

### ENERGETIC IONIC LIQUIDS: FUNDAMENTAL STUDIES RELATING TARGET STRUCTURES AND KEY PHYSICAL PROPERTIES

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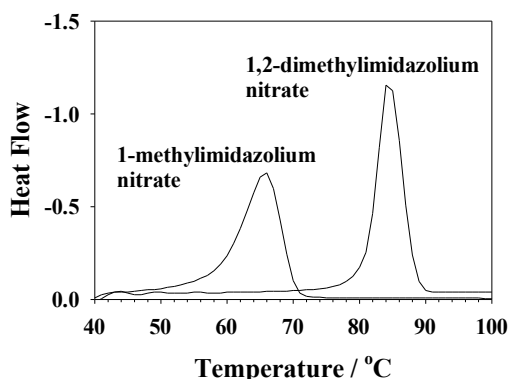
The most challenging, and initially counter intuitive aspect of ionic liquids, is that they exist at room temperature. ILs are wholly dissociated liquid salts, yet are liquids at low (room) temperature and have essentially no vapor pressure, in contrast to most inorganic salts which exhibit high melting points and high vapor pressures in the molten state. Salts are conventionally considered as high melting materials, as a consequence of highly associative, and structuring Coulombic cation-anion attractive forces - whereas by observation, ILs exhibit low melting behavior as a result of disrupting the attractive ion-ion interactions by introducing structural 'buffer-zones' of van der Waals-only regions into the ions, principally cations which suppress crystallization leading to formation of either glasses on cooling, or low lattice energy solids, with opportunities for both polymorphism and plastic crystal formation.

Some existing propellant and fuel components such as trimethylammonium nitrate, are ionic liquid materials and a limited number of ILs with 'energetic' anions are known (e.g., nitrate [NO<sub>3</sub>], perchlorate [ClO<sub>4</sub>], and dicyanamide [N(CN)<sub>2</sub>]), but have not been systematically investigated.

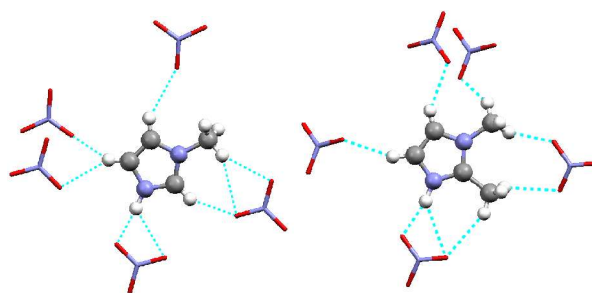
Thus there exists a need to understand the relationship between introduction of different chemical functions and components into potential ionic liquid cations and anions, and the resultant physical/rheological properties as criteria for developing new ionic liquid materials. The effects of introducing different functional groups around the periphery of cations, and varying the types of anions of organic salts has been investigated using simple substituted imidazolium and pyrrolidinium systems which were chosen to furnish solid salts for which single crystal X-ray diffraction could be used to probe interactions in the solid state while the range and stability of the ionic liquid phases was monitored by DSC, TGA-MS and Accelerated Rate Calorimetry.

Two approaches have been taken, preparing protonated and quaternized salts with a series of methyl, nitro, and nitrile substituents on the cations, and with nitrate, picrate and dicyanamide anions, using either alkylation with dimethylcarbonate followed by metathesis (quaternized systems) or neutralization of the heterocyclic bases with appropriate acids (protonated salts).

Crystalline salts such as 1-methyl-3-H-imidazolium nitrate (space group: P2<sub>1</sub>/c, mp: 65.8 °C, ΔH<sub>fus</sub>: 103 J g<sup>-1</sup>, T<sub>decomp</sub>: 155 °C), 1,2-dimethyl-3-H-imidazolium nitrate (space group: P2<sub>1</sub>/n, mp: 84.4 °C, ΔH<sub>fus</sub>: 110 J g<sup>-1</sup>, T<sub>decomp</sub>: 159 °C), 1,3-dimethylimidazolium picrate (space group: P-1, mp: 149 °C, ΔH<sub>fus</sub>: 110 J g<sup>-1</sup>, T<sub>decomp</sub>: 227 °C), and 1,2,3-trimethylimidazolium picrate (space group: P-1, mp: 118 °C, ΔH<sub>fus</sub>: 76 J g<sup>-1</sup>, T<sub>decomp</sub>: 271 °C) have been prepared, isolated, and characterized. The properties of these and related IL salts, and the effects of introducing different anions and cation substituents will be described.



Melting point transitions from the solid to liquid phases for 1-methyl-3H-imidazolium nitrate and 1,2-dimethyl-3-H-imidazolium nitrate determined by DSC.



Packing of anions around the cations in the crystal structures of 1-methyl-3H-imidazolium nitrate (*left*) and 1,2-dimethyl-3-H-imidazolium nitrate (*right*).

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