

REPORT DOCUMENTATION PAGE

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MEMORANDUM FOR PRS (In-House Publication)

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31 Mar 2003

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2003-076**
Karl Christe (AFRL/PRSP (ERC)); Ralf Haiges, Stefan Schneider, Thorsten Schroer (Loker
Hydrocarbon Research Institute); Ashwani Vij, Vandana Vij, and William W. Wilson (AFRL/PRSP
(ERC)), "New Polynitrogen Compounds"

Boatz
5364

Christe
5194

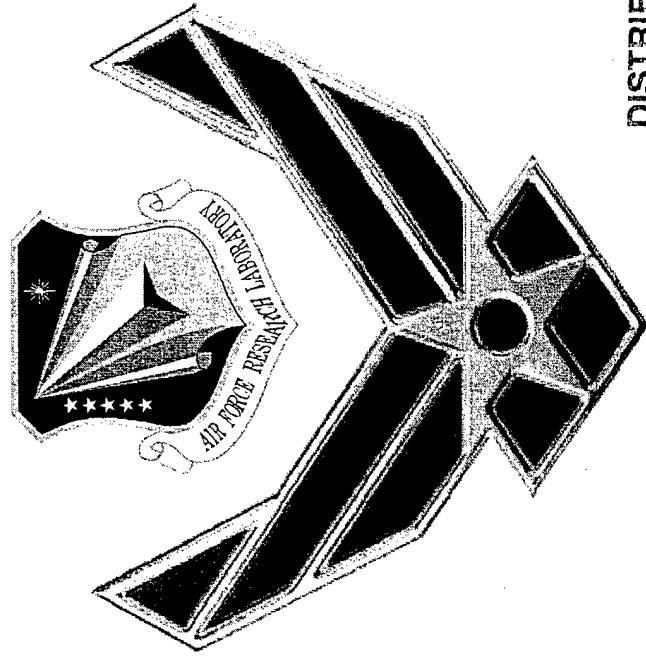
AFOSR Molecular Dynamics Contractors Conference
(San Diego, CA, 18-20 May 2003) (Deadline: 18 May 2003)

(Statement A)

Towards New Polynitrogen Species: The Search for Viable Precursors

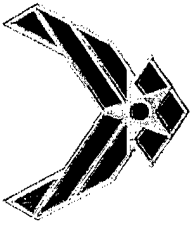
**AFSR Molecular Dynamics Contractors
Conference**

May 18-20, 2003

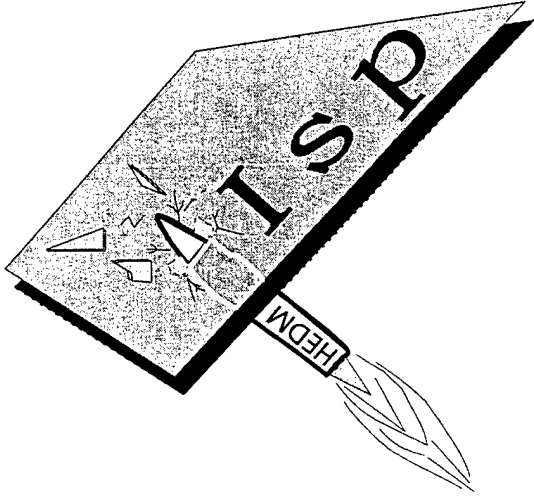


Dr. Jerry A. Boatz
Senior Research Chemist
Propellants Branch
Air Force Research Laboratory
jerry.boatz@edwards.af.mil
(661) 275-5364

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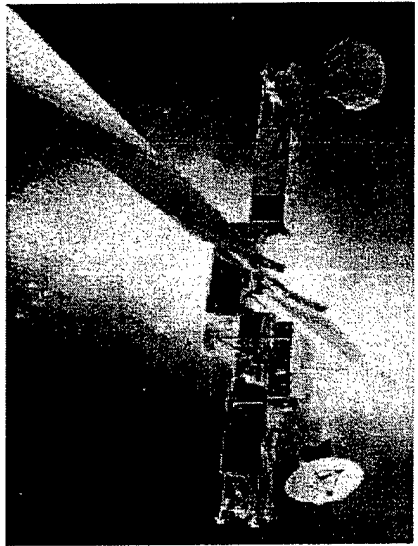
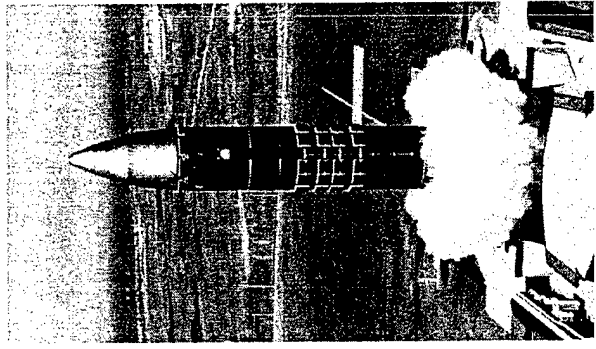
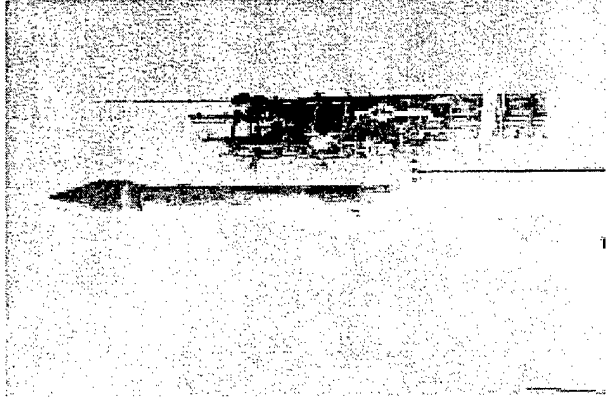
HEDM Program Objective

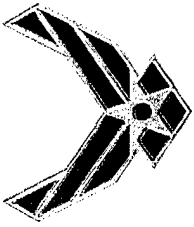


*Breaking the
performance barrier*

Identify and develop advanced chemical propellants for rocket propulsion applications

- Hydrocarbons for liquid boosters
- Liquid & solid oxidizers for boost and upper stages
- Monopropellants for upper stages and satellites





Current State of the Art



Monopropellants

| | Isp (sec) | Density (g/cm ³) |
|--|-----------|------------------------------|
| Hydrazine (N ₂ H ₄) | 200 | 1.01 |
| Hydrogen Peroxide (H ₂ O ₂) | 175 | 1.41 |

Solids

Ammonium Perchlorate (AP)

260

1.69

~20%Al/~10% polymer binder

Liquids

N₂O₄/Hydrazine

280

1.45/1.01

RP-1/Liquid Oxygen (LOX)

300

0.81/1.15

Cryogenic

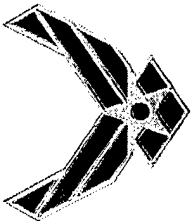
Liquid Hydrogen (LH₂)/LOX

390

0.07/1.15

I_{sp} at sea level 1000 psi chamber pressure

Isp = (pounds of thrust/pounds of propellant/second)



HEDM Propellant Payoffs



“The highest leverage technology area impacting launch vehicles is the development of high-energy-density materials for use as propellants.”

-- New World Vistas Panel on Space Technology (1995)

| Vehicle Type | Baseline Vehicle | Propellant | Takeoff Mass (lb) | Payload Mass (lb) | Payload Mass (lb) With 10% Isp Increase |
|-----------------------------|--------------------------|---|-------------------|-------------------|---|
| Two-stage ELV | Atlas II // Centaur D-1A | RP-1/LOX (Isp = 295 s) // LH2/LOX (Isp = 455 s) | 360,000 | 12,500 | 15,600 (+25%) |
| SSTO RLV | Lockheed SSTO | LH2/LOX (Isp = 455 s) | 1,900,000 | 40,000 | 68,000 (+70%) |
| Missile Defense Interceptor | Boost-Phase Interceptor | HTPB/Al/HMX (Isp = 270 s) | 1,847 | 74 | 110 (+49%) |

Our research is aimed at increasing propellant Isp by 5 to 50%



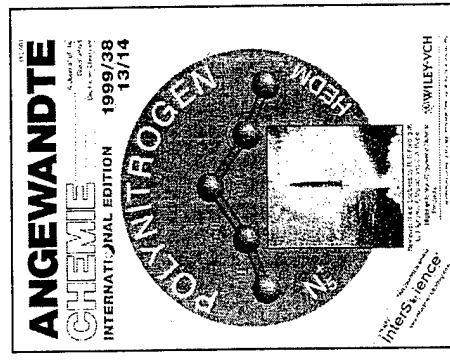
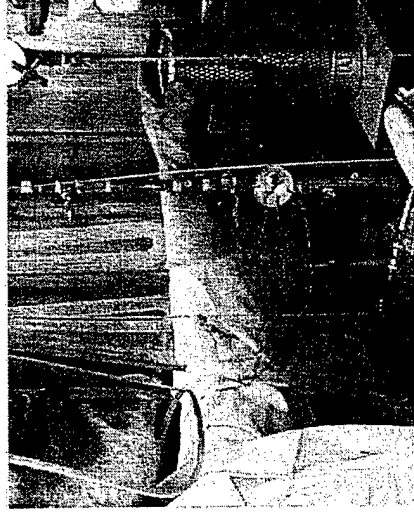
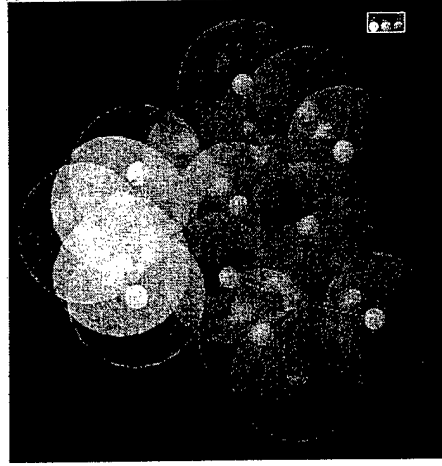
Polynitrogen Project



Discover, synthesize, characterize, and scale-up novel, highly energetic polynitrogen allotropes

Modeling and simulation guides the experimental program:

- ◆ Determines which molecules should exist and how energetic they are
- ◆ Gives information on how to synthesize promising molecules
- ◆ Provides critical data for identification and characterization of new molecules

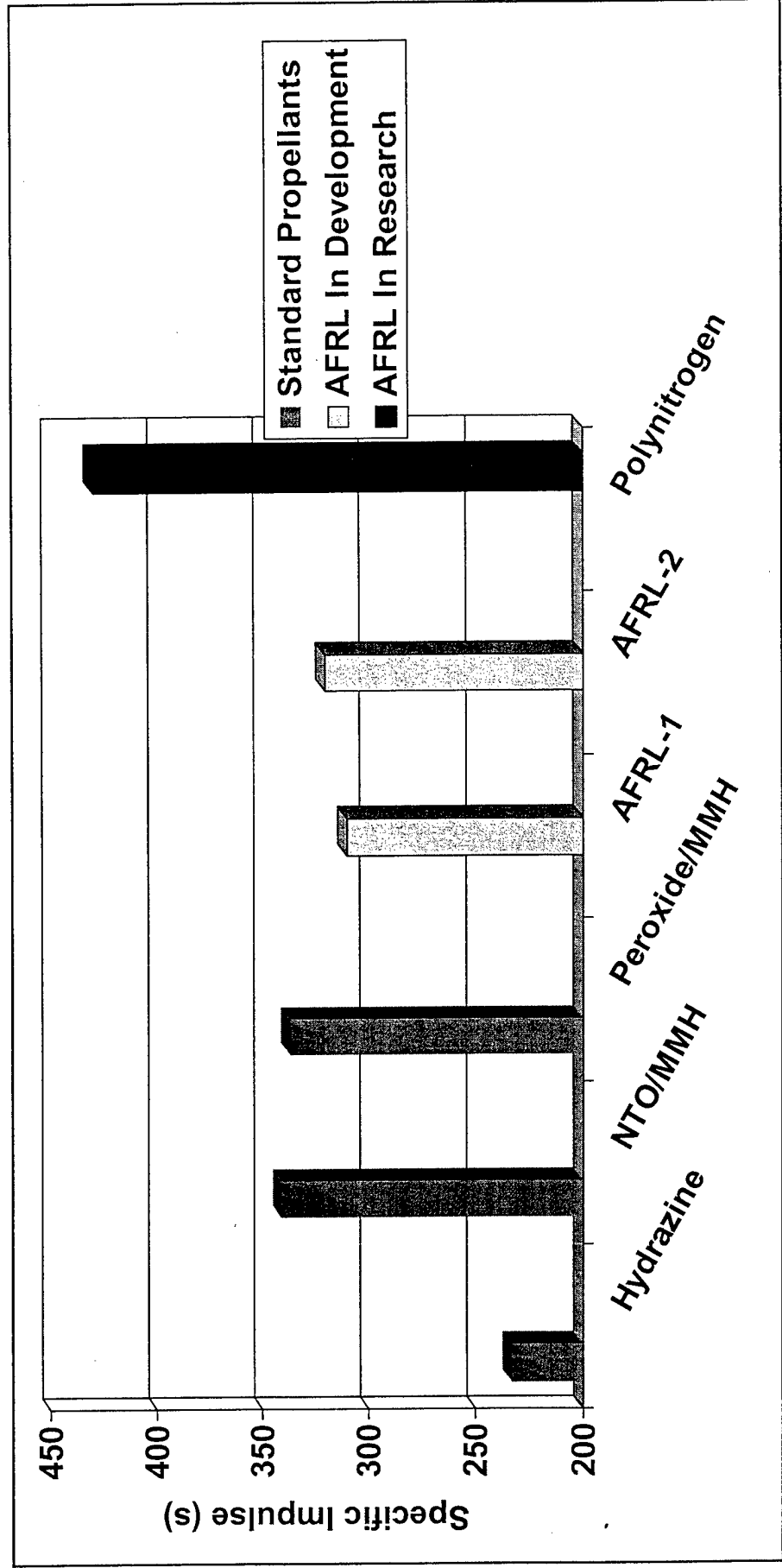


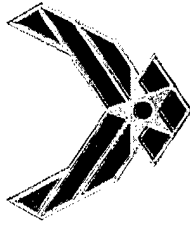


Performance of Polynitrogen Monopropellants



The performance of polynitrogens as monopropellants would dwarf that of hydrazine, and would greatly exceed even bipropellants

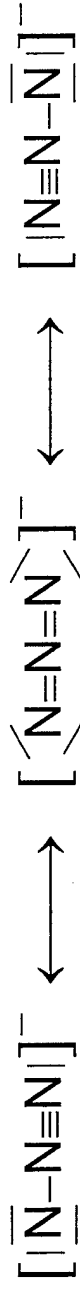




The Search for New Polynitrogens



- All polynitrogens are unstable with respect to N_2 molecules
- Their activation energy for N_2 elimination is largely determined by the weakest bond in the compound
- Their metastability is enhanced if suitable resonance structures exist:



- The double-bond character of the $\text{N}=\overline{\text{N}}$ bonds in the azide anion explains its exceptional stability
- How can this stabilization effect be used to our advantage in preparing new compounds?

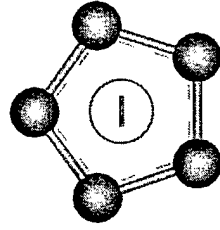


Pentazolate (N_5^-)?

- Substituted pentazoles $R-N_5$ have been known for decades ($R=aryl$)
- Cyclic N_5^- is aromatic
- Conversion of the diazonium salt, RN_2^+ , to the substituted pentazole ring $R-N_5$ by the reaction with azide ion, N_3^- , has been demonstrated many years ago by Ugi and Huisgen.
- N_5^- has been recently detected in the gas phase for the first time, using collisional fragmentation (electrospray ion mass spectroscopy).
- Can a chemical route to N_5^- be found? (e.g., can a suitable R group be found for the reaction $R-N_2^+ + N_3^- \rightarrow R-N_5 \rightarrow R^+ + N_5^-$?)

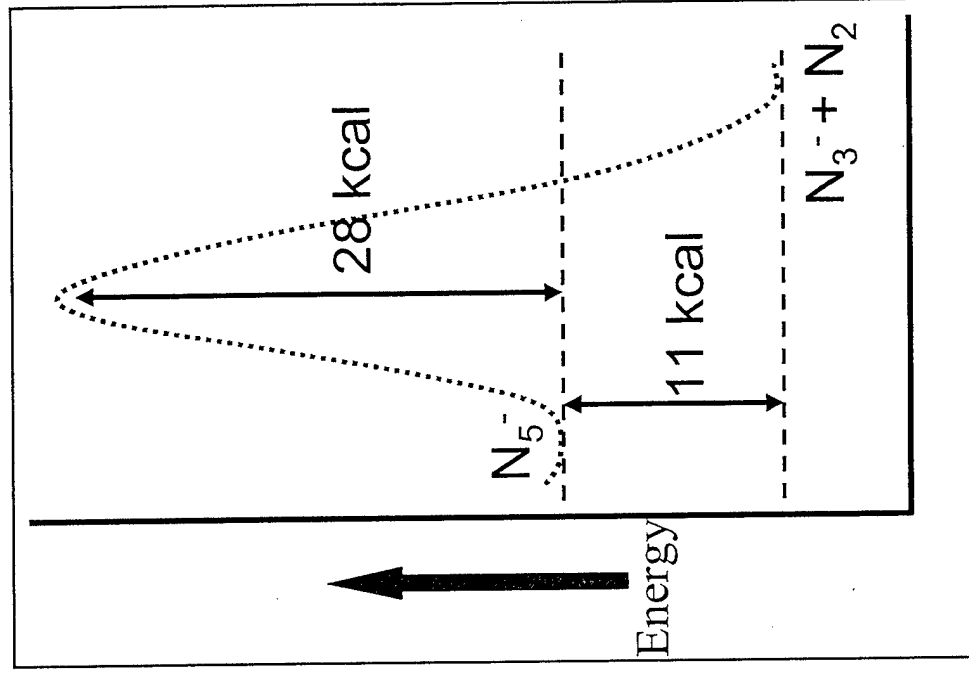


New Polynitrogen Anions



Pentazole anion (N_5^-)

- Theoretical calculations show that this anion has a 28 kcal/mole activation energy barrier for decomposition and its decomposition to N_3^- and N_2 is only 11 kcal/mol exothermic
- Aryl substituted pentazoles can be isolated as stable compounds only if stored at low temperatures. In methanol, these compounds rapidly decompose at room temperature to form aryl azides and N_2 gas

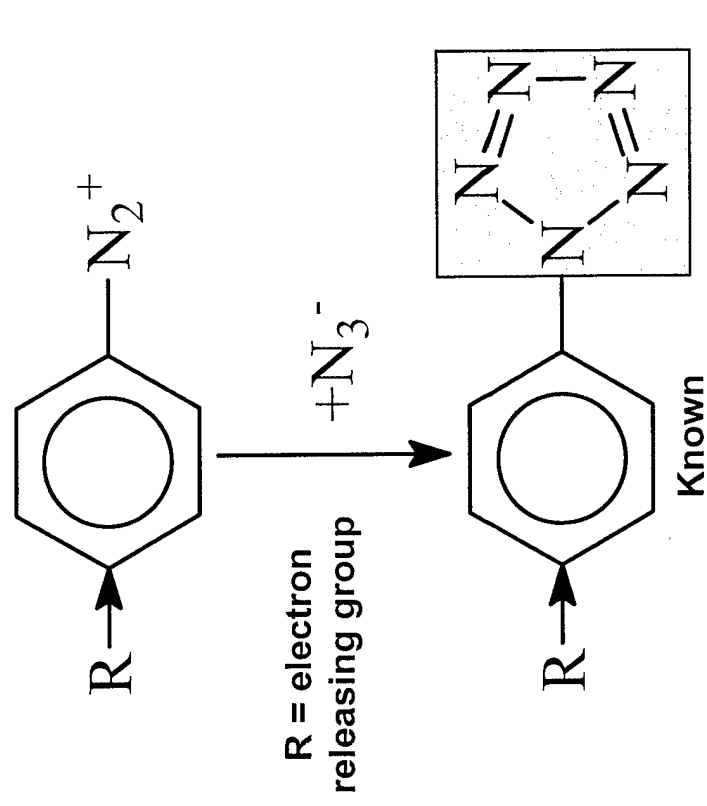
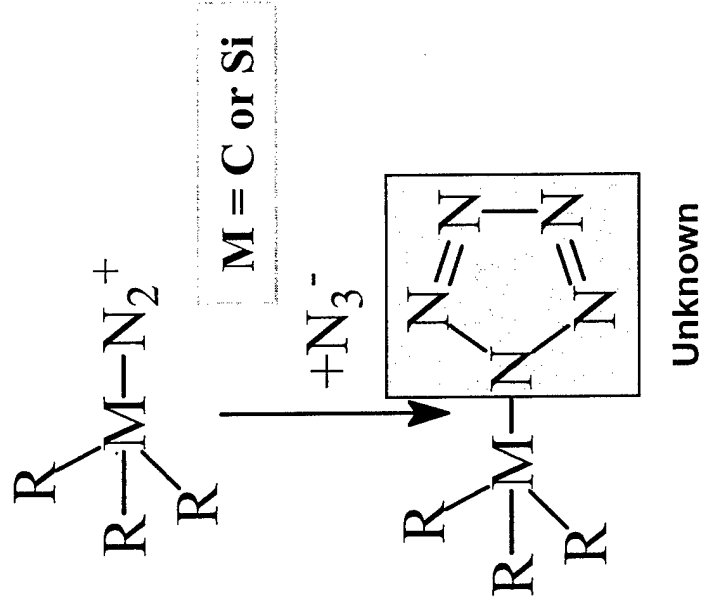


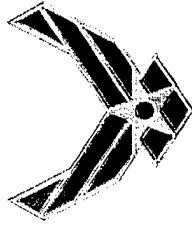


Synthetic Challenge – How do we make These New Anions??

Synthesis of Substituted Pentazoles

Sources for the Pentazole Anion (N_5^-)





Theoretical Challenge - Can we design and predict viable precursors to N_5^- ?



Find a substituent R so that

1. $R-N_2^+$ is stable wrt $R^+ + N_2$.
2. The R-N bond in $R-N_5$ is weak, thereby suitable for the reaction $R-N_5 + M^+X^- \rightarrow M^+N_5^- + R-X$

Approach

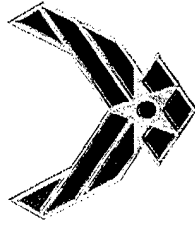
Use quantum chemical calculations to predict the stability of $R-N_2^+$ diazonium salts and the length/strength of the R- N_5 bond.

MBPT(2)/6-31G(d) level of theory

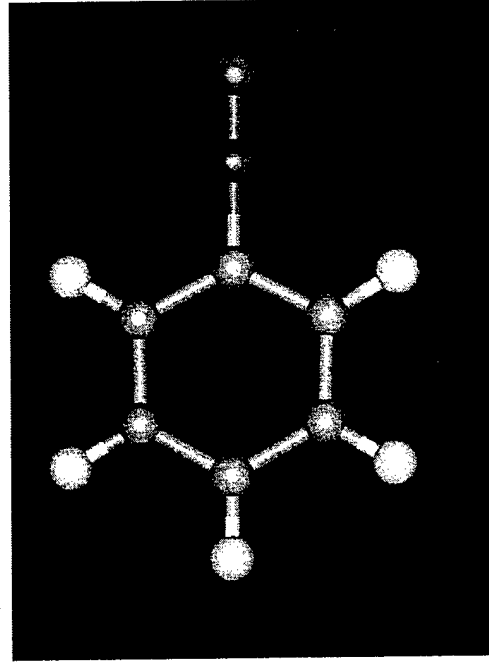


M = C, Si

L = F, Cl, CH_3 , CF_3 , NO_2 , phenyl, etc.

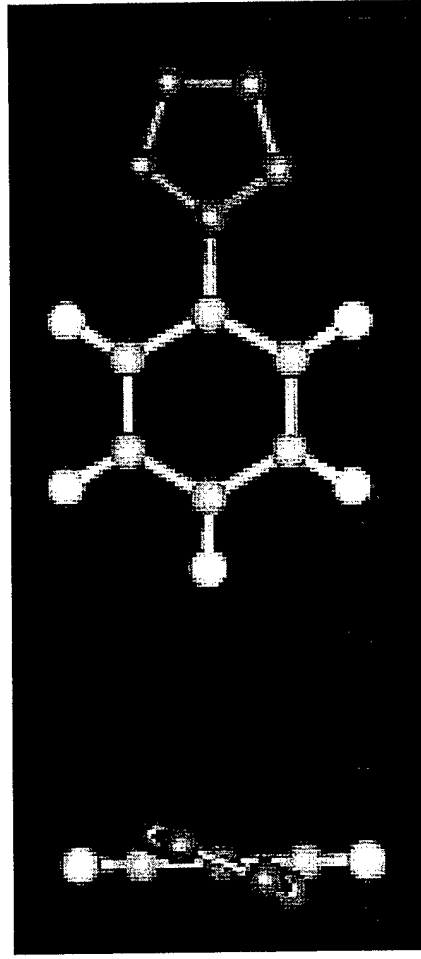


Phenyldiazonium -- too stable!



$$R(\text{C-N}_2^+) = 1.39 \text{ \AA}$$

$$D_e = 37.9 \text{ kcal/mol}$$

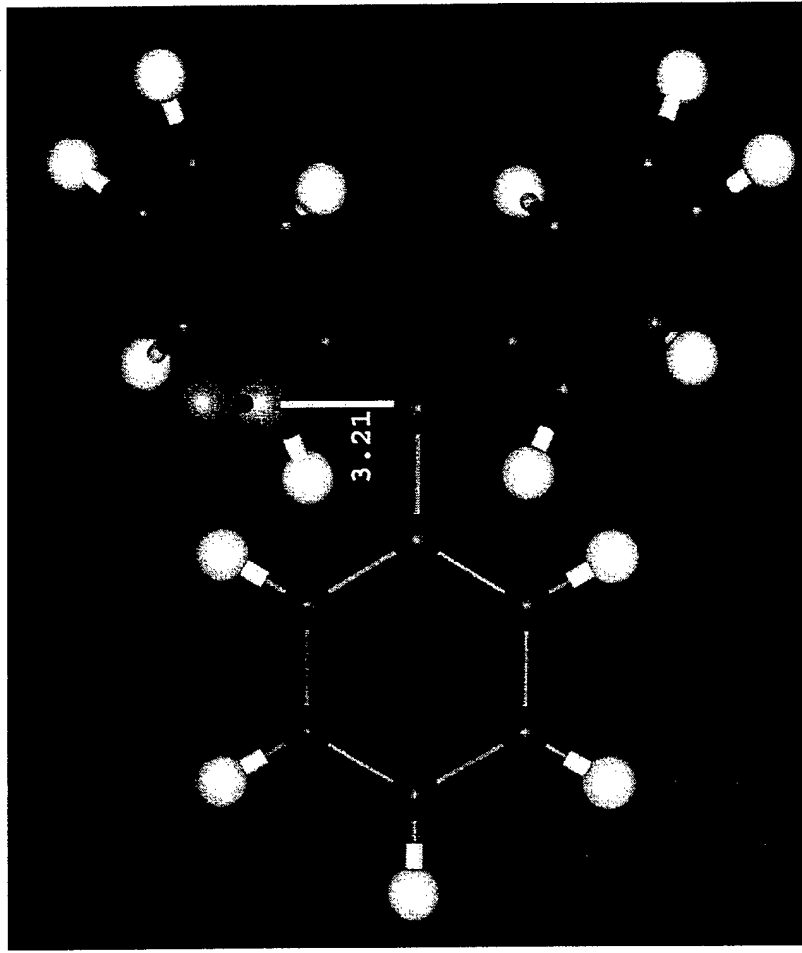
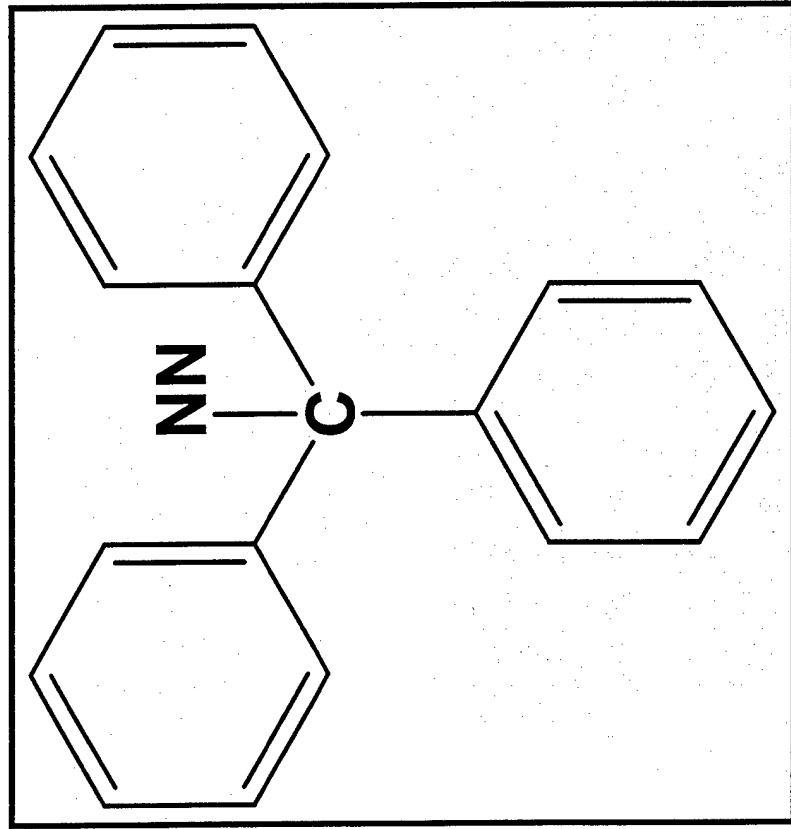


$$R(\text{C-N}_5) = 1.43 \text{ \AA}$$

Try replacing Ph+ with a more stable cation (Ph_3C^+)...



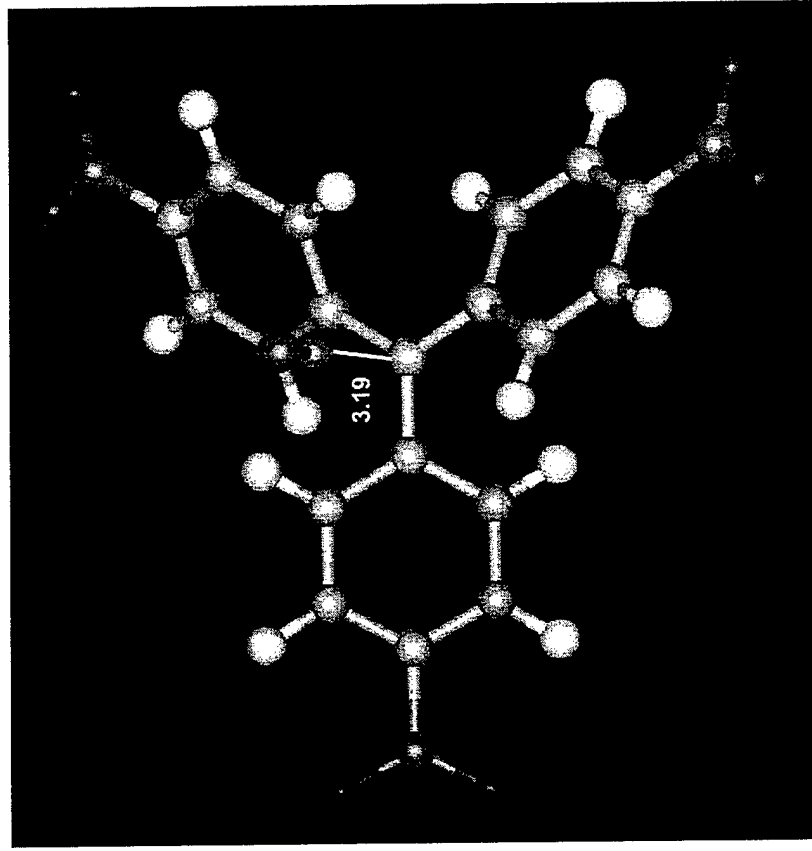
Trityldiazonium -- unstable!



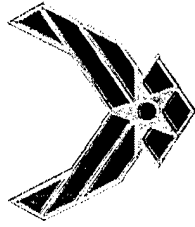
Trityl cation Ph_3C^+ is too stable -- can it be destabilized by placing e-withdrawing groups on the phenyl rings (e.g. NO_2)?



tris(para-nitrophenyl) methyldiazoniumium

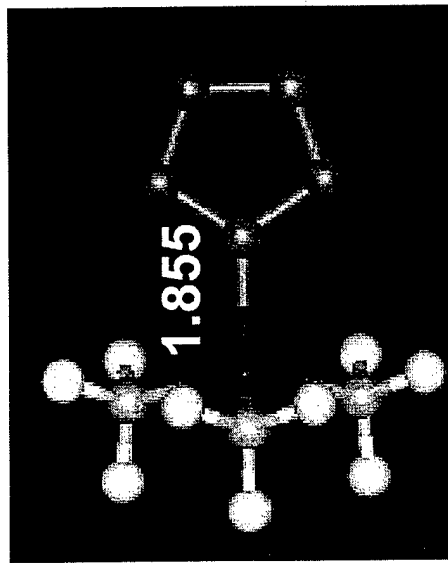
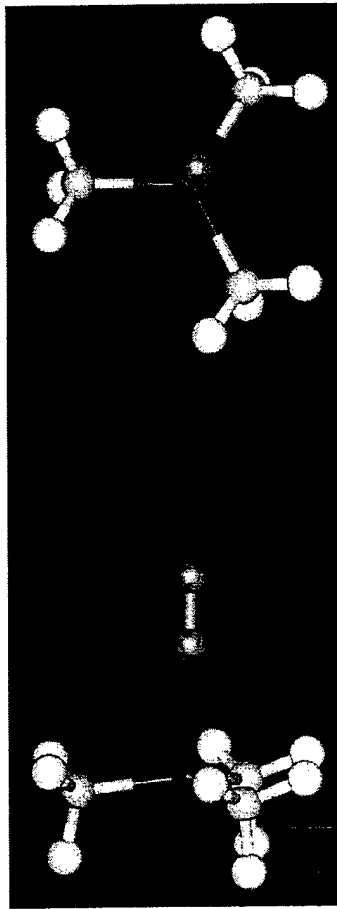
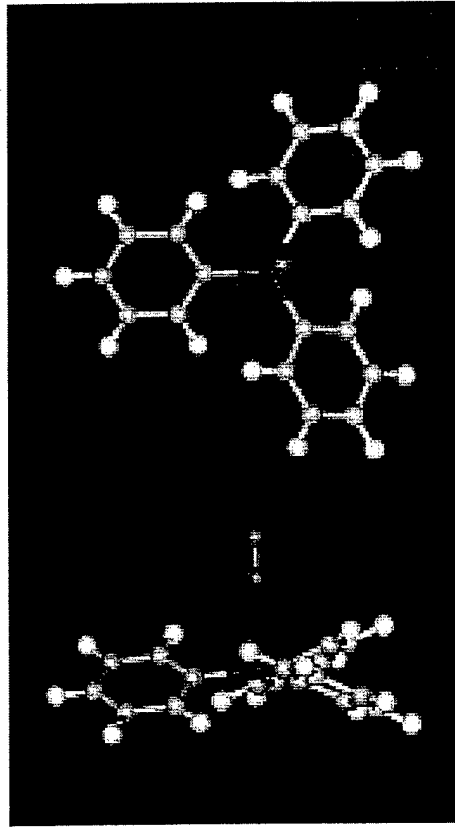


| R_3 | $R_3C-N_2^+$ distance(Å) | $D_e(C-N_2^+)$ (kcal/mol) |
|-------------------------|--------------------------|---------------------------|
| 3Ph | > 3.0 | -3.0 |
| 3(pNO ₂ -Ph) | > 3.0 | -3.4 |

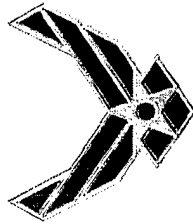


What about some silicon analogues?

| R_3 | $R_3Si-N_2^+$ distance(Å) | $D_e(Si-N_2^+)$ (kcal/mol) |
|-------|---------------------------|----------------------------|
| 3Ph | > 2.5 | -6.0 |
| 3Me | 2.151 | -13.8 |



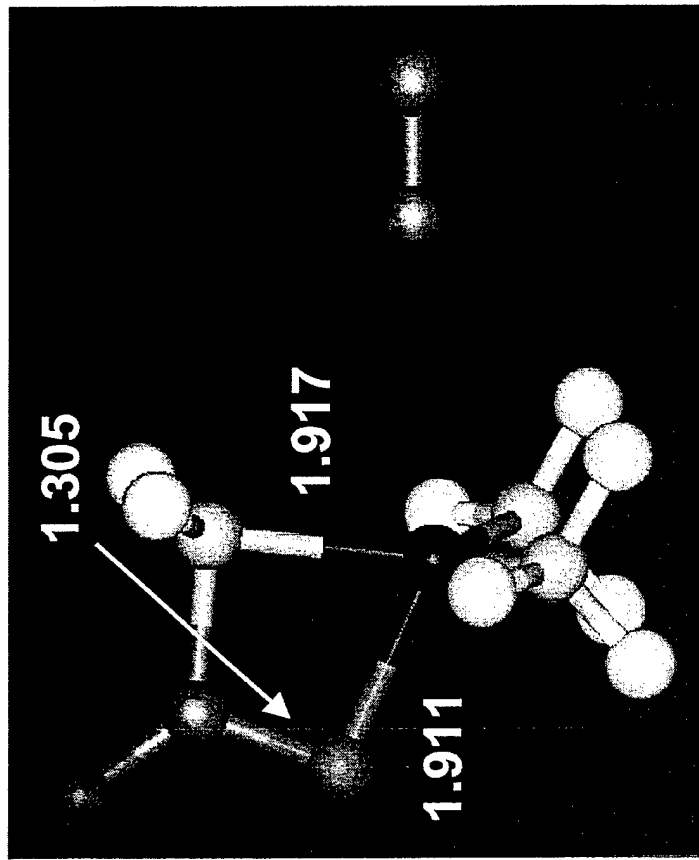
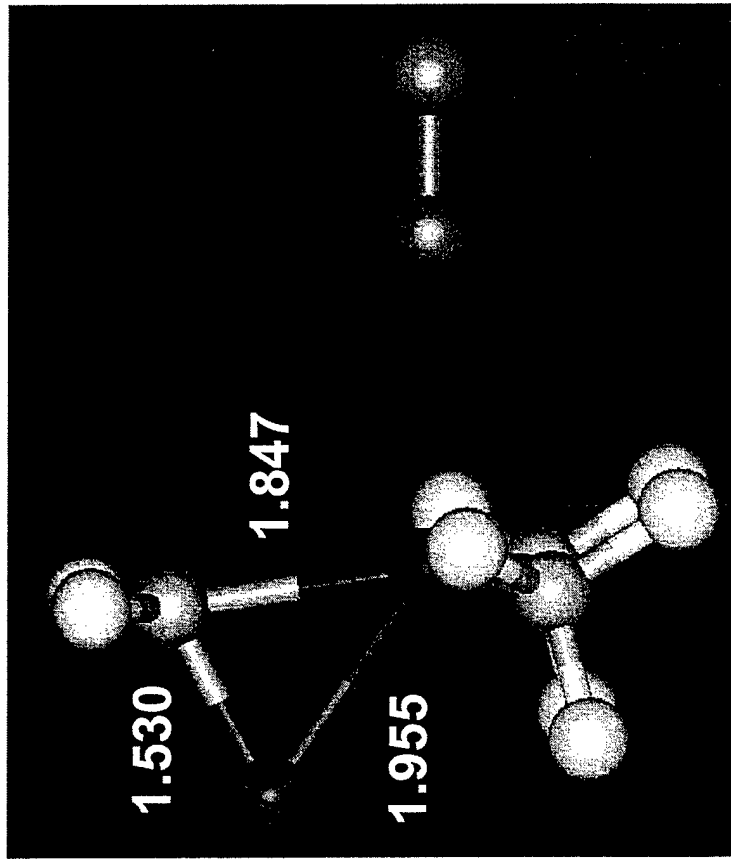
Trimethylsilyl cation looks promising --
can it be "fine-tuned" to give a slightly
more stable Si-N bond?

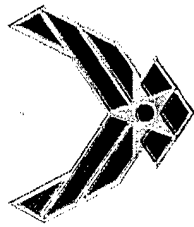


Derivatives of trimethylsilyldiazonium



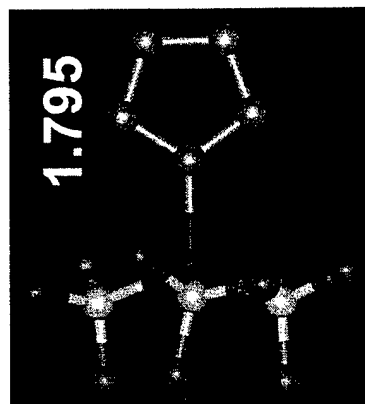
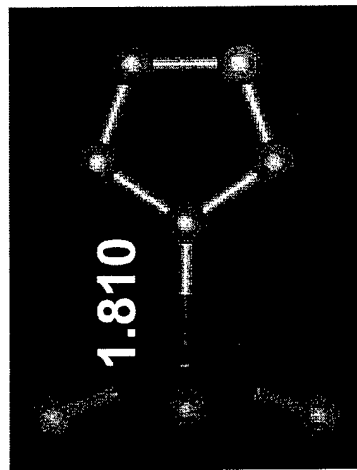
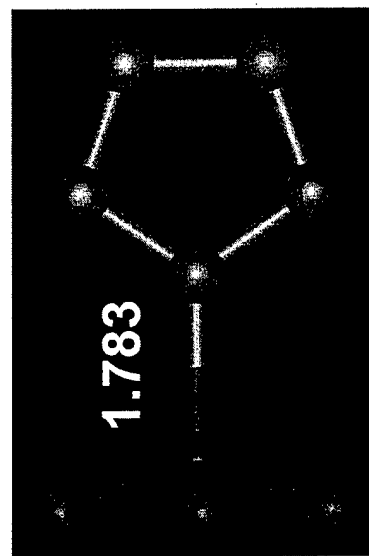
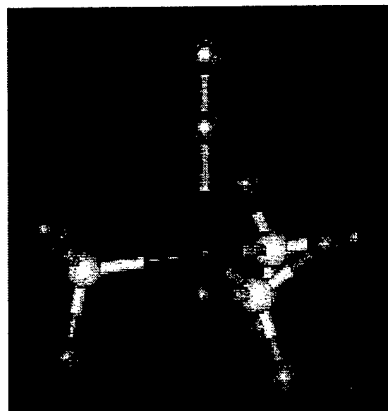
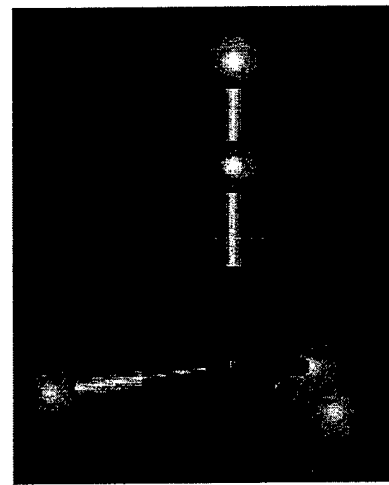
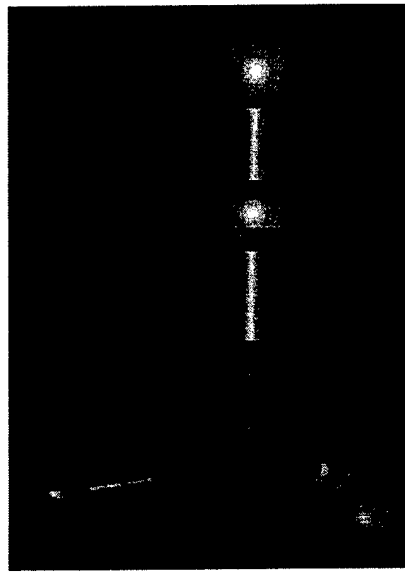
| R_3 | $R_3Si-N_2^+$ distance(Å) | $D_e(Si-N_2^+)$ (kcal/mol) |
|--------------------------------------|---------------------------|----------------------------|
| 2Me, FCH ₂ | 2.410 | -7.4 |
| 2Me, NO ₂ CH ₂ | > 2.5 | -5.2 |

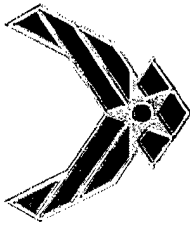




Silicon analogues, continued

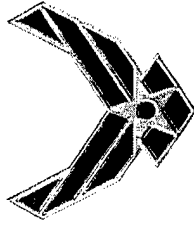
| R_3 | $R_3Si-N_2^+$ distance(Å) | $D_e(Si-N_2^+)$ (kcal/mol) |
|------------------|---------------------------|----------------------------|
| 3F | 1.973 | -33.4 |
| 3Cl | 2.125 | -14.5 |
| 3CF ₃ | 1.994 | n/a |





Conclusions

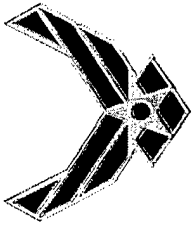
- Trityldiazonium ($\text{Ph}_3\text{C-N}_2^+$) and its tris(para- NO_2) analogue are predicted to be unstable wrt dissociation of N_2
- $\text{Ph}_3\text{Si-N}_2^+$ is also predicted to be unstable wrt dissociation of N_2
- $\text{Me}_3\text{Si-N}_2^+$ and $\text{Cl}_3\text{Si-N}_2^+$ are marginally stable ($D_e \sim 14$ kcal/mol; $R(\text{Si-N}) \sim 2.1$ Å)
- Of the silyl derivatives considered, $\text{F}_3\text{Si-N}_2^+$ is the most stable ($D_e = 33.4$ kcal/mol; $R(\text{Si-N}_2^+) = 1.97$ Å)
- Secondary (i.e., not directly bonded to Si) electronegative groups such as F and NO_2 interact strongly with Si in silyldiazonium cations, leading to displacement of N_2



Future/ongoing work



- Calculation of the structures and stabilities of $\text{Me}_x\text{F}_y\text{Cl}_z\text{Si-N}_2^+$ and $\text{Me}_x\text{F}_y\text{Cl}_z\text{Si-N}_5$
- Calculation of the reaction enthalpies $\text{R-N}_5 + \text{M}^+\text{X}^- \rightarrow \text{M}^+\text{N}_5^- + \text{R-X}$
- Other high-nitrogen/polynitrogen species (e.g. $\text{Fe}(\text{N}_5)_2$)



Acknowledgements



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DoD HPC Modernization Program

New Materials Design Challenge Project

Aeronautical System Center

AFFTC Distributed Center

Army HPC Research Center

Common HPC Software Support Initiative

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