CHEMISTRY OF DIFLUORAMINE DERIVATIVES

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<td>Chemistry of Difluoramine Derivatives</td>
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<th>5f. WORK UNIT NUMBER</th>
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14. ABSTRACT

15. SUBJECT TERMS

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## Calculated Performance Characteristics

<table>
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<tr>
<th>Compound</th>
<th>Density(^1) (\rho (\text{g} \cdot \text{cm}^{-3})) (HMX = 1.894)</th>
<th>Detonation pressure(^2) (P_{ CJ} \text{(KBar)}) (HMX = 390)</th>
<th>Specific impulse(^3) (I_{sp} \text{(sec)}) (HMX = 265)</th>
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<tr>
<td>(\text{NN} \text{O}_2 \text{O}_2 \text{N})</td>
<td>1.999</td>
<td>474</td>
<td>285</td>
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<tr>
<td>(\text{NF}_2 \text{F}_2)</td>
<td>1.973</td>
<td>444</td>
<td>274</td>
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<tr>
<td>(\text{F}_2 \text{N}_2 \text{F}_2)</td>
<td>1.949</td>
<td>443</td>
<td>291</td>
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</table>

1. Ammon, H.L. (University of Maryland, College Park), personal communication.
2. Adolph, H.G.; Koppes, W.M.; Lawrence, G.W. (Naval Surface Warfare Center, Silver Spring, MD), personal communications.
3. Baroody, E. (Naval Ordnance Station, Indian Head, MD), personal communication.
The Best Demonstrated Route to HNFX

Chapman, Kreutzberger & Welker / TPL, Inc.
Complications in Nitrolysis

Welker / TPL, Inc.
The Proof

• X-ray analysis (Richard Gilardi, NRL) of a minor impurity crystal in HNFX

Interestingly, \( \rho = 1.863 \)
Polymorphism in HNFX

- Original crystal preparation (needles) had solvent channels $\rightarrow \rho = 1.784$ (theor. $\rho = 1.999$)

- New recrystallization from CHCl$_3$ gives m.p. 216–218 °C without solvent (old m.p. 202~203 °C), but same polymorph!

- New recrystallizations from acetone give new morphologies: prisms and plates rather than needles
Typical HNFX Needles

~80×
New HNFX Crystal Habits

- Unit cells measured by Prof. Alan Pinkerton by CCD detector
- But...all crystals are the same polymorph!
- Can you believe it?
HNFX Properties

• M.P. 216–218 °C(dec)

• Readily forms solvent adducts as HMX does

• “Solvent-channel” form (“α-HNFX”) ρ 1.784

• Comparison of solvent adduct densities:

\[
\begin{align*}
\alpha\text{-HMX} & : \rho = 1.838 \quad HNFX\cdot\text{solvent} & : \rho = 1.784 \\
HMX\cdot\text{DMF} & : \rho = 1.607 & \Delta\rho \approx 0.25 \\
HMX\cdot\text{NMP} & : \rho = 1.570 & \Delta\rho \approx 0.25 \\
\end{align*}
\]

• Impact sensitivity of “α-HNFX” comparable to PETN
Difluorosulfamic Acid (DFSA): A Recent History

\[
\begin{align*}
\text{BrNO}_2 & \quad \text{HNF}_2 \quad \text{SO}_3 \quad \text{H}_2\text{SO}_4 \\
& \quad \rightarrow \quad \text{decomposition} \\
& \quad \text{products} \\
& \quad \text{(CH}_2\text{Cl}_2 \text{ layer)} \quad \text{+} \quad \text{H}_2\text{O \ layer} \\
\end{align*}
\]

- Chapman, Fluorochem, Jan. 1990

\[
\begin{align*}
\text{NHSO}_3\text{H} & \quad \text{F}_2 \quad \text{H}_2\text{O} \\
& \quad \rightarrow \quad \text{19F} \quad \delta \quad 36.8 \\
& \quad \text{(H}_2\text{O \ layer)} \\
\end{align*}
\]

- Archibald, Fluorochem, Jan. 1990

⇒ “Could this be aqueous F\textsubscript{2}NSO\textsubscript{3}H?”
Sodium Difluorosulfaminate

- But dilute aqueous $\text{F}_2\text{NSO}_3^{-}\text{Na}^+$ is stable for weeks at pH 7–8
Acknowledgments

Funding

- Office of Naval Research (Dr. Richard Miller)