Update in Ionic Liquids Research

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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

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, \(-\text{O-NH}_2\), is an analogue to hydrazine linkage \(-\text{NH-NH}_2\)
- \(\text{CH}_2(\text{O-NH}_2)_2\) 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!


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1,2-bis(oxyamine)ethane

1,2-bis(oxyamine)ethane mono salts
X⁻ = NO₃⁻, ClO₄⁻, C(NO₂)₃⁻, N(NO₂)₂⁻

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

1,3-bis(oxyamine)propane mono salts
X⁻ = NO₃⁻, ClO₄⁻, C(NO₂)₃⁻, N(NO₂)₂⁻

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

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X-ray diffraction confirmed structure, lots of hydrogen bonding!

H(1) and H(8) are partial occupancy 70%/30%


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


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X-ray structure ethylene bisoxyamine dinitrate was also solved


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

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

\[ H-X \rightarrow X^- = NO_3^-, ClO_4^-, N(NO_2)_2^- \]

<table>
<thead>
<tr>
<th>Salt</th>
<th>m.p.</th>
<th>DSC onset</th>
<th>Impact (kg·cm)</th>
<th>Friction (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Serinol nitrate</td>
<td>61-66°C</td>
<td>215°C</td>
<td>180</td>
<td>18.0</td>
</tr>
<tr>
<td>Serinol perchlorate</td>
<td>55-60°C</td>
<td>250°C</td>
<td>200</td>
<td>&gt;37.8</td>
</tr>
<tr>
<td>Serinol dinitramide</td>
<td>41-44°C</td>
<td>135°C</td>
<td>16</td>
<td>23.4</td>
</tr>
</tbody>
</table>


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Single Crystal x-ray diffraction study of serinol perchlorate

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.


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

\[ \text{H-X} \quad \xrightarrow{\text{SALT}} \quad \text{x}^+ \text{X}^- \]

\[ \text{X}^- = \text{NO}_3^-, \text{ClO}_4^-, \text{N(NO}_2)_2^- \]

<table>
<thead>
<tr>
<th>SALT</th>
<th>Melting Point</th>
<th>Decomposition Onset</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dihydroxy-3-aminopropane nitrate</td>
<td>-40°C</td>
<td>220°C</td>
</tr>
<tr>
<td>1,2-dihydroxy-3-aminopropane perchlorate</td>
<td>?</td>
<td>225°C</td>
</tr>
<tr>
<td>1,2-dihydroxy-3-aminopropane dinitramide</td>
<td>-5°C</td>
<td>135°C</td>
</tr>
</tbody>
</table>


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4-amino-1,2,4-triazole

H-X

X⁻ = NO₃⁻, ClO₄⁻, N(NO₂)₂⁻

<table>
<thead>
<tr>
<th>SALT</th>
<th>Melting Point</th>
<th>Decomposition Onset</th>
<th>Impact kg/㎝³</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-amino-1,2,4-triazolium nitrate</td>
<td>69° C</td>
<td>180° C</td>
<td>&gt;200</td>
</tr>
<tr>
<td>4-amino-1,2,4-triazolium perchlorate</td>
<td>84° C</td>
<td>210° C</td>
<td>30</td>
</tr>
<tr>
<td>4-amino-1,2,4-triazolium dinitramide</td>
<td>20° C</td>
<td>145° C</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>


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

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

\[
\text{O} + 3\text{N}_2\text{H}_4 \xrightarrow{1.0 \text{ C}} \text{H}_2\text{N-N} \xrightarrow{2. \Delta, 75-80\text{C}} \text{N-NH}_2 \xrightarrow{\text{MnO}_2, \text{CH}_3\text{CN}} \text{N-NH}_2
\]


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

\[
\begin{align*}
\text{N} & \quad \text{N} & \quad \text{N} \quad \text{NH}_2 \\
\text{R} & \quad \text{N} \quad \text{X} & \quad \text{N} \quad \text{NH}_2 & \quad \text{X}^{-} \\
\end{align*}
\]

+ 3 R-X

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

Not Ionic Liquids!

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


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


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


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

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Straight-forward metathesis forms desired nitrate salts

![Chemical structures](image)

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

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

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

\[ + H-X \to \text{New Salt} + X^- \]

\[ X^- = \text{NO}_3^-, \text{ClO}_4^-, \text{N(NO}_2)_2^- \]

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

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


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


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Theoretical Calculations of protonated 3,4,5-triamino-1,2,4-triazole


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

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


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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.


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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 affects.

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....

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