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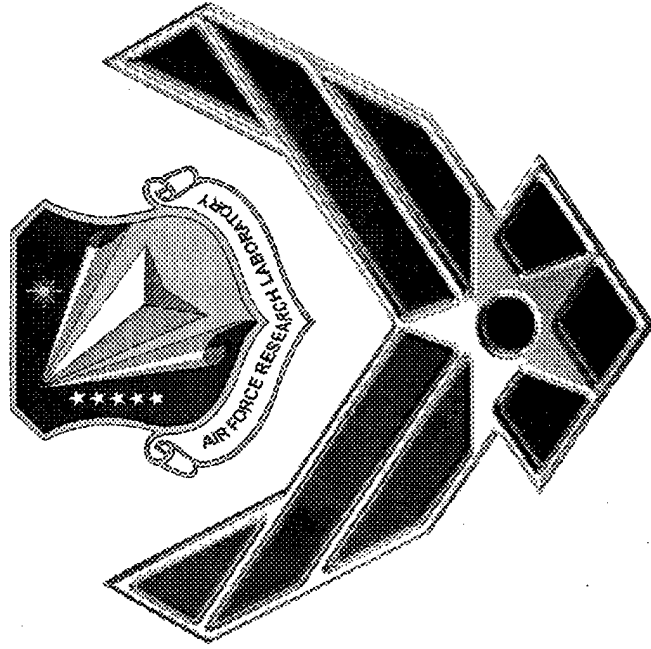
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New Ionic Liquids

ACS Ionic Liquids Symposium September 9, 2003



**Greg Drake, Tommy Hawkins, Kerri Tollison*,
Leslie Hall, Ashwani Vij, Sarah Sabowski*
AFRL/PRSP and *ERC, Inc.**

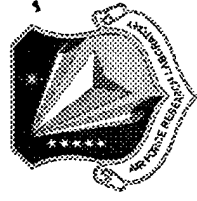
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Edwards Air Force Base, CA 93524-7680

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New Ionic Liquids



What are Ionic Liquids?

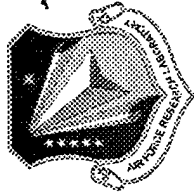
A class of salts consisting of cation/anion pair that has a very low melting point.

- (1) An ionic compound that melts below 100 °C (b.p. of H₂O). J. Wilkes, P. Wasserscheid, K. Seddon.
- (2) An ionic compound that has a melting point at or below ambient temperatures. These are often called RTILs (Room Temperature Ionic Liquids) T. Welton, R. Rogers.

But many of the salts fit both definitions and 2 is really a more specific class of (1), and all are low melting salts.

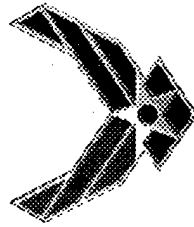


New Ionic Liquids

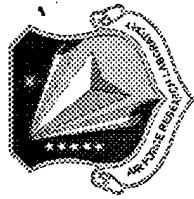


Important factors affecting the physical properties of ionic liquids

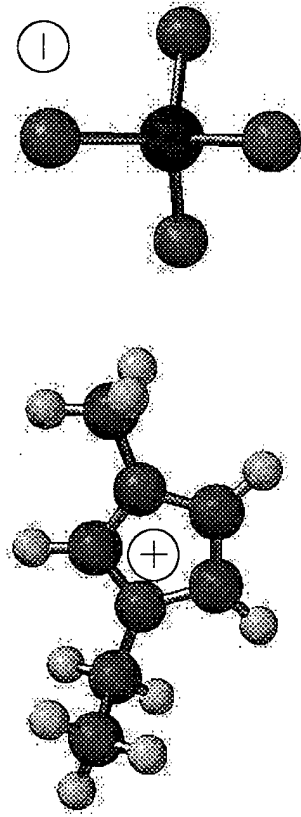
1. Asymmetry of cation as well as anion
2. Packing efficiency
3. Charge delocalization in cationic/anionic species
4. "Sheer size" differentials



New Ionic Liquids

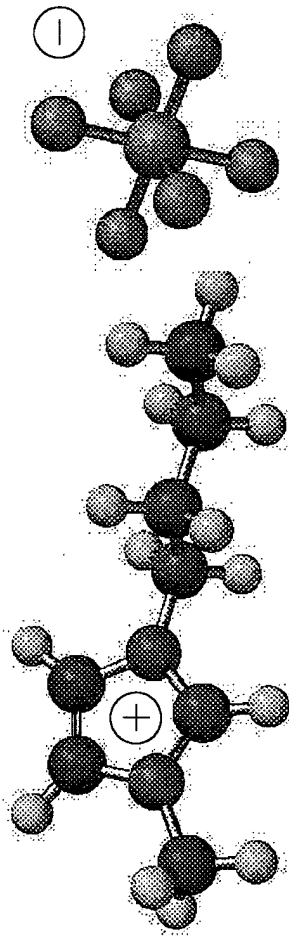


Ionic liquids research was really opened up by the pioneering work of King, Wilkes, and Hussey under USAF research looking for new battery electrolytes.¹ Dealt heavily with aluminum halide anions early on.



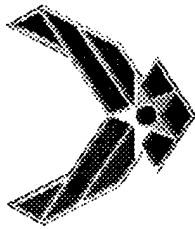
1-ethyl-3-methylimidazolium tetrachloroaluminate

Later, water stable ionic liquids were synthesized by Wilkes and coworkers which opened up the currently rapidly expanding field that we see today².

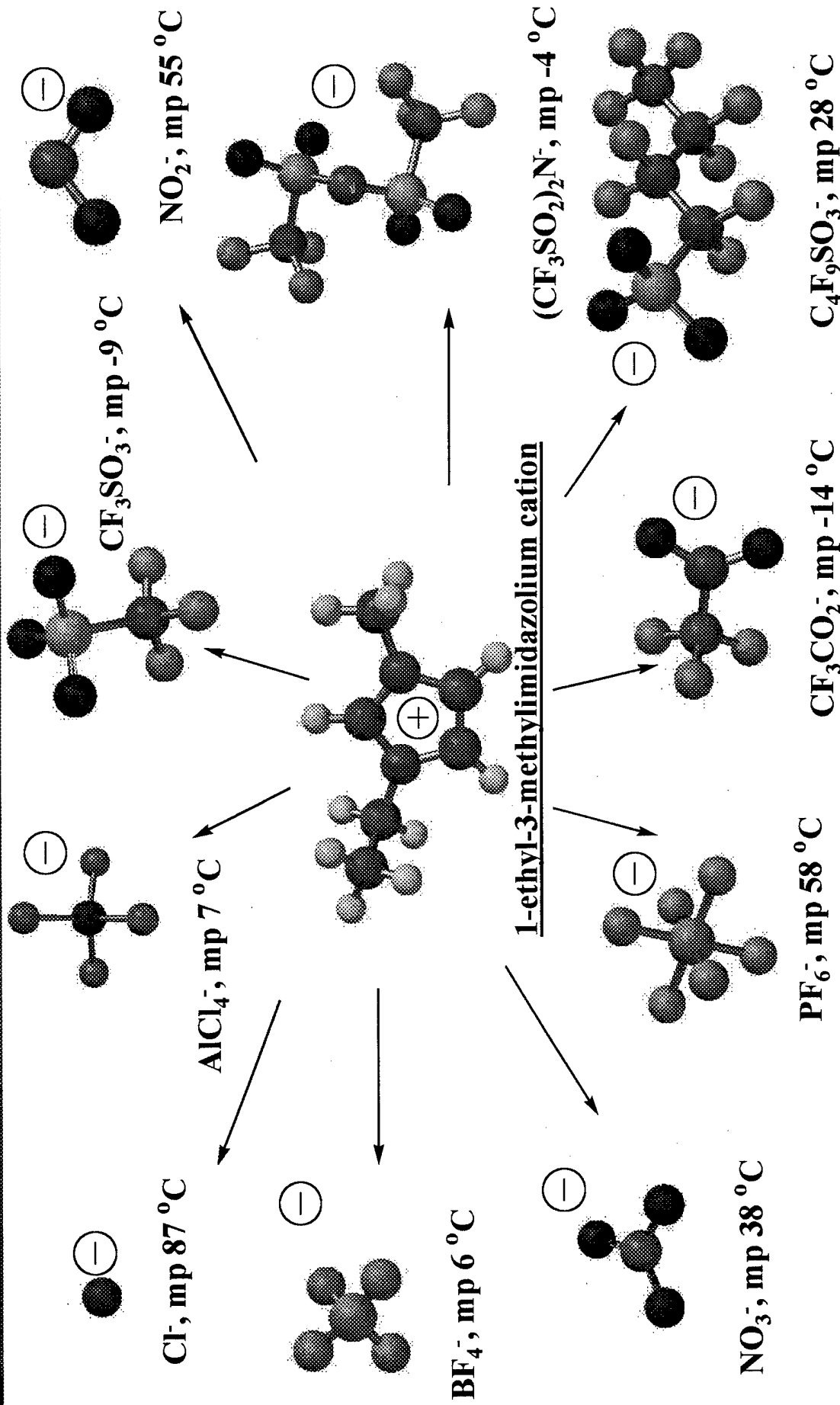


1-butyl-3-methylimidazolium hexafluorophosphate

¹Fannin, A.; Floreani, D.; King, L.; Landers, J.; Piersma, B.; Stech, D.; Vaughn, R.; Wilkes, J.S. *J. Phys. Chem.* 1984, 88, 2614. ²Wilkes, J.; Zaworotko, M.J. *Chem. Soc. Chem. Commun.* 1992, 965.



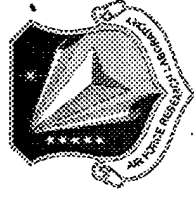
New Ionic Liquids



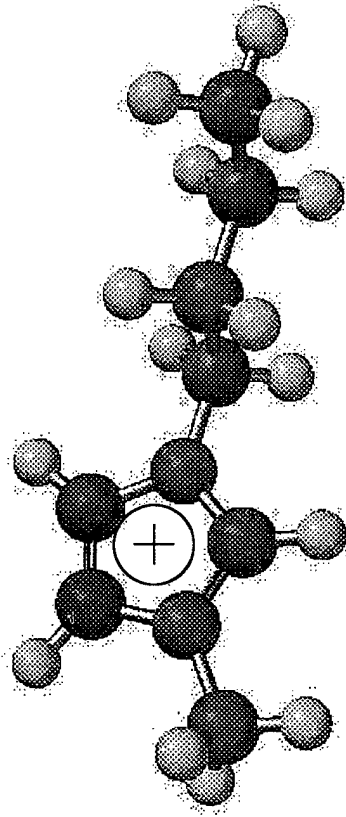
Wasserscheid, P.; Keim, W. *Angew. Chem. Int. Ed. Engl.* 2000, 39, 3772. Wasserscheid, P., Welton, T. (eds.) *Ionic Liquids in Synthesis* Wiley-VCH, FRG, 2003. Seddon, K.R.; Holbrey, J. D. *Clean Products and Processes* 1999, 1, 223. Rogers, R.; Seddon, K. (eds.) *Ionic Liquids* A.C.S. Symp. Ser. 818 2002 A.C.S. Publ. Co.



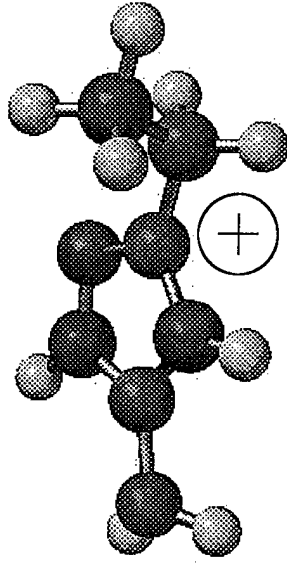
New Ionic Liquids



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.

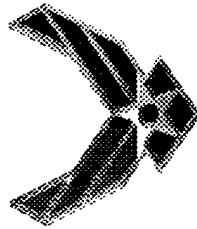


**1-n-butyl-3-methyl imidazolium
cation**

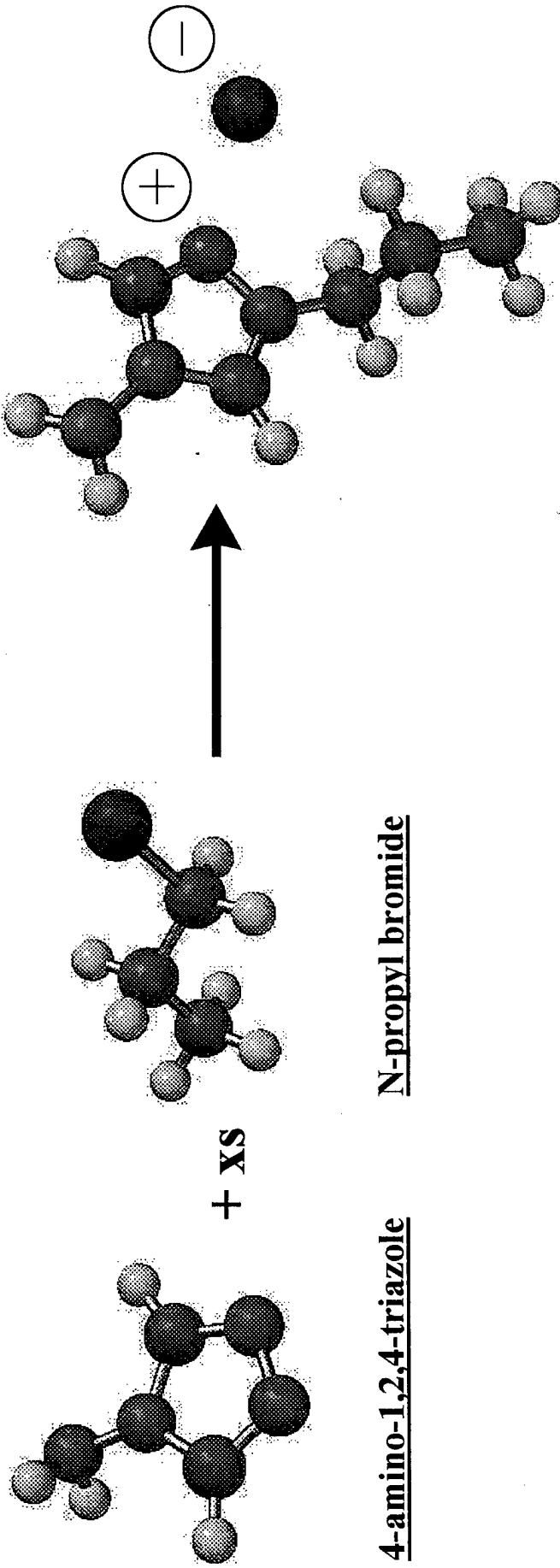


**1-ethyl-4-amino-1,2,4-
triazolium cation**

These new ionic liquids have similar shapes and physical properties, BUT higher ΔH_f , higher densities, and better oxygen balances.

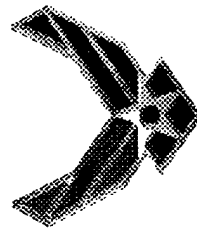


New Ionic Liquids

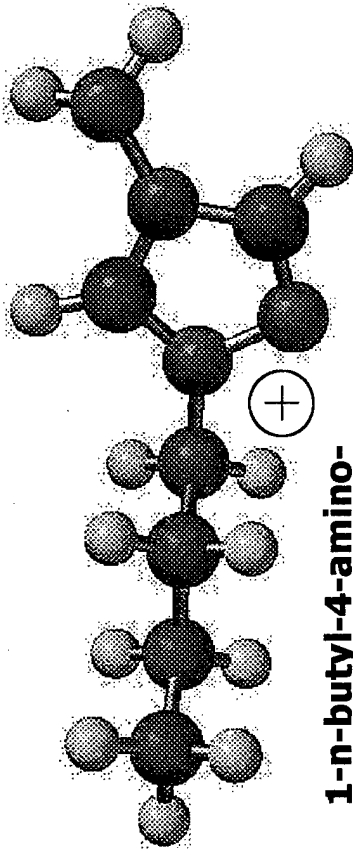


Synthesis is from commercial materials
High yield simple isolation has been known
in literature for quite sometime.

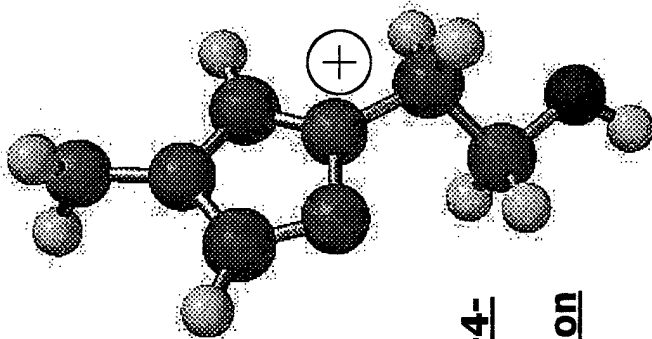
Scriven; Keay; Goe; Astleford J. Org. Chem. **1989**, *54*, 731.



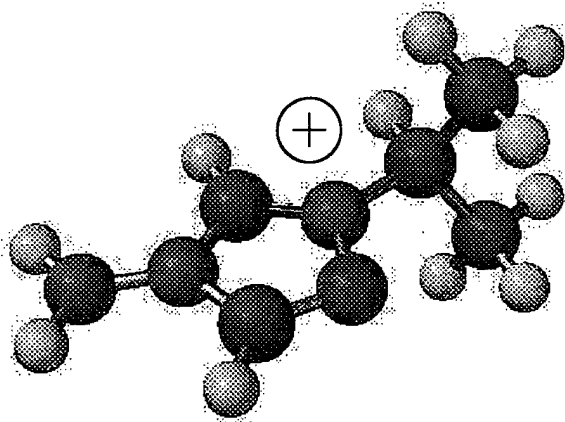
New Ionic Liquids



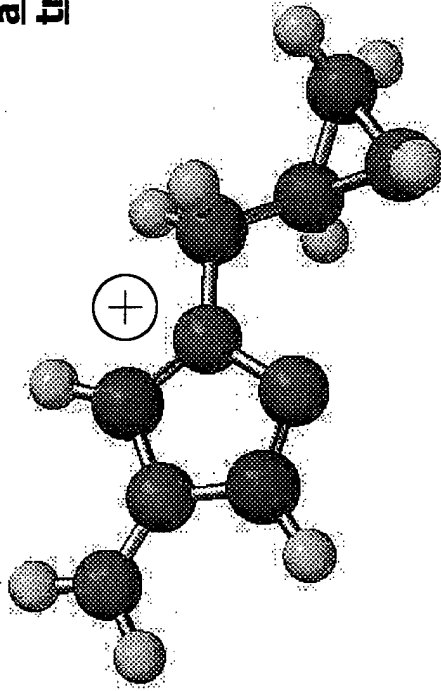
1-n-butyl-4-amino-1,2,4-triazolium cation



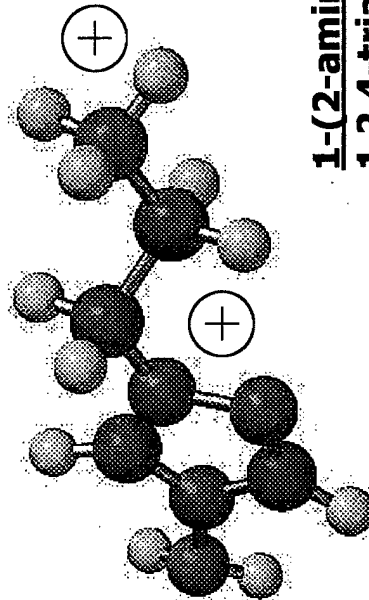
1-(2-ethanol)-4-amino-1,2,4-triazolium cation



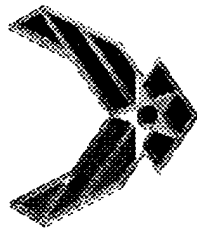
1-isopropyl-4-amino-1,2,4-triazolium cation



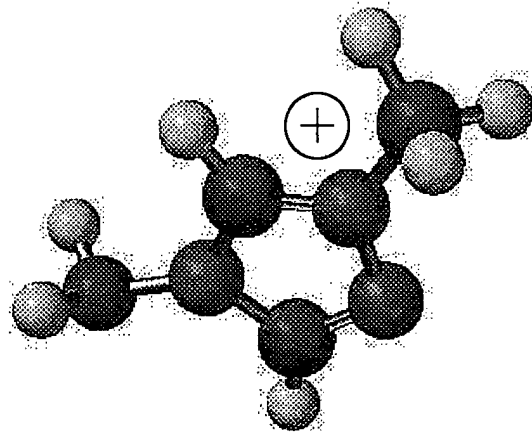
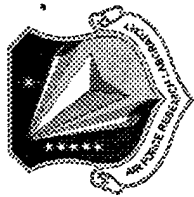
1-methylcyclopropyl-4-amino-1,2,4-triazolium cation



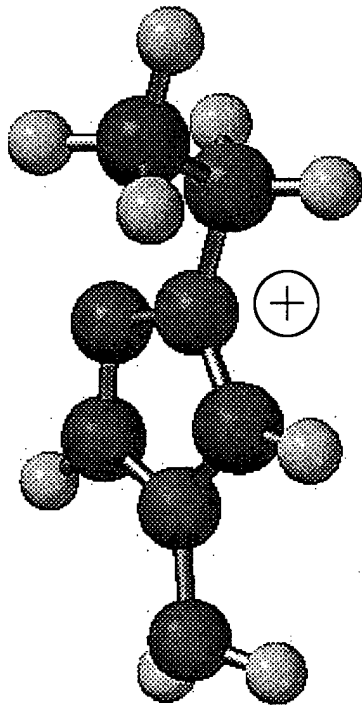
1-(2-aminoethyl)-4-amino-1,2,4-triazolium dication



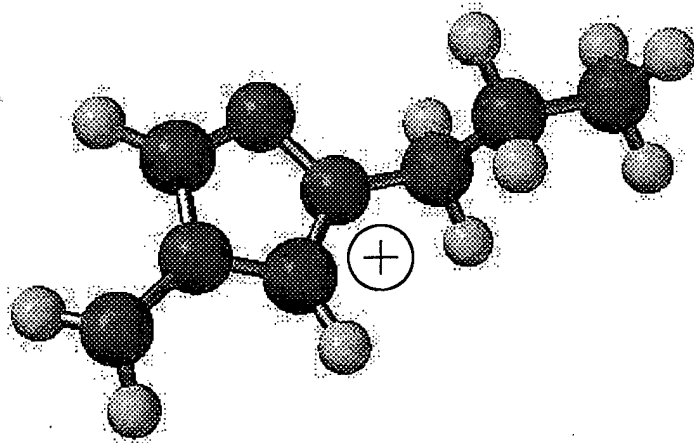
New Ionic Liquids



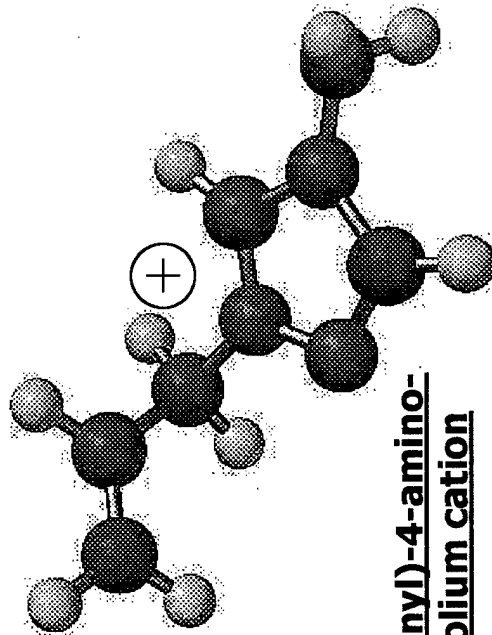
1-methyl-4-amino-1,2,4-triazolium cation



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



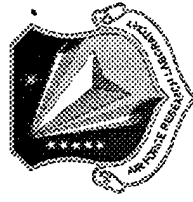
1-n-propyl-4-amino-1,2,4-triazolium cation



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



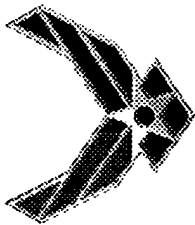
New Ionic Liquids



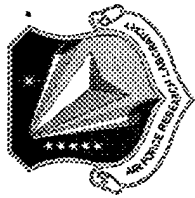
Physical properties of 1-n-alkyl substituted-4-amino-1,2,4-triazolium bromides.

- increasing melting points with increasing molecular weights,
- decomposition onsets that are relatively low
- densities decrease with increasing alkyl chain length.

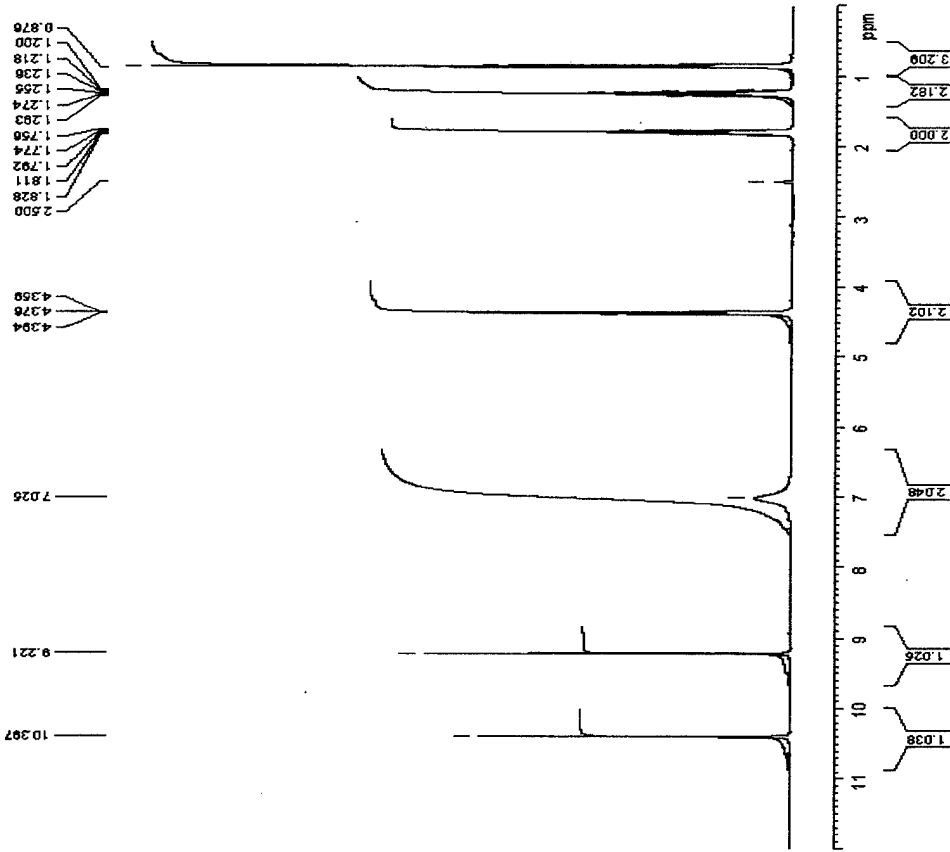
<u>Substituted 4AT salts</u>	<u>m.p. (°C)</u>	<u>dec. onset (°C)</u>	<u>density (g/cm³)</u>
1-ethyl	63°	110	1.69
1-n-propyl	60°	120	1.56
1-isopropyl	90°	110	1.60
1-butyl	48°	130	1.46
1-n-pentyl	54°	130	1.37
1-n-hexyl	76°	120	1.34
1-n-heptyl	94°	120	1.30
1-n-octyl	80°	135	1.27
1-n-nonyl	81°	140	1.26
1-n-decyl	90°	135	1.23



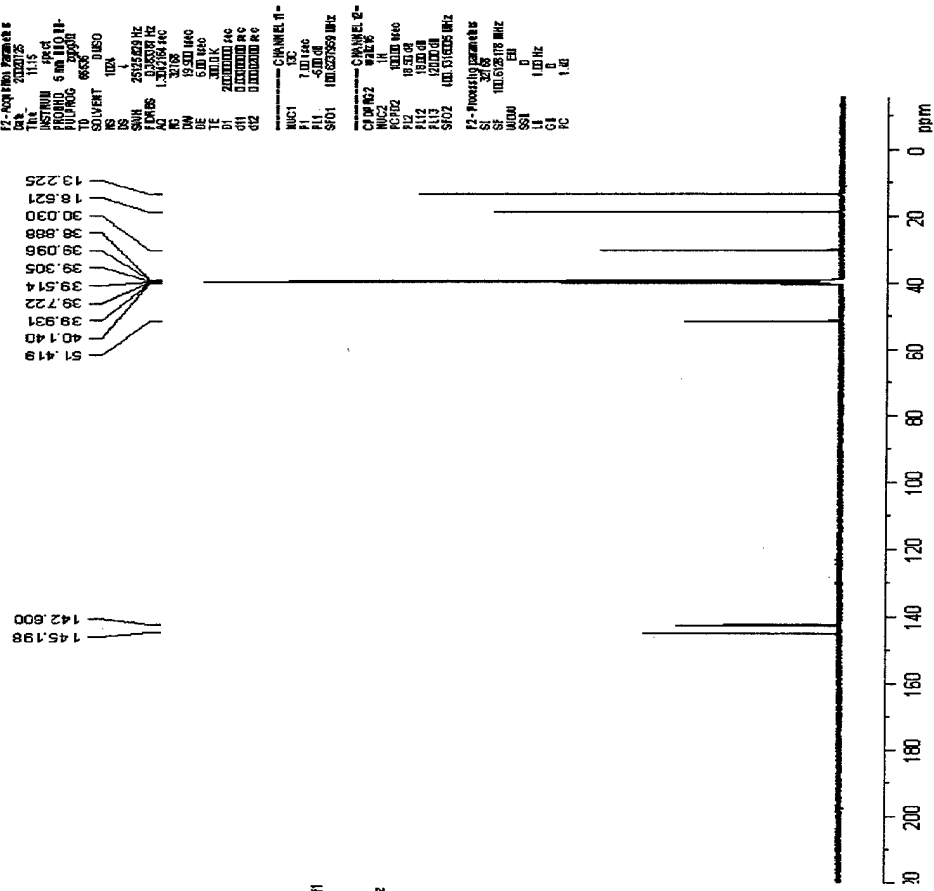
New Ionic Liquids



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



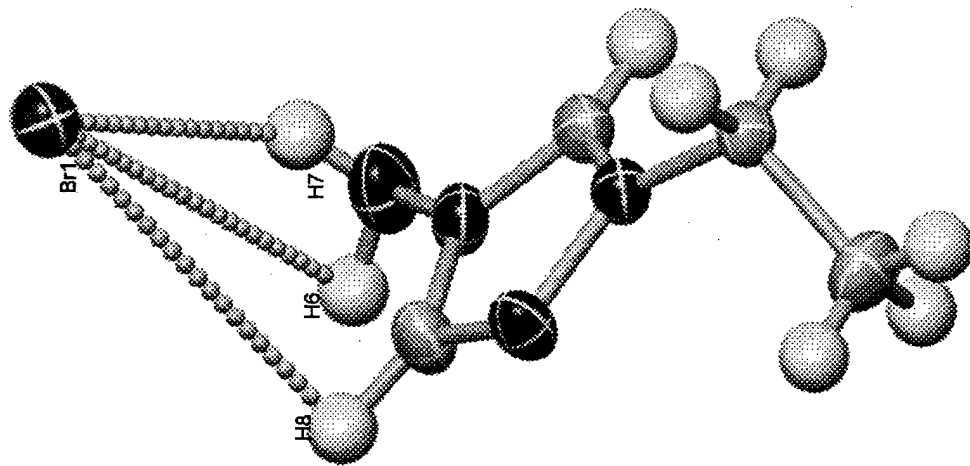
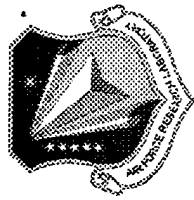
carbon of 1-n-butyl-4-amino-1,2,4-triazolium bromide solid in d6-DMSO



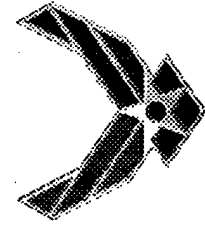
¹H(left) and ¹³C nmr spectra of 1-butyl-4-amino-1,2,4-triazolium bromide.



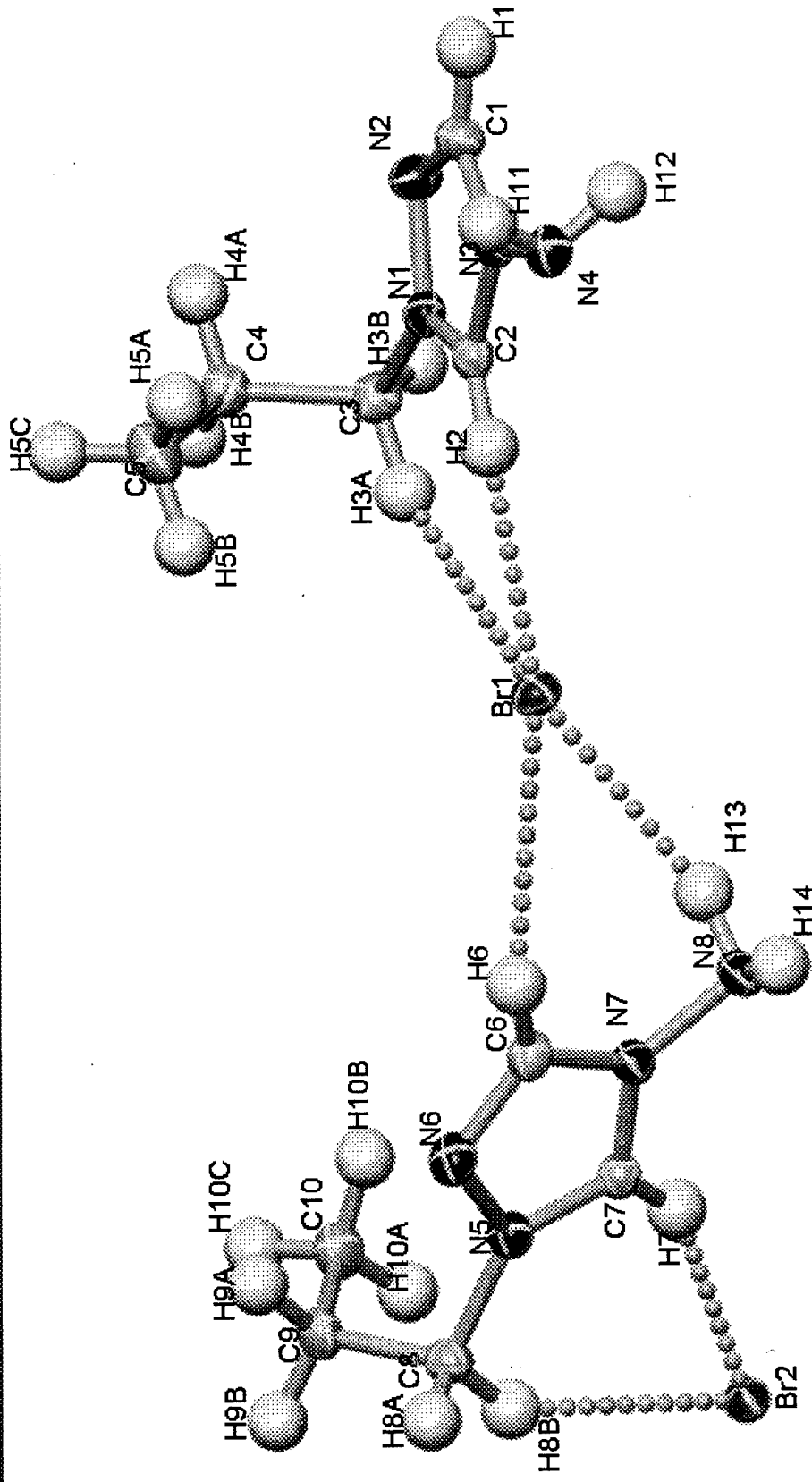
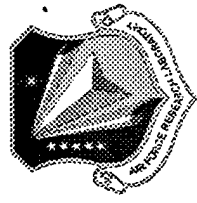
New Ionic Liquids



Single x-ray diffraction study of 1-ethyl-4-amino-1,2,4-triazolium bromide.



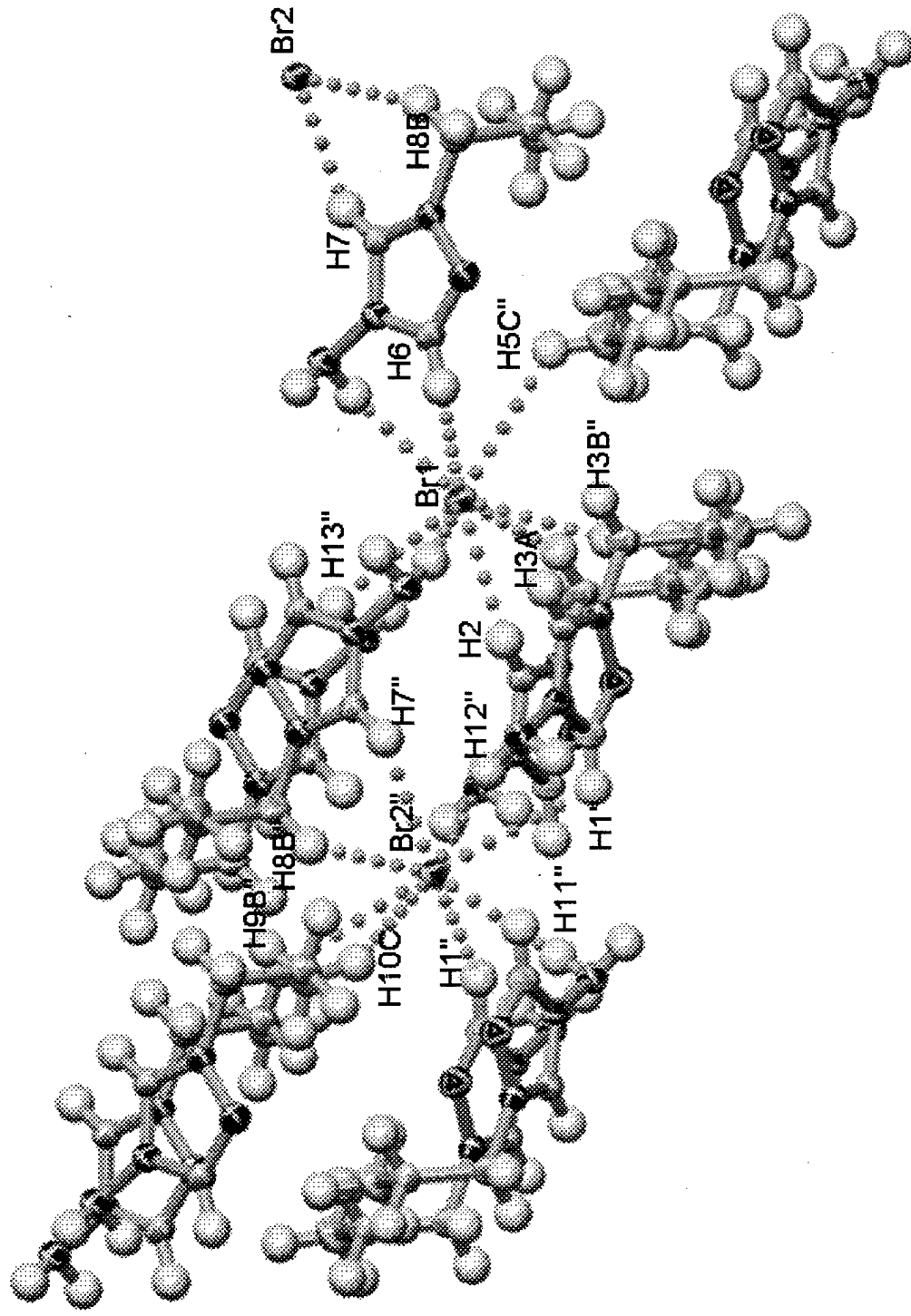
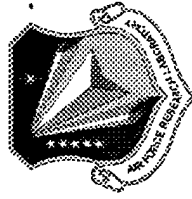
New Ionic Liquids



Single crystal x-ray diffraction study of 1-n-propyl-4-amino-1,2,4-triazolium bromide showing significant hydrogen bond contacts.



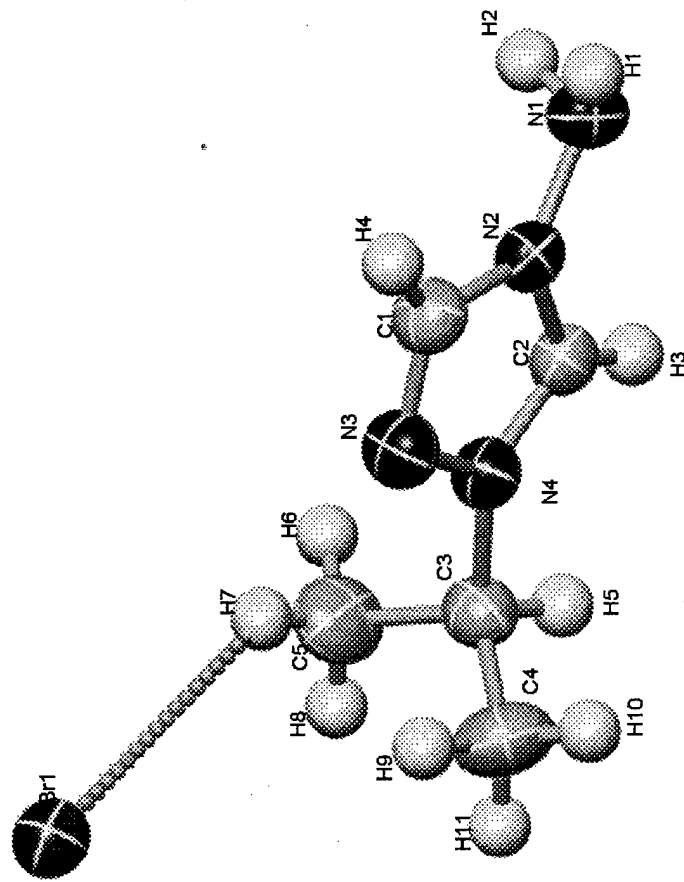
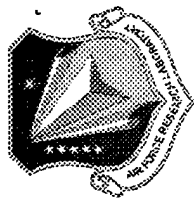
New Ionic Liquids



Extensive hydrogen bonding in 1-n-propyl-4-amino-1,2,4-triazolium bromide



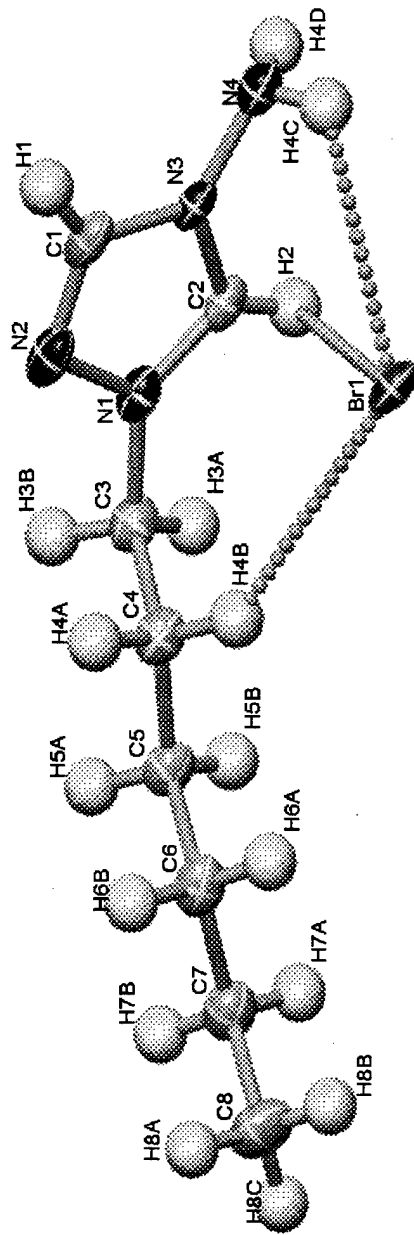
New Ionic Liquids



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



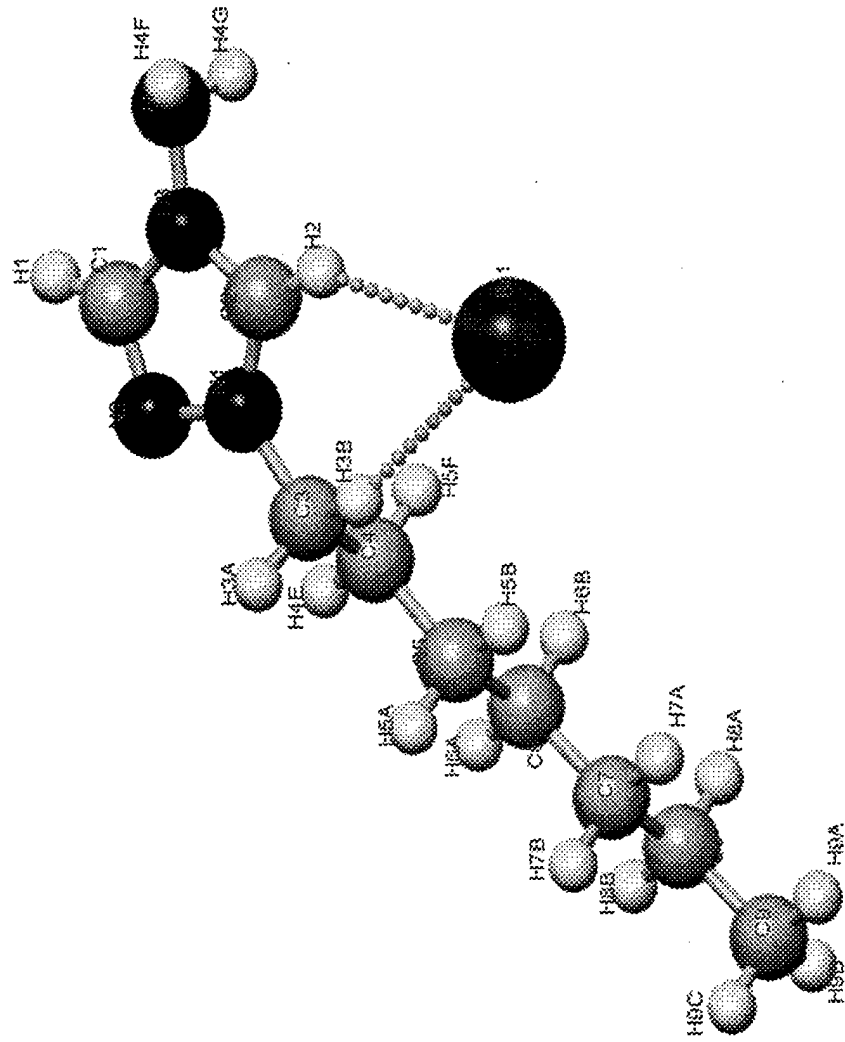
New Ionic Liquids



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



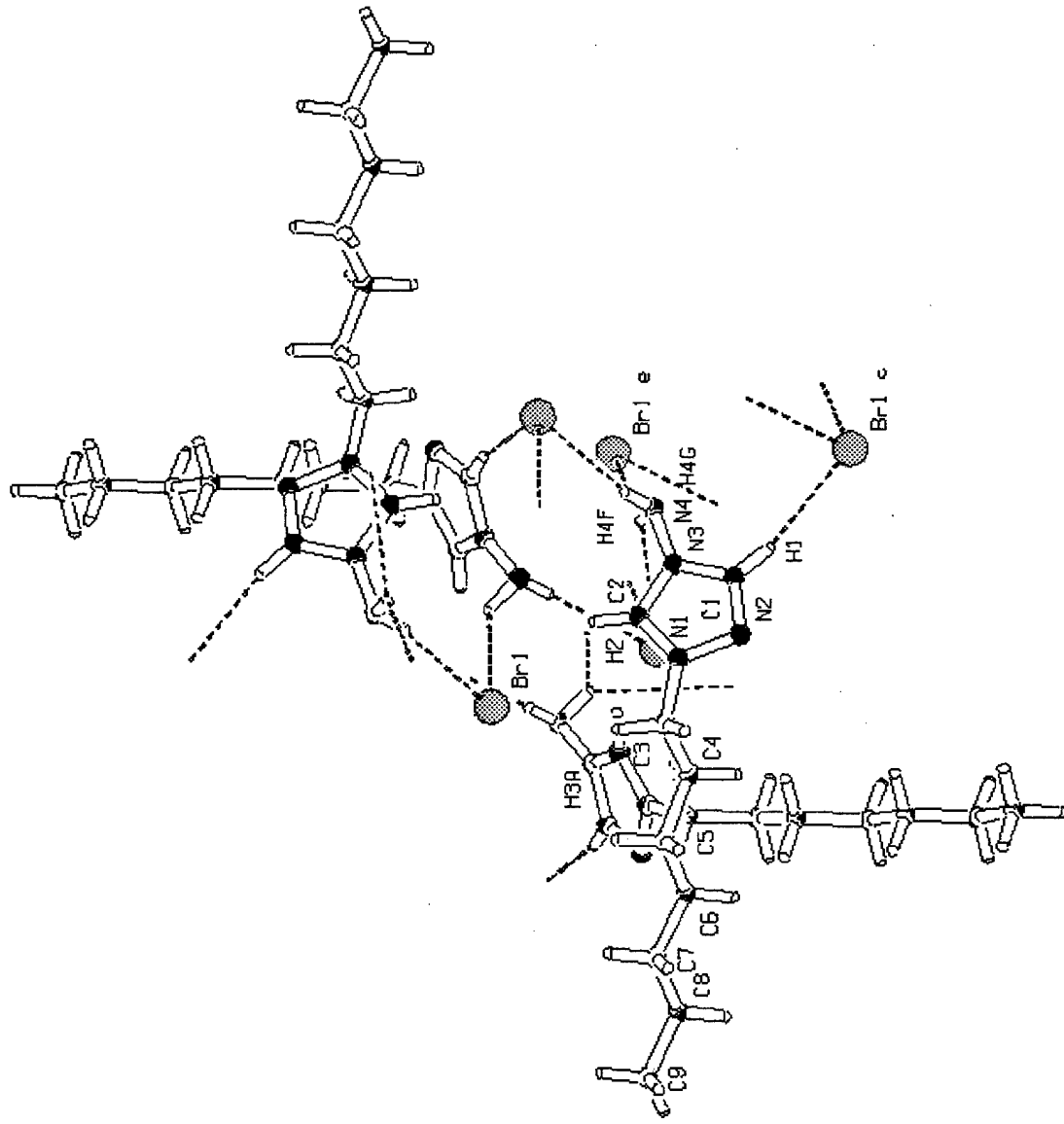
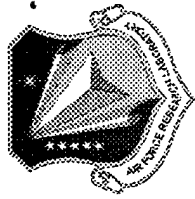
New Ionic Liquids



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



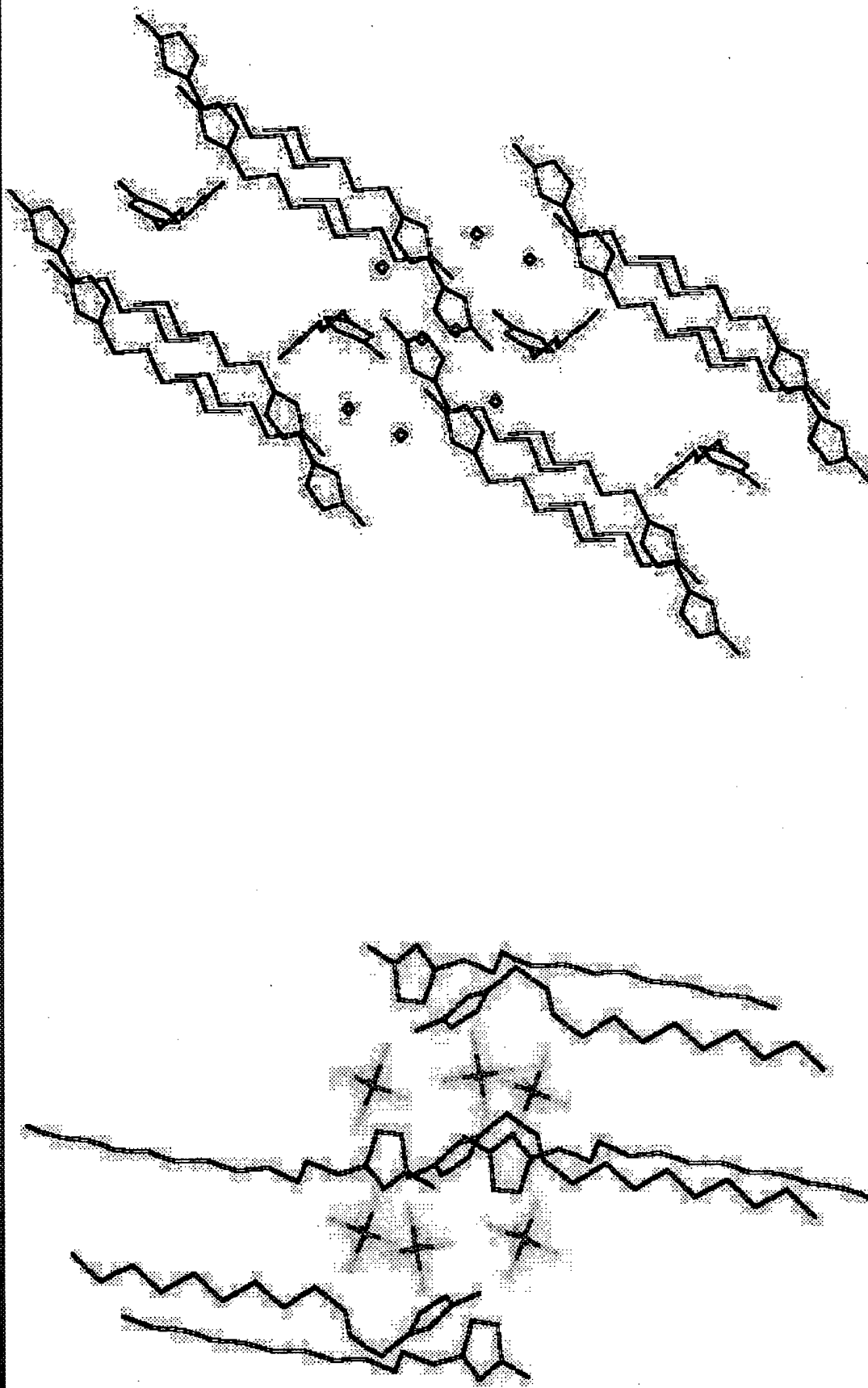
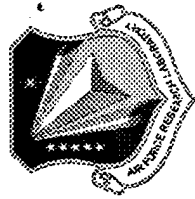
New Ionic Liquids



Hydrogen bond contacts in 1-heptyl-4-amino-1,2,4-triazolium bromide



New Ionic Liquids



1-dodecyl-3-methylimidazolium hexafluorophosphate*

1-hexyl-4-amino-1,2,4-triazolium bromide#

*Gordon, C. M.; Holbrey, J. D.; Kennedy, A. R.; Seddon, K. R. *J. Mater. Chem.* **1998**, *8*, 2627. #Drake, G. W.; Hawkins, T. W.; Tollison, K.; Hall, L.; Vij, A. 2003 manuscript in progress.

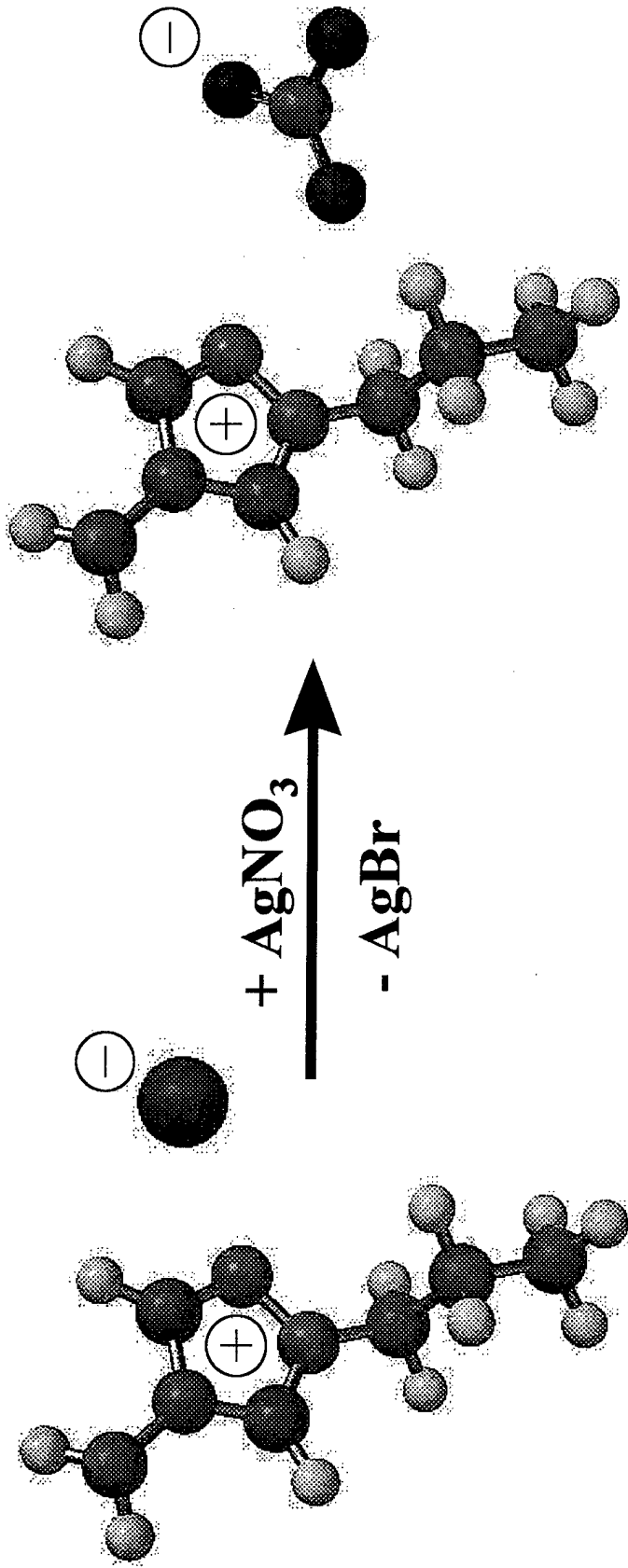


New Ionic Liquids



But halides are only the start...

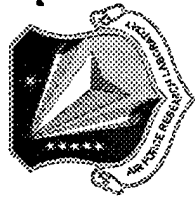
Nitrates were best made through silver nitrate metathesis in methanol.



This route led to the best materials as the silver bromide was easily removed.



New Ionic Liquids



1-substituted-4-amino-1,2,4-triazolium nitrate salts are more stable.

<u>Salt</u>	<u>melting point(°C)</u>	<u>decomp onset(°C)</u>	<u>$\rho(\text{g}/\text{cm}^3, \text{est.})$</u>
1-methyl	54	185	1.57
1-ethyl	5	185	1.39 (1.38)
1-n-propyl	34	190	1.35
1-isopropyl	53	175	1.37 (1.43)
1-n-butyl	-10	190	1.31
1-(2-ethanol)	10	180	1.48
1-methylcyclopropyl	56	190	1.36 (1.44)
1-(2-propenyl)	10	165	1.23
1-n-pentyl	26	170	1.29
1-n-hexyl	-2	160	1.26
1-n-heptyl	31	160	1.24
1-n-octyl	29	170	1.22
1-n-nonyl	53	175	1.20
1-n-decyl	49	185	1.18



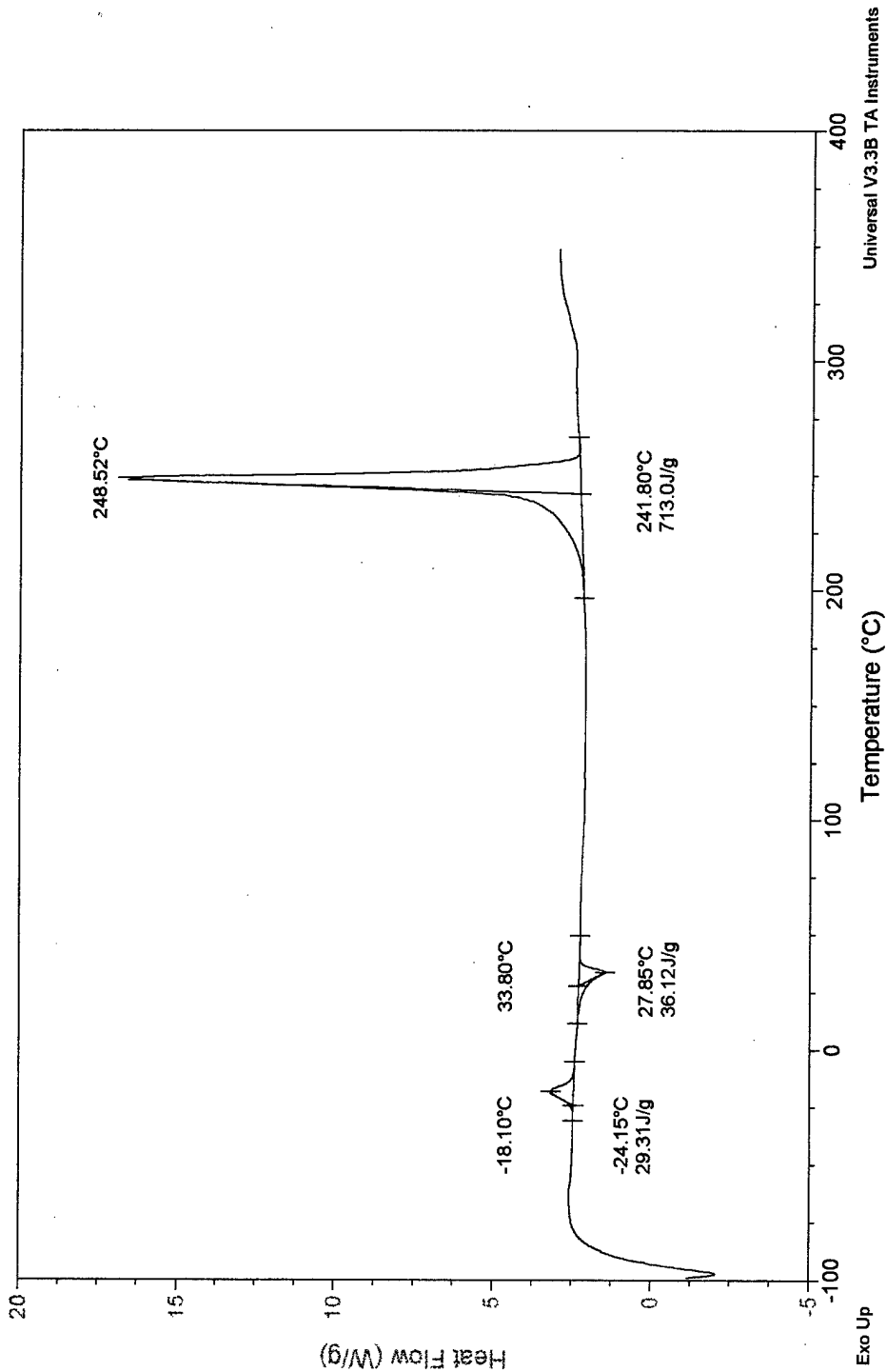
New Ionic Liquids



Sample: 1-PROPYL-4-AT NITRATE
Size: 1.9000 mg
Method: greg
Comment: 10C/min/10ml/minhermeticalpans

DSC

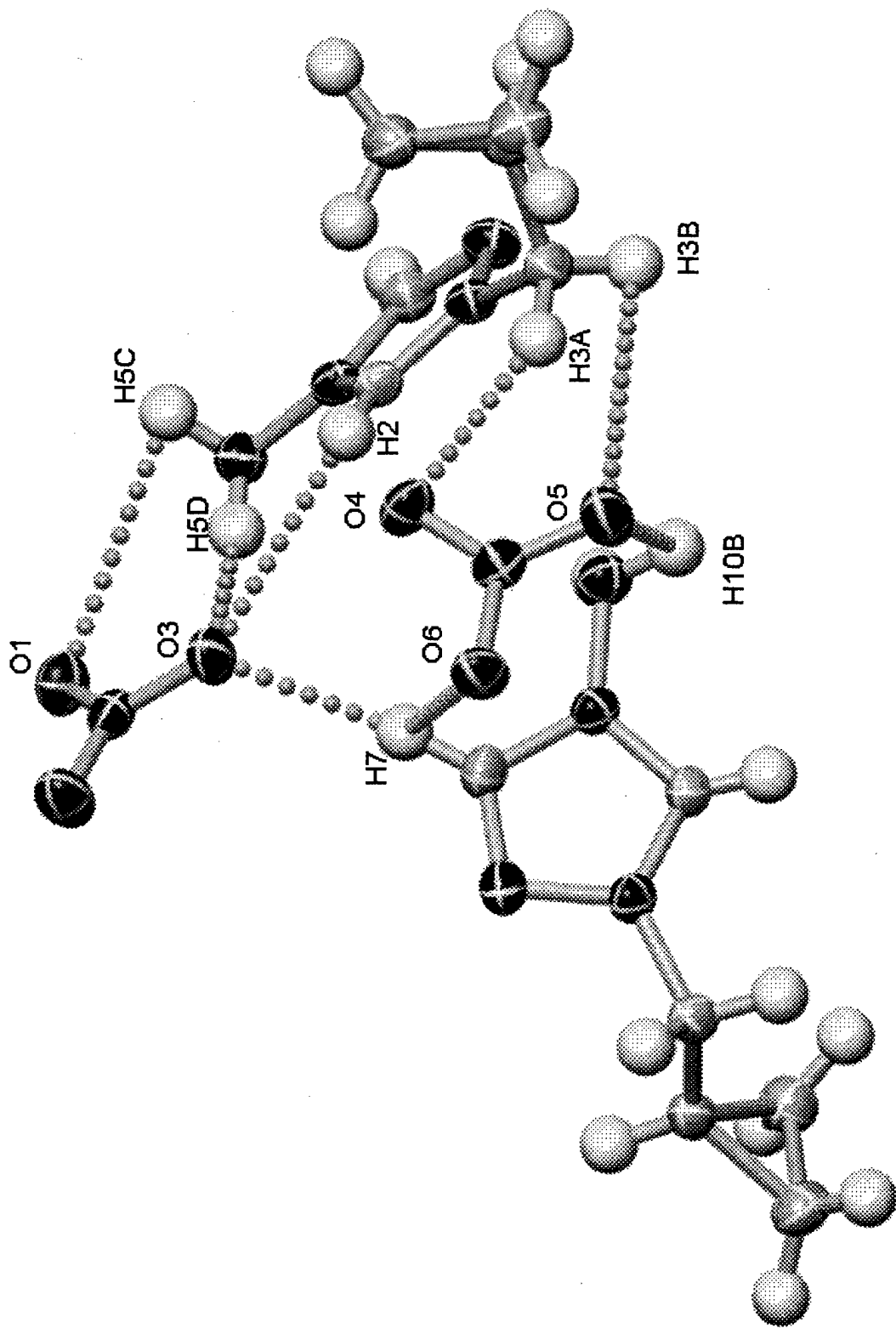
File: C:\...files from old DSC\4at propyl no3
Operator: DRAKE
Run Date: 16-Jan-02 23:04



DSC of 1-n-propyl-4-amino-1,2,4-triazolium nitrate



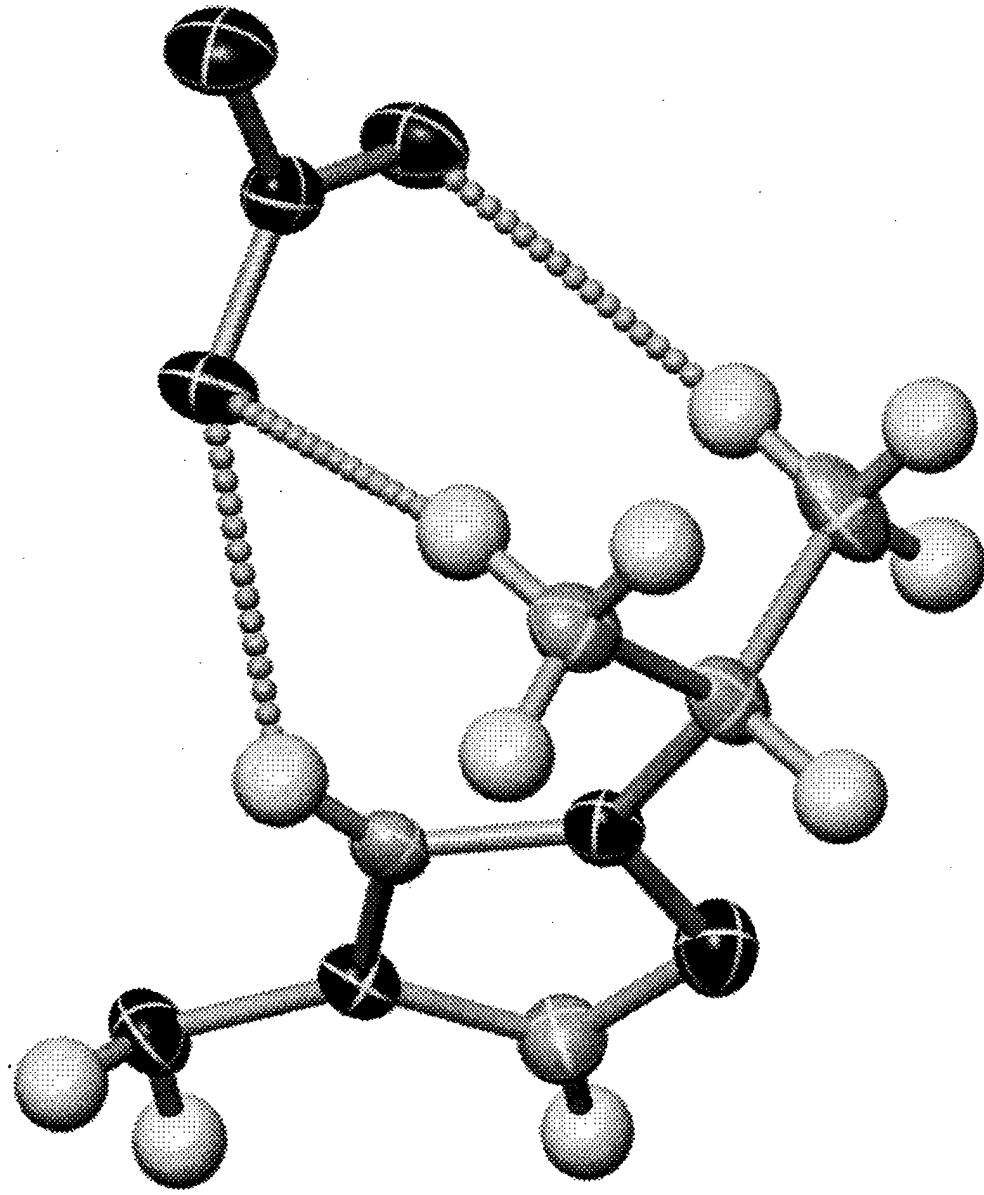
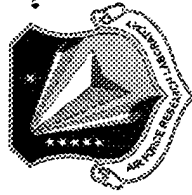
New Ionic Liquids



Single crystal x-ray diffraction study of 1-methylcyclopropyl-4-amino-1,2,4-triazolium nitrate.



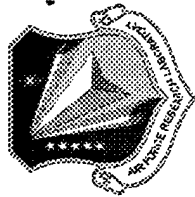
New Ionic Liquids



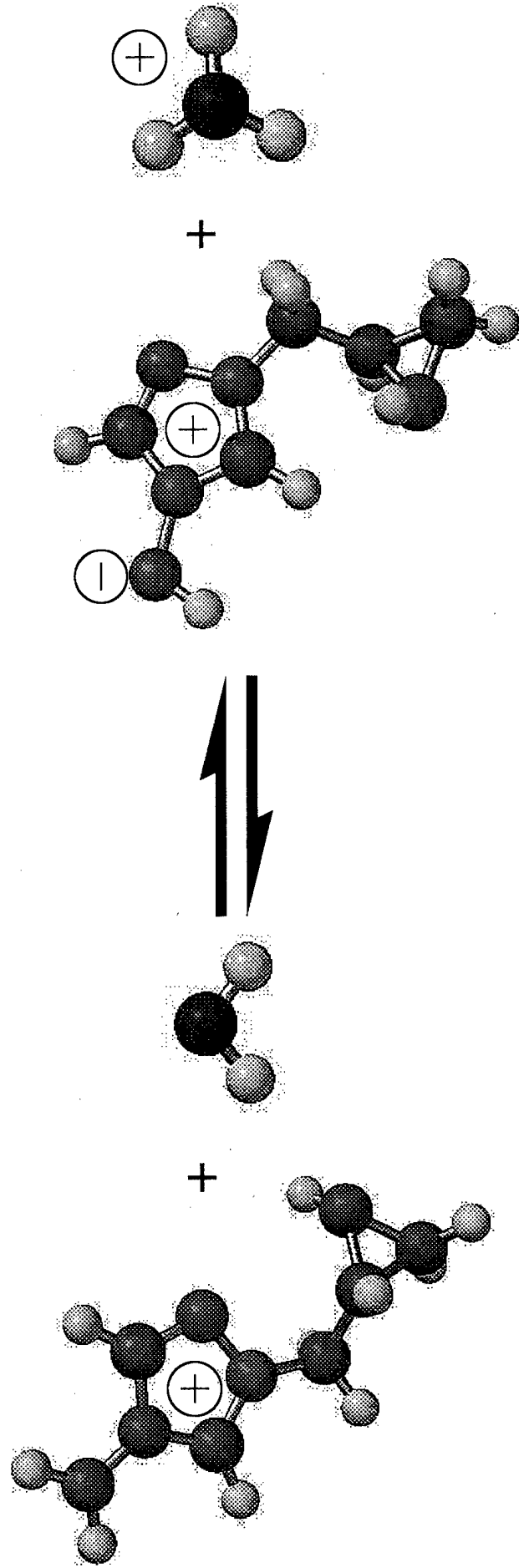
Single crystal x-ray diffraction structure of 1-isopropyl-4-amino-1,2,4-triazolium nitrate



New Ionic Liquids

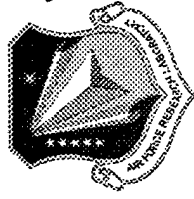


The new energetic cations are weakly acidic in nature, aqueous solutions have a pH of around 4 which suggests the equilibrium involving a zwitterionic 1-alkyl-4-amido-1,2,4-triazolium species. This equilibrium could be one possible way for the ionic liquids to “come apart”.





New Ionic Liquids



Summary and Conclusions

A large new class of low melting salts which should be considered as new members of the well known class of materials referred to as ionic liquids has been synthesized and well characterized.

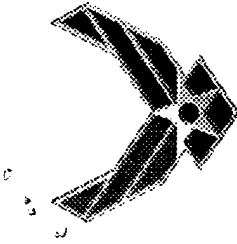
Using asymmetric cation shapes and poor cation-anion fit, an analogue system to the well known 1,3-dialkylsubstituted imidazolium cation family, based upon 1-substituted-4-amino-1,2,4-triazolium cations paired with the bromide and nitrate ions has been explored.

Facile synthesis routes from commercially available materials coupled with high yield and purity reactions make these new materials very exciting.

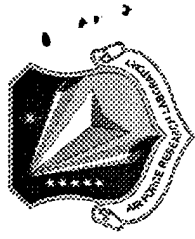
Several single crystal x-ray diffraction studies of several structures have been carried out proving the expected structure as well as revealing extensive hydrogen bonding in the solid state.

Physical properties of 1-substituted-4-amino-1,2,4-triazolium salts included much higher viscosities, higher densities, and much more polar behavior than that of imidazolium ionic liquids.

Further work is being carried out with other ions.



New Ionic Liquids



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