

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. REPORT DATE (DD-MM-YYYY) 6 May 2003		2. REPORT TYPE View Graphs		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Structural Effects on the Physical Properties of Ionic Liquids				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Greg Drake, et al.				5d. PROJECT NUMBER 2303	
				5e. TASK NUMBER M2C8	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRSP 10 E. Saturn Blvd. Edwards AFB, CA 93524				8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-PR-ED-VG-2003-122	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-VG-2003-122	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
20030616 039					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified	A		Sheila Benner
				19b. TELEPHONE NUMBER (include area code) (661) 275-5693	

FILE

MEMORANDUM FOR PRS (In-House Publication)

06 May 2003

FROM: PROI (STINFO)

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2003-122**
Greg Drake (AFRL/PRSP) et al., "Structural Effects on the Physical Properties of Ionic Liquids"

5355

2003 AFOSR Molec Dynamics & Theo Chem Contr Mtg
(San Diego, CA, no date provided) (Deadline: 19 May 2003)

(Statement A)

Structural Effects on the Physical Properties of Ionic Liquids

Greg Drake and Tom Hawkins
AFRL/PRSP
Air Force Research Laboratory
Edwards AFB, CA 93524

and

John Wilkes
Department of Chemistry
United States Air Force Academy
USAF Academy, CO 80840

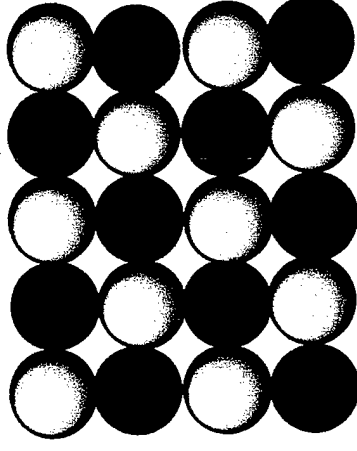




Ionic Liquids



versus



Extended lattice

NOT

Table salt Na^+Cl^- m.p. = 804 °C Very high
Cryolite Na_3AlF_6 m.p. nearly 1000 °C (Hall Process for Al production)
Eutectic of Li^+Cl^- and K^+Cl^- m.p. 355 °C

Molten salts are very hot!

Not commercially viable

Corrosion and energy issues

Giant lattice of miniature magnets stuck together



Ionic Liquids



What are Ionic Liquids?

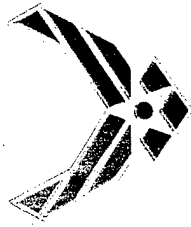
A class of salts consisting of cation/anion pair that has a very low melting point.

Definition of an ionic liquid is open to some debate amongst researchers in the area, but most in the area use one of two.

(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).

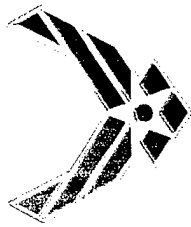


Ionic Liquids

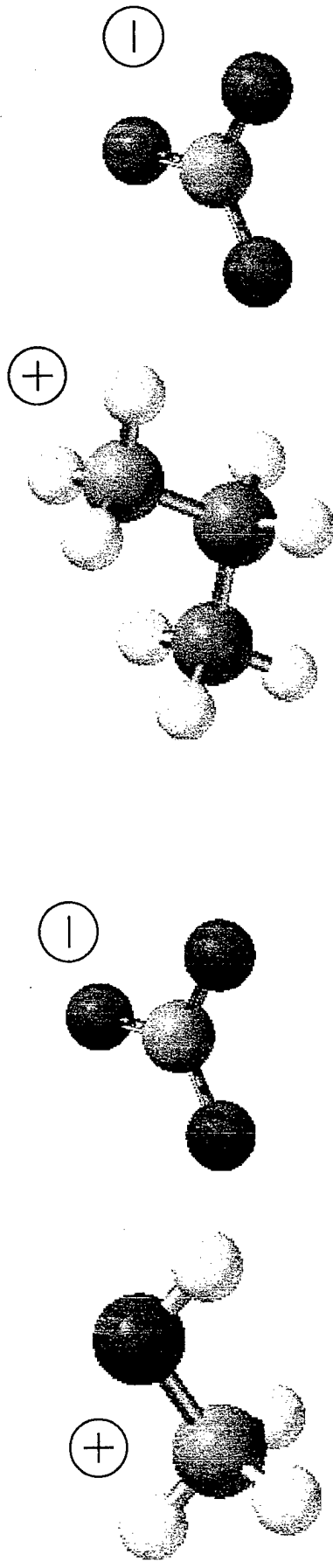


Important factors affecting the physical properties of ionic liquids

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



Ionic Liquids



Hydroxylammonium nitrate (HAN)

$[\text{NH}_3\text{OH}^+][\text{NO}_3^-]$ m.p. 39-40 °C

Ethylammonium nitrate

$[\text{CH}_3\text{CH}_2\text{NH}_3^+][\text{NO}_3^-]$ m.p. 12 °C

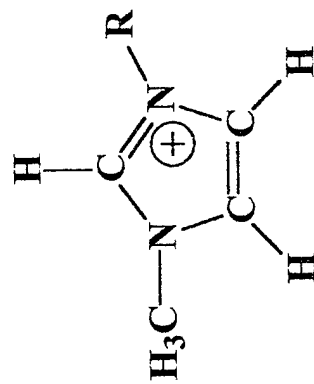
Serious issues...

- can be treacherous
- acidic
- very hygroscopic

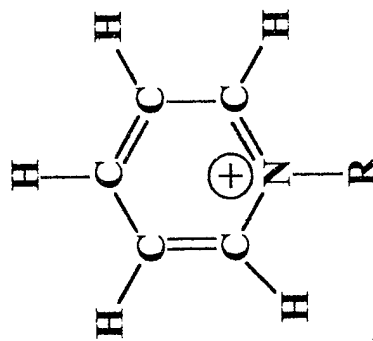


Ionic Liquids

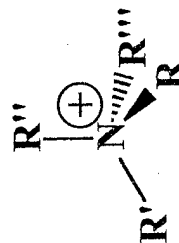
Some major shapes for organic based cations



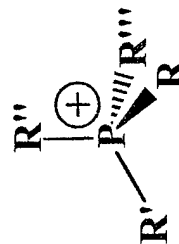
1-methyl-3-alkyl-imidazolium



1-alkylpyridinium



Tetralkylammonium



Tetralkylphosphonium



Ionic Liquids



The group of anions for ionic liquids is much larger and growing....

<u>water soluble</u>	<u>water insoluble</u>
CH_3CO_2^-	PF_6^-
CF_3CO_2^-	$[\text{BR}_1\text{R}_2\text{R}_3\text{R}_4]^-$
Cl^- , Br^- , I^-	$[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$
NO_3^-	BF_4^-
BF_4^-	R-SO_3^-
NO_2^-	
$[\text{AlCl}_4^-$, $\text{Al}_2\text{Cl}_7^-]$	

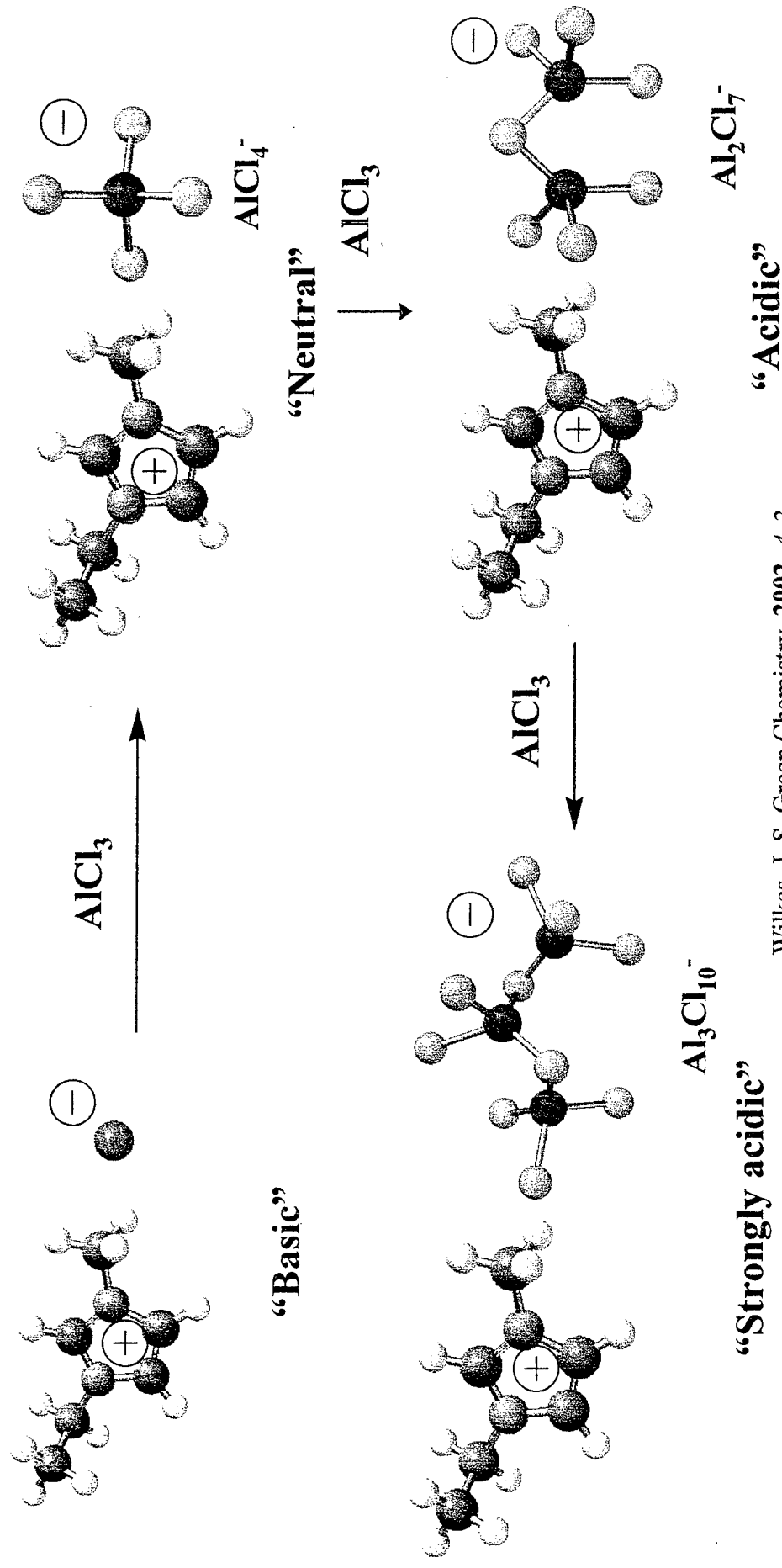
Typically R groups are n-alkyl groups

This list is not comprehensive but it covers the majority of what is out there.



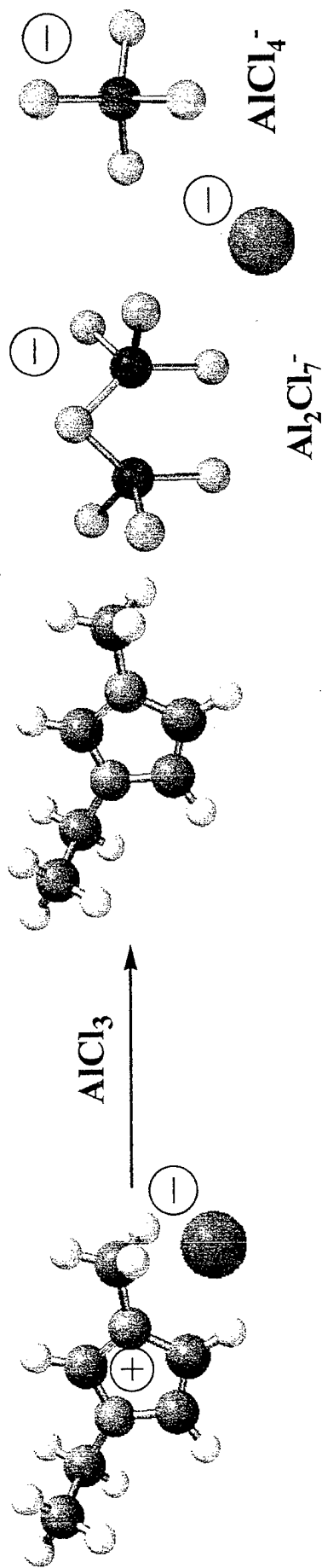
Ionic Liquids

Significant efforts spent on 1-ethyl-3-methyl-imidazolium based systems and aluminum trichloride systems. More complex than originally thought as AlCl_3 and Cl^- have an equilibrium based on their respective concentrations.

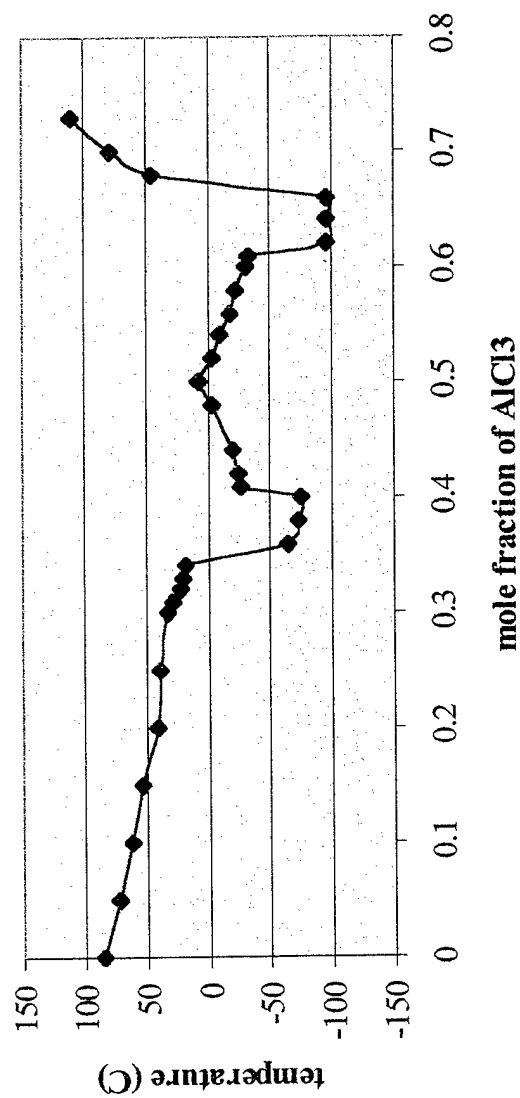




Ionic Liquids

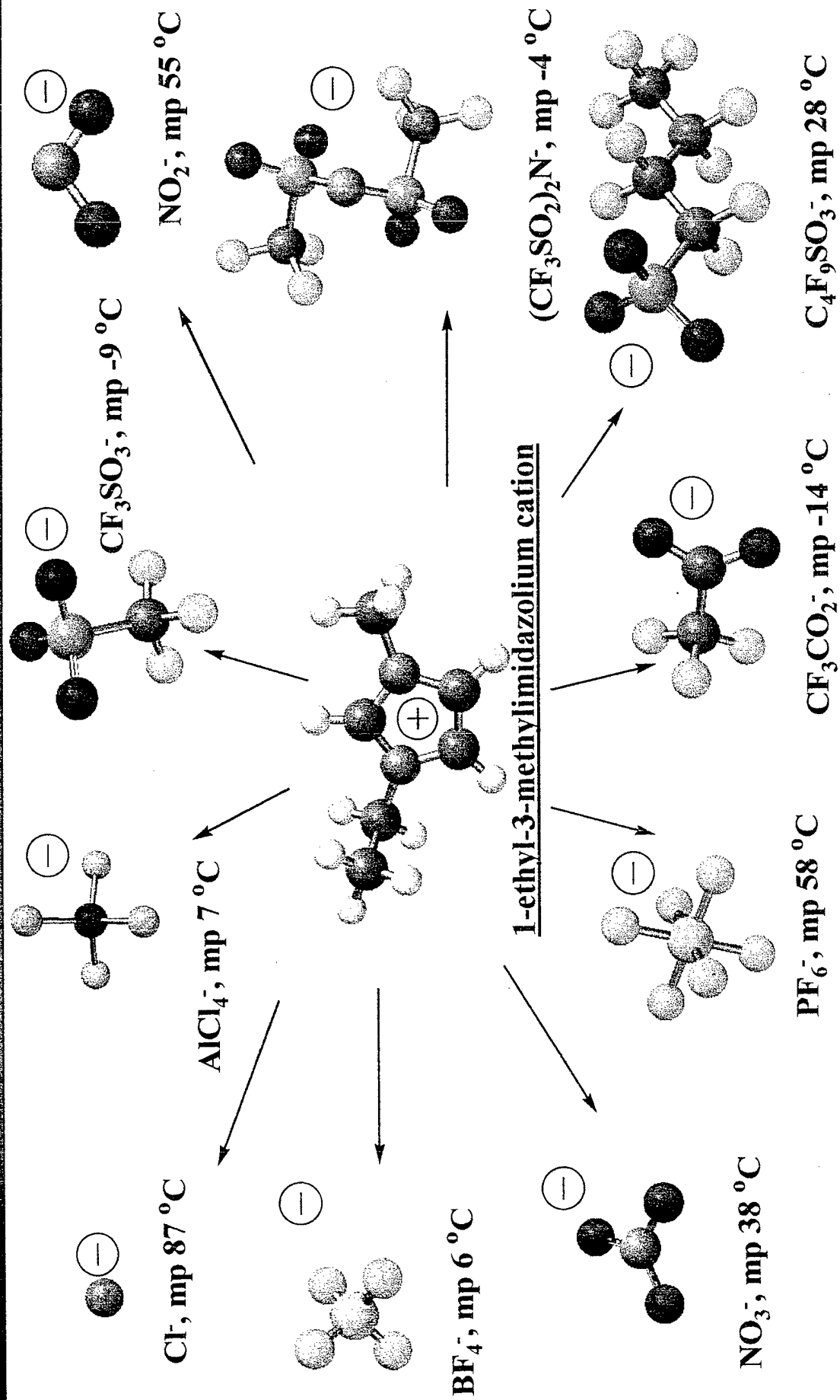


Melting point of MeEtImCl and AlCl₃ mixtures





Ionic Liquids

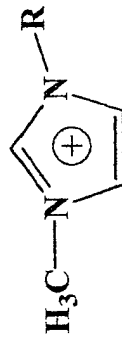




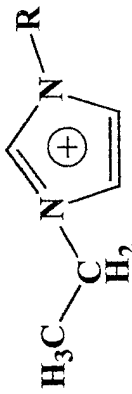
Ionic Liquids melting points



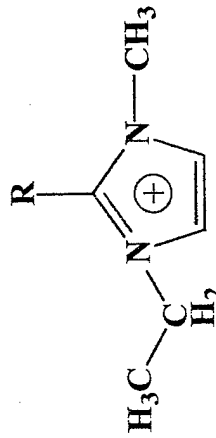
Substituent	Triflate (m.p.)	Bis(trifluorosulfonamide) m.p.
1-methyl	39	22
1-ethyl	-9	-3
1-butyl	16	-4
1-CH ₂ OCH ₂ CH ₃	27	<-30(Tg)
1-CH ₂ -CF ₃	45	<-30(Tg)



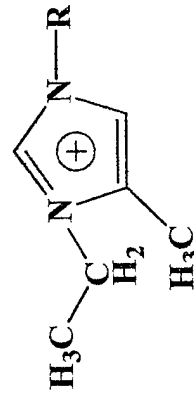
3-methyl-1-R-imidazolium



3-ethyl-1-R-imidazolium



1-ethyl-2-R-3-methyl-imidazolium



1-ethyl-3-R-5-methyl-imidazolium

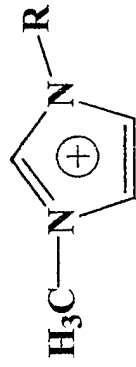
Substituent	Triflate (m.p.)	Bis(trifluorosulfonamide) m.p.
1-ethyl	23	14
1-butyl	2	<-30(Tg)

Substituent	Triflate (m.p.)	Bis(trifluorosulfonamide) m.p.
2,3-dimethyl	109	20
2-ethyl-3-methyl	113	28

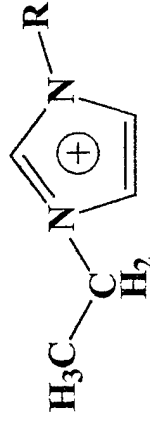
Substituent	Triflate (m.p.)	Bis(trifluorosulfonamide) m.p.
3-methyl	6	-3
3-ethyl	35	-22



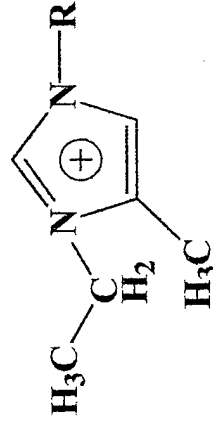
Ionic Liquids



3-methyl-1-R-imidazolium



3-ethyl-1-R-imidazolium



1-ethyl-3-R-5-methyl-imidazolium

Bis(trifluoromethylsulfonamide)	η (cP)	Λ (mS/cm)
1-methyl	44	8.4
1-ethyl	34 (45)	8.8 (8.6)
1-butyl	52 (90)	3.9 (3.7)
1-CH ₂ OCH ₂ CH ₃	54 (74)	4.2 (3.6)
1-CH ₂ -CF ₃	248	0.98

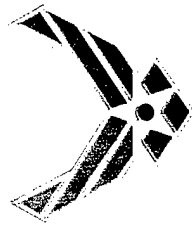
Bis(trifluoromethylsulfonamide)	η (cP)	Λ (mS/cm)
1-ethyl	35 (53)	8.5 (7.5)
1-butyl	48	4.1

Bis(trifluoromethylsulfonamide)	η (cP)	Λ (mS/cm)
3-methyl	37 (51)	6.6 (6.4)
3-ethyl	36	6.2

Red values in () are for corresponding CF₃SO₃⁻ salt

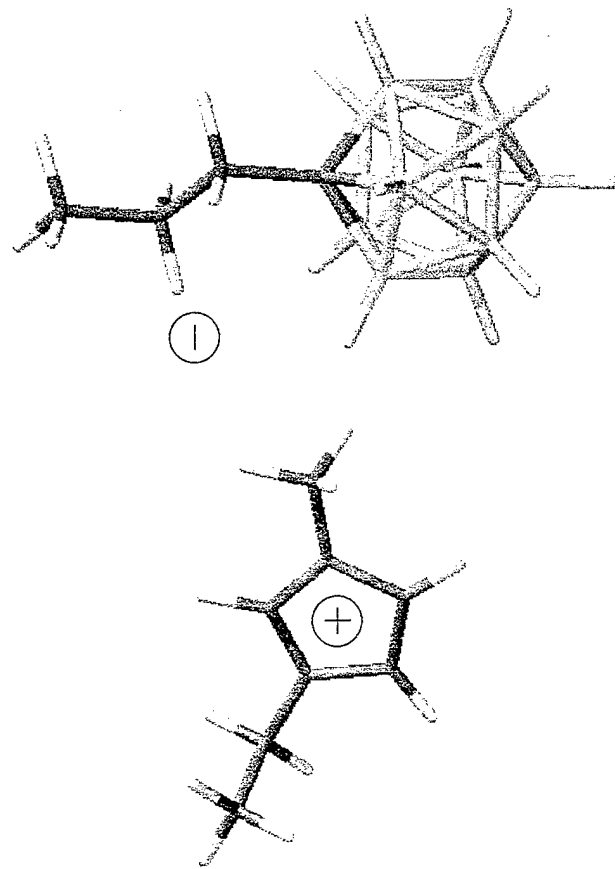
Viscosity and conductivity increase with increasing chain length but intramolecular hydrogen bonding can be important. Size and “charge” of anion also significant.

Bonhote, P. ; Diaz, A. ; Papageorgiou, N. ; Kalyanasundaram, K. ; Gratzel, M. Inorg. Chem. 1996, 35, 1168.



Ionic Liquids

The end extreme of non-coordinating anions has been achieved through the use of carborane anion in the formation of ionic liquids. Essentially no hydrogen bonding.

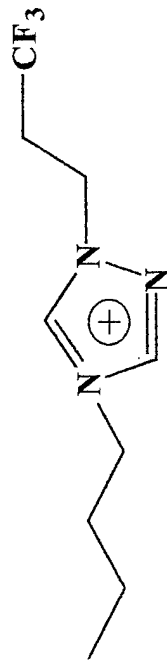


<u>Ionic liquid</u>	<u>m.p. °C</u>
[EMIM][HCB ₁₁ H ₁₁]	122
[EMIM][1-CH ₃ -CB ₁₁ H ₁₁]	59
[EMIM][1-CH ₂ CH ₃ -CB ₁₁ H ₁₁]	64
[EMIM][1-CH ₂ CH ₂ CH ₃ -CB ₁₁ H ₁₁]	45
[EMIM][1-CH ₂ CH ₂ CH ₂ CH ₃ -CB ₁₁ H ₁₁]	49

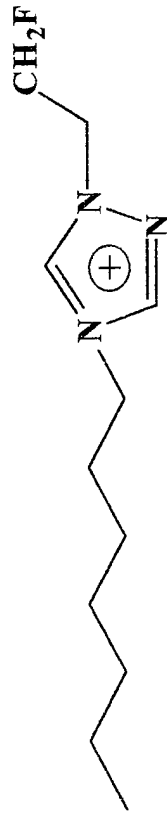
1-ethyl-3-methyl-imidazolium icosahedral
1-propyl-1-carborane [EMIM][1-prop-CB₁₁H₁₁]



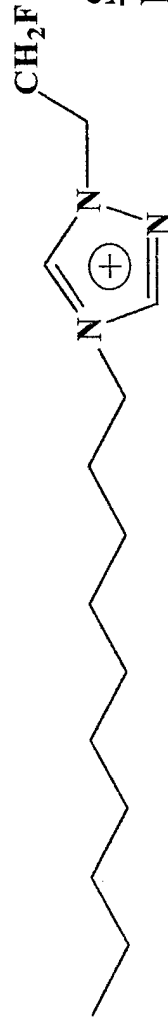
Ionic Liquids



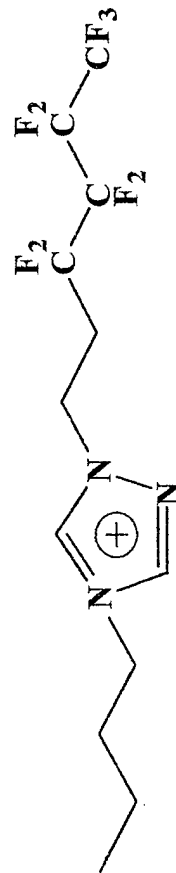
1-(3',3'-trifluoro-n-propyl)-3-n-butyl-1,2,4-triazolium



1-(2'-fluoroethyl)-3-n-heptyl-1,2,4-triazolium



1-(2'-fluoroethyl)-3-n-decyl-1,2,4-triazolium



1-(1H,1H,2H,2H-perfluoro-n-hexyl)-3-n-butyl-1,2,4-triazolium

Salt	m.p.(°C)	DSC onset (°C)
NTf ₂ ⁻	-67	395
TfO ⁻	33	379

Salt	m.p.(°C)	DSC onset (°C)
NTf ₂ ⁻	-70	359
BF ₄ ⁻	52	336

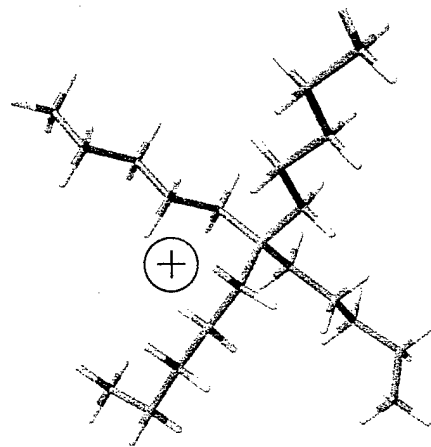
Salt	m.p.(°C)	DSC onset (°C)
NTf ₂ ⁻	-62	426
TfO ⁻	46	362

Salt	m.p.(°C)	DSC onset (°C)
NTf ₂ ⁻	69	394
TfO ⁻	173	391
PF ₆ ⁻	296	357



Ionic Liquids

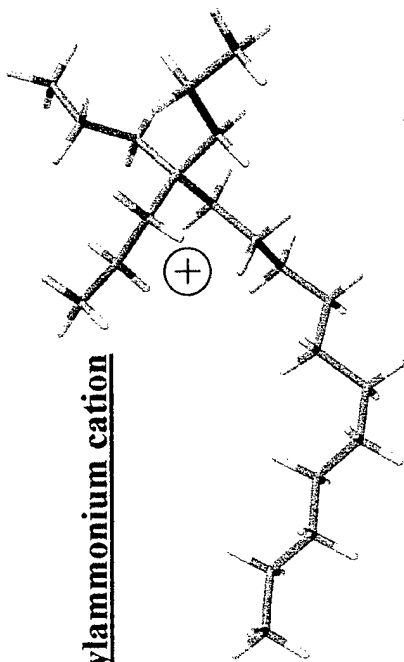
Substituted ammonium salts $R_4N^+X^-$ Variations in melting point based on cation structure.



Tetra-n-pentylammonium cation

Br^- m.p. = 101 °C

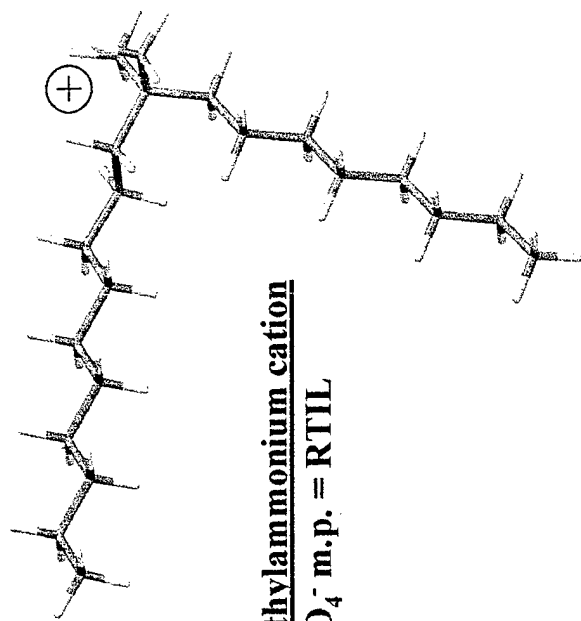
ClO_4^- m.p. = 118 °C



Tris-(n-propyl)-undecylammonium cation

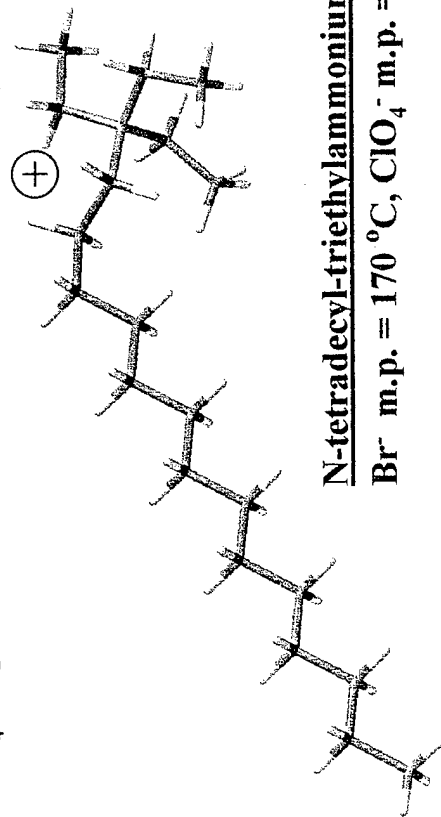
Br^- m.p. = 67 °C

ClO_4^- m.p. = 65 °C



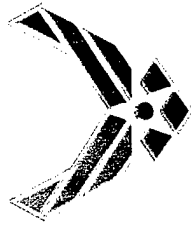
N-decyl-n-octyl-dimethylammonium cation

Br^- m.p. = RTIL, ClO_4^- m.p. = RTIL



N-tetradecyl-triethylammonium cation

Br^- m.p. = 170 °C, ClO_4^- m.p. = 152 °C



Ionic Liquids

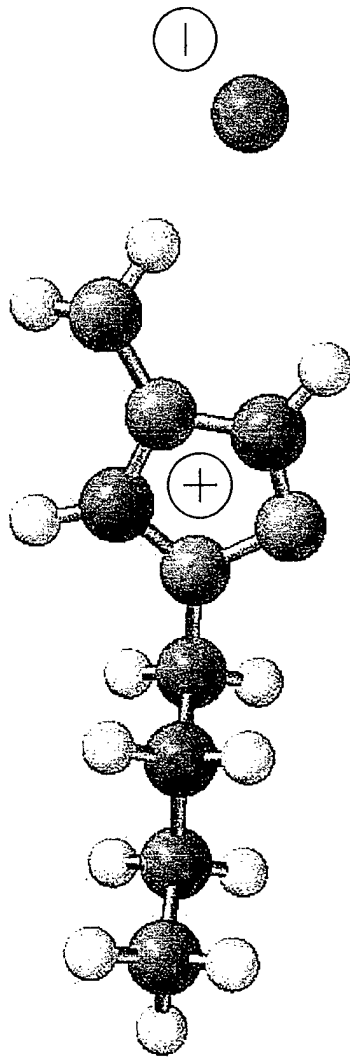
Substituted ammonium salts $[R_4N^+][X^-]$ Recently work has been done by using more desirable anions.

<u>Substituted Ammonium Salt</u>	<u>M.P.</u> (° C)	<u>Density</u> (g/cm ³)	<u>Viscosity</u> (cp)	<u>Λ</u> (Ω^{-1} cm ² /mole)
$[(n-C_6H_{13})(CH_3)_3N^+][N(SO_2CF_3)_2]^-$	-74 (g)	1.33	153	1.4
$[(n-C_7H_{15})(CH_3)_3N^+][N(SO_2CF_3)_2]^-$	-73 (g)	1.28	153	1.4
$[(n-C_8H_{17})(CH_3)_3N^+][N(SO_2CF_3)_2]^-$	-73(g)	1.27	181	1.3
$[(n-C_6H_{13})(CH_3CH_2)_3N^+][N(SO_2CF_3)_2]^-$	20	1.27	167	2.5
$[(n-C_7H_{15})(CH_3CH_2)_3N^+][N(SO_2CF_3)_2]^-$	-79	1.26	75	1.9
$[(n-C_8H_{17})(CH_3CH_2)_3N^+][N(SO_2CF_3)_2]^-$	-74	1.25	202	1.3
$[(n-C_6H_{13})(n-C_4H_9)_3N^+][N(SO_2CF_3)_2]^-$	26	1.15	595	0.8
$[(n-C_7H_{15})(n-C_4H_9)_3N^+][N(SO_2CF_3)_2]^-$	-67	1.17	606	0.8
$[(n-C_8H_{17})(n-C_4H_9)_3N^+][N(SO_2CF_3)_2]^-$	-63	1.12	574	0.7
$[(n-C_7H_{15})(Et)_3N^+][N(SO_2CF_3)_2]^-$	-82	1.27	362	1.2
$[(n-C_8H_{17})(n-C_4H_9)_3N^+][OSO_2CF_3]^-$	-57	1.02	2030	0.07

- most have very low glass points
- densities decrease as expected
- viscosity increases dramatically with increasing alkyl length
- conductivity decreases with cation size (mobility issue)



Ionic Liquids



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

<u>1-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

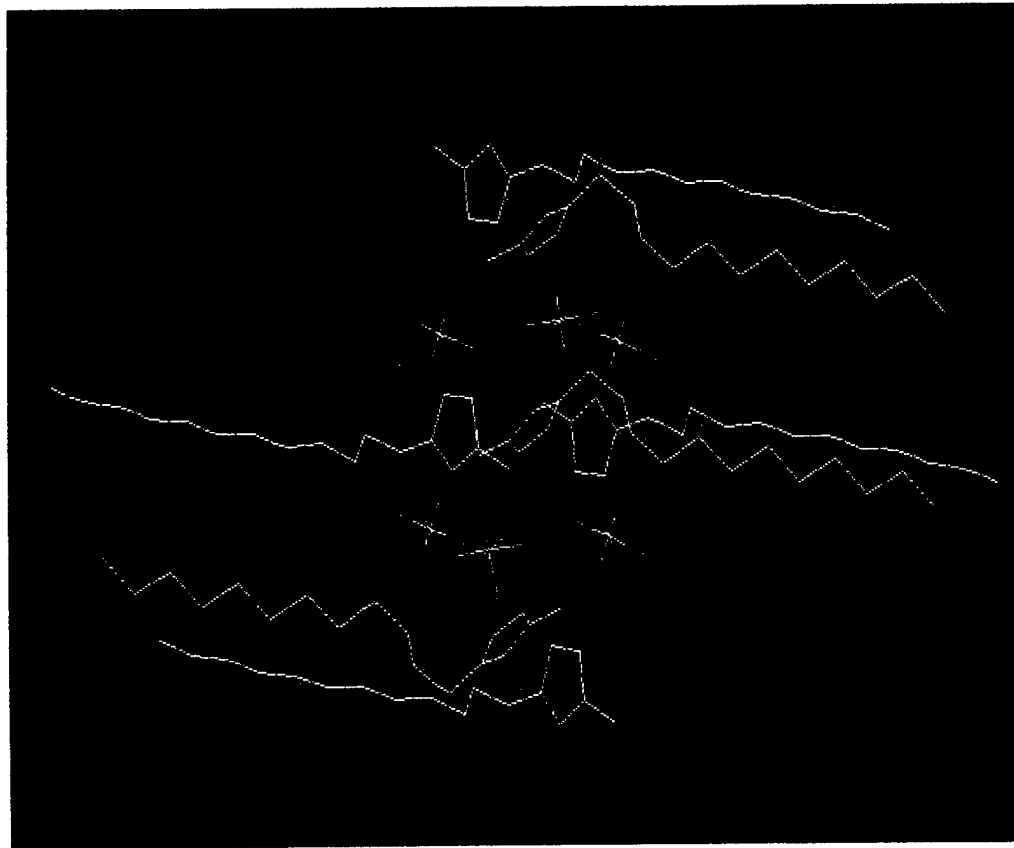


Extensive hydrogen bonding in 1-n-propyl-4-amino-1,2,4-triazolium bromide

#Drake, G. W.; Hawkins, T. W.; Tollison, K.; Hall, L.; Vij, A. **2003** manuscript in progress.



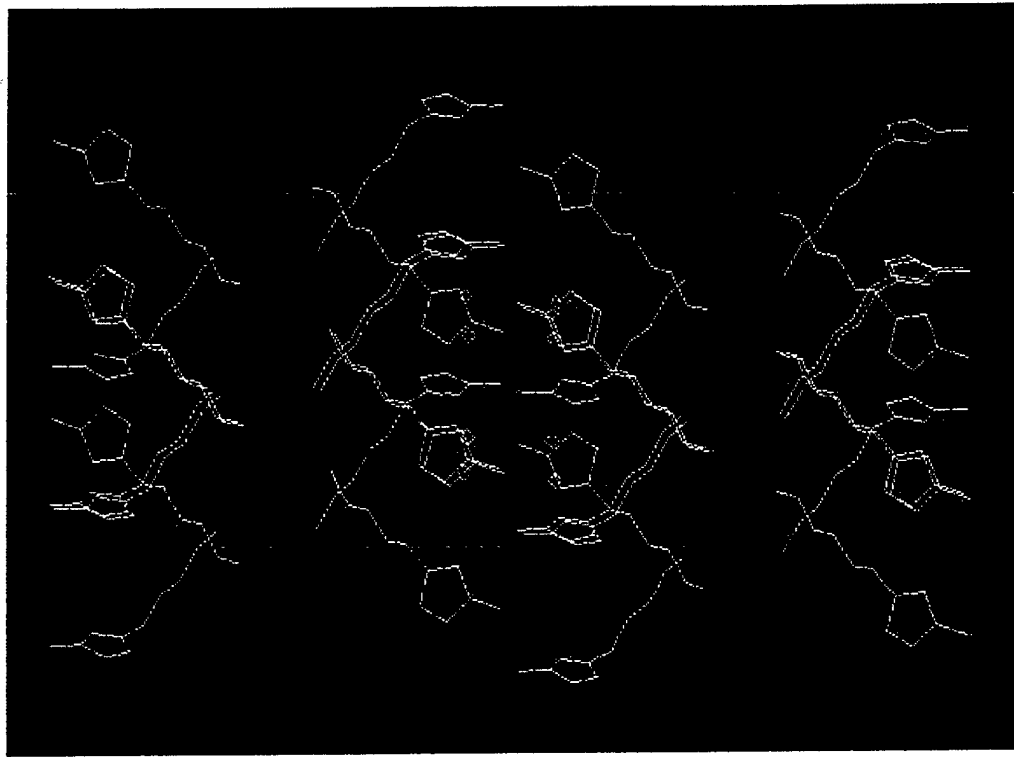
Ionic Liquids



1-dodecyl-3-methylimidazolium hexafluorophosphate*

*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.



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



Ionic Liquids



Summary and Conclusions

- Overall cation symmetry or lack thereof dramatically affects the physical properties of ionic liquids.
- Inter- as well as intra- molecular interactions especially hydrogen bonding are very important.
- Conductivity and viscosity are indirectly related, and both are significantly affected by the size and charge distribution of the cation and/or anion.
- New classes of ionic liquids are appearing and the field has tremendous promise for new and exciting breakthroughs.



Ionic Liquids



Acknowledgements:

- Mike Berman (AFOSR)
- Kerri Tollison, Leslie Hall, Greg Kaplan, Ashwani Vij (coworkers)
- Wayne Kalliomaa and Ronald Channell (AFRL/PRSP)
- Mike Huggins (AFRL/PRS)