C)	Time (h)	Yield (%)	mp* (°C)	$T_{5\%dec}$ ** (°C)	Form
1			21	3.5	98	78	182	Yellow, hygroscopic, crystalline solid
2			21	2	97	121	179	Yellow, hygroscopic, crystalline solid
3			25	1.5	99	96	215	Yellow crystalline solid
4			60	24	96	---‡	175	Yellow, extremely hygroscopic crystalline solid
5			60	24	97	86	192	Yellow, hygroscopic, amorphous solid

* Melting points (mp) were determined by DSC for the melting transition for the second cycle with the heating rate of 5 °C/min, after initial melting and then cooling the samples to -50 °C.

** Decomposition temperatures ($T_{5\%dec}$) were determined by TGA, from onset temperatures to initial 5 wt% loss of the sample, by heating the sample at the constant rate of 5 °C/min from room temperature to 600 °C under air atmosphere.

‡ due to extremely hygroscopic character of the sample the determination of the melting point was not possible under the DSC experiment conditions.

Appendix C
XRD data for EILs

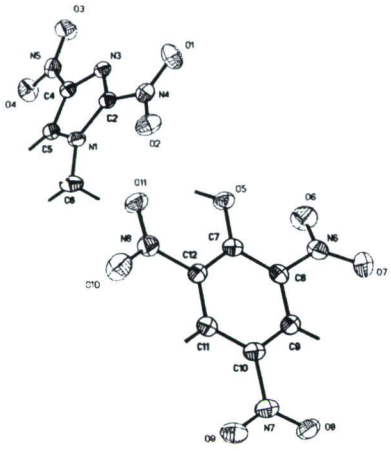
Appendix C1

Synthesis and extensive experimental and crystallographic analysis of the properties of protonated ILs, including nitro substituted 1-alkyl-3-H-imidazolium and 1-alkyl-2-methyl-3-H-imidazolium nitrate and picrate salts

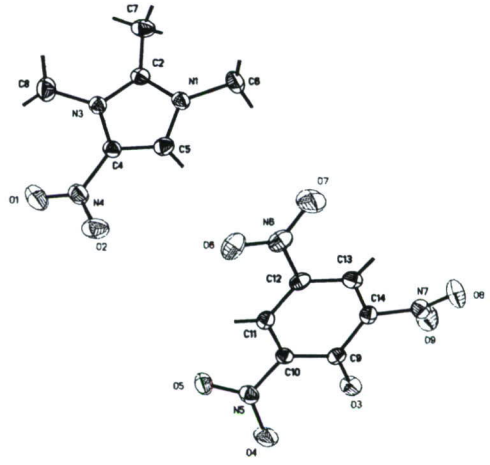
Table C1.1. Crystallographic parameters for picrate and nitrate based salts.

parameter	[1-Me-2,4-diNO_2-imiodazole][picric acid]	1,2,3-triMe-4-NO_2-im][picrate]	[1,3-diMe-4,5-diCN-imidazole][picric acid]	[1,2-diMe-3-H-im][picrate]	[1-Me-3-H-im][picrate]	[1,3-diMe-im][picrate]	[1-Me-3-H-im][NO_3]	[1,2-diMe-3-H-im][NO_3]
formula	$C_9H_5N_7O_{11}$	$C_{12}H_{12}N_6O_9$	$C_6H_{11}N_3O_6S$	$C_{11}H_{11}N_5O_7$	$C_{10}H_9N_5O_7$	$C_{11}H_{11}N_5O_7$	$C_4H_7N_3O_3$	$C_5H_9N_3O_3$
M_r	387.2	384.28	253.24	325.25	311.22	325.25	145.13	159.15
T [K]	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	Monoclinic
space group	$P2_1$	$P2_1/n$	$P2_1/n$	Cc	$P2_1/c$	$P1$	$P2_1/c$	$P2_1/n$
a [Å]	6.2866(10)	6.5665(10)	8.366(3)	6.0731(19)	8.018(2)	7.2105(15)	8.957(7)	7.8630(14)
b [Å]	11.646(2)	10.3324(17)	11.036(4)	15.082(5)	5.8847(15)	9.615(2)	9.917(7)	13.003(2)
c [Å]	10.3067(17)	23.031(4)	11.379(4)	14.764(5)	27.215(7)	10.265(2)	7.143(6)	7.9703(13)
α [°]	90	90	90	90	90	78.308(3)	90	90
β [°]	93.367(3)	92.417(3)	100.580(6)	90.963(5)	94.798(5)	82.099(4)	96.046(12)	111.875(3)
γ [°]	90	90	90	90	90	85.773(4)	90	90
V [Å^3]	753.3(2)	1561.2(4)	1032.8(6)	1352.1(7)	1279.7(6)	689.5(3)	630.9(8)	756.2(2)
Z	2	4	4	4	4	2	4	4
ρ_{calc} [g cm^{-3}]	1.335	1.635	1.629	1.598	1.615	1.567	1.528	1.398
independent/ obsd reflns	2075(R_{int} = 0.0143)/ 1985	2262(R_{int} = 0.0250)/ 1806	1490(R_{int} = 0.0497)/ 1210	1469(R_{int} = 0.0147)/ 1459	1841(R_{int} = 0.0509)/ 1352	1994(R_{int} = 0.0191)/ 1635	902(R_{int} = 0.0224)/ 769	1090(R_{int} = 0.0210)/ 945
GooF	1.084	1.091	1.029	1.083	1.076	1.057	0.981	1.034
R_1, wR_2 [$I > 2\theta(I)$]	0.0234, 0.0548	0.0349, 0.1008	0.0385, 0.0928	0.0199, 0.0510	0.0571, 0.1093	0.0440, 0.1155	0.0280, 0.0744	0.0308, 0.0751
R_1, wR_2[a] (all data)	0.0254, 0.0558	0.0495, 0.1082	0.0531, 0.0992	0.0201, 0.0512	0.0901, 0.1202	0.0561, 0.1231	0.0348, 0.0788	0.0373, 0.0786

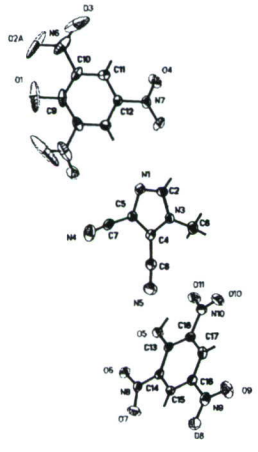
[a] $R = \sum| |F_o| - |F_c| |/\sum|F_o|$. $wR_2 = \{\sum[w(F^2_o - F^2_c)^2]/\sum(w(F^2_o)^2]\}^{1/2}$.



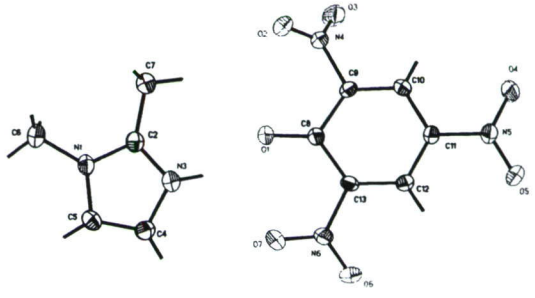
[1-Me-2,4-diNO_2-imidazole] [picric acid] (cocrystal)



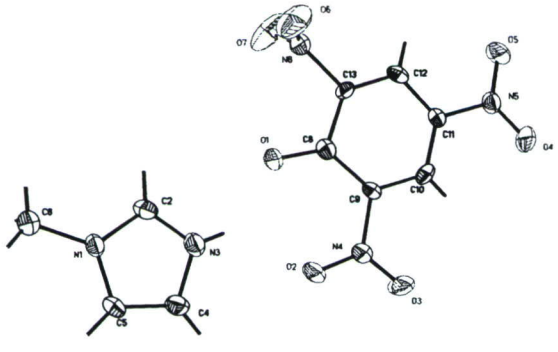
1,2,3-triMe-4-NO2-im][pic]



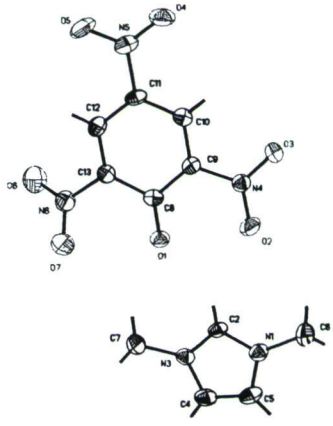
[1,3-diMe-4,5-diCN-imidazole] [picric acid] (cocrystal)



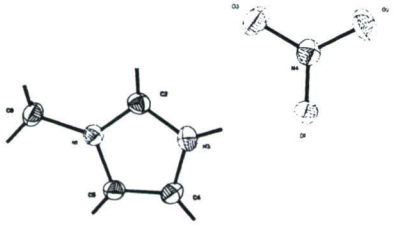
[1,2-diMe-3-H-im][pic]



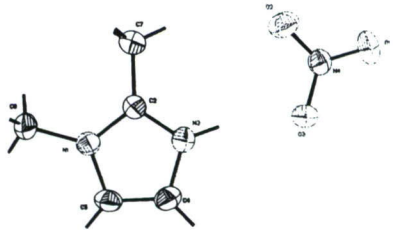
[1-Me-3-H-im][pic]



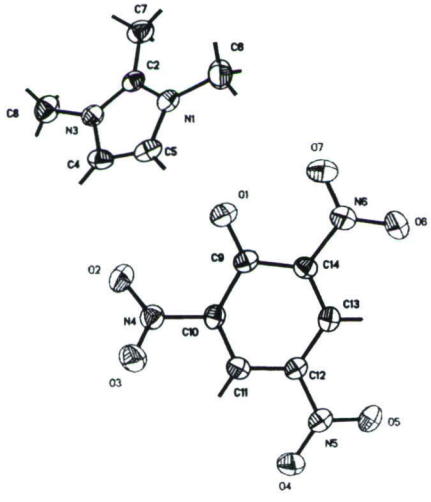
[1,3-diMe-im][pic]



[1-Me-3-H-im][NO_3]



[1,2-diMe-3-H-im][NO_3]



[1,2,3-triMe-im][pic]

Appendix C2

Synthesis and investigation of stability and thermal properties of azolate based ILs, along with crystal structure investigation of formed products

Table C2.2. Crystallographic data for phosphonium and ammonium based salts.

parameter	[Ph_4P][5-NO_2-benztri]	[Ph_4P][4-NO_2-tri]	[Ph_4P][4-NO_2-im]	[Ph_4P][3,5-NO_2-tri]	[Ph_4P][2,4-diNO_2-im]	[Ph_4P][4,5-diNO_2-im]	[Ph_4P][4,5-diCN-im]	[Ph_4P][1-H-tetr]
color/shape	yellow/plate	colorless/rod	colorless/fragment	colorless/rod	yellow/platelet	yellow/platelet	colorless/fragment	colorless/needle
formula	$C_{30}H_{23}N_4O_2P$	$C_{26}H_{21}N_4O_2P$	$C_{27}H_{22}N_3O_2P$	$C_{26}H_{20}N_5O_4P$	$C_{27}H_{21}N_4O_4P$	$C_{27}H_{21}N_4O_4P$	$C_{29}H_{21}N_4P$	$C_{25}H_{21}N_4P$
M_r	502.49	452.44	451.45	497.44	496.45	496.45	456.47	408.43
T [K]	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
crystal system	triclinic	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	tetragonal
space group	P-1	$P2_12_12_1$	$P2_1/n$	$P2_1$/c	P-1	$C2$	$P2_1/c$	$P\bar{4}$
a [Å]	10.3778(8)	7.707(2)	10.805(2)	11.248(2)	7.558(1)	16.678(3)	11.807(2)	11.910(1)
b [Å]	11.3027(9)	13.693(4)	13.150(3)	15.050(3)	10.548(2)	7.2763(13)	13.231(3)	11.910(1)
c [Å]	12.883(1)	21.335(7)	16.035(3)	13.863(2)	15.175(2)	11.583(2)	15.464(3)	7.074(2)
α [°]	66.162(1)	90	90	90	81.403(3)	90	90	90
β [°]	71.886(1)	90	105.910(3)	95.196(3)	83.228(3)	121.193(3)	101.973(4)	90
γ [°]	63.746(1)	90	90	90	81.397(3)	90	90	90
V [Å^3]	1223.42(17)	2251.4(12)	2191.0(8)	2337.1(7)	1177.1(3)	1202.4(4)	2363.3(8)	1003.3(3)
Z	2	4	4	4	2	2	4	2
ρ_{calcd} [g cm^{-3}]	1.364	1.335	1.369	1.414	1.401	1.371	1.283	1.352
independent/ obsd reflns	5591(R_{int} = 0.0226)/ 4669	5341(R_{int} = 0.0232)/ 5002	5085(R_{int} = 0.0285)/ 3987	5556(R_{int} = 0.0286)/ 4377	5347(R_{int} = 0.0126)/ 4675	2712(R_{int} = 0.0217)/ 2455	5106(R_{int} = 0.0360)/ 3811	2385(R_{int} = 0.0368)/ 2047
GooF	1.020	1.068	1.046	1.035	1.046	1.028	1.085	1.084
R_1, wR_2 [$I>2\theta>(I)$]	0.0410, 0.1049	0.0327, 0.0786	0.0487, 0.0956	0.0453, 0.0956	0.0459, 0.0935	0.0419, 0.1009	0.0596, 0.1046	0.0496, 0.1030
R_1, wR_2 (all data)	0.0522, 0.1122	0.0368, 0.0802	0.0690, 0.1022	0.0650, 0.1025	0.0465, 0.0975	0.0490, 0.1051	0.0896, 0.1140	0.0637, 0.1082

[a] $R = \sum| |F_o| - |F_c| |/\sum|F_o|$. $wR_2 = \{\sum[w(F^2_o-F^2_c)^2]/\sum(w(F^2_o)^2]\}^{1/2}$.

Table C2.2. continued

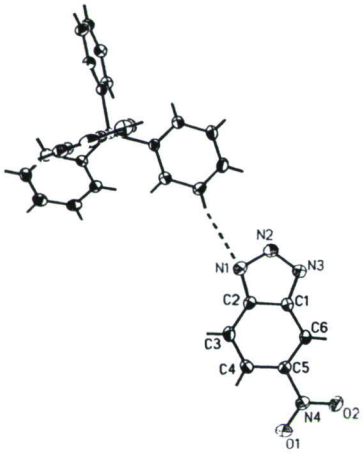
parameter	[Ph_3EtP][5-NO_2-benztri]	[Ph_3EtP][5-NO_2-benzim]·H_2O	[Ph_3EtP][3,5-diNO_2-tri]	[Ph3EtP][2,4-diNO_2-im]	[Ph3EtP][4,5-diNO_2-im]
color/shape	yellow/platelet	fragment/colorless	colorless/platelet	yellow/platelet	yellow/fragment
formula	$C_{26}H_{23}N_4O_2P$	$C_{27}H_{26}N_3O_3P$	$C_{22}H_{20}N_5O_4P$	$C_{23}H_{21}N_4O_4P$	$C_{23}H_{21}N_4O_4P$
M_r	454.45	471.48	449.4	448.41	448.41
T [K]	173(2)	173(2)	173(2)	173(2)	173(2)
crystal system	triclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	P-1	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$	$P2_1/n$
a [Å]	8.562(2)	14.465(3)	8.461(2)	8.434(2)	11.469(3)
b [Å]	11.435(2)	13.514(3)	14.282(3)	14.608(3)	15.228(3)
c [Å]	12.704(3)	13.555(3)	17.812(4)	17.616(3)	12.306(3)
α [°]	101.901(4)	90	90	90	90
β [°]	96.477(4)	114.331(4)	90	90	99.587(4)
γ [°]	105.445(4)	90	90	90	90
V [Å^3]	1154.4(4)	2414.3(8)	2152.6(7)	2170.4(7)	2119.4(8)
Z	2	4	4	4	4
ρ_{calc} [g cm^{-3}]	1.307	1.297	1.387	1.372	1.405
independent/ obsd reflns	5281(R_{int} = 0.0293)/ 3288	5731(R_{int} = 0.0714)/ 3544	4880(R_{int} = 0.0270)/ 4432	5417(R_{int} = 0.0241)/ 4522	5041(R_{int} = 0.0314)/ 3949
GooF	0.995	1.099	1.081	1.033	1.059
R_1, wR_2 [$I > 2\theta(I)$]	0.0538, 0.1048	0.0830, 0.1152	0.0367, 0.0732	0.0325, 0.0752	0.0494, 0.0978
R_1, wR_2 (all data)	0.1053, 0.1193	0.1512, 0.1315	0.0437, 0.0752	0.0417, 0.0784	0.0711, 0.1047

[a] $R = \sum| |F_o| - |F_c| |/\sum|F_o|$. $wR_2 = \{\sum[w(F^2_o - F^2_c)^2]/\sum(w(F^2_o)^2]\}^{1/2}$.

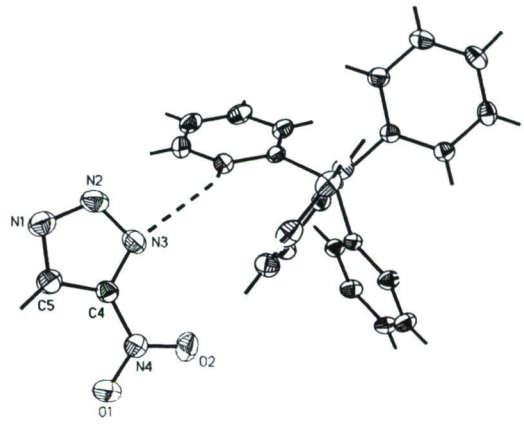
Table C2.2. continued

parameter	[*N*-ph-py][4-NO_2 tri]	[*N*-ph-py][3,5-diNO_2 tri]	[Bu_4N][5-NO_2-benztri]·H_2O	[Bu_4N][5-NO_2-benzim]·H_2O	[Me_4N][5-NO_2-benztri]
formula	$C_{13}H_{11}N_5O_2$	$C_{13}H_{10}N_6O_4$	$C_{22}H_{41}N_5O_3$	$C_{23}H_{40}N_4O_2$	$C_{10}H_{15}N_5O_2$
M_r	269.27	314.27	423.6	404.59	237.27
T [K]	173(2)	173(2)	173(2)	173(2)	173(2)
crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	*P*-1	*P*-1	*C*2/m	$P2_1/n$	$P2_1/c$
a [Å]	6.660(2)	3.812(1)	20.444(4)	9.5056(6)	5.717(1)
b [Å]	7.306(2)	9.972(3)	12.818(2)	19.4098(13)	25.634(5)
c [Å]	14.026(4)	17.938(5)	9.559(2)	26.7082(18)	7.987(2)
α [°]	93.205(5)	85.150(5)	90	90	90
β [°]	90.373(6)	87.310(6)	93.210(4)	96.0890(10)	100.642(4)
γ [°]	116.940(4)	82.144(6)	90	90	90
V [Å^3]	607.1(3)	672.6(3)	2501.1(8)	4899.9(6)	1150.2(4)
Z	2	2	4	4	4
ρ_{calc} [g cm^{-3}]	1.473	1.552	1.125	1.234	1.370
independent/ obsd reflns	2778(R_{int} = 0.0288)/ 1860	3024(R_{int} = 0.0476)/ 1272	3113(R_{int} = 0.0375)/ 1899	11528(R_{int} = 0.0476)/ 5868	2758(R_{int} = 0.0442)/ 1862
GooF	1.100	1.000	1.099	1.012	1.115
R_1, wR_2 [$I > 2\theta(I)$]	0.0929, 0.2031	0.0828, 0.1153	0.0719/0.1238	0.0637, 0.1534	0.0685, 0.1103
R_1, wR_2 (all data)	0.1376, 0.2237	0.2216, 0.1497	0.1305/0.1429	0.1448, 0.1843	0.1130, 0.1230

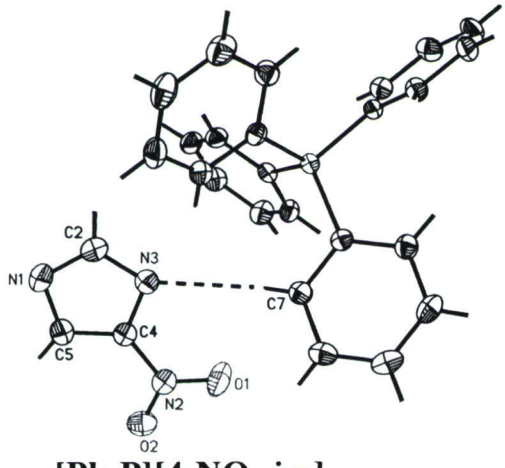
[a] $R = \sum| |F_o| - |F_c| |/\sum|F_o|$. $wR_2 = \{\sum[w(F^2_o - F^2_c)^2]/\sum(w(F^2_o)^2]\}^{1/2}$.



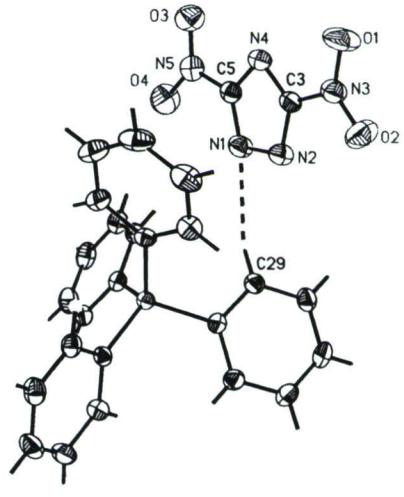
[Ph_4P][5-NO_2-benztri]



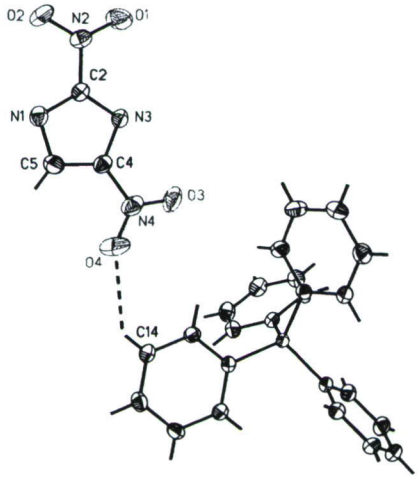
[Ph_4P][4-NO_2-1,2,3-tri]



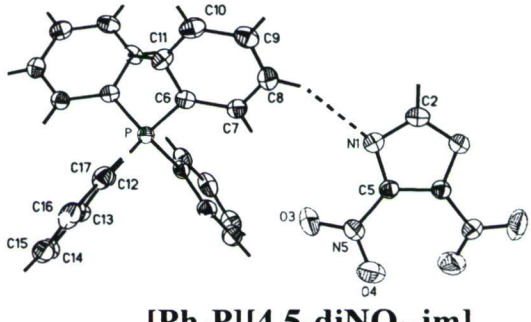
[Ph_4P][4-NO_2-im]



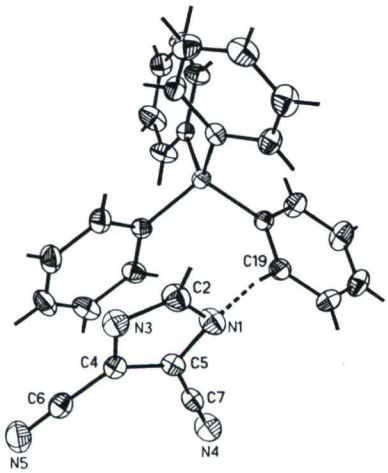
[Ph_4P][3,5-diNO_2-1,2,4-tri]



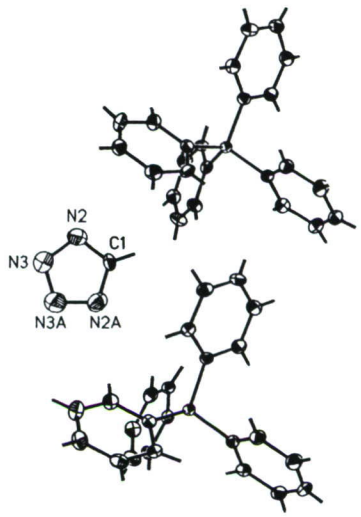
[Ph_4P][2,4-diNO_2-im]



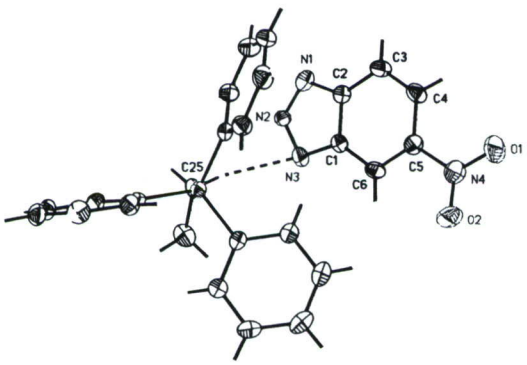
[Ph_4P][4,5-diNO_2-im]



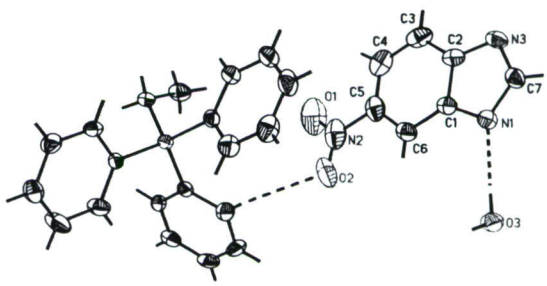
[Ph_4P][4,5-diCN-im]



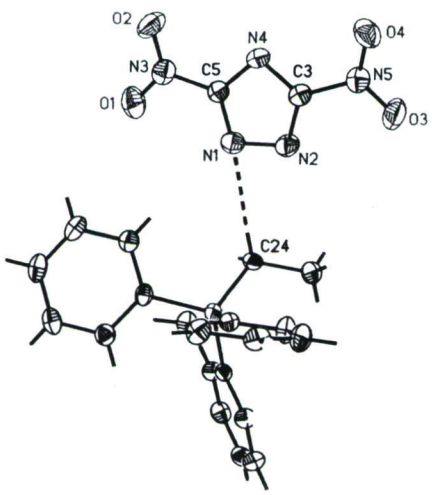
[Ph_4P][tetr]



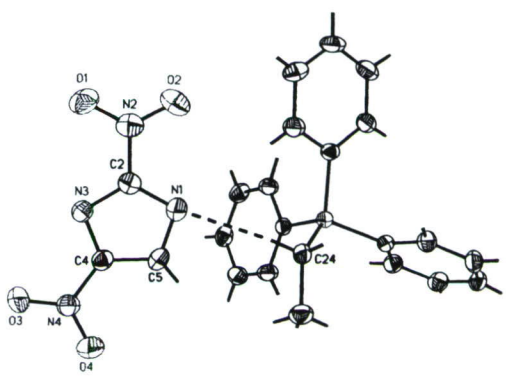
[$EtPh_3P$][5-NO_2-benztri]



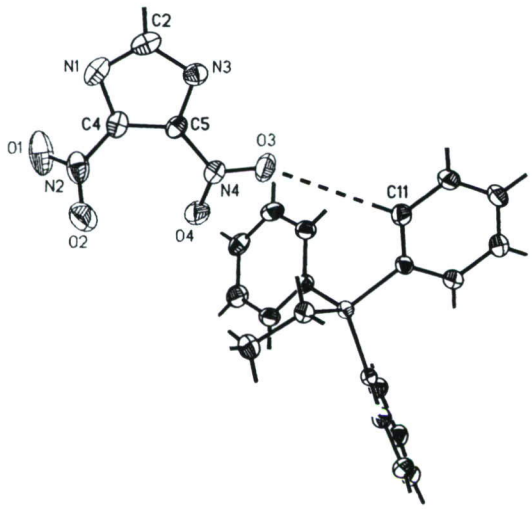
[$EtPh_3P$][5-NO_2-benzim]·H_2O



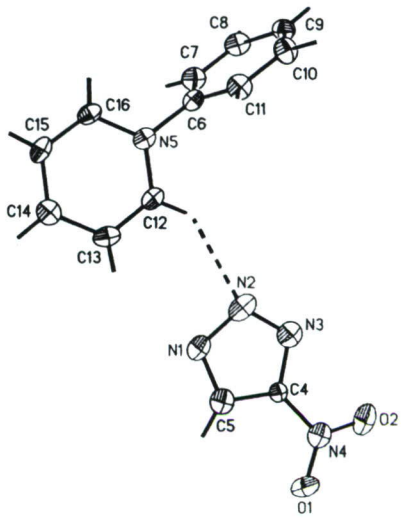
[$EtPh_3P$][3,5-diNO_2-1,2,4-tri]



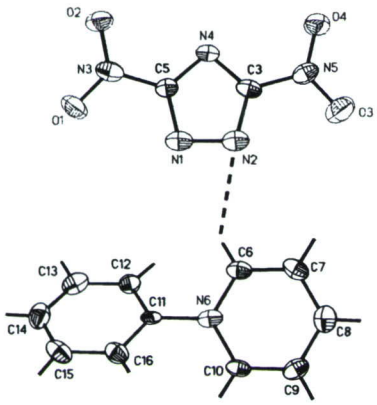
[$EtPh_3P$][2,4-diNO_2-im]



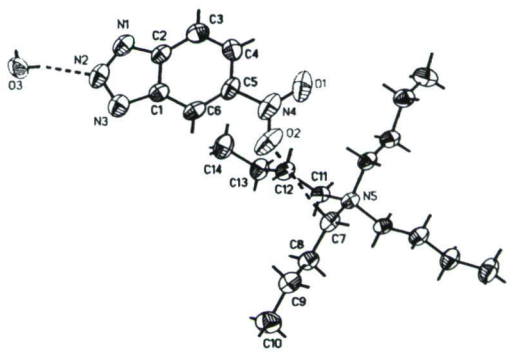
[EtPh$_3$P][4,5-diNO$_2$-im]



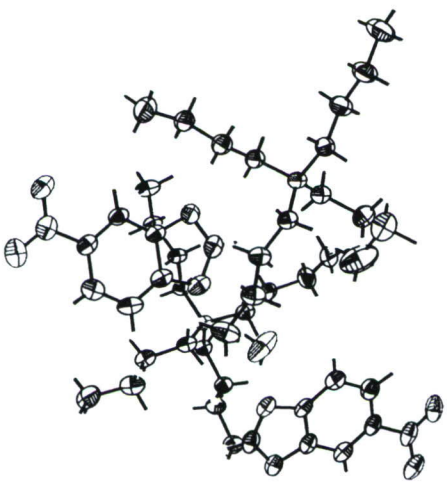
[PhPyr][4-NO$_2$-1,2,3-tri]



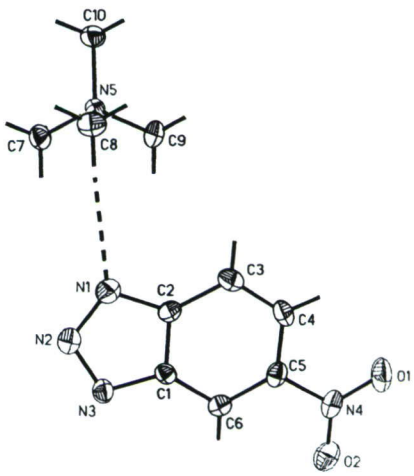
[PhPyr][3,5-diNO$_2$-1,2,4-tri]



[Bu$_4$N][5-NO$_2$-benztri]·H$_2$O



[Bu$_4$N][5-NO$_2$-benzim]·H$_2$O



[Me$_4$N][5-NO$_2$-benztri]

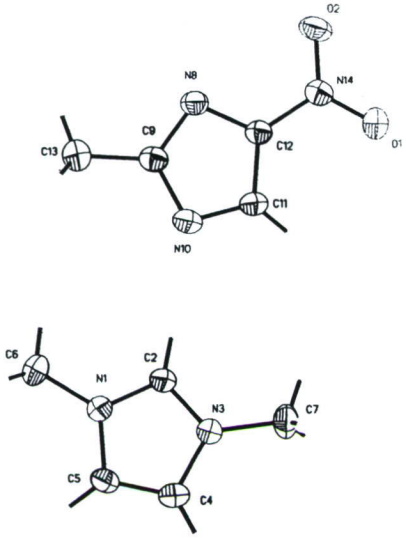
Appendix C3

Azolium Azolates via 1,3-dimethylimidazolium-2-carboxyalte system

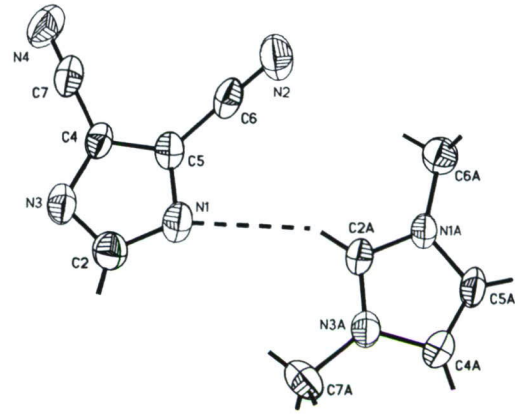
Table C3.2. Crystallographic data for azolium azolate based salts

parameter	[1,3-diMe-im][2-Me-5-NO_2-im]	[1,3-diMe-im][4,5-diCN-im]	[1,3-diMe-im][4-NO_2-im]	[1,3-diMe-im][4,5-diNO_2-im]
formula	$C_9H_{13}N_5O_2$	$C_{10}H_{10}N_6$	$C_8H_{11}N_5O_2$	$C_8H_{10}N_6O_4$
M_r	223.24	214.24	209.22	254.22
T [K]	173(2)	173(2)	173(2)	173(2)
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	P-1	Cc	$P2_1/c$	$P2_1/c$
a [Å]	6.9398(11)	15.839(4)	8.1437(17)	7.8099(17)
b [Å]	8.2348(14)	10.445(3)	10.197(2)	12.914(3)
c [Å]	10.8745(18)	6.8231(17)	12.090(3)	11.053(2)
α [°]	74.600(3)	90	90	90
β [°]	74.851(3)	98.940(5)	92.216(4)	97.967(4)
γ [°]	67.989(3)	90	90	90
V [Å^3]	546.29(16)	1115.0(5)	1003.2(4)	1104.1(4)
Z	--	4	4	4
ρ_{calc} [g cm^{-3}]	1.357	1.276	1.385	1.529
independent/ obsd reflns	--	1142(R_{int} = 0.0359)/ 946	2376(R_{int} = 0.0331)/ 1695	2644(R_{int} = 0.0272)/ 1986
GooF	--	1.131	1.106	1.064
R_1, wR_2 [$I>2\theta>(I)$]	0.0416, 0.1170	0.0560, 0.1165	0.0564, 0.0970	0.0533, 0.1125
R_1, wR_2[a] (all data)	0.0552, 0.1260	0.0707, 0.1216	0.0935, 0.1084	0.0777, 0.1220

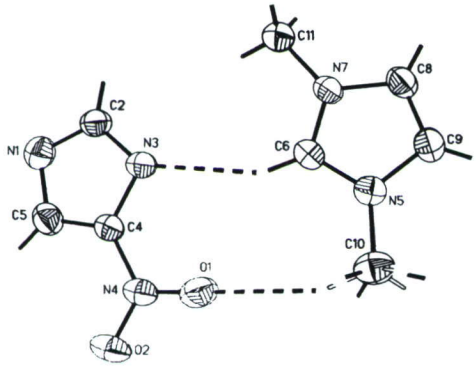
[a] $R = \sum| |F_o| - |F_c| |/\sum|F_o|$. $wR_2 = \{\sum[w(F^2_o-F^2_c)^2]/\sum(w(F^2_o)^2]\}^{1/2}$.



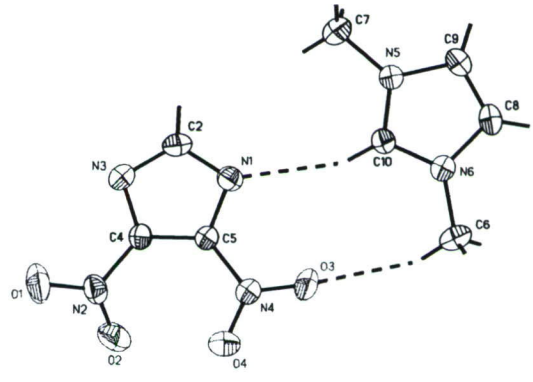
[1,3-diMe-im][2-Me-5-NO_2-im]



[1,3-diMe-im][4,5-diCN-im]



[1,3-diMe-im][4-NO_2-im]



[1,3-diMe-im][4,5-diNO_2-im]

Appendix D
Protocols and equipment

Appendix D1
NMR analyses.

NMR spectra were obtained in DMSO-d_6 or D_2O with TMS or residual hydrogen signals in the deuterated solvent used as the internal standard for ^{1}H (360 or 500 MHz) and for ^{13}C (90 or 125 MHz).

Appendix D2
TGA analysis

Thermal decomposition temperatures were measured in the dynamic heating regime using a TGA 2950 TA Instrument under helium, nitrogen, argon and air atmospheres. Samples between 2-10 mg were heated from 40–600 °C under constant heating at 5 °C min^{-1}.

Appendix D3
DSC analysis

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, $\Delta H = 28.71$ J g^{-1}). Data were collected at constant atmospheric pressure, using samples between 10-40 mg in aluminum sample pans sealed using pin-hole caps. 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; matched sample and reference pans (within ± 0.20 mg) were used.

Appendix D4
PXRD analysis (powder X-ray diffraction)

Bulk sample compositions were investigated using a Rigaku Powder Diffractometer (Woodlands, TX) at 25 °C with Cu/Kα radiation ($\lambda = 1.5418$ Å) in the 2θ range 10-50 °. Step intervals were taken at 0.1 ° steps at 1.2 ° min^{-1}. Peaks were normalized in each scan to the highest peak in the spectrum. Then each spectrum was overlaid, offset, and combined to a single graph.

XRD analysis (single crystal X-ray diffraction)

Data for all single crystal structural determinations were collected on a Bruker CCD area detector-equipped diffractometer with graphite monochromated Mo/Kα radiation ($\lambda =$ 0.71073 Å) and structures solved using SHELXTL [i]. Absorption corrections were made with SADABS [ii]. All non-hydrogen atoms were readily located and refined anisotropically. The structures were refined by full-matrix least squares on F^2. In cases of disorder, alternate positions were found and refined with alternating least-squares cycles. All hydrogen atoms were found from a difference Fourier map unless otherwise stated.

[i] Sheldrick, G. M. *SHELXTL, Version 6.14*; Bruker AXS, Inc.: Madison, WI, 2003.
[ii] Sheldrick, G. M. *Program for Semiempirical Absorption Correction of Area Detector Data*, University of Göttingen: Germany, 1997.

Appendix D5

ARC analysis

Accelerating rate calorimetry measurements were obtained under adiabatic conditions in a sealed titanium bomb under oxygen at 100 psig pressure using an Arthur D. Little ARC 2000^{TM} accelerating rate calorimeter. Samples (0.2–0.5 g) were heated 10 °C min^{-1}, using a stepping heat-wait-search protocol with each step of 10 °C to determine the onset of self-heating (excess heating rate > 0.02 °C min^{-1}).