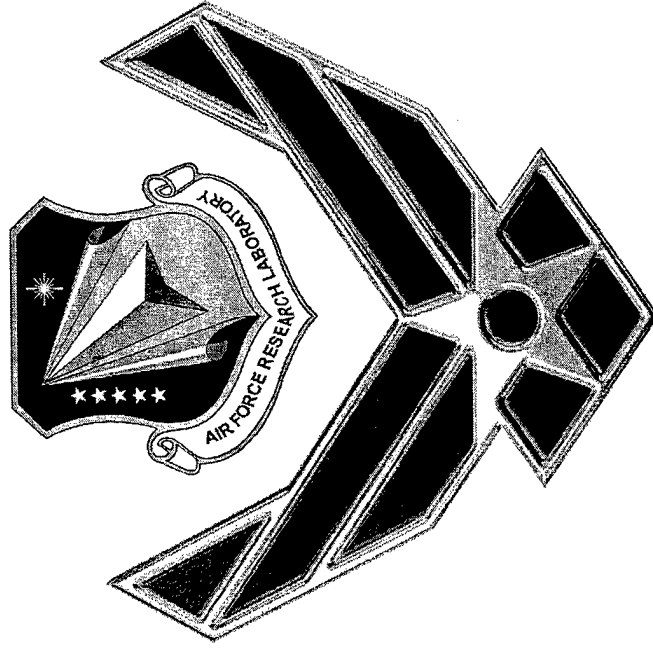


Research in Energetic Ionic Liquids

October 2002



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High Energy Density Materials

Research

AFRL/PRSP

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Air Force Research Laboratory

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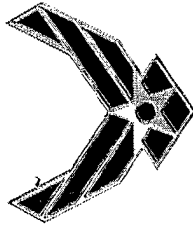
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55355

AFOSR Workshop hosting gov't & academic researchers
(Dulles, VA, 9-10 October 2002)

(Statement A)



Energetic Ionic Liquids



Before we get started....

People who have been and are critical to our research project

Tommy Hawkins

Kerri Tollison

Adam Brand and Milton Mckay

Lt. Leslie Hall and Ashwani Vij

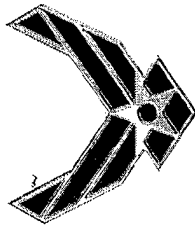
Mike Berman AFOSR

Tommy Highsmith ATK/Thiokol

Mark Petrie /Jeff Bottaro SRI Int.

Mike Huggins

Jeff Sheehy



Energetic Ionic Liquids

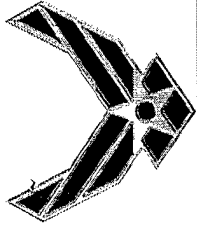


Energetic Ionic Liquids- one of the new focal points for HEDM research. Why are we here today? HEDM research effort has shifted away from cryogenic/matrix isolation and now is pointing into synthetic endeavors

Goal: Build a solid working relationship between theoretical/computational and synthetic chemists as well as having work going on in decomposition areas in trying to fully understand energetic ionic liquids. Both sides of the fence need guidance from each other to be truly productive in a practical sense.

Ionic liquids have been around a very long time (100 years), and recently they have really taken off. But in this "take off" most researchers are looking for applications in the use of ionic liquids. Few people are looking at ionic liquids for the "why" these materials are low melting and how this unusual class of compounds might be more useful for other applications.

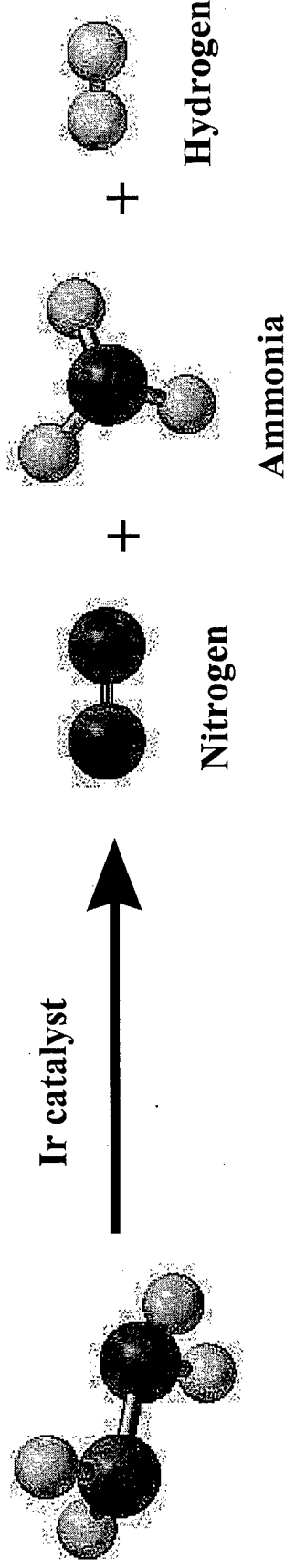
Our research at AFRL has been working on designing, synthesizing, and fully characterizing new low melting energetic salts which are useful.



Energetic Ionic Liquids



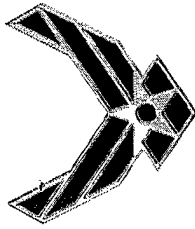
State of the art is hydrazine, N_2H_4 , which is used in many satellite systems



Advantages: Tried and true for several decades, relatively cool burning for hardware.

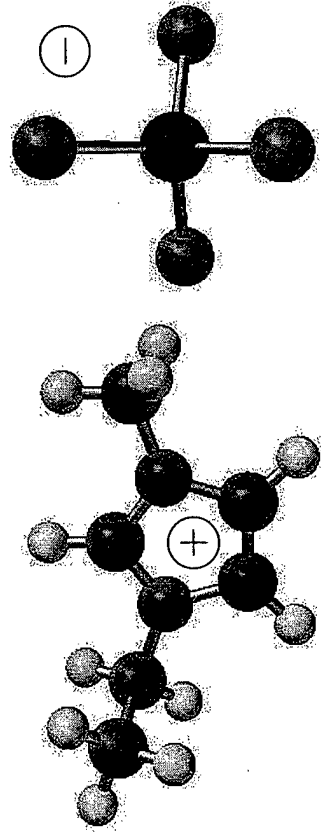
Disadvantages: Hydrazine is extremely toxic (carcinogenic), has a high vapor pressure, a high melting point ($1^\circ C$), and results in workers using self contained suits.

Our approach at AFRL has been investigating new low melting salts as they have inherent advantages including higher densities and negligible vapor pressures.



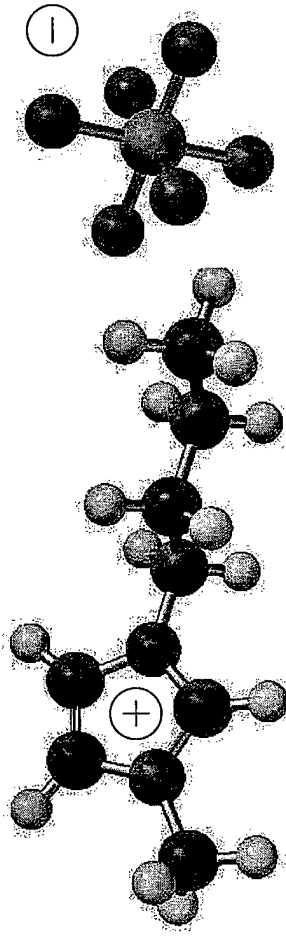
Energetic Ionic Liquids

Ionic liquids research was really opened up by the pioneering work of John Wilkes, Charles Hussey and others under USAF research looking for new battery electrolytes. Dealt heavily with aluminum halide anions early on.

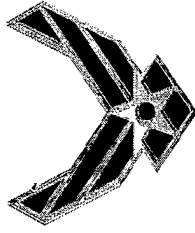


1-ethyl-3-methylimidazolium tetrachloroaluminate

Later, water stable ionic liquids were synthesized by Wilkes and coworkers which opened up the currently rapidly expanding field that we see today.

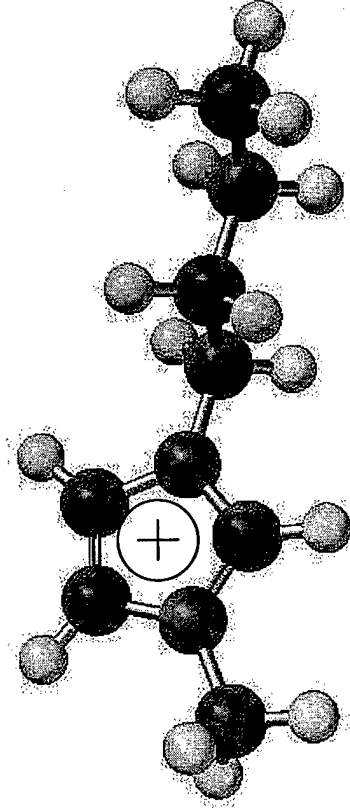


1-butyl-3-methylimidazolium hexafluorophosphate

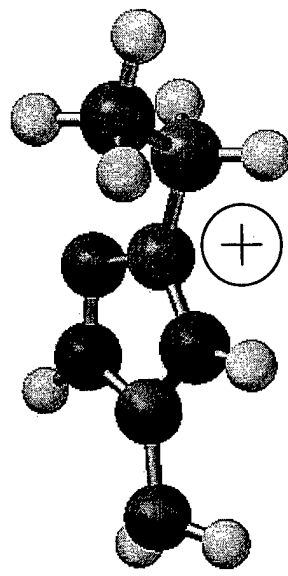


Energetic Ionic Liquids

Most ionic liquids are based upon imidazolium rings and “heavy” or “dead” anions. We felt that we could use the shape of the cation and the poor fit idea to make much more energetic salts in a simple manner.

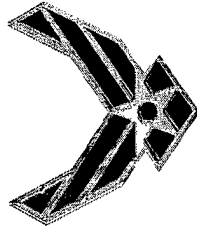


1-n-butyl-3-methyl imidazolium cation

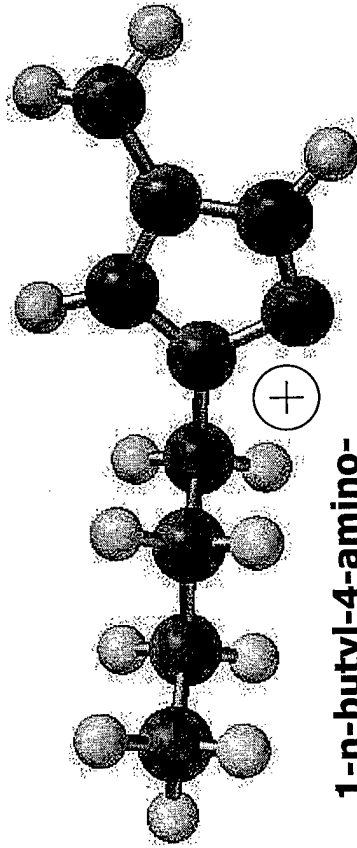


1-ethyl-4-amino-1,2,4-triazolium cation

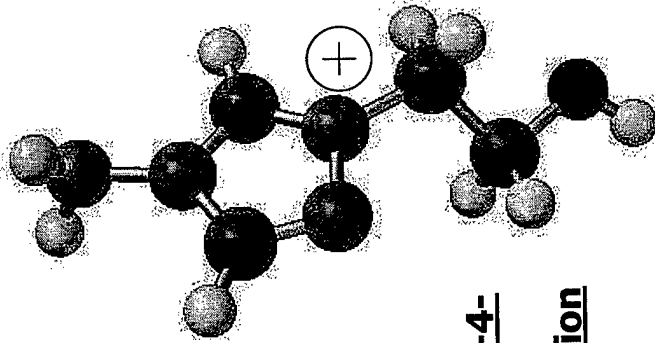
AFRL energetic ionic liquids have similar shapes and physical properties, BUT higher ΔH_f , higher density, and better oxygen balances.



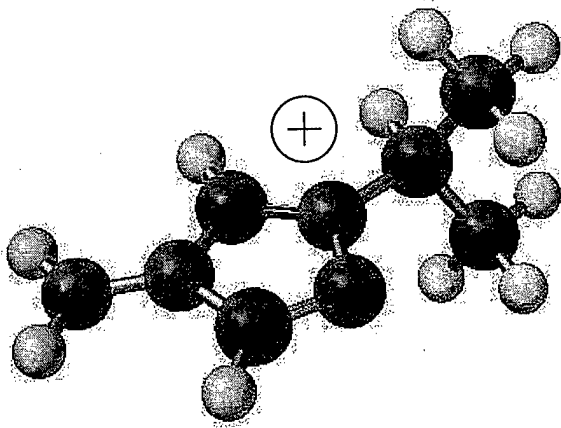
Energetic Ionic Liquids



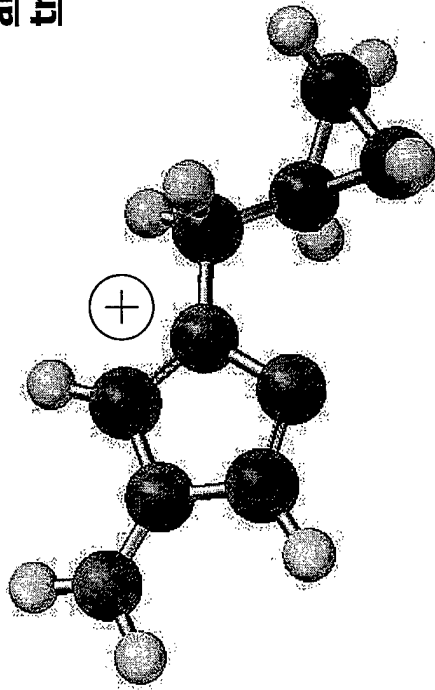
1-n-butyl-4-amino-
1,2,4-triazolium cation



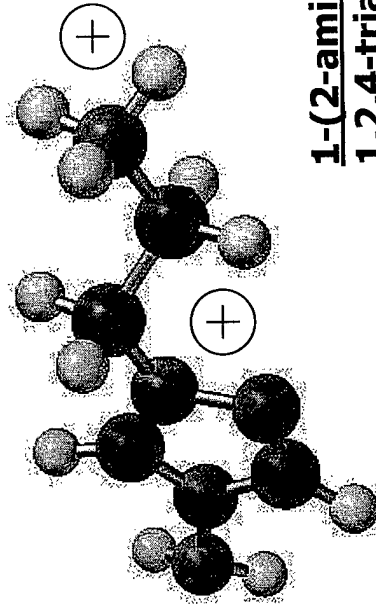
1-(2-ethanol)-4-
amino-1,2,4-
triazolium cation



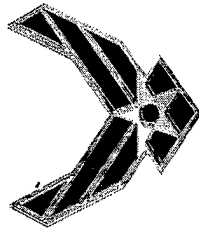
1-isopropyl-4-amino-
1,2,4-triazolium cation



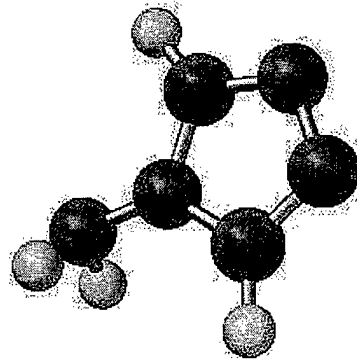
1-methylcyclopropyl-4-amino-
1,2,4-triazolium cation



1-(2-aminoethyl)-4-amino-
1,2,4-triazolium dication

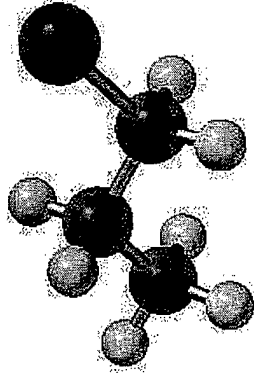


Energetic Ionic Liquids

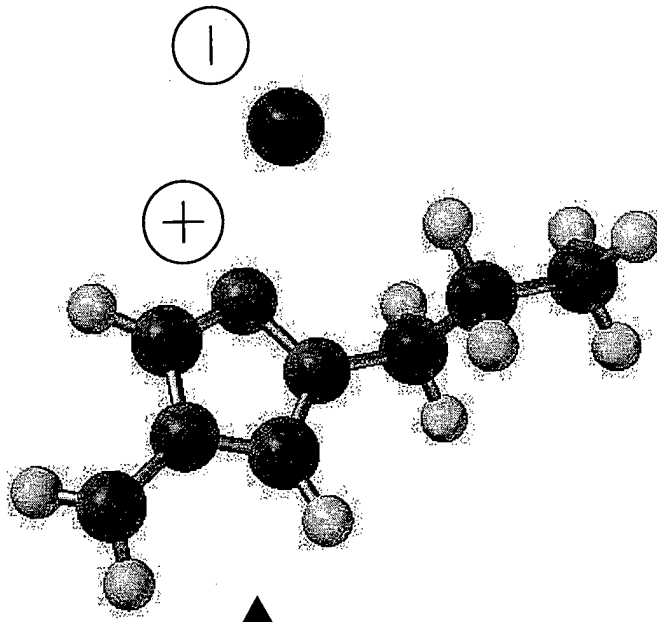


4-amino-1,2,4-triazole

+ XS



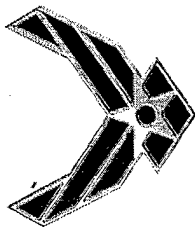
N-propyl bromide



1-n-propyl-4-amino-1,2,4-triazolium bromide
(yield >95% very pure)

Synthesis is from commercial materials
High yield simple isolation has been known
in literature for quite sometime.

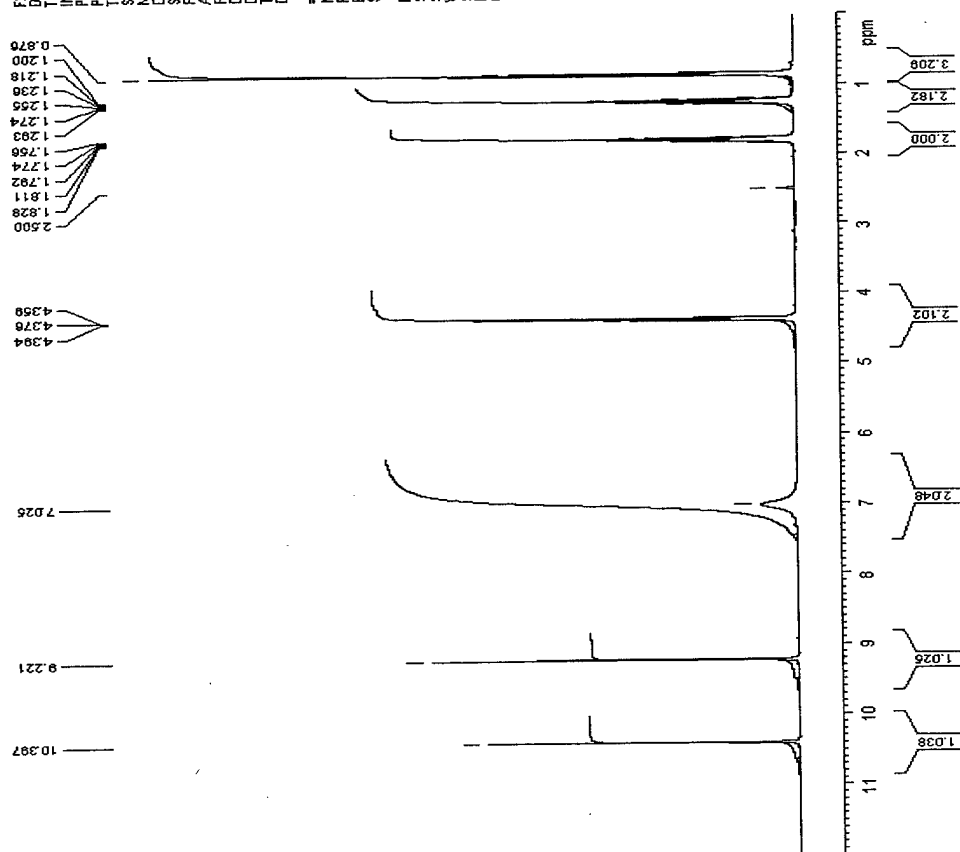
Scriven; Keay; Goe; Astleford J. Org. Chem. **1989**, *54*, 731.



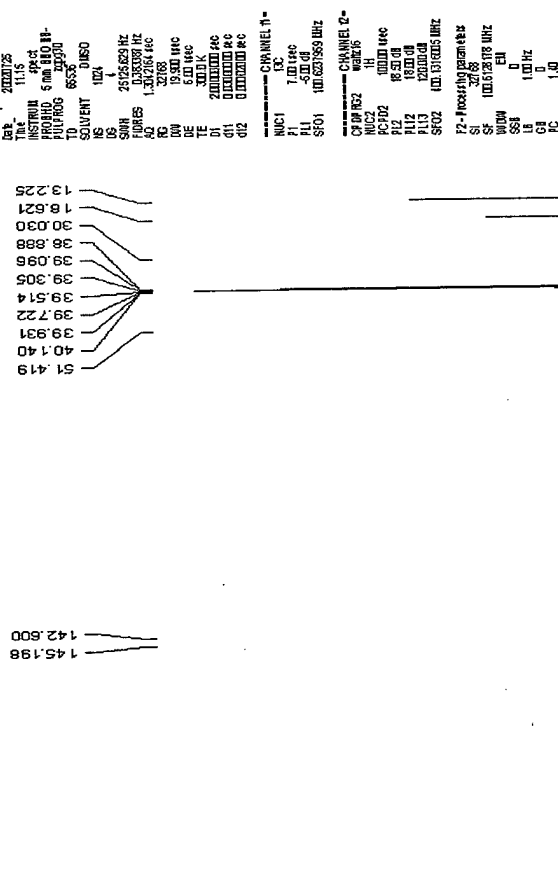
Energetic Ionic Liquids



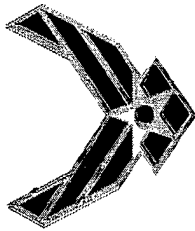
proton of 1-n-butyl 4-amino-1,2,4-triazolium bromide solid in d6-DMSO



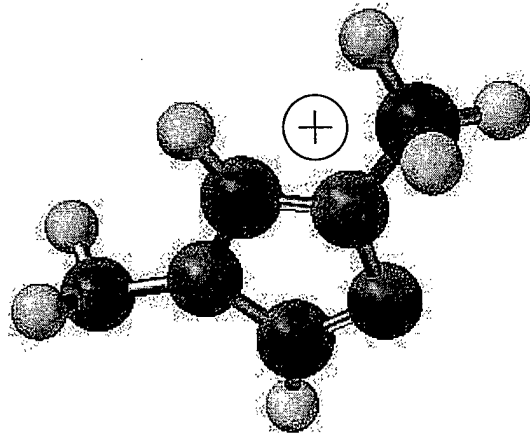
carbon of 1-n-butyl 4-amino-1,2,4-triazolium bromide solid in d6-DMSO



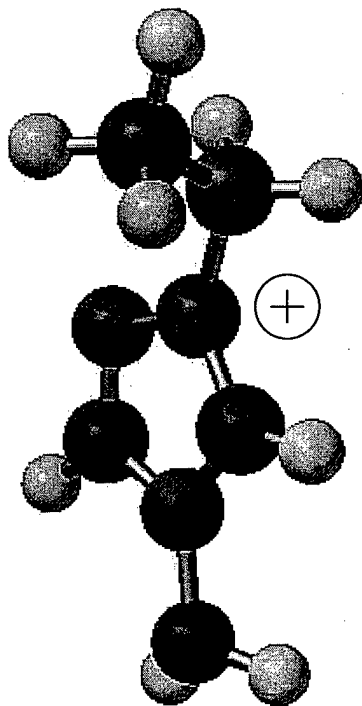
¹H(left) and ¹³C nmr spectra of 1-butyl-4-amino-1,2,4-triazolium bromide.



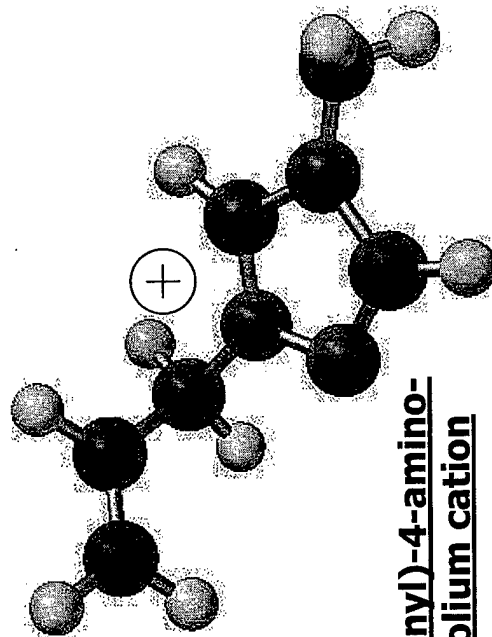
Energetic Ionic Liquids



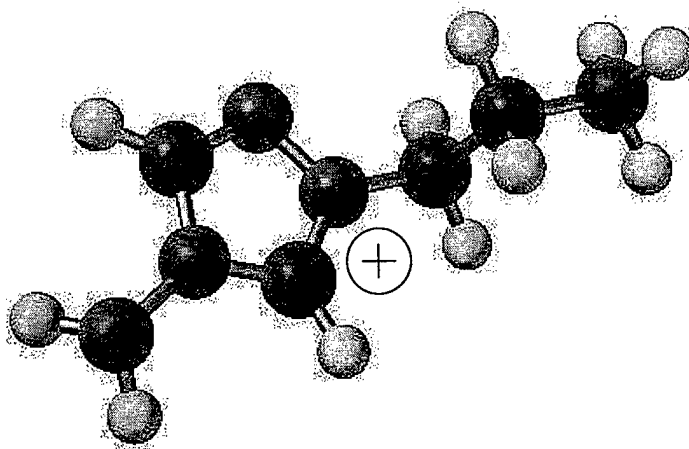
1-methyl-4-amino-
1,2,4-triazolium cation



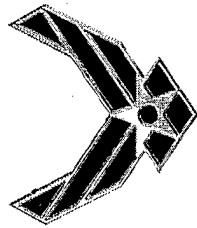
1-ethyl-4-amino-
1,2,4-triazolium cation



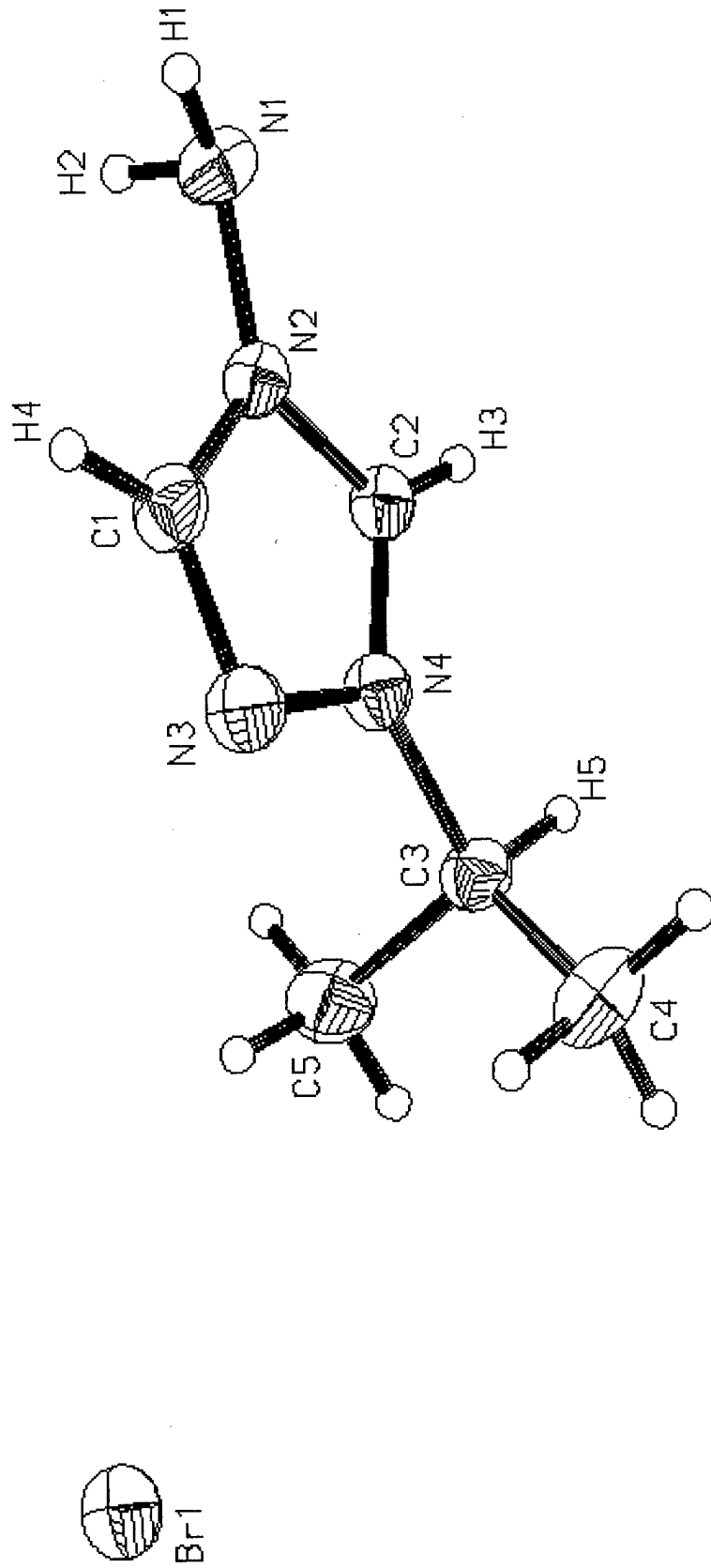
1-(2-propenyl)-4-amino-
1,2,4-triazolium cation



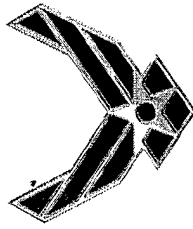
1-n-propyl-4-amino-
1,2,4-triazolium cation



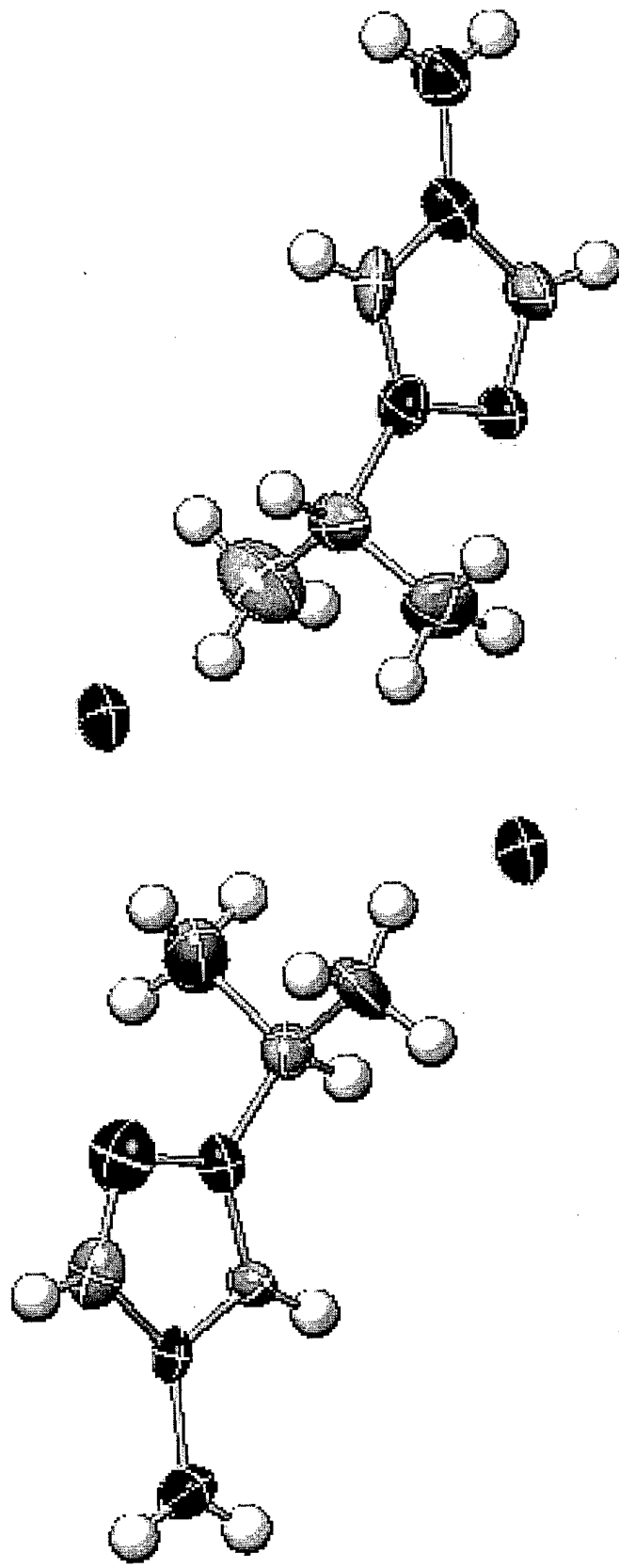
Energetic Ionic Liquids



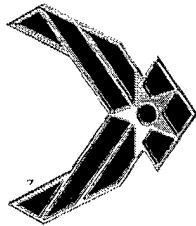
Single crystal x-ray diffraction study ORTEP view of 1-isopropyl-4-amino-1,2,4-triazolium bromide(Dr. A. Vij and Lt L. Hall)



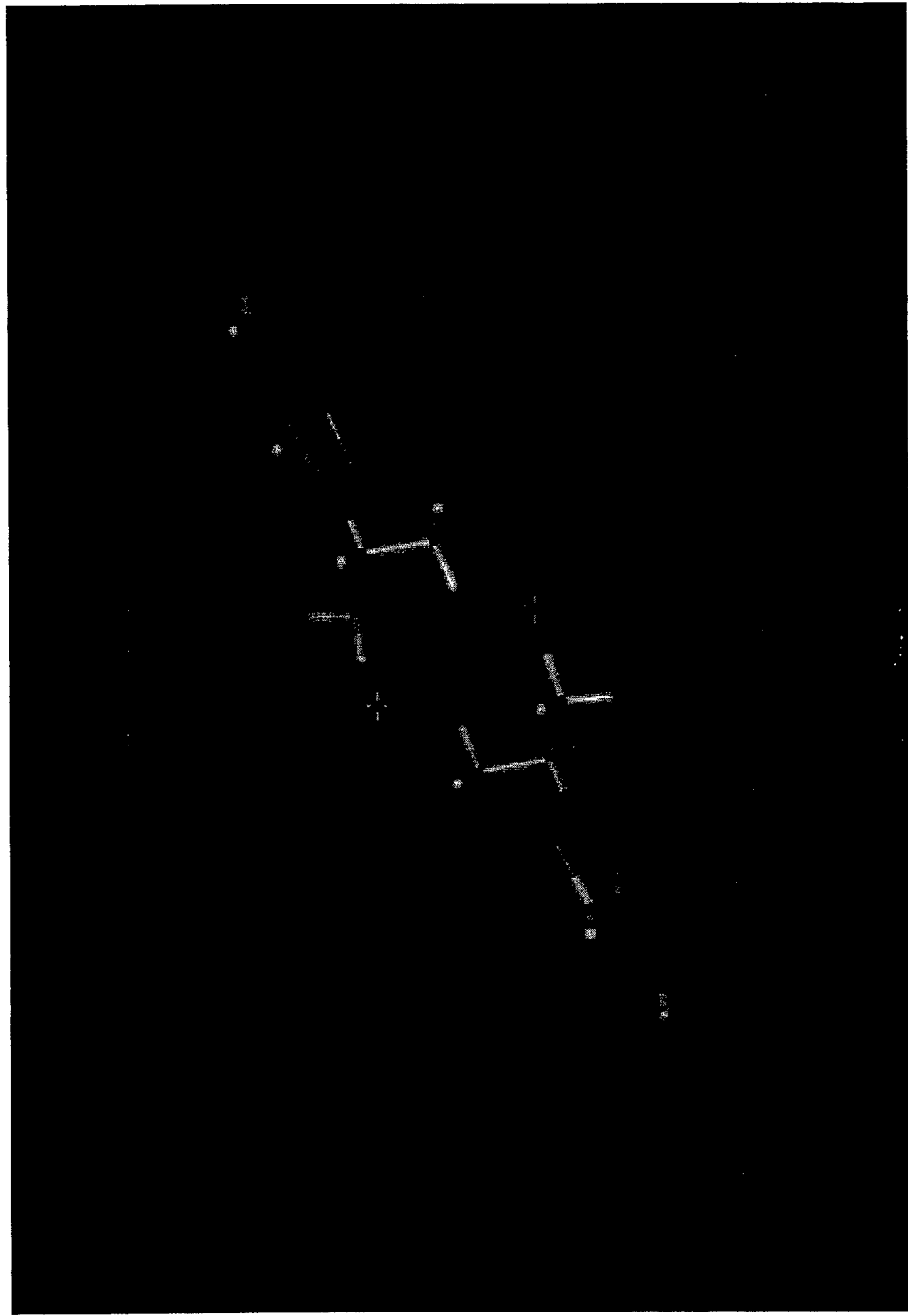
Energetic Ionic Liquids



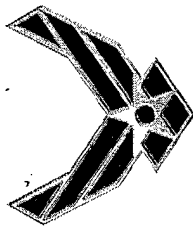
Single crystal x-ray diffraction study of 1-isopropyl-4-amino-1,2,4-triazolium bromide



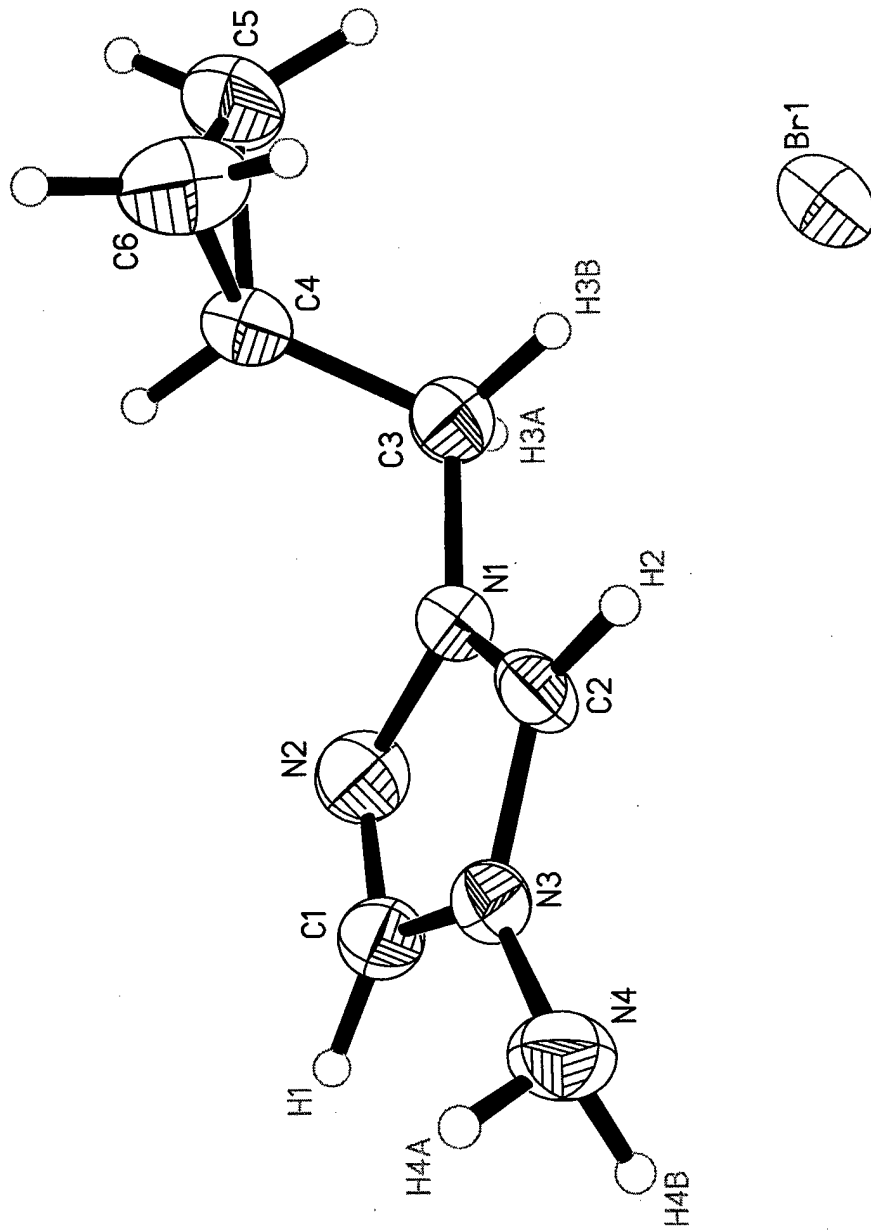
Energetic Ionic Liquids



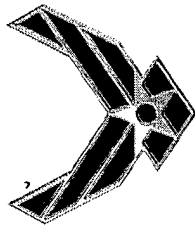
Single crystal x-ray diffraction study of 1-isopropyl-4-amino-1,2,4-triazolium bromide



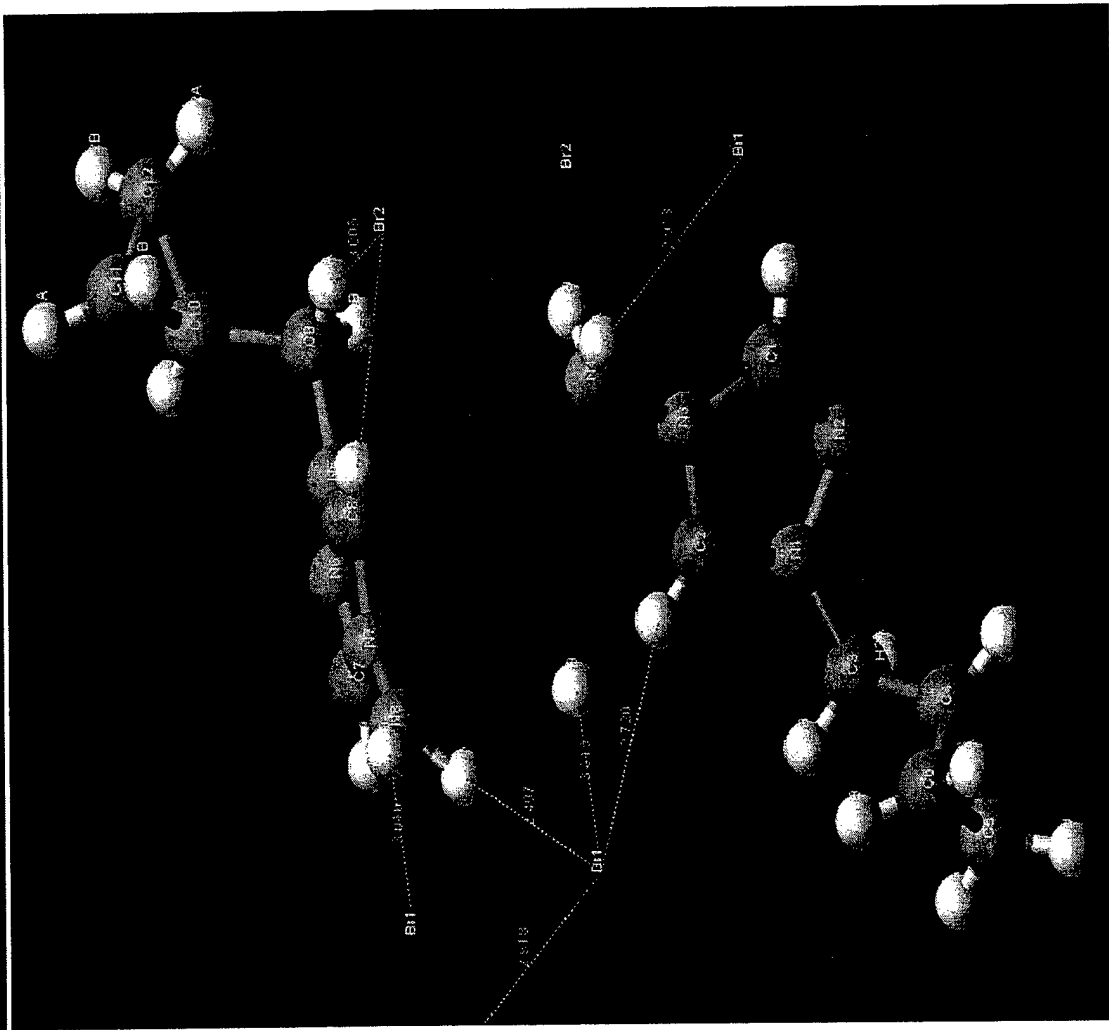
Energetic Ionic Liquids



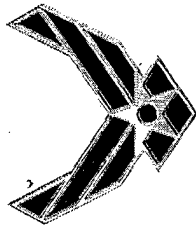
Single crystal x-ray diffraction study ORTEP view of 1-cyclopropylmethyl-4-amino-1,2,4-triazolium bromide(Dr. A. Vij and Lt L. Hall)



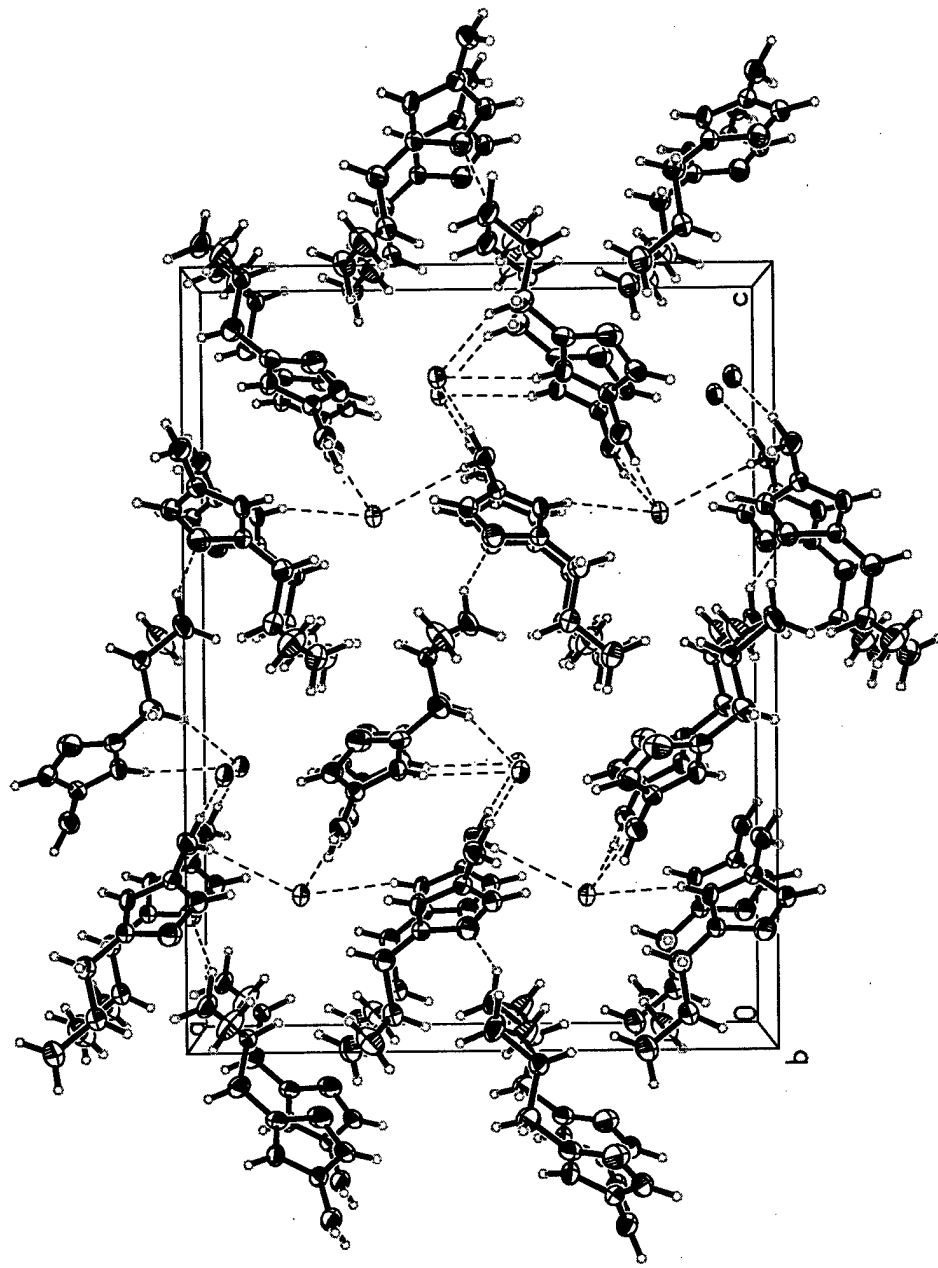
Energetic Ionic Liquids



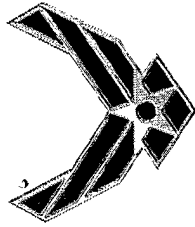
Br...H-N interactions in 1-cyclopropylmethyl-4-amino-1,2,4-triazolium bromide



Energetic Ionic Liquids



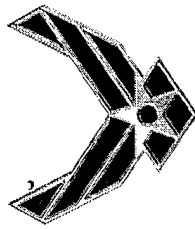
Packing in unit cell of 1-cyclopropylmethyl-4-amino-1,2,4-triazolium bromide



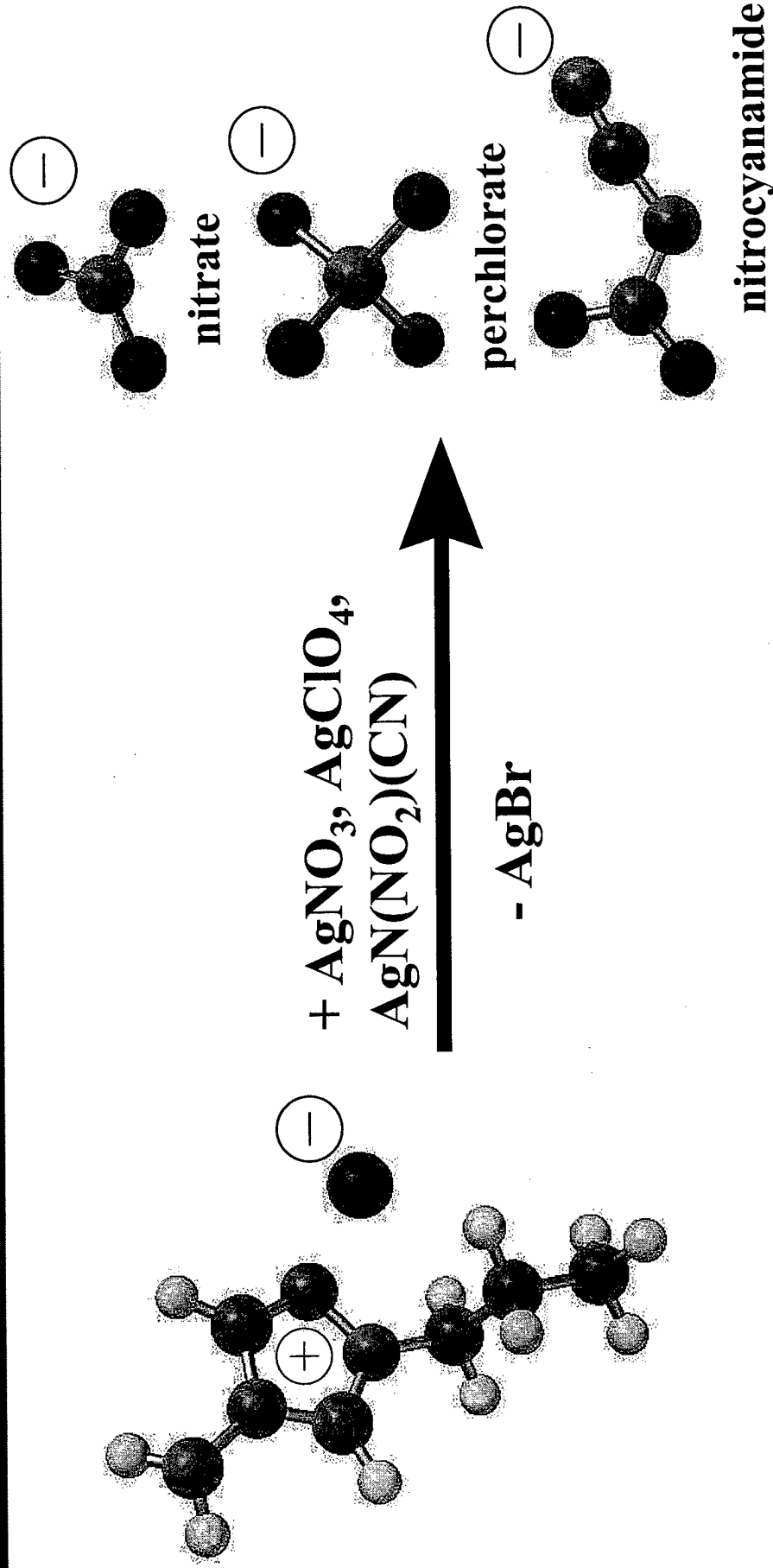
Energetic Ionic Liquids

Physical property trends of 1-n-alkyl substituted-4-amino-1,2,4-triazolium bromide salts roughly follow some trends but not all. Substituted 4-amino-1,2,4-triazolium bromide salts have increasing melting points with increasing molecular weights, decomposition onsets that are relatively low, and densities which follow the expected decreasing trend with increasing alkyl chain length.

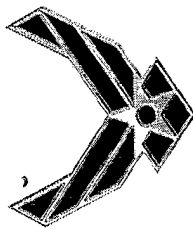
Substituted 4AT salts	m.p. (°C)	dec. onset (°C)	density (g/cm ³)
1-ethyl	63°	110	1.69
1-n-propyl	60°	120	1.56
1-isopropyl	90°	110	1.60
1-butyl	48°	130	1.46
1-n-pentyl	54°	130	1.37
1-n-hexyl	76°	120	1.34
1-n-heptyl	94°	120	1.30
1-n-octyl	80°	135	1.27
1-n-nonyl	81°	140	1.26
1-n-decyl	90°	135	



Energetic Ionic Liquids



Synthesis is straight-forward and high yield with simple filtration to remove silver halide to give high purity ionic liquid. We have synthesized a large family of new salts based on this methodology.



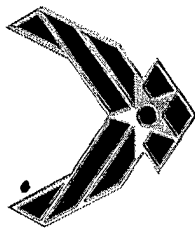
Energetic Ionic Liquids



We have studied many but not all of the cation systems and have found some intriguing physical properties. The nitrate salts are much more thermally stable than their halide precursors and are extremely interesting.

1-substituted-4-amino-1,2,4-triazolium nitrate salts

<u>Salt</u>	<u>melting point(°C)</u>	<u>decomp onset(°C)</u>	<u>density(g/cm³, est.)</u>
1-methyl	54	185	1.57
1-ethyl	5	185	1.39
1-n-propyl	37	190	1.35
1-n-butyl	-10	190	1.31
1-(2-ethanol)	10	180	1.48
1-methylcyclopropyl	56	190	
1-(2-propenyl)	10	165	



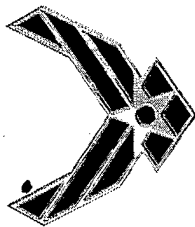
Energetic Ionic Liquids



The perchlorate salts are even more thermally stable than the nitrate salts and are interesting as well.

1-substituted-4-amino-1,2,4-triazolium perchlorate salts

<u>Salt</u>	<u>melting point(°C)</u>	<u>decomp onset(°C)</u>	<u>density(g/cm³, est.)</u>
1-methyl	83	250	1.62(1.59m)
1-ethyl	5	195	1.54
1-n-propyl	0	190	1.49
1-n-butyl	39	240	1.44
1-(2-ethanol)	10	175	1.63
1-methylcyclopropyl	5	150	
1-(2-propenyl)	-11	185	



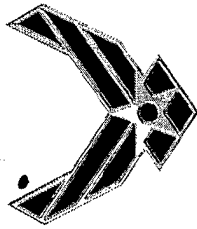
Energetic Ionic Liquids



The nitrocyuanamide salts are similar to the nitrate salts, are the least viscous, and have the lowest melting points.

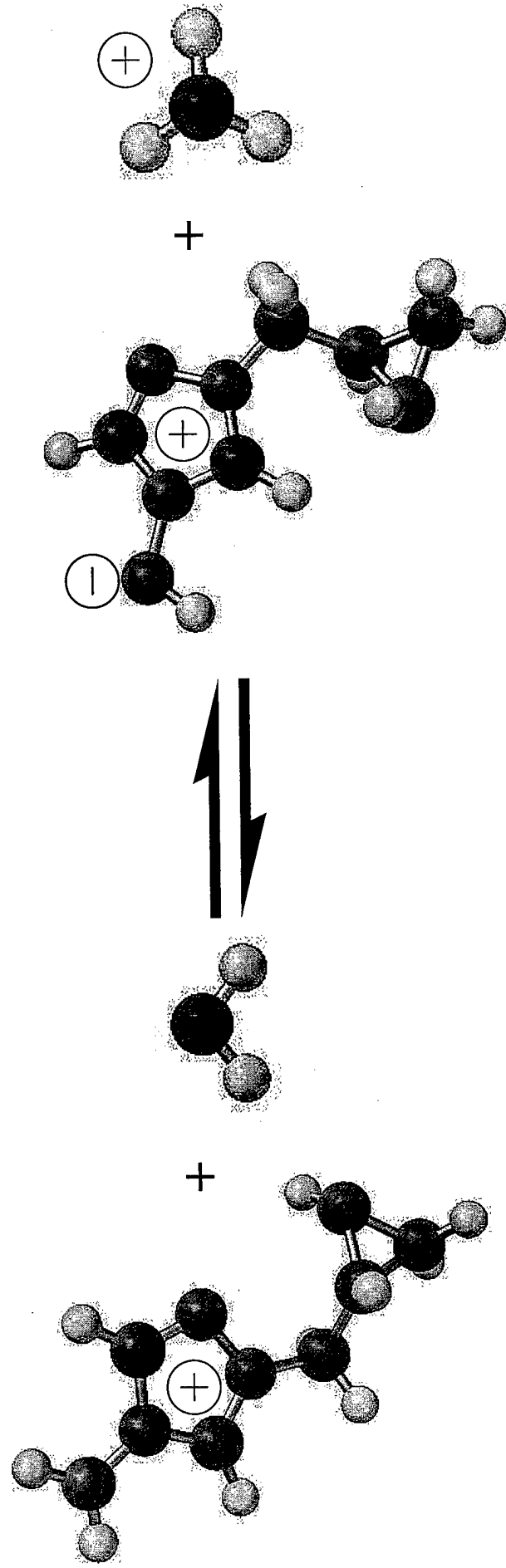
1-substituted-4-amino-1,2,4-triazolium nitrocyuanamide salts

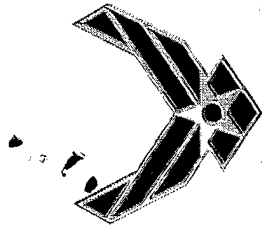
<u>Salt</u>	<u>melting point(°C)</u>	<u>decomp onset(°C)</u>	<u>density(g/cm³, est.)</u>
1-methyl	11	180	
1-ethyl	10	175	1.37
1-n-propyl	5	185	1.33
1-n-butyl	<0 ?	175	1.30
1-(2-ethanol)	<0 ?	175	1.43
1-methylcyclopropyl	-10	195	
1-(2-propenyl)	-11	185	



Energetic Ionic Liquids

The new energetic cations are weakly acidic in nature, aqueous solutions have a pH of around 5 which suggests the following equilibrium involving a zwitterionic 1-alkyl-4-amido-1,2,4-triazolium species. We have not tried to isolate this species yet to see if it exists. But similar chemistry has been observed with the acidic parent heterocycle 4-amino-1,2,4-triazole. This equilibrium could be one possible way for the ionic liquids to “come apart”.





Energetic Ionic Liquids

Important issues for energetic ionic liquids

Structural features affect physical properties

Poor fit between cation and anion

5 or 6 membered heterocyclic rings appear to be important with asymmetric substituents.

Size, overall shape, and nature(basicity) of anion

Hydrogen bonding can make major impact on physical properties
intra- versus inter- molecular interactions especially melting point and viscosity

Cation-anion interactions affecting melting point/viscosity

Decomposition routes

pKa of parent heterocyclic ring

basicity of counterion

“active” hydrogens (-OH, NH₂, CHX)