

REPORT DOCUMENTATION PAGE

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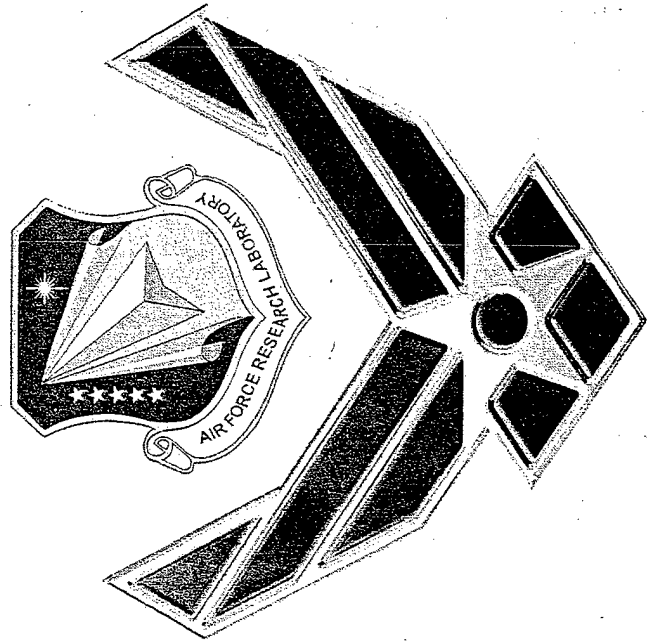
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Update in Ionic Liquids Research



Greg Drake and Tommy Hawkins

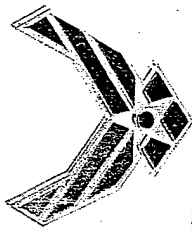
AFRL/PRSP

AFOSR Ionic Liquids Workshop

March 7 & 8, 2004

Tampa, FL

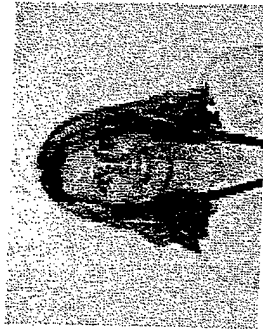
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AFRL Ionic Liquids



Those involved in this work



Ms. Kerri Tollison
Synthesis and
Characterization



Greg Kaplan
Synthesis and
Characterization



Jerry Boatz
Theoretical
Calculations



Jeff Mills
Theoretical
Calculations



Leslie Hall
Synthesis &
x-ray work



Ashwani Vij
X-ray
crystallography

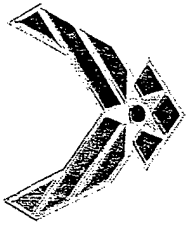


Tommy Hawkins
6.2 Propellant
Development

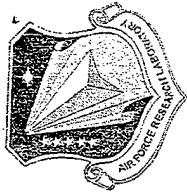


Greg Drake
6.1 Research
Synthesis

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HOW WE GOT TO WHERE WE ARE

- SIMPLE SALTS USING PROTIC ACIDS

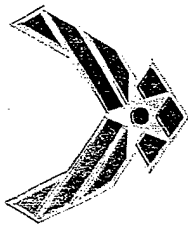
- OPEN CHAIN WORK
HYDROGEN BONDING EFFECTS

HYDRAZINE ANALOGUES

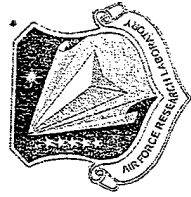
SOME SIMPLE AMINES

- HETEROCYCLIC APPROACH

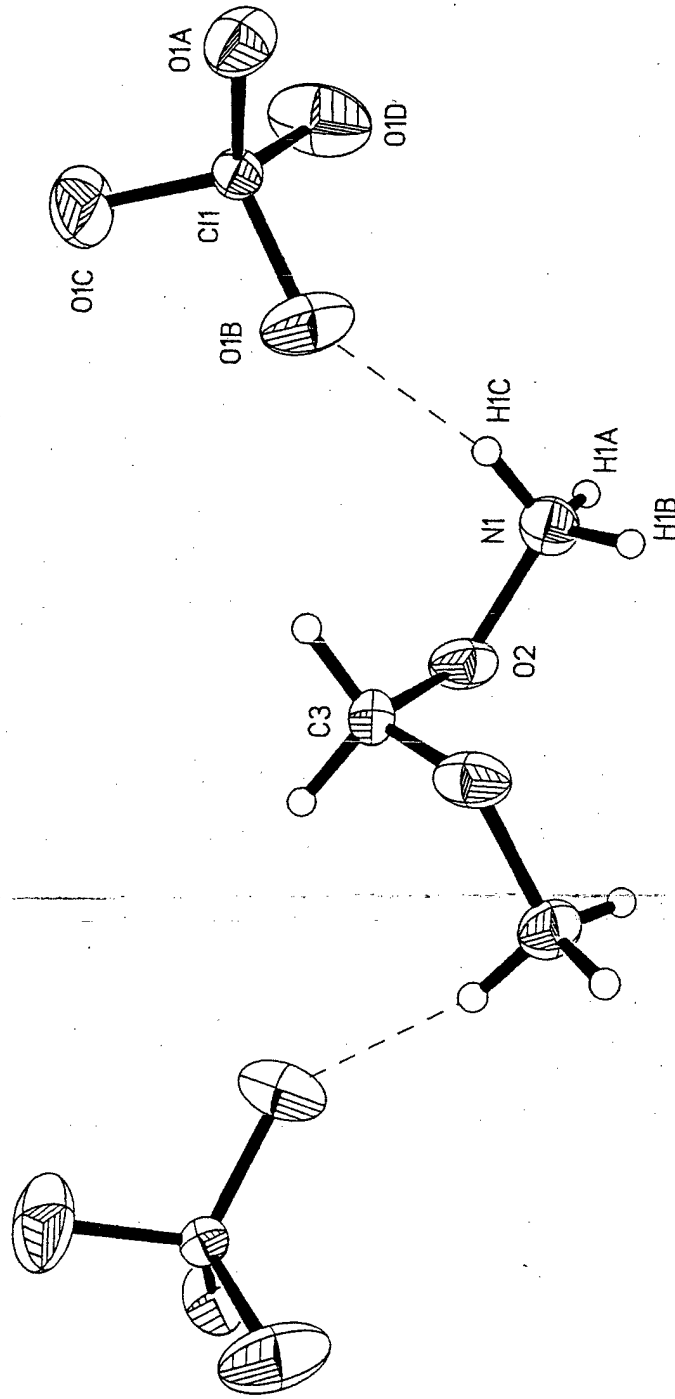
SHAPE CONSIDERATIONS



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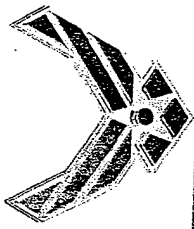


- Oxyamine, $-O-NH_2$, is analogue to hydrazine linkage $-NH-NH_2$
- $CH_2(O-NH_2)_2$ Explored at Edwards in late 1960's (Claude Merrill)
- Reinvestigation of mono- and di- salts
- Several of the salts met the definition of an ionic liquid
- Treacherous! Sensitive to mechanical stimuli! Explode unexpectedly!

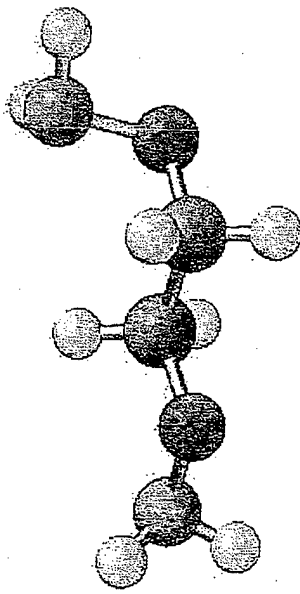
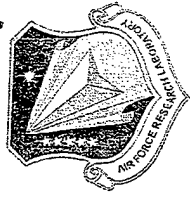


Tollison, K.; Drake, G.; Hawkins, T.; Brand, A.; McKay, M.; Ismail, I.; Merrill, C.; Petrie, M.; Bottaro, J.; Highsmith, T.; Gilardi, R. *J. Energet. Mater.* **2001**, *19*, 277.

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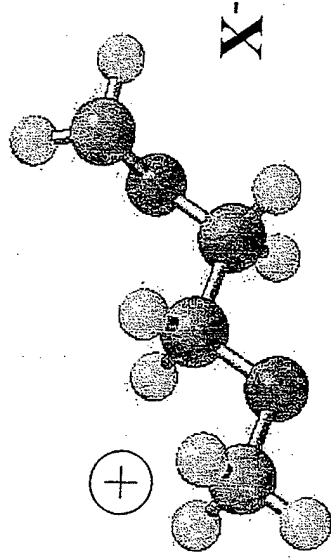
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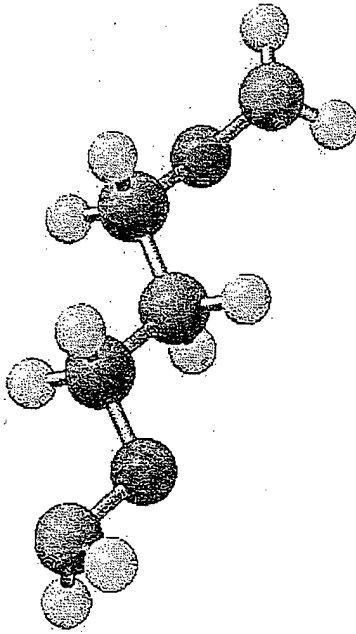
1,2-bis(oxyamine)ethane

Dixon, D. W.; Weiss, R. H. *J Org. Chem.* 1984,49, 4487.

H-X

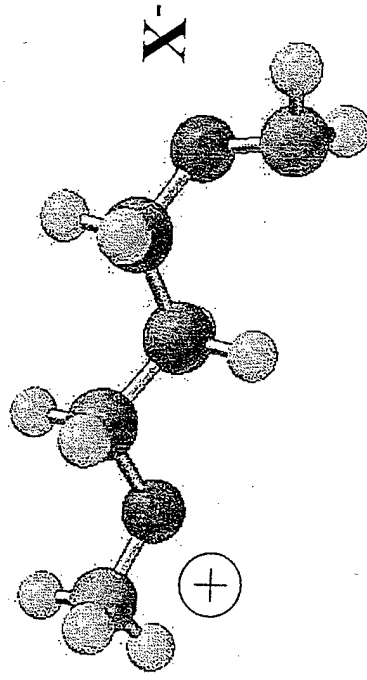


1,2-bis(oxyamine)ethane mono salts
 $X^- = NO_3^- , ClO_4^- , C(NO_2)_3^- , N(NO_2)_2^-$



1,3-bis(oxyamine)propane very stable, watery liquid
b.p. = 65-70 C @ 0.3 torr; f.p. = glasses at -40 C

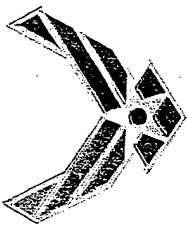
H-X



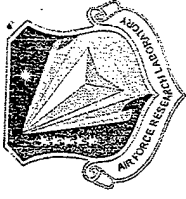
1,3-bis(oxyamine)propane mono salts
 $X^- = NO_3^- , ClO_4^- , C(NO_2)_3^- , N(NO_2)_2^-$

In either case, the oxyamines yield extremely friction and impact sensitive materials.

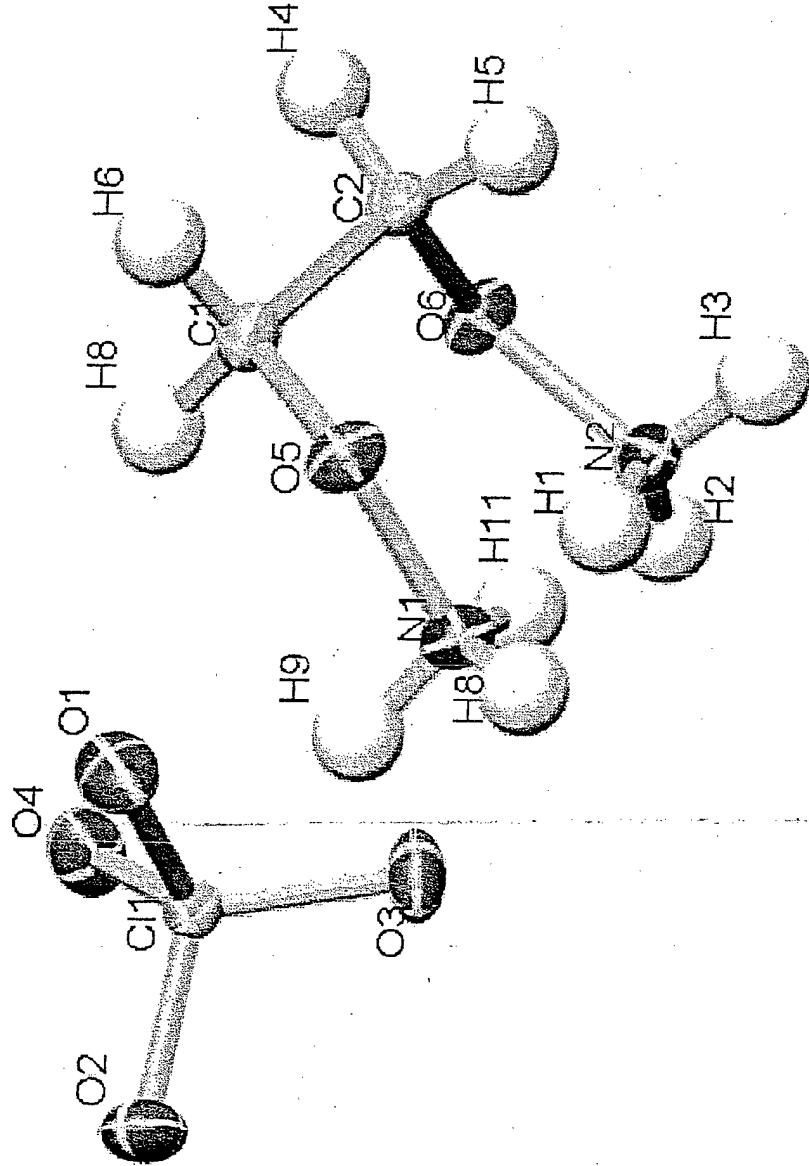
Drake, G.; Hawkins, T.; Hall, L.; Sheehy, J. Prop. Energ. Pyrotech. Submitted 2004.
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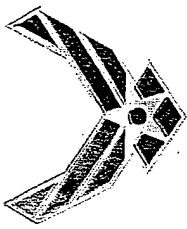
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X-ray diffraction confirmed structure, lots of hydrogen bonding!
H(1) and H(8) are partial occupancy 70%/30%



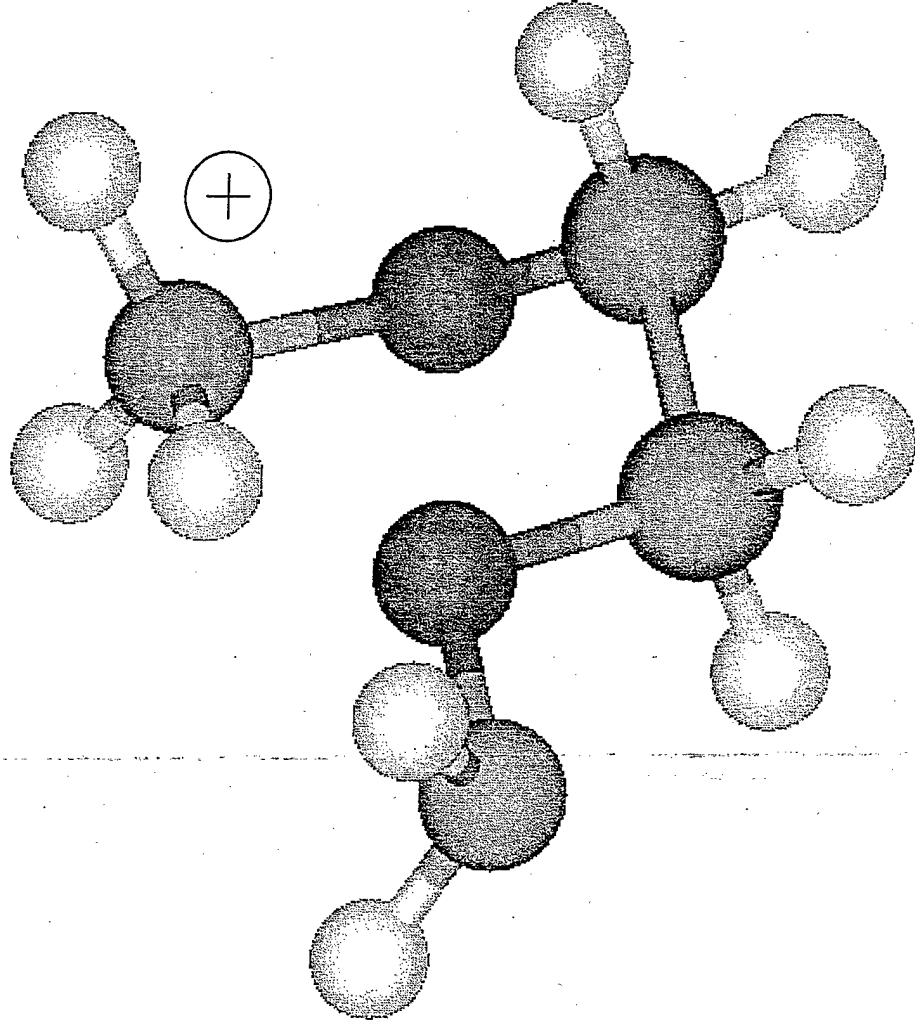
Drake, G.; Hawkins, T.; Hall, L.; Sheehy, J. *Prop. Energ. Pyrotech.* Submitted 2004.
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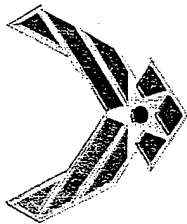
AFRL Ionic Liquids



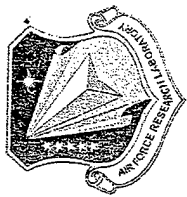
High level computational studies (Dr. Jeff Sheehy NASA/Marshall) revealed a slightly different structure. Comparison of bond distances matched well though



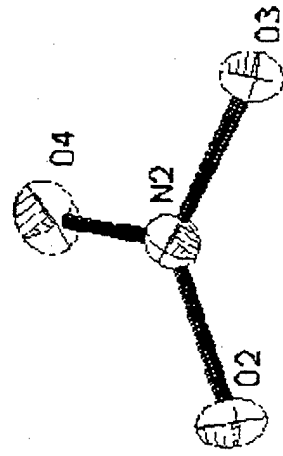
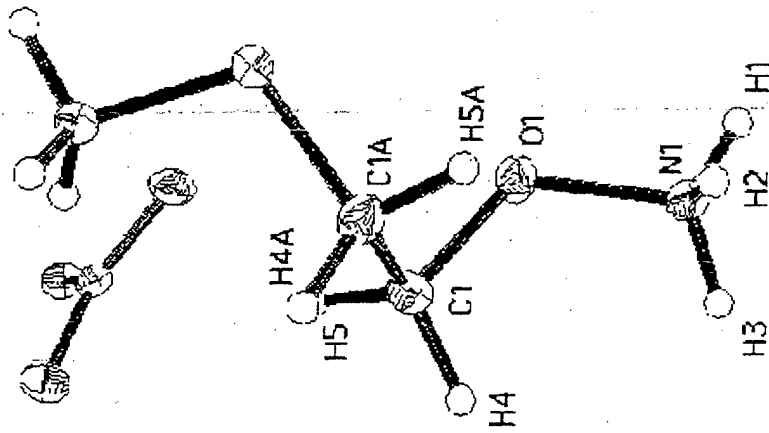
Drake, G.; Hawkins, T.; Hall, L.; Sheehy, J. Prop. Energ. Pyrotech. Submitted 2004.
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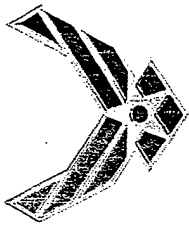


X-ray structure ethylene bisoxyamine dinitrate was also solved

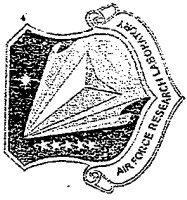


Drake, G.; Hawkins, T.; Hall, L.; Sheehy, J. *Prop. Energ. Pyrotech.* Submitted 2004.

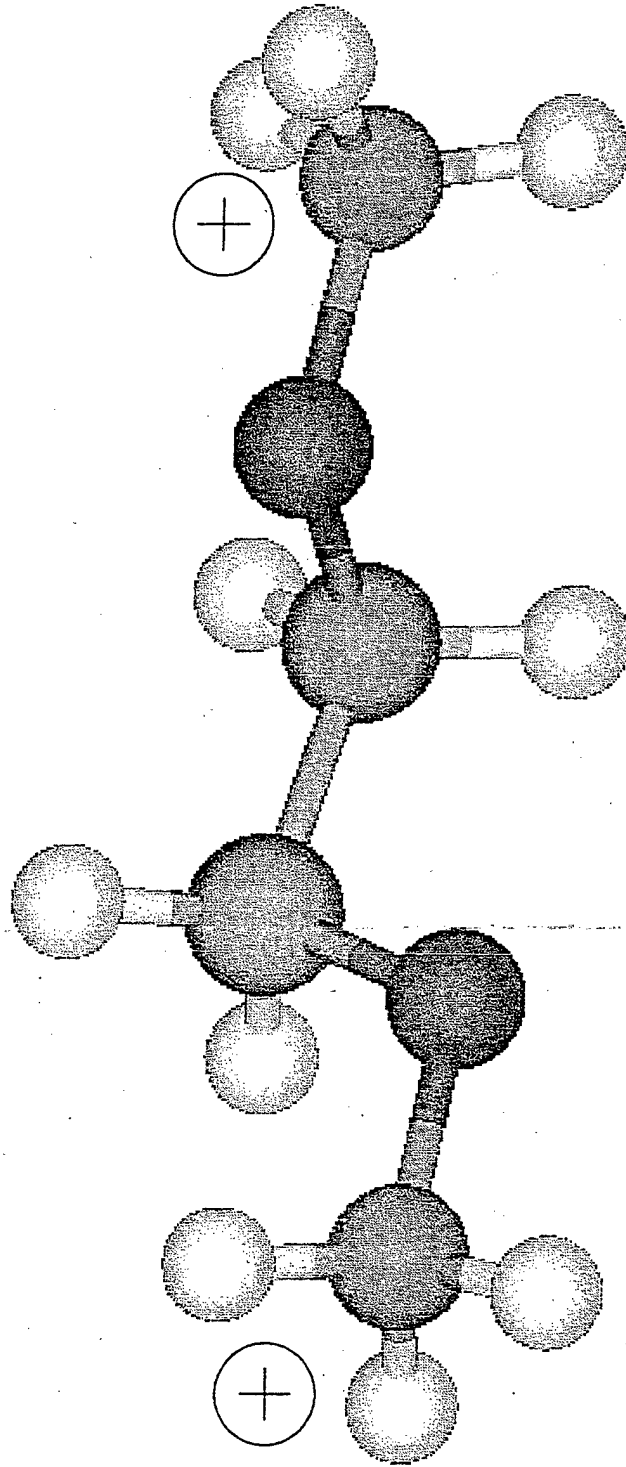
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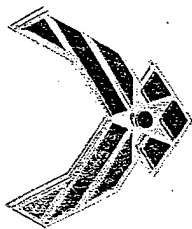
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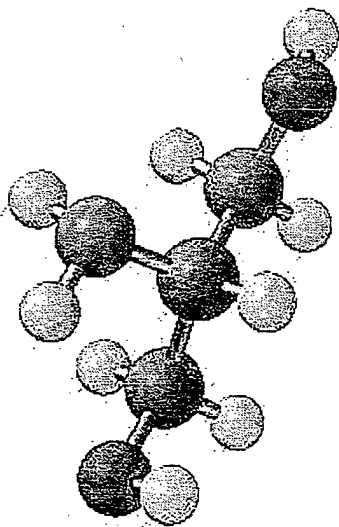
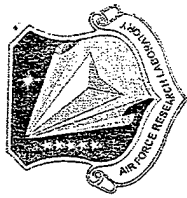
High level calculations (Jeff Sheehy) of the gas phase ethylene bisoxoammonium cation revealed a similar structure with accurately predicted bond distances.



Drake, G.; Hawkins, T.; Hall, L.; Sheehy, J. *Prop. Energ. Pyrotech.* Submitted 2004.
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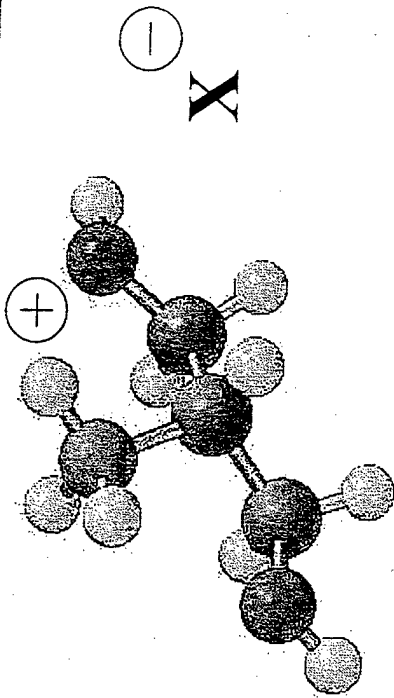


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1,3-dihydroxy-2-aminopropane
(serinol)

H-X

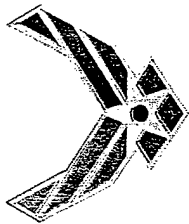


X⁻ = NO₃⁻, ClO₄⁻, N(NO₂)₂⁻

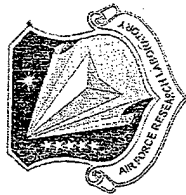
Salt	m.p.	DSC onset	Impact (kg·cm)	Friction (kg)
Serinol nitrate	61-66° C	215° C	180	18.0
Serinol perchlorate	55-60° C	250° C	200	>37.8
Serinol dinitramide	41-44° C	135° C	16	23.4

Drake, G.; Hawkins, T.; Tollison, K.; Hall, L.; Boatz, J. *Prop. Energ. Pyrotech.* 2004 submitted.

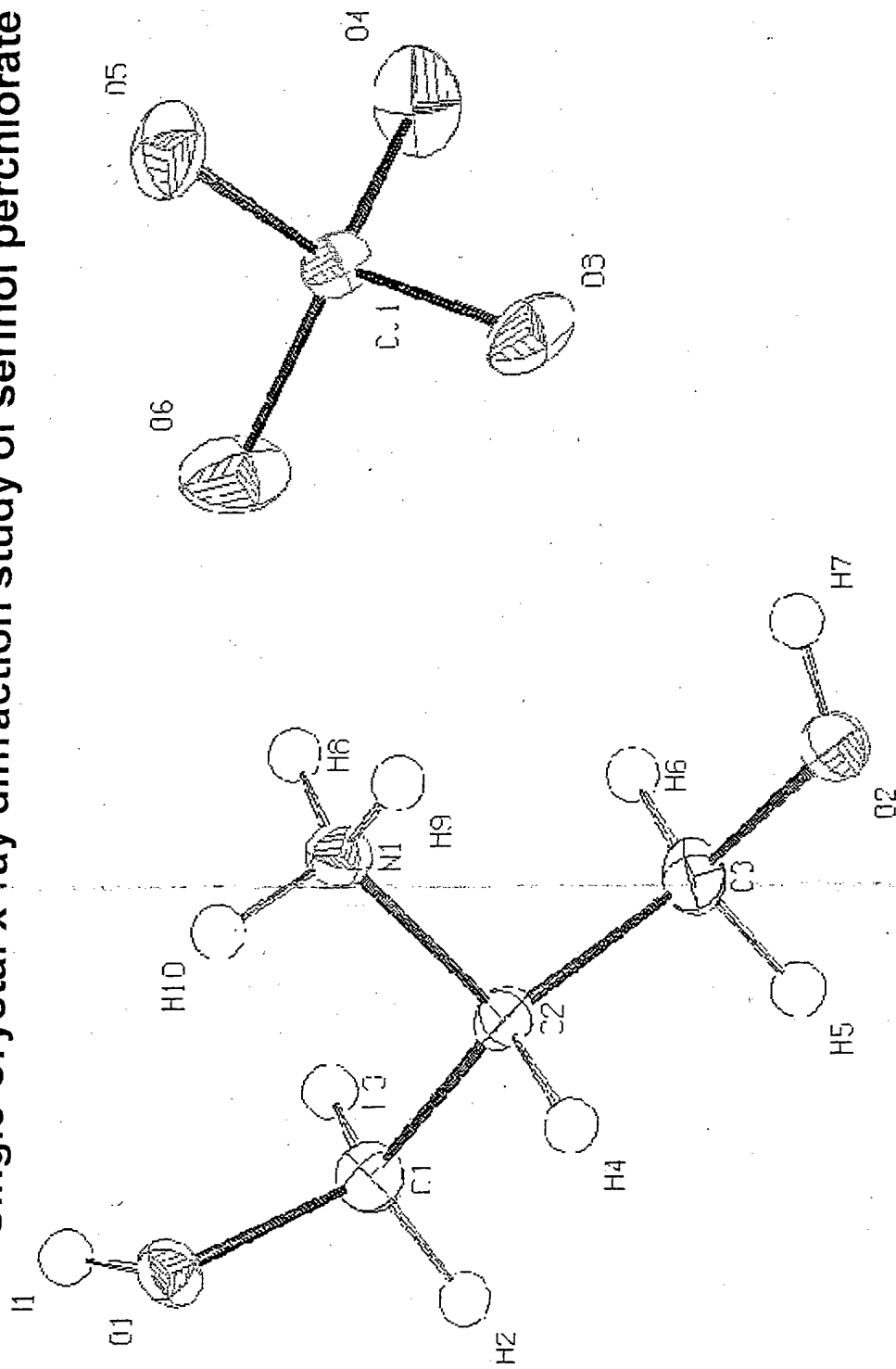
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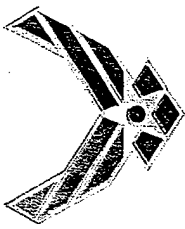
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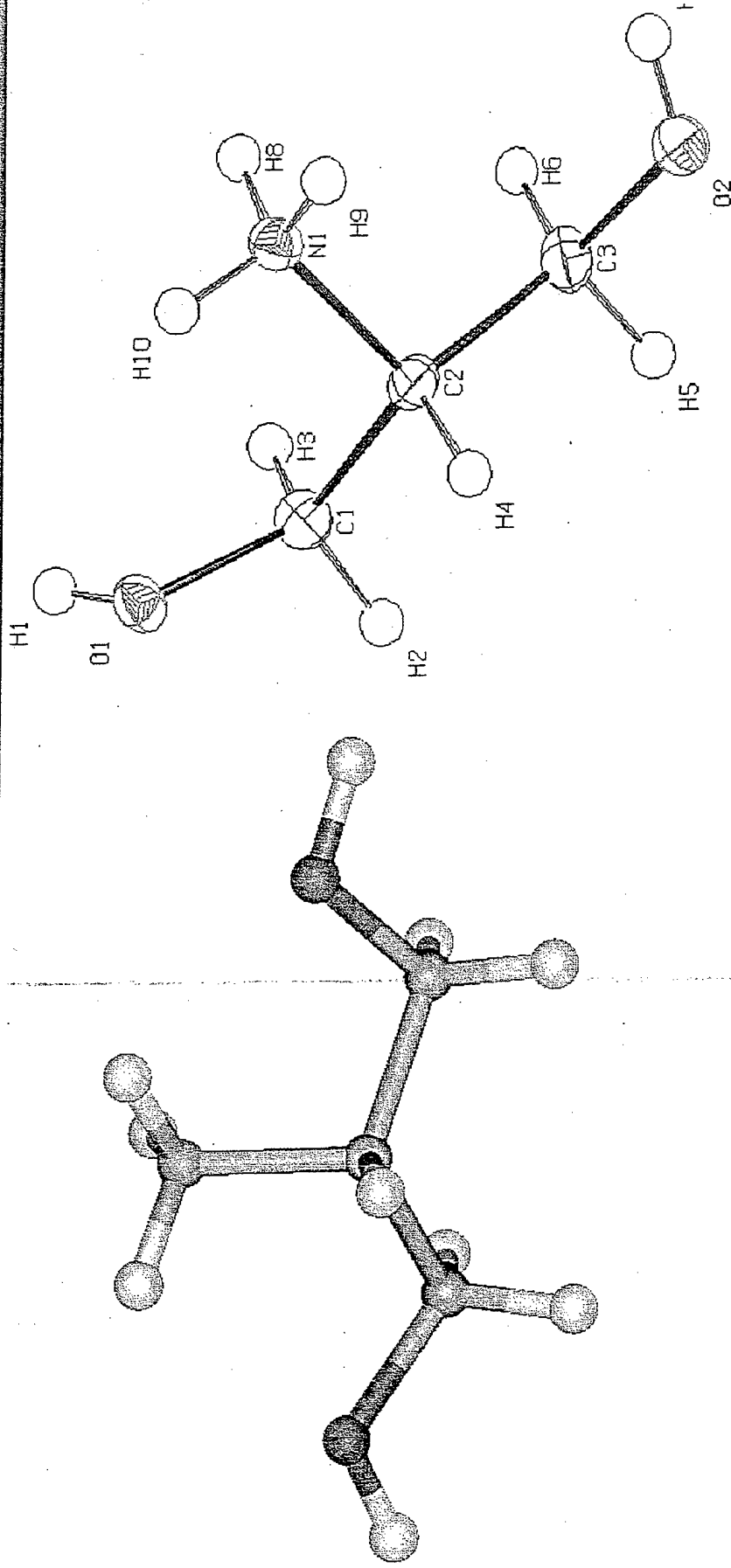
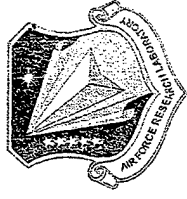
Single Crystal x-ray diffraction study of serinol perchlorate



Drake, G.; Hawkins, T.; Tollison, K.; Hall, L.; Boatz, J. Prop. Energ. Pyrotech. 2004 submitted.
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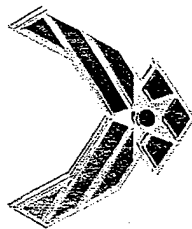


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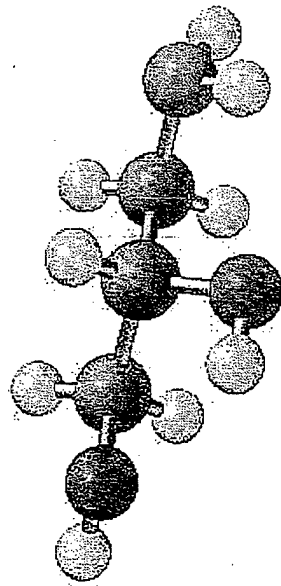
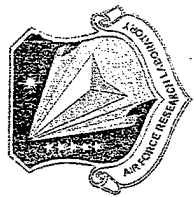


Theoretical computations by Dr. Jerry Boatz (AFRL) using B3LYP/6-31G(d,p) of serinol cation in the gas phase (C_s symmetry) as compared to that observed in the single crystal x-ray diffraction study of serinol perchlorate

Drake, G.; Hawkins, T.; Tollison, K.; Hall, L.; Boatz, J. *Prop. Energ. Pyrotech.* **2004** submitted.
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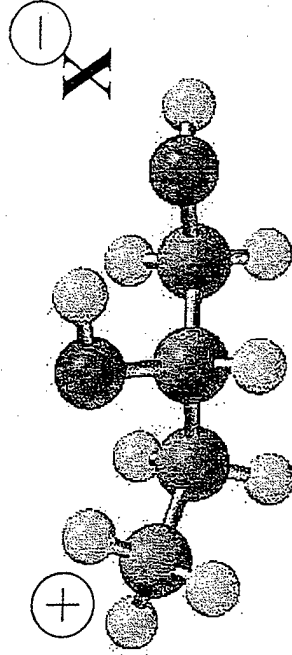


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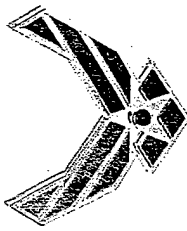
1,2-dihydroxy-3-aminopropane
(chiral)

H-X

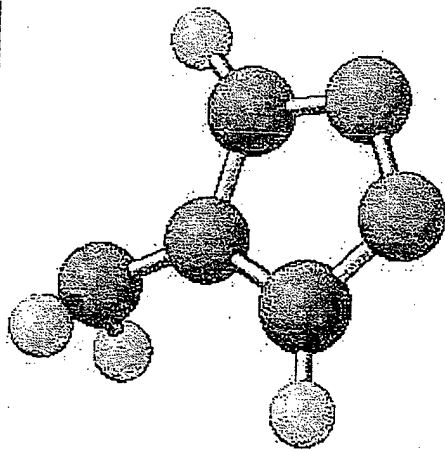


<u>SALT</u>	<u>Melting Point</u>	<u>Decomposition Onset</u>
1,2-dihydroxy-3-aminopropane nitrate	-40° C	220° C
1,2-dihydroxy-3-aminopropane perchlorate	?	225° C
1,2-dihydroxy-3-aminopropane dinitramide	-5° C	135° C

Drake, G.; Hawkins, T.; Tollison, K.; Hall, L.; Boatz, J. manuscript in progress, 2004.
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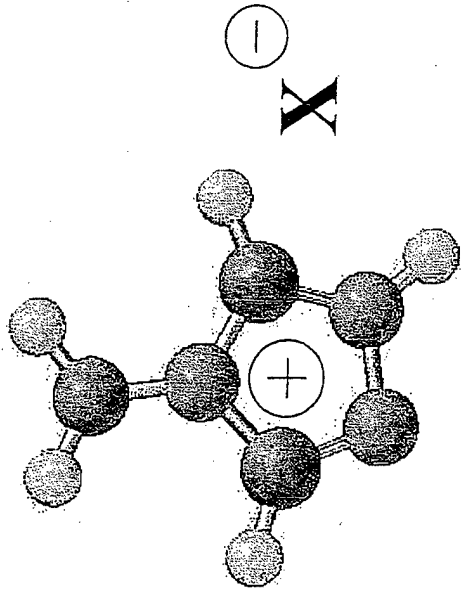


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4-amino-1,2,4-triazole

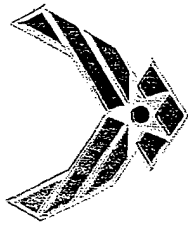
H-X



<u>SALT</u>	<u>Melting Point</u>	<u>Decomposition Onset</u>	<u>Impact</u> kgcm
4-amino-1,2,4-triazolium nitrate	69° C	180° C	>200
4-amino-1,2,4-triazolium perchlorate	84° C	210° C	30
4-amino-1,2,4-triazolium dinitramide	20° C	145° C	<5

Drake, G.; Hawkins, T.; Brand, A.; Hall, L.; McKay, M.; Vij, A.; Ismail, I. Prop. Expl. Pyrotech. 2003, 28, 174.

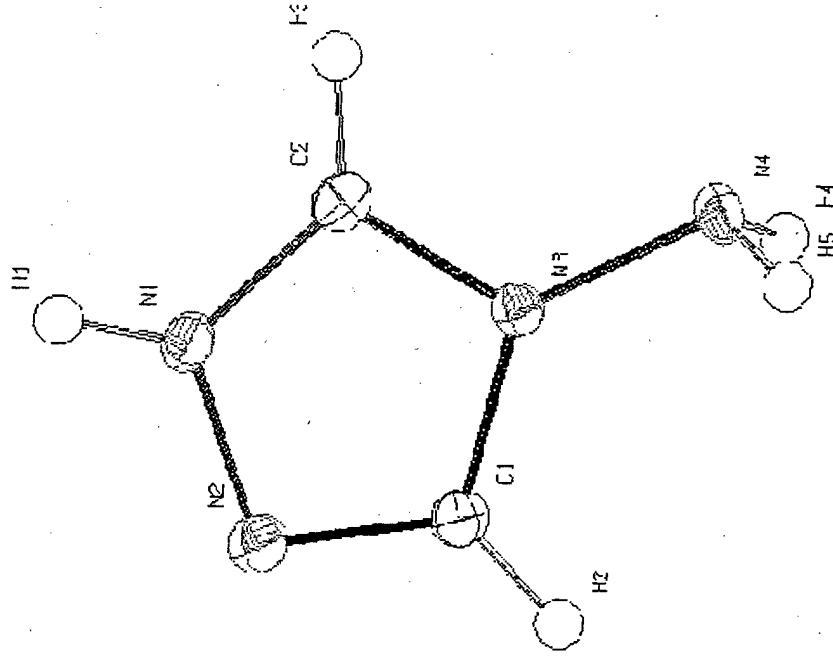
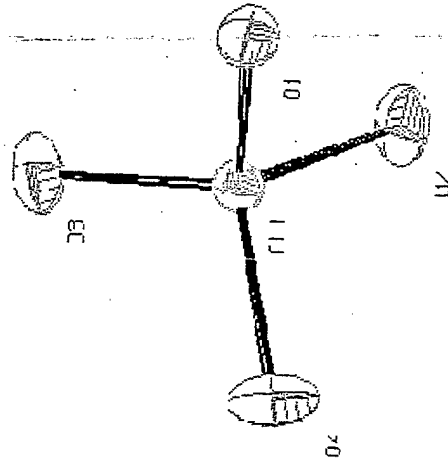
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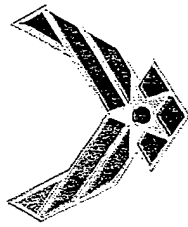
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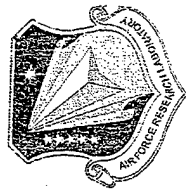
Single crystal x-ray diffraction study revealed the expected structure for 4-amino-1,2,4-triazolium perchlorate.



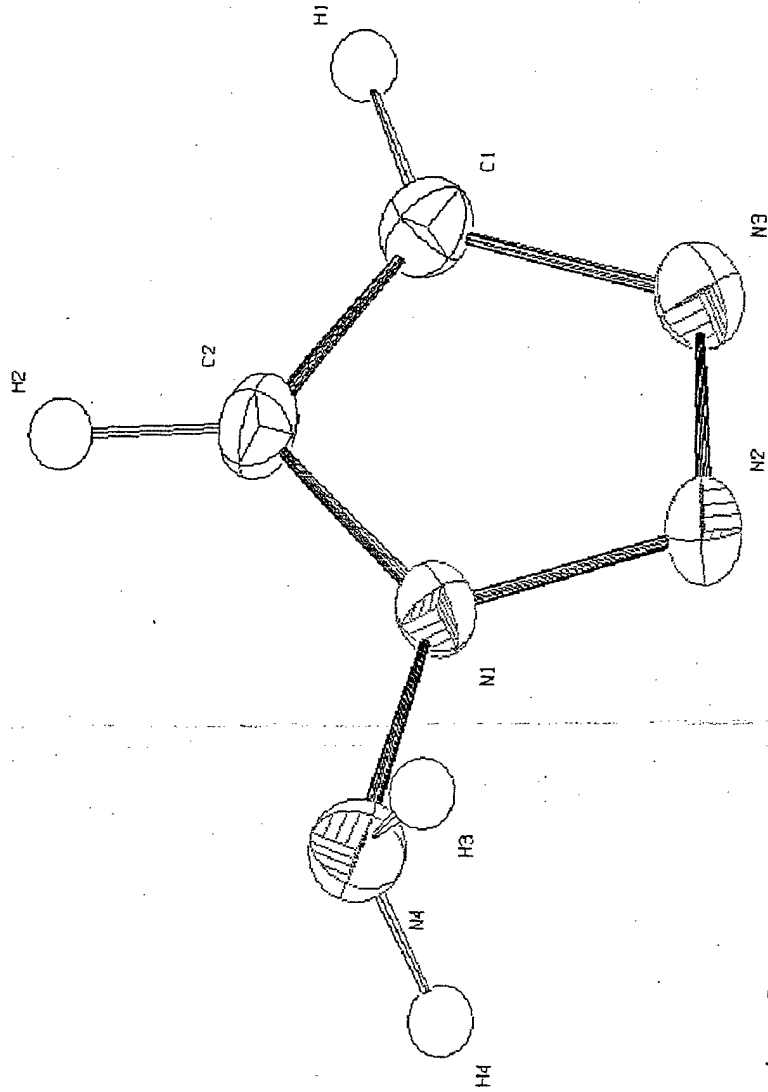
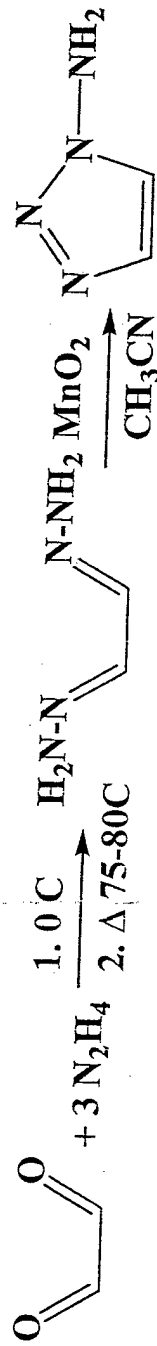
Hall, L.; Drake, G. Unpublished results 2004.
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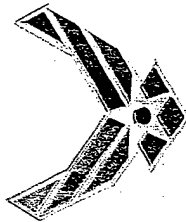


New Effort with 1-amino-1,2,3-triazole

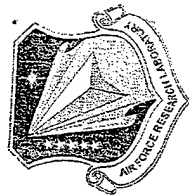


Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. *J. Heterocyc. Chem.* submitted 2004.

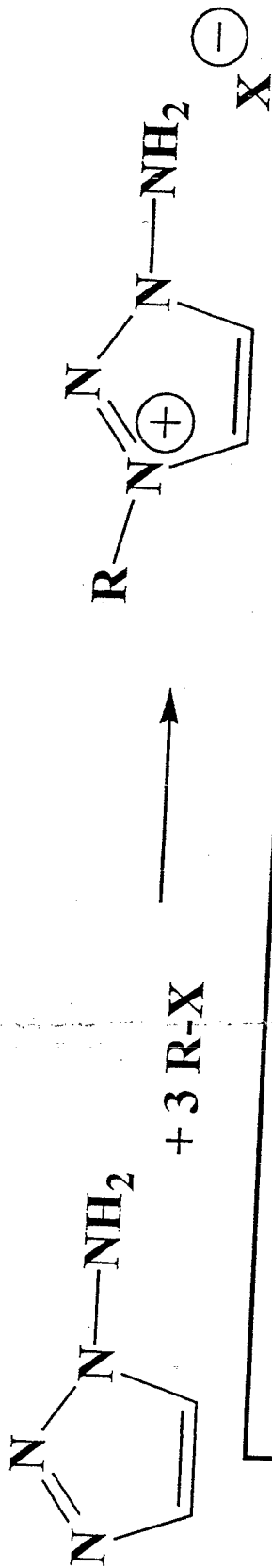
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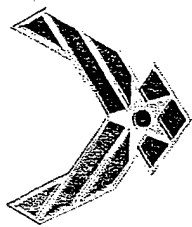
Synthesis of 1-amino-3-alkyl-1,2,3-triazolium halides



<u>New Salt</u>	M.P. (°C)	Decomp.
1-amino-3-methyl-1,2,3-triazolium iodide	146	150
1-amino-3-ethyl-1,2,3-triazolium bromide	118	149
1-amino-3-propyl-1,2,3-triazolium bromide	128	135
1-amino-3-allyl-1,2,3-triazolium bromide	100	135
1-amino-3-butyl-1,2,3-triazolium bromide	131	145

Not Ionic Liquids!

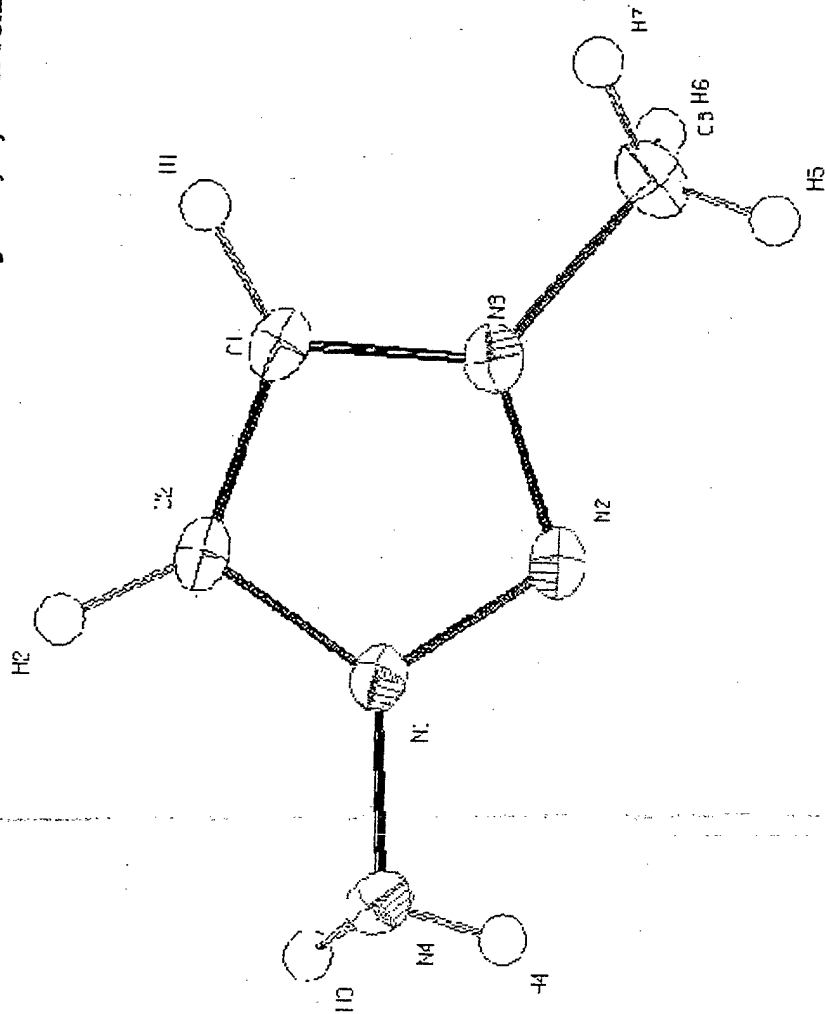
Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. *Heterocyc. Chem.* submitted 2004.
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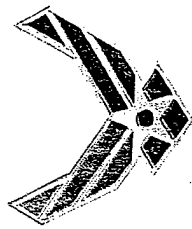


Single crystal x-ray diffraction study of 1-amino-3-methyl-1,2,3-triazolium iodide

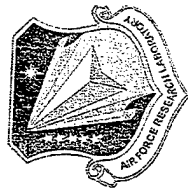


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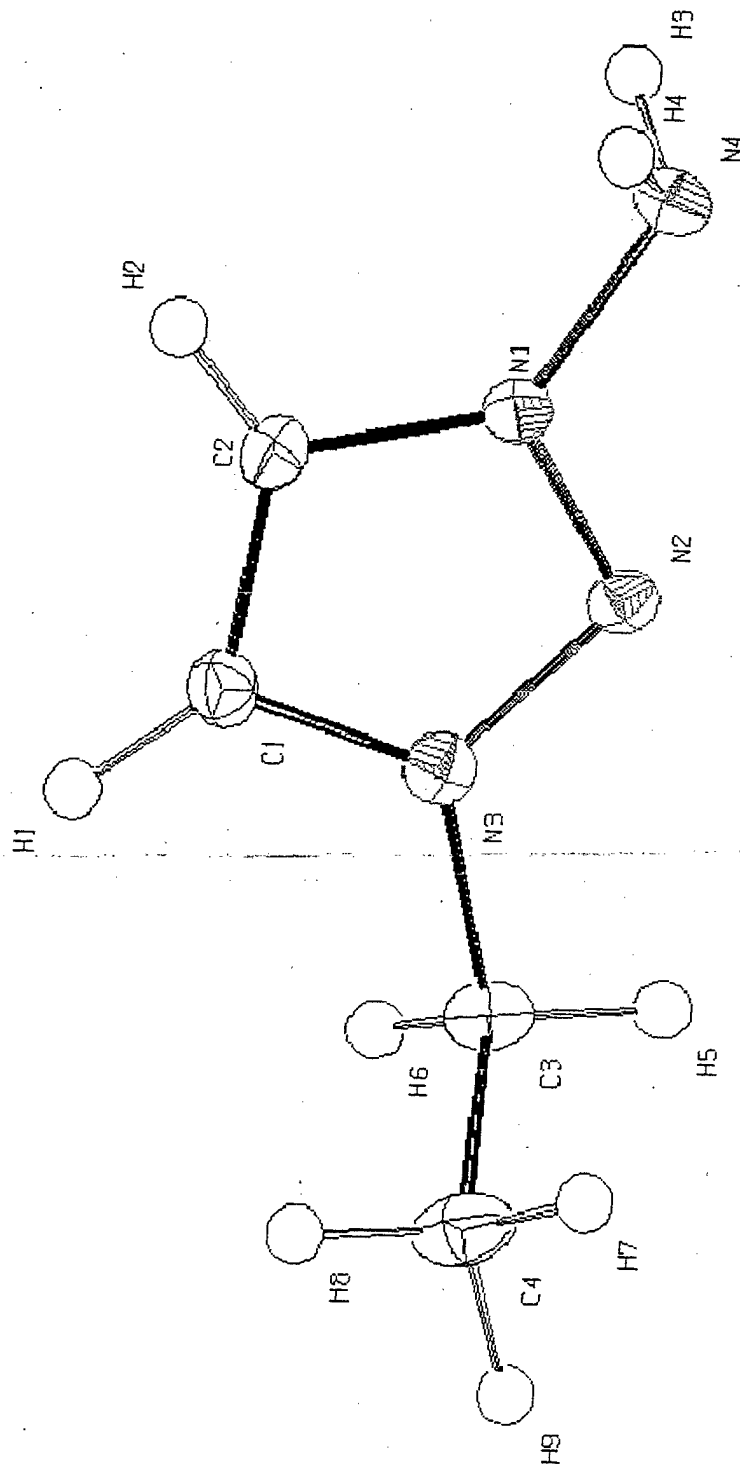
Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. *Heterocyc. Chem.* submitted 2004.
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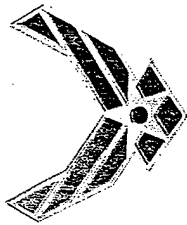
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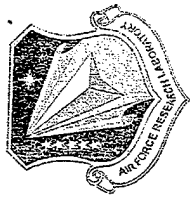
Single crystal x-ray diffraction study of 1-amino-3-ethyl-1,2,3-triazolium bromide



Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. *Heterocyc. Chem.* submitted 2004.
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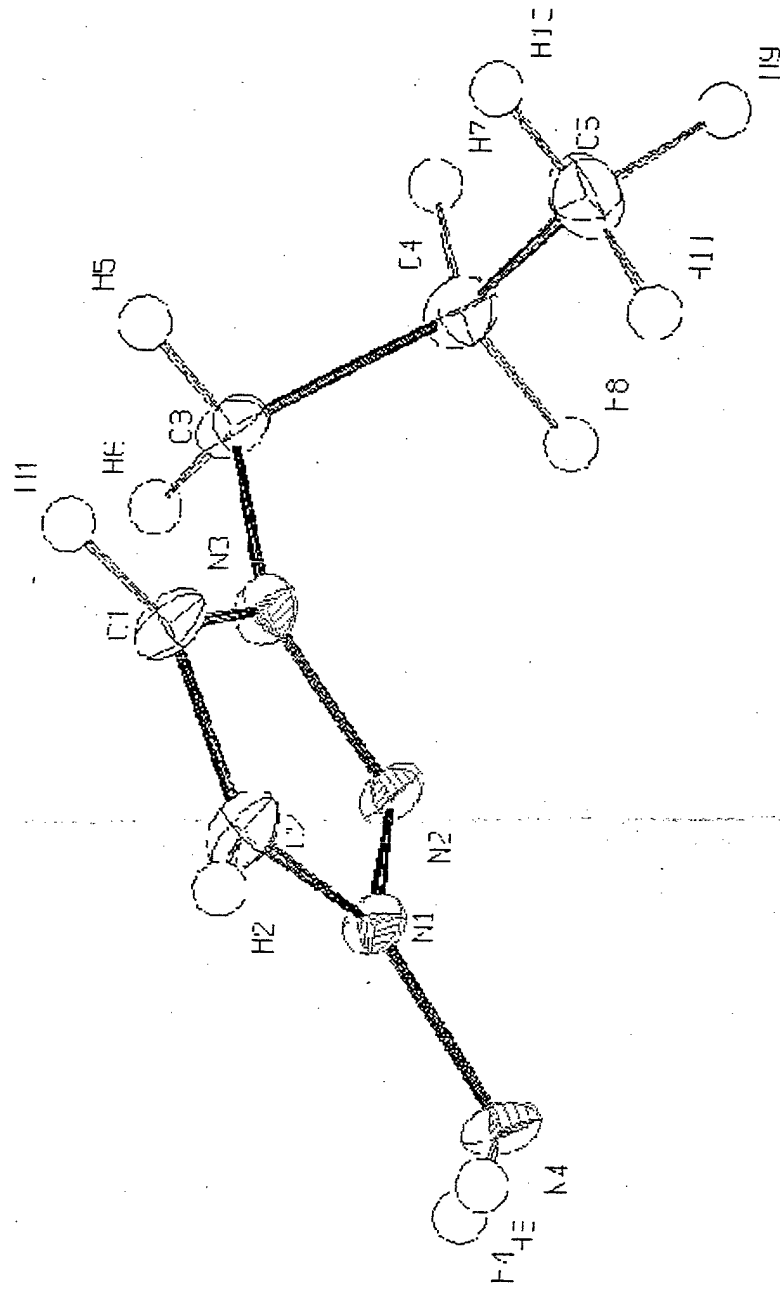


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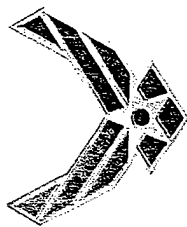


Single crystal x-ray diffraction study of 1-amino-3-propyl-1,2,3-triazolium bromide

Br 1



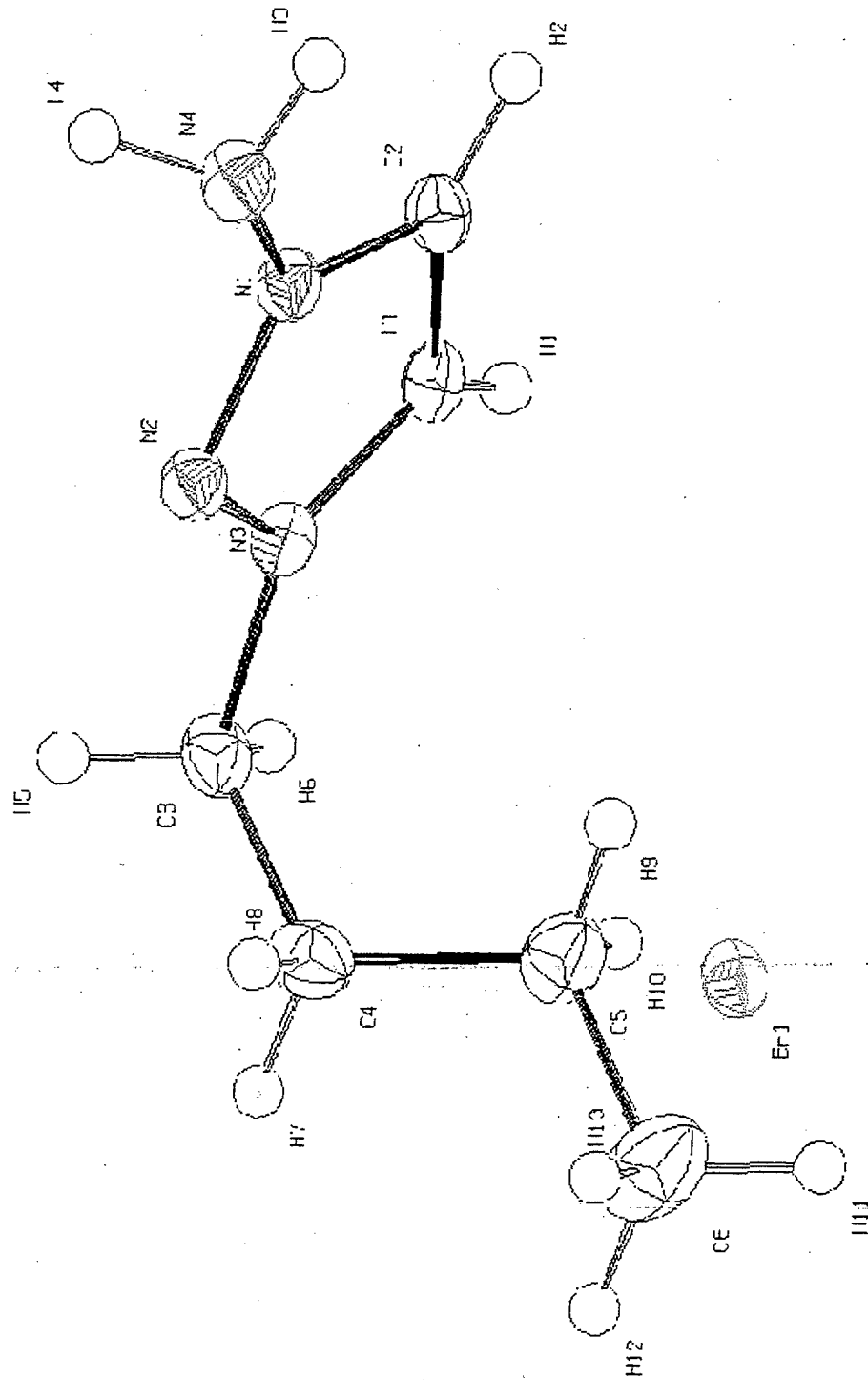
Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. *Heterocyc. Chem.* submitted 2004.
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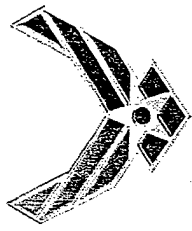


Single crystal x-ray structure of 1-amino-3-butyl-1,2,3-triazolium bromide



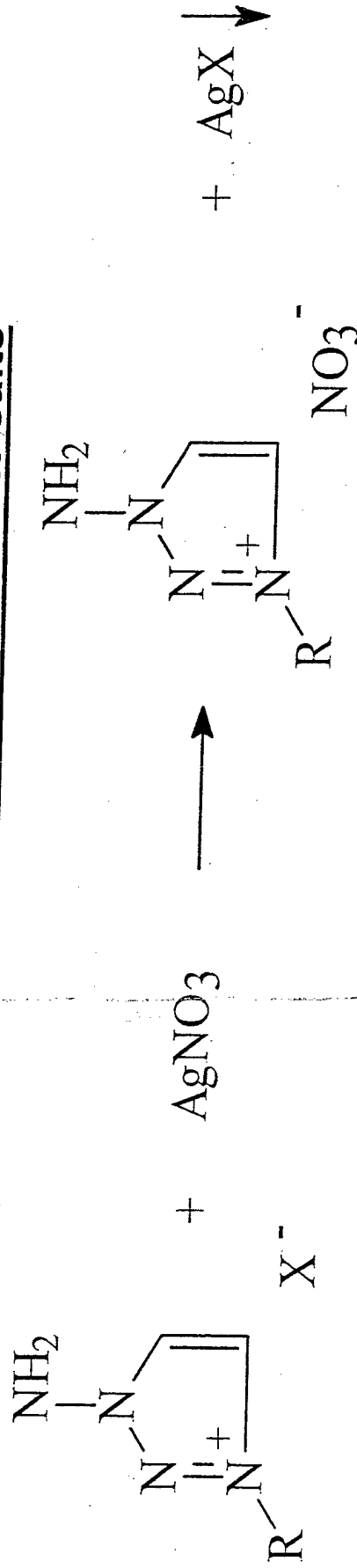
Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. *Heterocyc. Chem.* submitted 2004.

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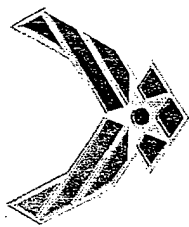
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Straight-forward metathesis forms desired nitrate salts

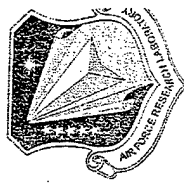


<u>NEW SALT</u>	M.P. (°C)
1-amino-3-methyl-1,2,3-triazolium nitrate	86
1-amino-3-ethyl-1,2,3-triazolium nitrate	30
1-amino-3-propyl-1,2,3-triazolium nitrate	33
1-amino-3-allyl-1,2,3-triazolium nitrate	8
1-amino-3-butyl-1,2,3-triazolium nitrate	48

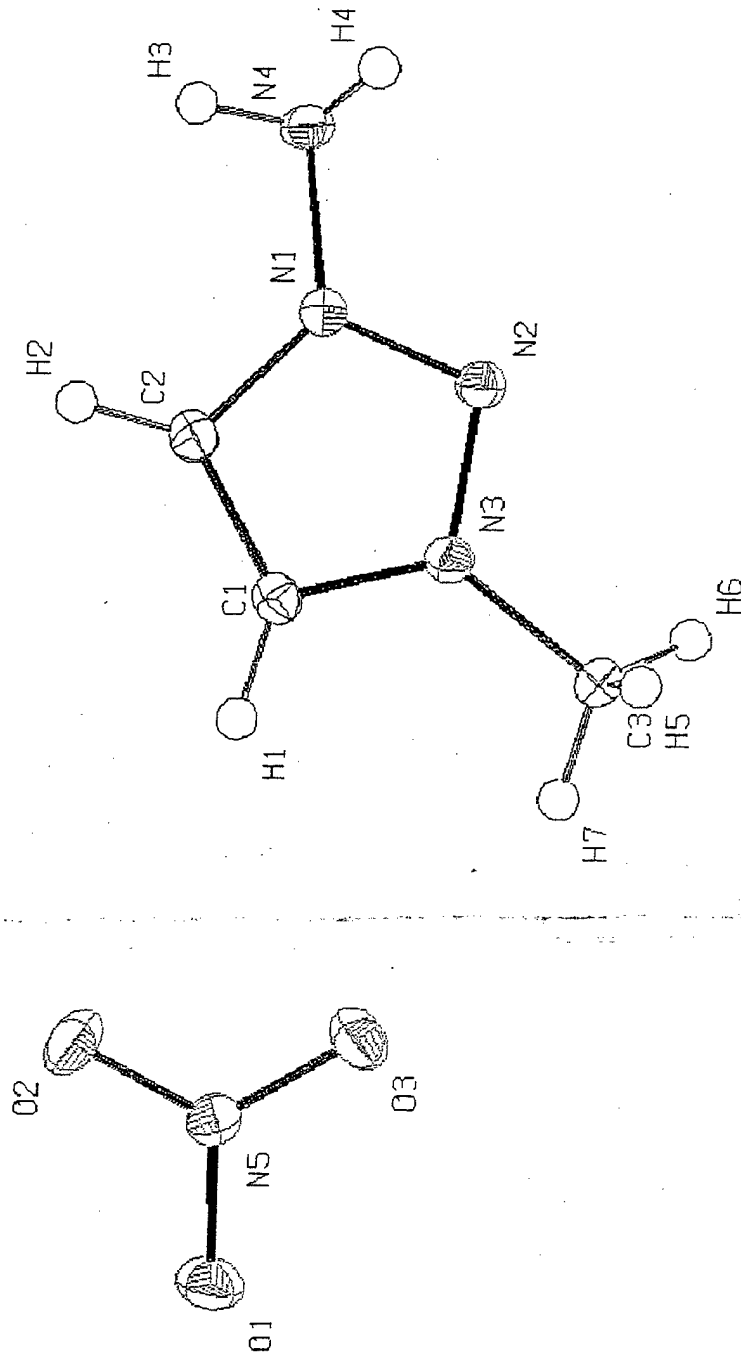
Kaplan, G.; Drake, G.; Tollison, K.; Hawkins, T.; Hall, L. Manuscript in progress 2004.
Distribution A. Public Release, Distribution unlimited.



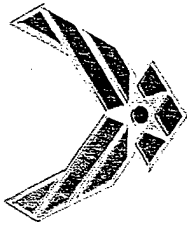
AFRL Ionic Liquids



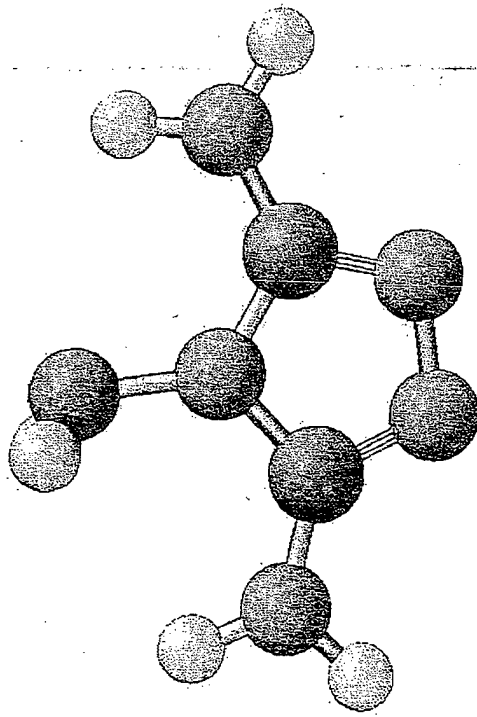
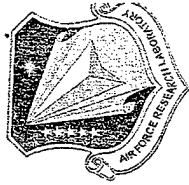
Single crystal x-ray diffraction study of 1-amino-3-methyl-1,2,3-triazolium nitrate



Kaplan, G.; Drake, G.; Hawkins, T.; Hall, L.; Tollison, K. Manuscript in progress 2004
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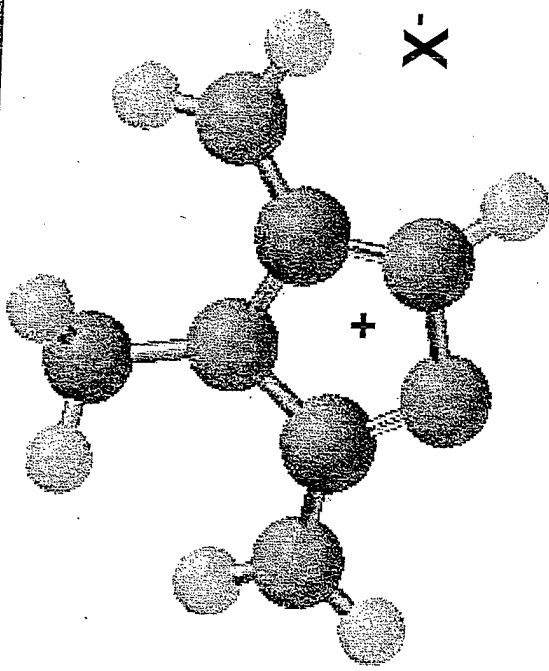


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3,4,5-triamino-1,2,4-triazole
(Guanazine)

+ H-X

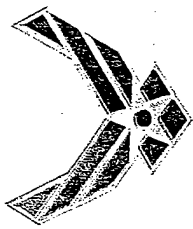


X⁻ = NO₃⁻, ClO₄⁻, N(NO₂)₂⁻

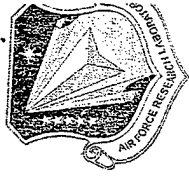
<u>New Salt</u>	M.P. (°C)	Impact (kgcm)	Friction (Kg)
Guanazinium nitrate	225	200	16
Guanazinium perchlorate	215	50	15.2
Guanazinium dinitramide	145	196	15.2

Not Ionic Liquids!

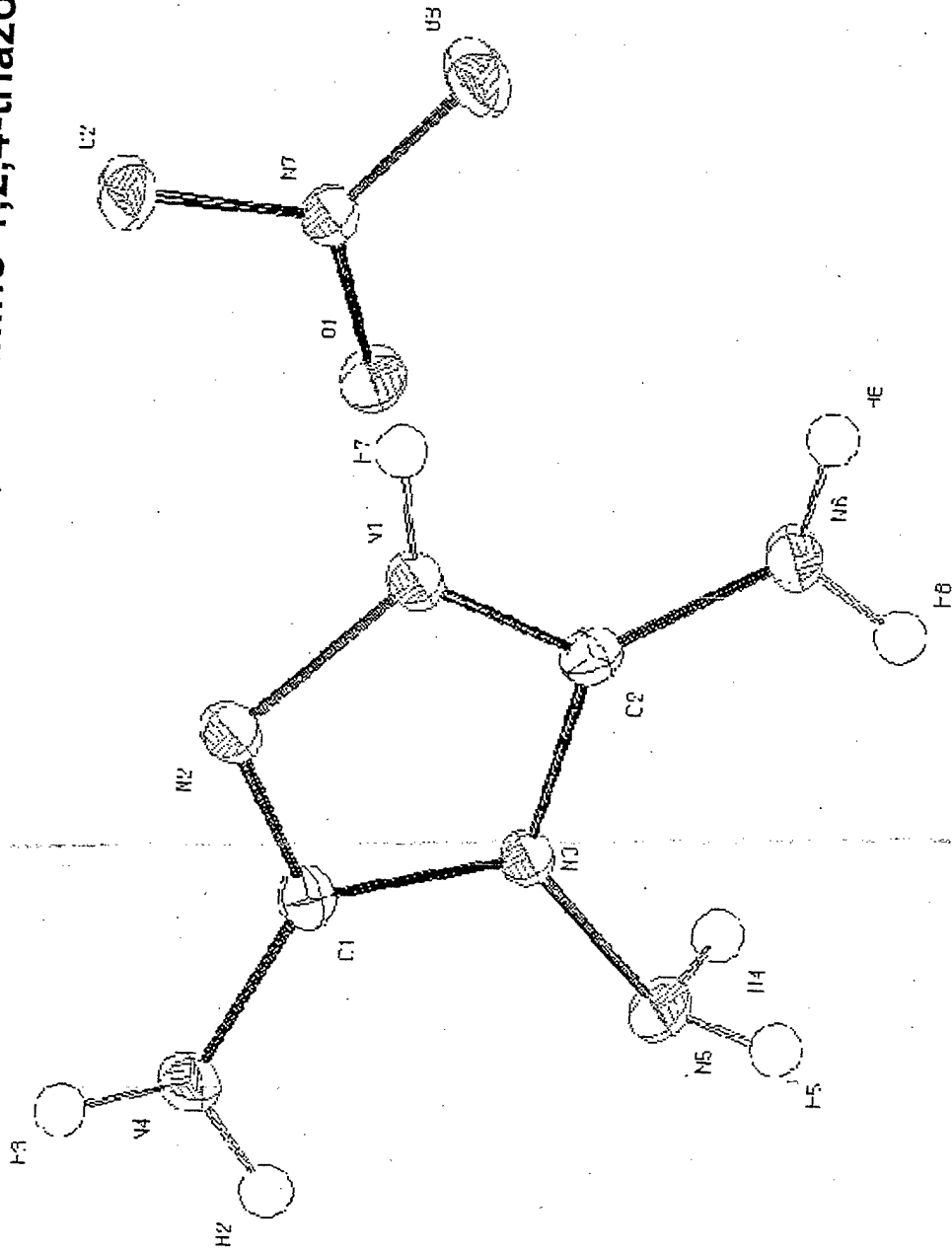
Drake, G.; Hawkins, T.; Hall, L.; Brand, A. *Prop. Expl. Pyrotech.* 2004, to be submitted
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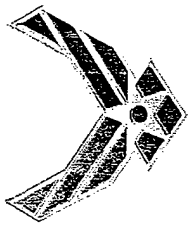
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Single crystal x-ray diffraction study of 3,4,5-triamino-1,2,4-triazolium nitrate



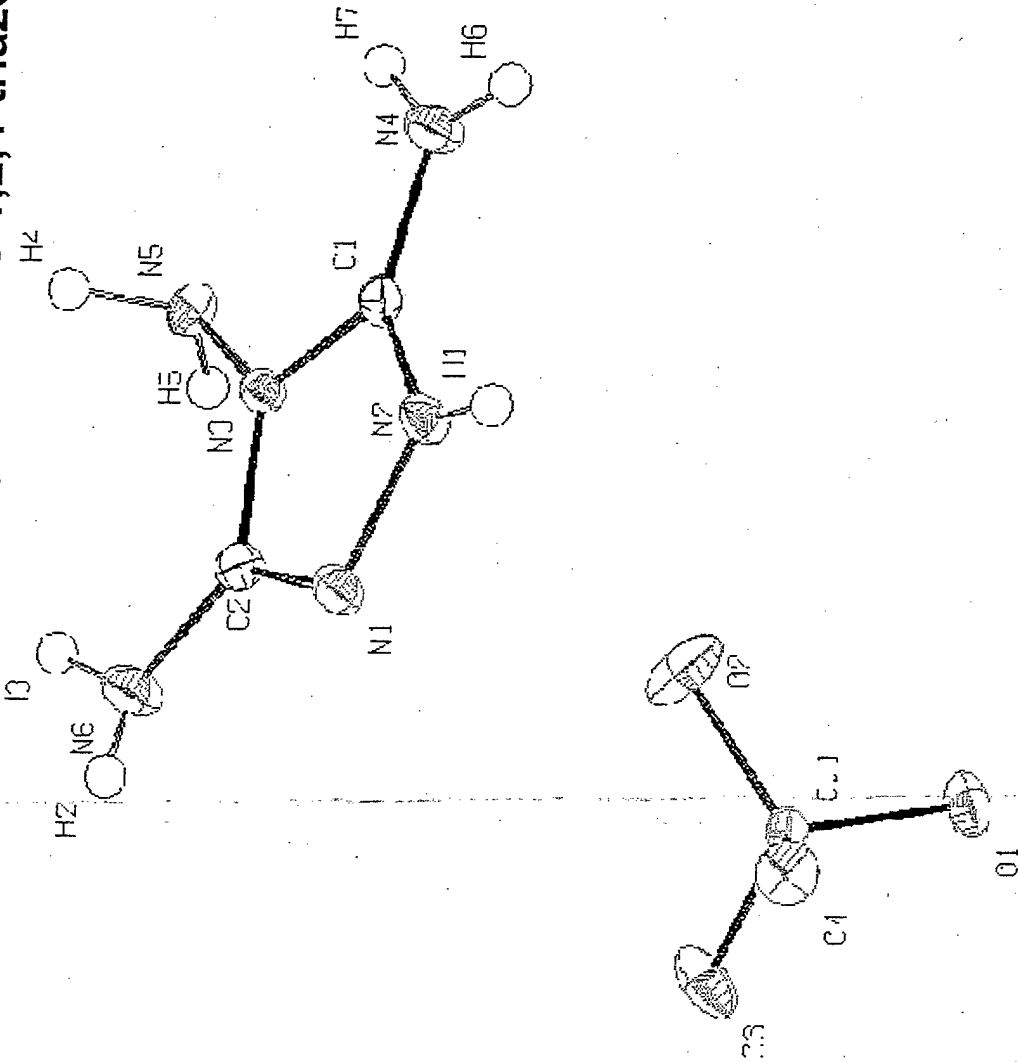
Drake, G.; Hawkins, T.; Hall, L.; Brand, A. Prop. Expl. Pyrotech. **2004**, to be submitted
Distribution A. Public Release, Distribution unlimited



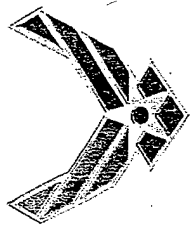
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Single crystal x-ray diffraction study of 3,4,5-triamino-1,2,4-triazolium perchlorate



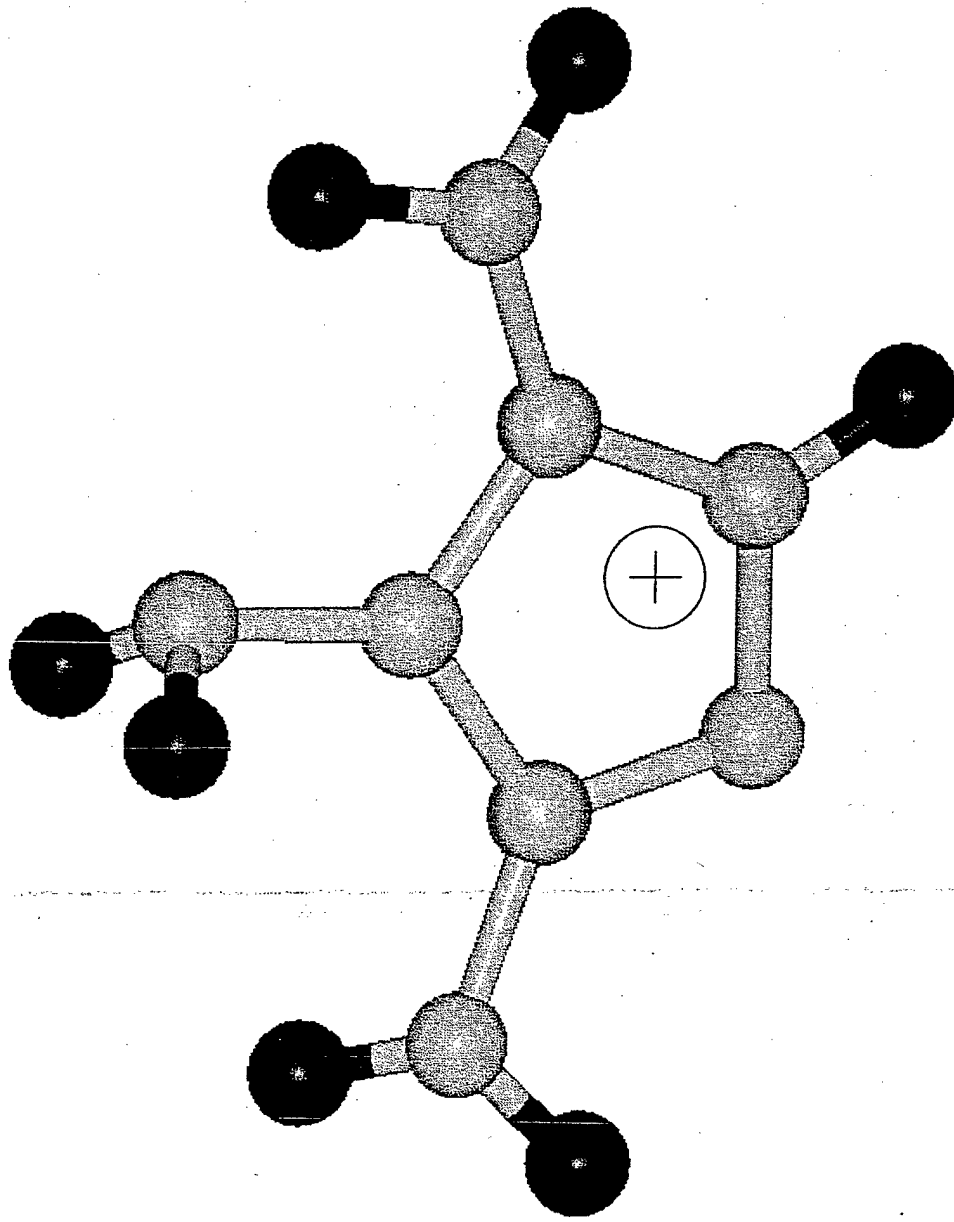
Drake, G.; Hawkins, T.; Boatz, J.; Hall, L.; Brand, A. *Prop. Expl. Pyrotech.* **2004**, to be submitted
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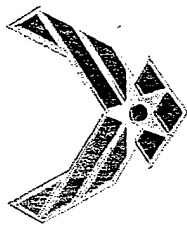
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Theoretical Calculations of protonated 3,4,5-triamino-1,2,4-triazole



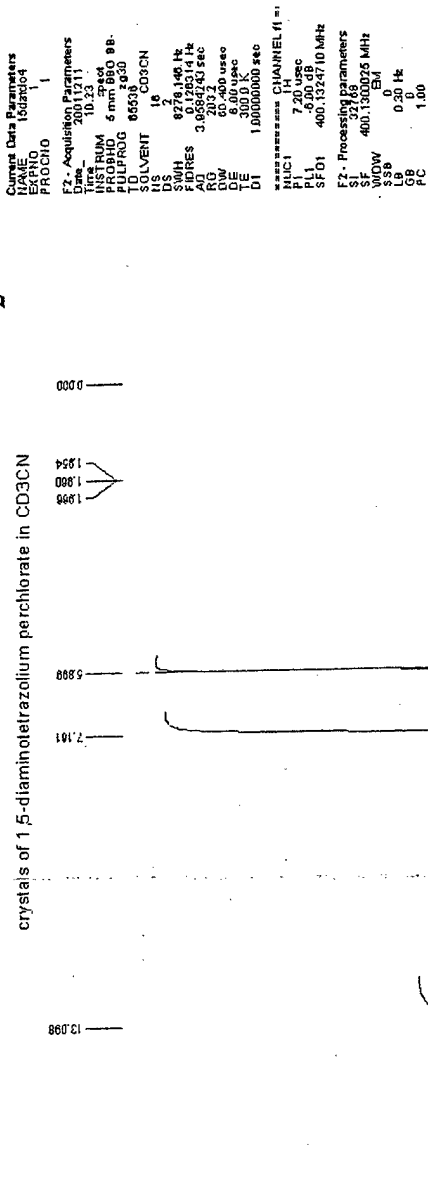
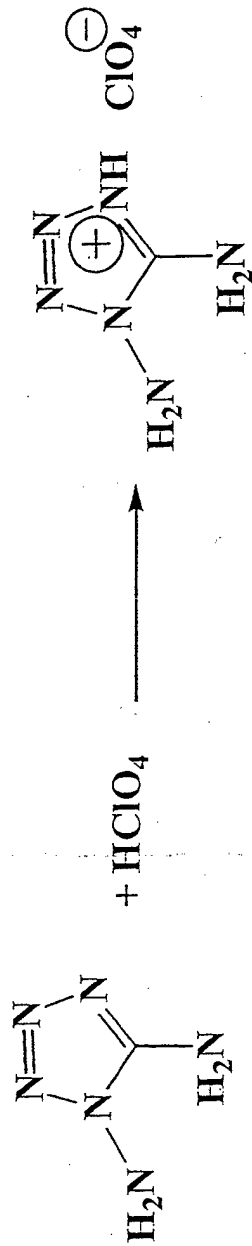
Drake, G.; Hawkins, T.; Boatz, J; Hall, L.; Brand, A. Prop. Expl. Pyrotech. **2004**, to be submitted
Distribution A. Public Release, Distribution unlimited



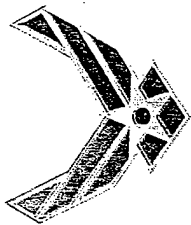
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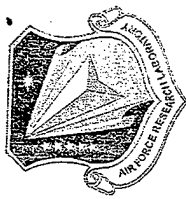
Experimental points to proton going on tetrazole ring, which disagrees from Russian findings



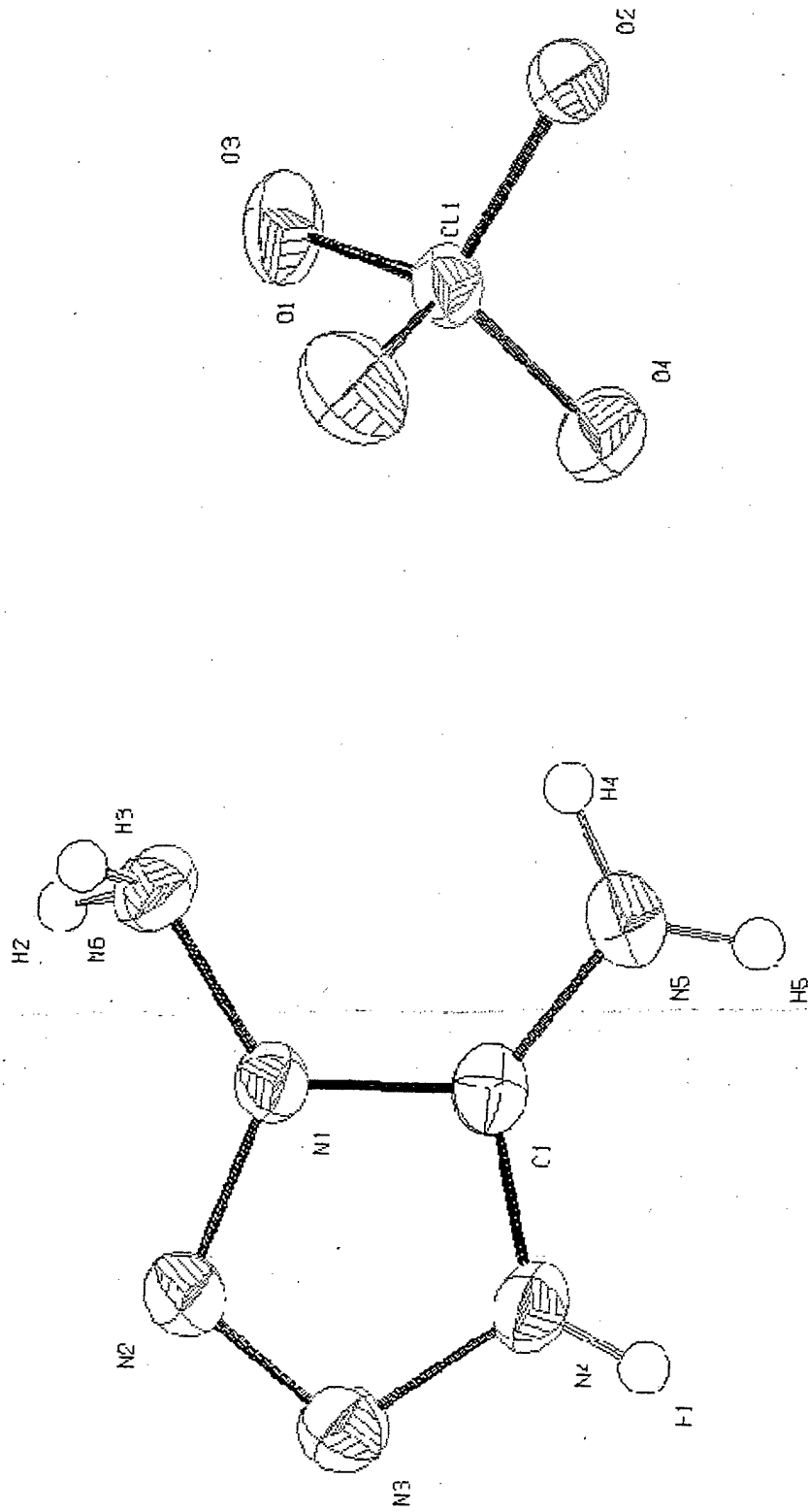
P. Gaponik; V. Karavai "Synthesis and properties of 1,5-diaminotetrazole" Khim. Geterotsikl. Soedin. 1984, 1683.
Distribution A. Public Release, Distribution unlimited



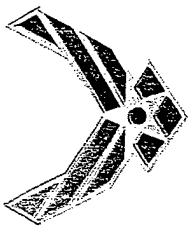
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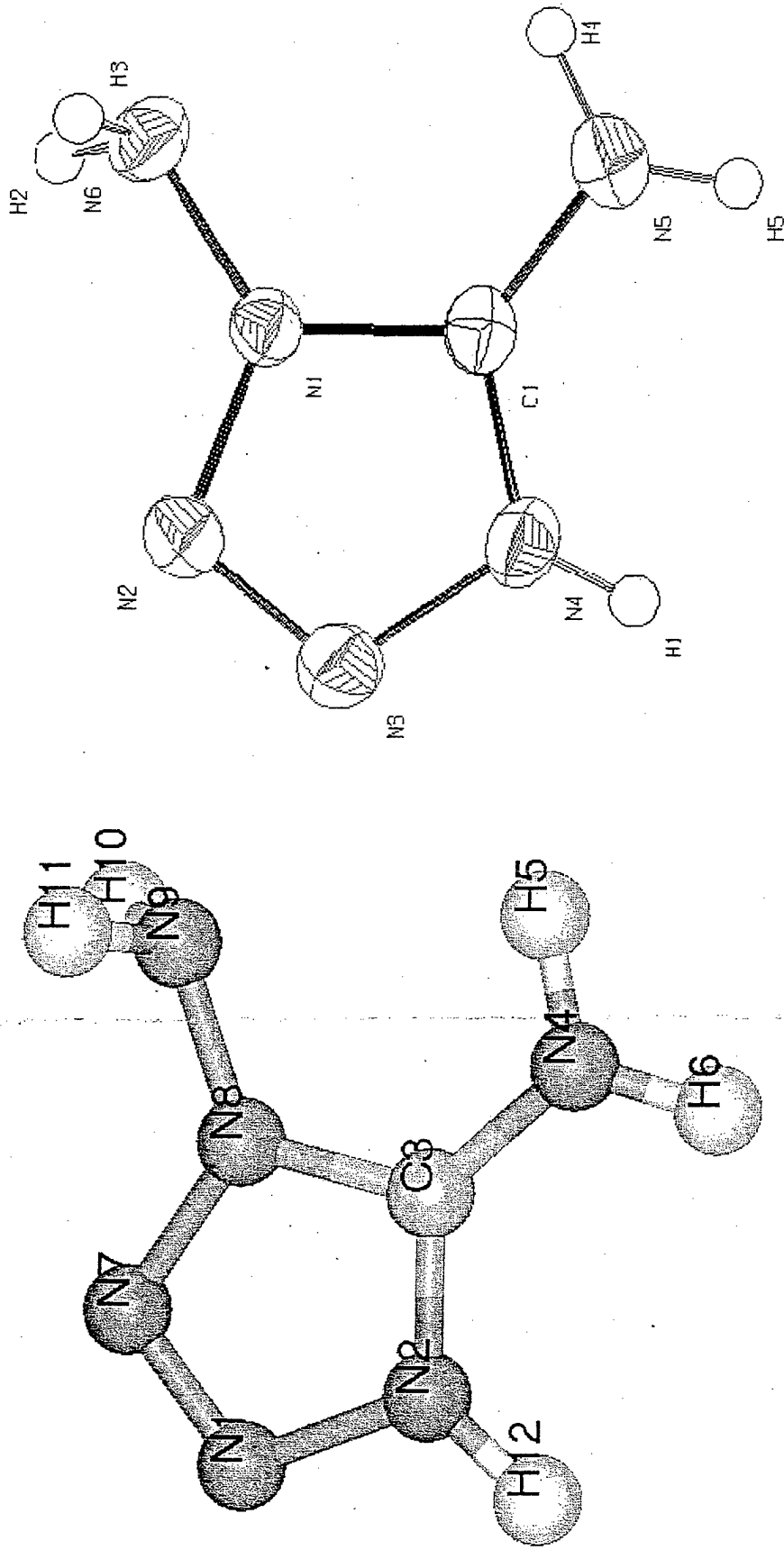
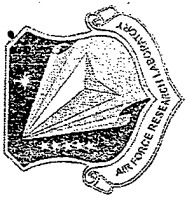
Single crystal x-ray diffraction study of 1,5-diamino-1,2,3,4-tetrazolium perchlorate



Drake, G.; Hawkins, T.; Vij, A.; Hall, L.; Boatz, J. Prop. Explos. Pyro. **2004**, Submitted
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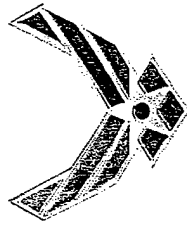


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Theory and Experimental Structures of 1,5-diamino-1,2,3,4-tetrazolium perchlorate
are in close agreement in distances and angles.

Drake, G.; Hawkins, T.; Vij, A.; Hall, L.; Boatz, J. *Prop. Explos. Pyro.* 2004, Submitted
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Summary and Conclusions

Hydrogen bonding is highly important in all systems

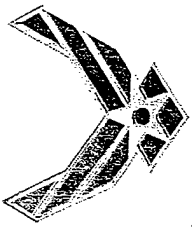
Asymmetry can dramatically affect physical properties and modest changes can have drastic effects.

N-amino heterocycles offer a rich platform for ionic liquids

New triazole and tetrazole systems have been identified as ionic liquid precursors

X-ray crystallography continues to be a powerful tool in identifying interactions in the solid state.

There are a lot of possibilities out there that await development....



AFRL Ionic Liquids

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Jeff Bottaro Mark Petrie (SRI Int.)