High nitrogen compounds are the focus of advanced energetic material research aimed at future needs in the area of advanced explosives and propellants. One method of building nitrogen rich molecules consists of using a core heterocycle, e.g. a tetrazole, and nitrogen containing pendant groups like amines and azides. Hydrazine and its derivatives are widely used as propellants and a combination of two energetic compounds, i.e. hydrazines and tetrazoles, might provide materials with advantageous properties for energetic applications. Instead of coupling the hydrazine moiety directly to the tetrazole ring, we decided to incorporate an alkyl spacer which can help to increase thermal stability and lower the sensitivity towards impact and friction.
Synthesis and Characterization Of 5-(hydrazino-alkyl) tetrazoles

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Objectives

- Development and fielding of new energetic materials for advanced chemical propulsion in space and missile applications

- Design energy dense, ionic liquids with very fast (hypergolic) ignition response
  - Anion control hypergolic activity,
  - Cation influences ignition delay times (IDs)

Combining energetic functional groups such as hydrazines and heterocyclic rings such as tetrazoles, triazoles etc.
Combination of energetic functional groups and heterocycles

Triazolium cation

\[
\text{H}_2\text{NNH}_n\text{N}^+\text{N}H\text{NH}_2
\]

Tetrazolium cation

\[
\text{R}\text{N}^+\text{N}^\text{N}n\text{N}H\text{NH}_2
\]

Tetrazolate anion

\[
\text{N}^\text{N}n\text{N}H\text{NH}_2
\]
Reported 5-hydrazino -1H - tetrazoles


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Targeted molecules

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Synthesis of 5-(halo-alkyl)-tetrazoles

Single X-ray crystal structures of 5-(halo-alkyl)-Tetrazoles 1-3

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Synthesis of 5-(hydrazino-alkyl)-tetrazoles

\[
\begin{align*}
\text{Br} & \quad \overset{\text{N}_2\text{H}_4}{\text{MeOH}} \quad \text{NH}_2\text{NH}_2 & \quad + & \quad \text{N}_2\text{H}_5\text{Br}
\end{align*}
\]

\[n = 1 - 3\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility</th>
<th>Physical state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H(_2)O</td>
<td>CH(_3)OH</td>
</tr>
<tr>
<td>n = 1</td>
<td>soluble</td>
<td>Sparingly soluble</td>
</tr>
<tr>
<td>n = 2</td>
<td>soluble</td>
<td>soluble</td>
</tr>
<tr>
<td>n = 3</td>
<td>soluble</td>
<td>soluble</td>
</tr>
</tbody>
</table>

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Synthesis of 5-(hydrazino-propyl) tetrazole

\[
\text{N}_2\text{H}_4 > 6 \text{ eq} \quad \text{MeOH} \quad \text{N}_2\text{H}_4 \sim 3 - 4 \text{ eq} \quad \text{MeOH}
\]

\[
\begin{align*}
&\text{3} \\
\end{align*}
\]

\[
\begin{align*}
&\text{5} \\
\end{align*}
\]

\[
\begin{align*}
&\text{5} \quad \text{+} \quad \text{6} \\
&\text{2.5 : 1}
\end{align*}
\]

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$^1$H NMR spectra of 1, 5-trimethylene tetrazole (6) and 5-(hydrazino-propyl) tetrazole
DSC, Single crystal X-Ray structure and $^1$H NMR spectrum of 5-(hydrazino-propyl) tetrazole

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Difficult to separate due to poor solubility of the zwitter ions

Unprecedented in the literature
Reactions of crude 5-(hydrazino-alkyl)tetrazoles with 2-nitrobenzaldehyde

1, n = 1
2, n = 2

\[
\begin{align*}
\text{N}_2\text{H}_4 & \rightarrow \text{N}_2\text{H}_5\text{Br} \\
\text{MeOH} & \rightarrow \text{N}_2\text{H}_4\text{NH}_2 + \text{N}_2\text{H}_5\text{Br}
\end{align*}
\]

7, n = 1
8, n = 2

Distribution A: Approved for public release; distribution unlimited
Single crystal X-Ray structure and $^1$H NMR spectrum of hydrazone 7
Synthesis of 5-(hydrazino-alkyl) tetrazole via BOC hydrazine

Amino acid-BOC → Amino acid·HCl

Tetrazole-R-N₂H₂-BOC → Tetrazole-R-N₂H₂·HCl → Tetrazole-R-N₂H₂

- Address solubility issues
- Solid state structures of hydrochloride salt
- Hydrochloride salt as substrate for metathesis reaction with energetic anions e.g. [NO₃], [N₃], etc.
Synthesis of 5-(hydrazino-alkyl) tetrazole via BOC hydrazine

\[
\text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{(H}_3\text{C)}_3\text{C} \quad \text{O} \quad \text{C} \quad \text{N} \quad \text{H} \quad \text{N} \quad \text{H} \quad \text{N} \quad \text{H} \\
\text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \\
\text{O} \quad \text{C} \quad \text{C} \quad \text{H}_3\text{C}_3
\]

\[
\begin{align*}
9, & \quad n = 1 \\
10, & \quad n = 2
\end{align*}
\]

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Removal of BOC protecting group

\[
\text{HCl/MeOH} \quad \rightarrow \\
\begin{align*}
11, n &= 1 \\
12, n &= 2
\end{align*}
\]

\(^1\text{H NMR and DSC of 5-(hydrazino-methyl)tetrazole mono-hydrochloride 11}\)

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Neutralization of 5-(hydrazino-alkyl)tetrazole monohydrochlorides salts 11 and 12

\[
\text{Inseparable mixture}
\]

\[\text{NaOH / NaOMe} \quad \text{C}_3\text{H}_7\text{NH}_2 \quad \text{NaCl} \]

11, \( n = 1 \)
12, \( n = 2 \)
13, \( n = 1 \)
14, \( n = 2 \)

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DSC and $^1$H NMR spectrum of 5-(hydrazino-methyl)tetrazole

Distribution A: Approved for public release; distribution unlimited
Metathesis reaction of 5-(hydrazino-methyl)tetrazole mono-hydrochloride with silver nitrate

1H NMR and DSC of 15

Distribution A: Approved for public release; distribution unlimited
Synthesis of 5- (azido-methyl) tetrazole

\[
\begin{align*}
16, n &= 1 \\
17, n &= 2
\end{align*}
\]

1H NMR and DSC of 5-(azido-methyl) tetrazole

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DSC and $^1$H NMR spectrum of 5-(azido-ethyl) tetrazole
Reaction of 5- (chloro-methyl) tetrazole with mono-methyl hydrazine (MMH)

\[
\text{CH}_3\text{NNHNH}_2 > 6 \text{ eq} \rightarrow \begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N}
\end{array}
\text{Cl} \\
\text{CH}_3
\]

\[
\text{CH}_3\text{NNHNH}_2 \sim 3 \text{ eq} \rightarrow \begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N}
\end{array}
\text{CH}_3\text{-NNH}_2\text{NNH}_2\text{Cl} \\
\text{CH}_3
\]

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Successfully synthesized several 5-(hydrazino alkyl) tetrazole

Fairly stable, $T_d > 150$, and difficult to work with due poor solubility

Bicyclic tetrazole derivative formed via intramolecular cyclization

Generated energetic nitrate salt and tetrazole-alkyl azides from reaction intermediates

Reaction of MMH with 5-chloromethyl tetrazole also leads to di-alkylated derivative depending on concentration of MMH
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