ENERGETIC MATERIALS PROGRAMS AT USC

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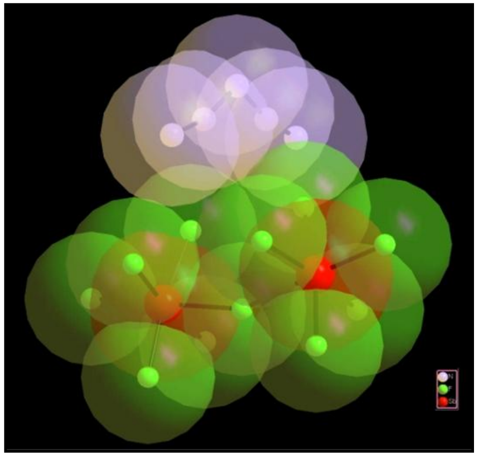
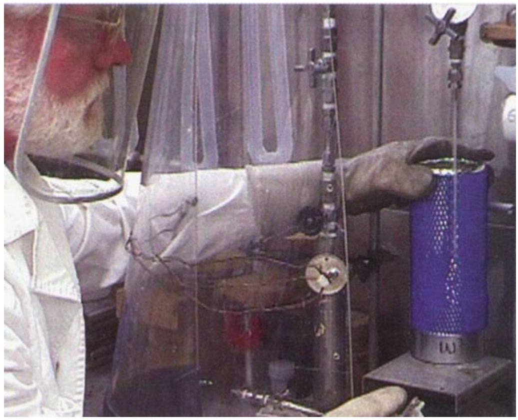
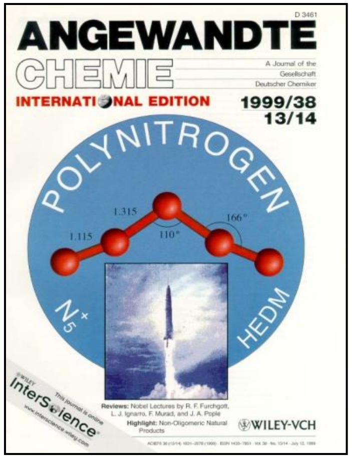
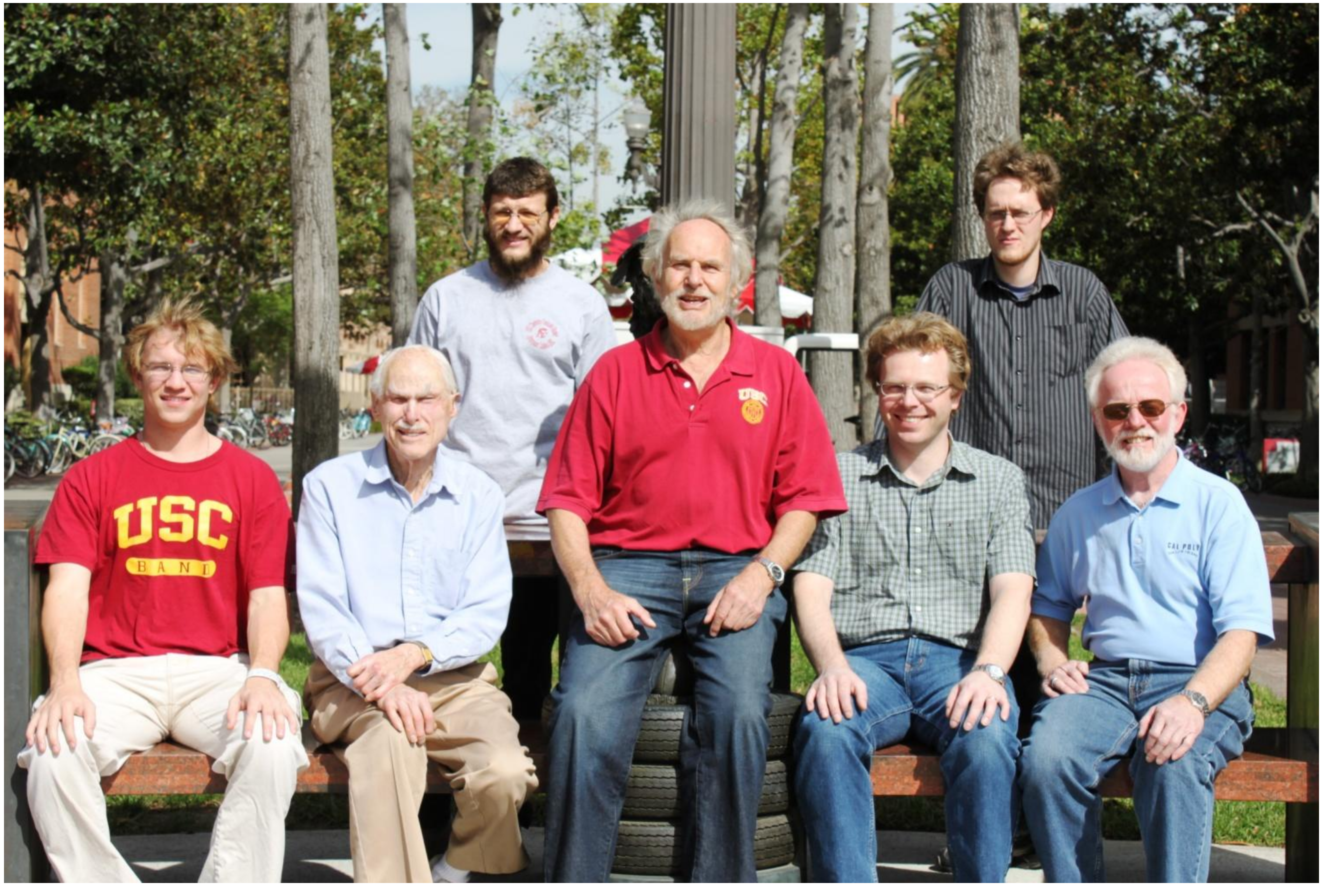






Coworkers and Sponsors



Office of Naval Research

AF Office of Scientific Research

Defense Threat Reduction Agency, Tenth Anniversary, United States of America, 1998 - 2008

NSF

Outline

- High-Oxygen Carriers as Green Replacements for AP and Hydrazine (ONR)
- Polyazide Chemistry (NSF)
- Polynitrogen Chemistry (AFOSR/DARPA)
- Dense High-Energy Materials for Agent Defeat (DTRA)

ONR Programs and Why Are We Interested in High-Oxygen Carriers?

- Compounds currently used for solids and their drawbacks:
  - NH_4ClO_4, (Ammonium Perchlorate, AP), halogen containing combustion product (HCl)
  - $NH_4N(NO_2)_2$, (Ammonium Dinitramide, ADN), thermal stability problems
  - NH_4NO_3, (Ammonium Nitrate, AN), burning rate problems

- Currently used liquid monopropellant: Hydrazine, carcinogen and low I_{sp}

- Goal of this Study:
  - ➢ Replacement of ClO_4^-, $N(NO_2)_2^-$, or NO_3^- anions by a green, thermally stable, high performing novel anion which carries a very large excess of oxygen and can oxidize large amounts of metal and binder in solids or large organic cations in ionic liquids.
  - ➢ Finding a green, high-performing replacement for AP has been pursued for a century, but the problem has not been solved as yet.

Technical Approach

- Combine a fuel cation with a complex anion which carries a large excess of oxygen, does not contain any halogen and has a large positive heat of formation

- Use crystal engineering to prepare either a high-melting solid (small hard cation) for AP replacement or a low-melting ionic liquid (large asymmetric soft cation) for hydrazine replacement

- Synthesize and characterize the complex high-oxygen anions and combine them with suitable cations.

- Study the stability and properties of the resulting salts and evaluate their performance

Results

- Prepared and characterized solid and ionic-liquid tetranitrato-borate salts but the thermal stability of the tetranitrato-borate anion was insufficient.
- Replaced the boron central atom by aluminum which improved the thermal stability.
- Increased the energy content of the cation by replacing imidazolium cations by tetrazolium cations.
- Prepared with 4-ethyl-1,5-dimethyl-tetrazolium tetranitrato-aluminate (TTNA) a high performing (*Isp* 280 – 290 sec) ionic-liquid monopropellant.
- Carried out successful ignition tests with TTNA.
- However, the long-term stability of these salts was still insufficient due to the relatively weak $M\text{-}O\text{-}NO_2$ linkage of the nitrato anions.
- Initiated efforts to replace the weak M-O-N linkage by stronger B-N or B-C bonds.
- Successfully prepared and characterized by “Umpolung” reactions several $B(NX)_4^-$ skeletons which are ideal precursors for the synthesis of the $B(NO_2)_4^-$ anion.

Predicted Properties of $B(NO_2)_4^-$

- This anion would hold great potential for an ionic liquid monopropellant and also as a green replacement for AP.
- Theoretical calculations predict $B(NO_2)_4^-$ to be vibrationally stable and allow to estimate the heat of formation ($\Delta_f H^0_{298}$ = -613 kJ/mol) and density (ρ = 1.79 g/cm^3) of Ammonium TetranitroBorate, (ATNB), $NH_4B(NO_2)_4$.
- Specific Impulse calculations with the Cheetah program 4.0 for optimized propellant formulations using either aluminum or alane as a fuel and hydroxyterminated polybutadiene as a binder predict ATNB to deliver an I_{sp} (in sec) comparable to that of AP.

	Al	AlH_3
ATNB	259 (15.3% binder)	278 (9.1% binder)
AP	266 (11.3% binder)	279 (9% binder)

Potential Syntheses Routes for $B(NO_2)_4^-$

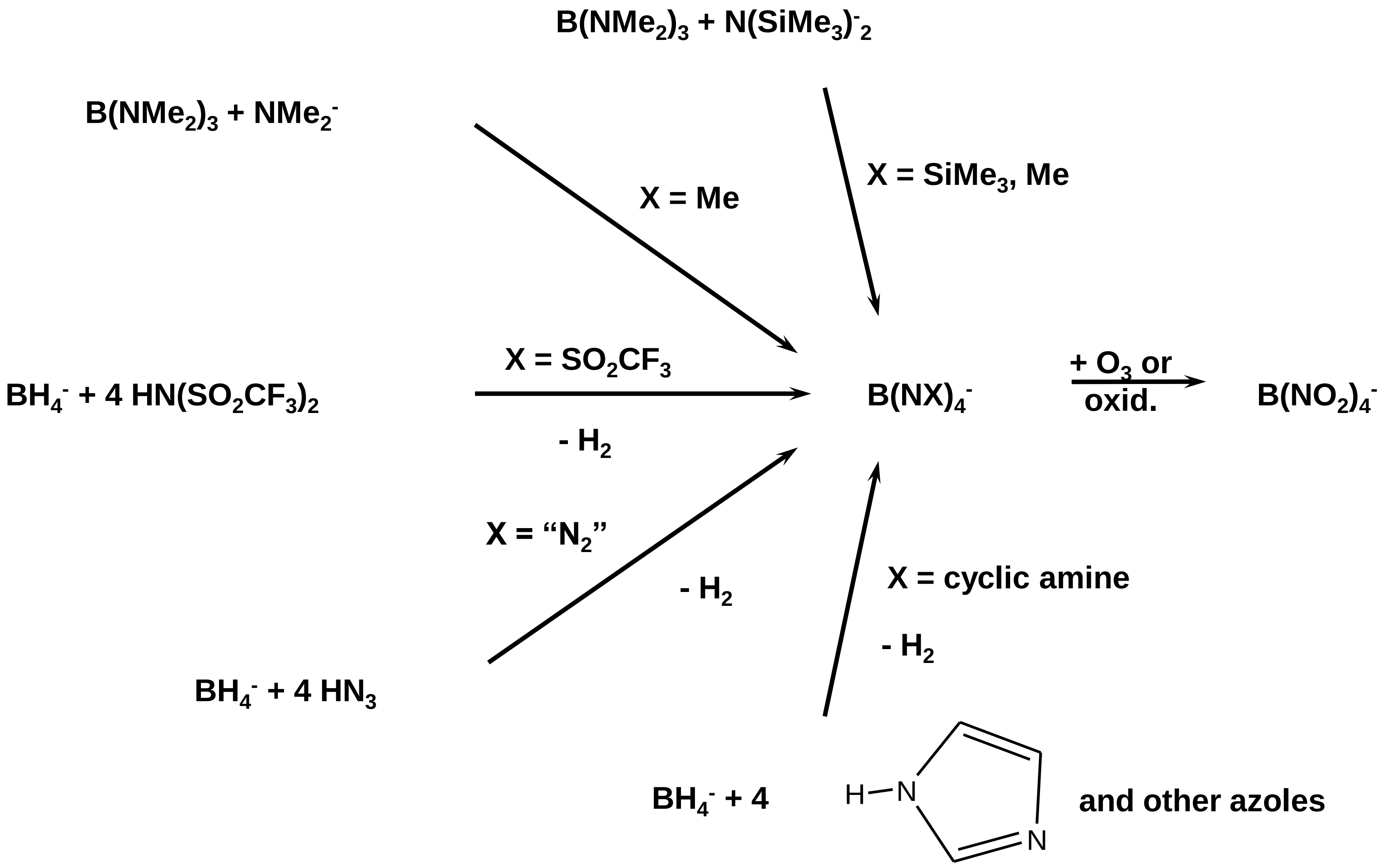
- Direct synthesis of $B(NO_2)_4^-$ from BCl_4^- and NO_2^- ions not possible because the negative charge in NO_2^- is on the oxygen atoms, resulting in the formation of nitrito compounds with weak B-O-NO bonds.
- Our approach is based on "Umpolung" reactions using NX ligands in which the negative charge is on the nitrogen atom. This allows us to construct $B(NX)_4^-$ skeletons:

$$BCl_4^- + 4\ NX^- \rightarrow B(NX)_4^- + 4\ Cl^-$$

In a subsequent reaction, the N-X bonds could be oxidatively cleaved with ozone or peroxide to give the desired tetranitro compound:

$$B(NX)_4^- + 8\ O_3 \rightarrow B(NO_2)_4^- + 8\ O_2 + 4\ X$$

Some Approaches to $B(NX)_4^-$ Skeletons



$B(NMe_2)_3 + N(SiMe_3)^-_2$

X = $SiMe_3$, Me

$B(NMe_2)_3 + NMe_2^-$

X = Me

$BH_4^- + 4\ HN(SO_2CF_3)_2$

X = SO_2CF_3

- H_2

$B(NX)_4^-$ $\xrightarrow[\text{oxid.}]{+\ O_3\ \text{or}}$ $B(NO_2)_4^-$

$BH_4^- + 4\ HN_3$

X = "N_2"

- H_2

BH_4^- + 4

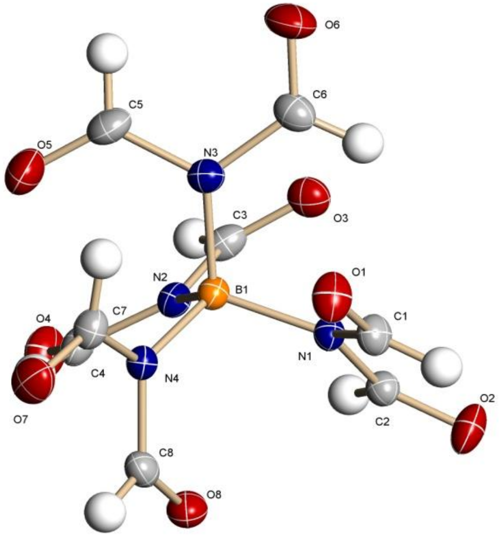
X = cyclic amine

- H_2

and other azoles

$B(NO_2)_4^-$ Synthesis

- Have synthesized and characterized the following $[B(NX)_4]^-$ skeletons: $[B(NCO)_4]^-$, $[B(NCS)_4]^-$, $[B(N_3)_4]^-$, and $[B(imidazolate)_4]^-$.
- Cleavage experiments of the latter two skeletons using ozone, HOF, RuO_4, PbO_2, basic peroxide, or acid have been studied.
- Ozonization of $[B(imidazolate)_4]^-$ produced the tetrakis-bis-formyl amido borate anion.
- Attempts to cleave the tetrakis-bis-formyl-amidoborate anion were unsuccessful.



$B(NO_2)_4^-$ Synthesis

- The ozonisation of the $[B(N_3)_4]^-$ produced only NO_3^- and borate.
- The tetraazidoborate was then converted into a phosphazene and then ozonized.

$$Li[B(N_3)_4] + 4\ PMe_3 \rightarrow Li[B(N{=}PMe_3)_4] + 4\ N_2$$

- The ozonization of the phosphazene gave again only nitrate and borate.
- The reactions of the phosphazene and the azide with HOF produced BF_4^- and again NO_3^-.

$B(NO_2)_4^-$ Synthesis

- We prepared the tetraisothiocyanoborate-anion by treatment of BCl_3 with an excess of KSCN in THF:

$$BCl_3 + 4\ KSCN \rightarrow K[B(NCS)_4] + 3\ KCl$$

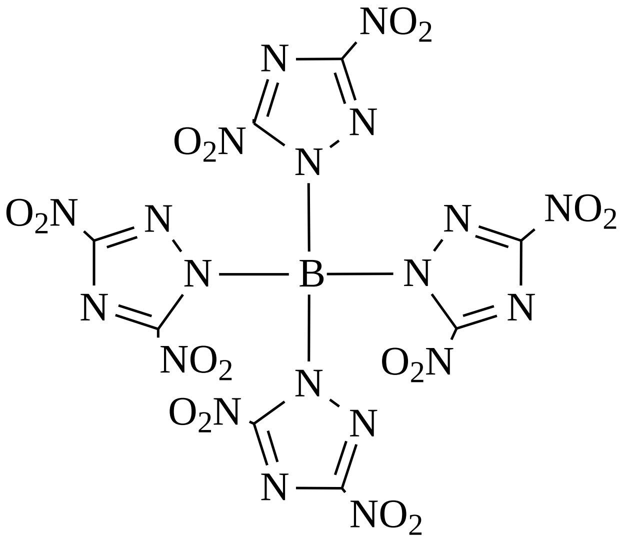
- We also prepared the $[B(N(SO_2CF_3)_2)_4]^-$ anion:

$$BH_4^- + 4\ H(SO_2CF_3)_2 \rightarrow K[B(NSO_2CF_3)_2)_4] + 4\ H_2$$

- Cleavage reactions of these two anions will be investigated.
- We are also working on the synthesis of $[H_2NB(NMe_2)_3]^-$ as an alternate precursor for the oxidative cleavage reactions.

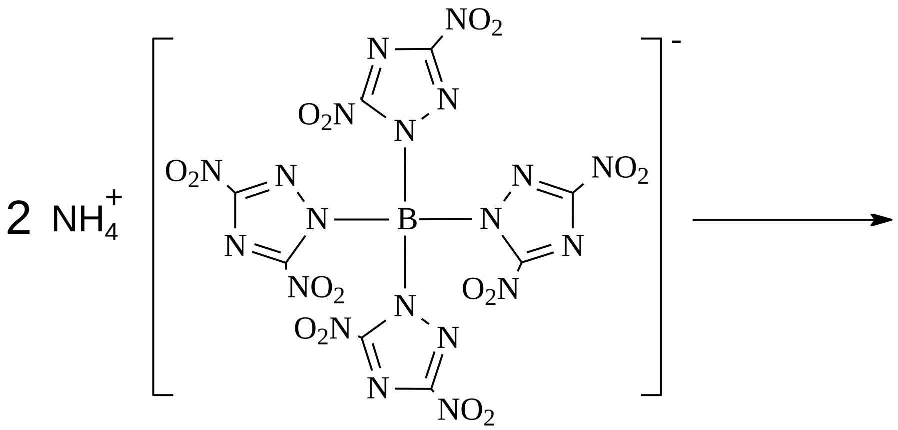
$[B(DNT)_4]^-$, a Superior Alternative to $[B(NO_2)_4]^-$

- To circumvent the difficulties with the oxidative cleavage reactions, we have also pursued alternative concepts.
- We have found that the $B(DNT)_4^-$ anion offers numerous advantages. It promises superior performance and better stability and, synthetically, should be more readily accessible.



$B(DNT)_4^-$

$[B(DNT)_4]^-$, a Superior Alternative to $[B(NO_2)_4]^-$



$B_2O_3 + 21\ N_2 + 4\ H_2O + 16\ CO + 4½O_2$

- Good oxygen balance

- Performance calculations for NH_4DNTB:

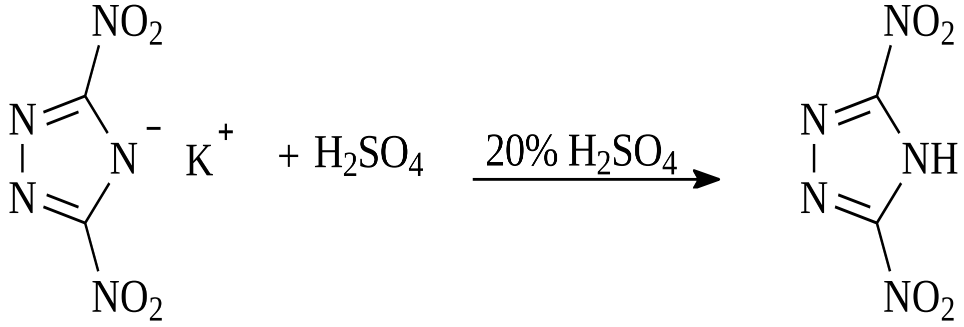
  $\Delta_f H^0 = 138.9$ kcal/mol

  $\rho = 1.74\ g/cm^3$

  max *Isp* of aluminized propellant approximates that of AP

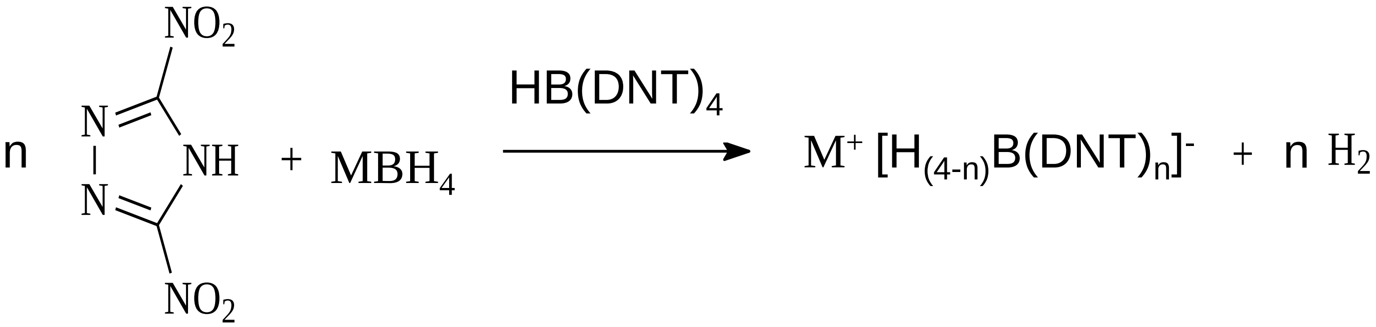
Syntheses of Dinitrotriazolatoborate Salts

KDNT



HDNT

Potassium (3,5-dinitro-1,2,4-triazolate)



$$n\,\mathrm{HDNT} + MBH_4 \xrightarrow{HB(DNT)_4} M^+[H_{(4-n)}B(DNT)_n]^- + n\,H_2$$

$M[H_2B(DNT)_2]$ Syntheses

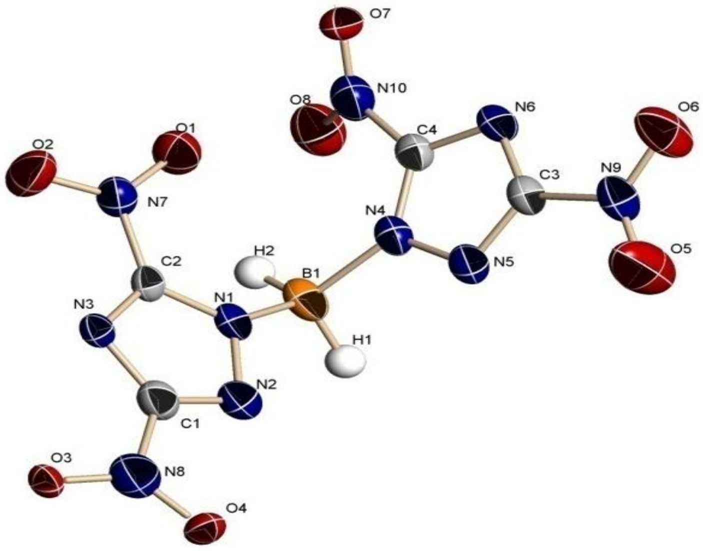
- Reaction of MBH_4 with an excess of HDNT in diethylether at ambient temperature replaced only two of the four hydrogens (conditions, conditions, conditions):

$$M[BH_4] + 4\ HDNT \rightarrow M[BH_2(DNT)_2] + 2\ H_2 + 2\ HDNT$$

- The Li^+ salt exploded in dry box without provocation, but the Na^+ and $N(CH_3)_4^+$ salts were found to be stable. $N(CH_3)_4[H_2B(DNT)_2]$ is hydrolytically stable and has a density of $\rho = 1.52$ g/cm^3.

Crystal structure of

$[N(CH_3)_4]^+[BH_2(DNT)_2]^-$

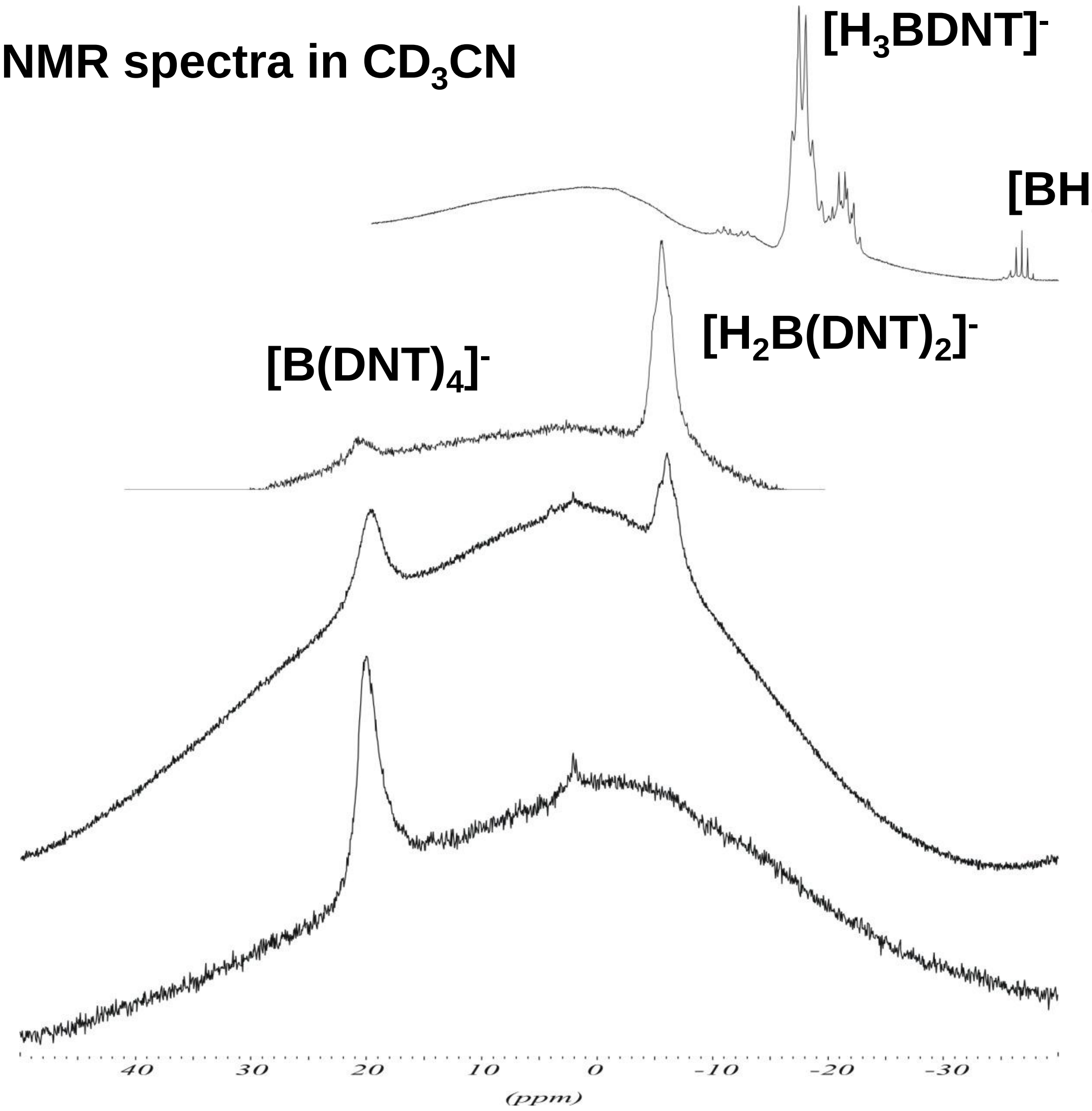


Syntheses of $[N(CH_3)_4]^+$ Salts of H_3BDNT^-, $H_2B(DNT)_2^-$, $HB(DNT)_3^-$, and $B(DNT)_4^-$

- Reactions of $[TMA][BH_4]$ with HDNT in stoichiometric ratios in THF at 85 C resulted in mono-, di-, tri-, and tetra-substitution.
- In solution, the tri-substituted compound disproportionates to the di- and tetra-substituted ones.
- Compounds were characterized by NMR and vibrational spectroscopy.
- So far, we have only the crystal structure of the di-substituted compound, but efforts continue to obtain single crystals for the mono and tetra-substituted compounds.

Multinuclear NMR Spectroscopy

^{11}B NMR spectra in CD_3CN



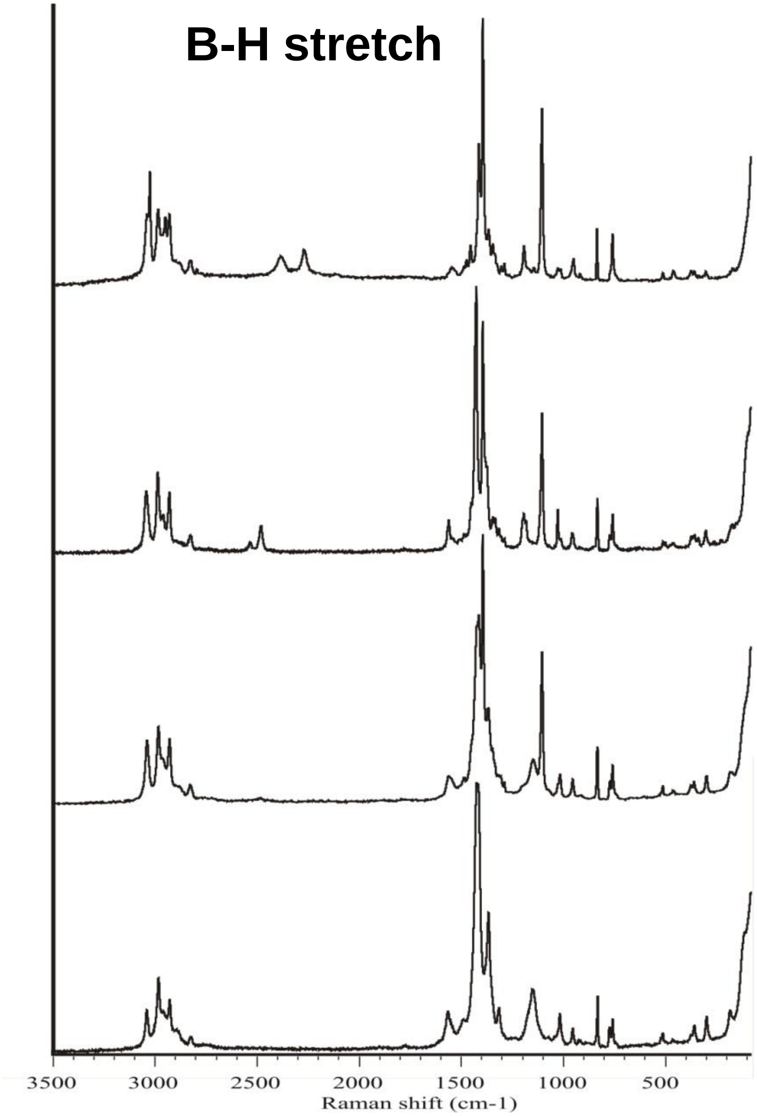
1 $TMABH_4$: 1 HDNT

1 $TMABH_4$: 2 HDNT

1 $TMABH_4$: 3 HDNT

1 $TMABH_4$: 4 HDNT

Raman Spectra



1 $TMABH_4$: 1 HDNT

1 $TMABH_4$: 2 HDNT

1 $TMABH_4$: 3 HDNT

1 $TMABH_4$: 4 HDNT

Stability of [TMA][B(DNT)$_4$]

- [TMA][B(DNT)$_4$] is thermally stable up at least 150 ºC (TGA).
- [TMA][B(DNT)$_4$] is also hydrolytically stable. It was dissolved in water and recovered from the solution unchanged based on its NMR spectra.
- [TMA][B(DNT)$_4$] is insensitive.
    - Negative hammer test
    - Burns without explosion
    - Negative qualitative friction test
    - Smooth decomposition in TGA

Improved $M[B(DNT)_4]$ Syntheses

- Although the displacement reaction with excess HDNT at 125 °C in THF resulted in the quantitative evolution of the expected amount of H_2 and the formation of the tetra-substituted compound,

$$M[BH_4] + 4\ HDNT \rightarrow M[B(DNT)_4] + 4\ H_2$$

there were problems with THF side reactions.

- Side reactions can be avoided by using glyme as a solvent.

- The $B(DNT)_4^-$ salts of Na^+, PNP^+ and PPh_4^+ were prepared in this manner, and the Na^+ salt was converted to the NH_4^+ salt by ion exchange.

- So far, these salts were amorphous solids, but efforts continue to obtain their crystal structures.

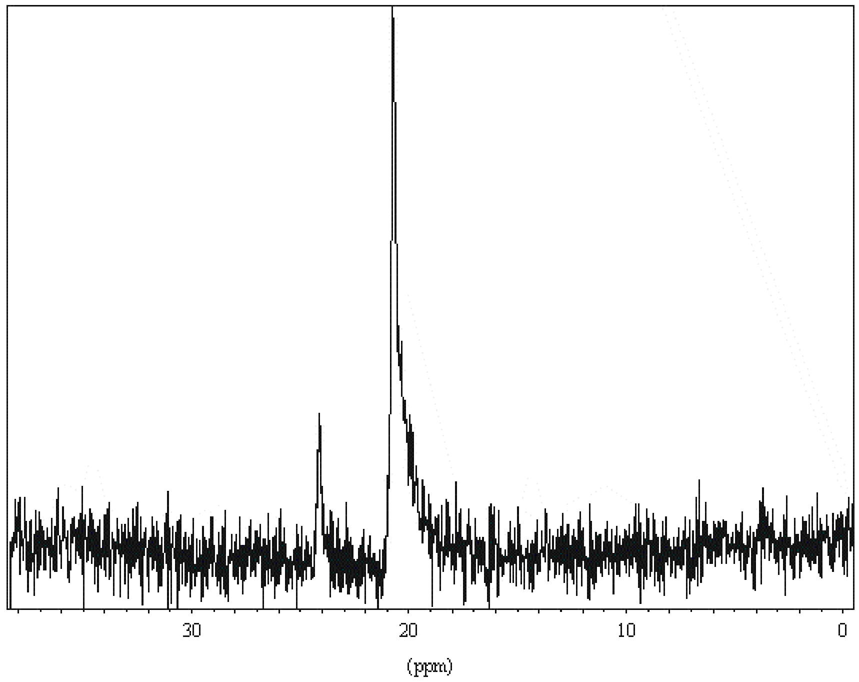
- The reaction in glyme was also used successfully to scale up the synthesis of $Na[H_2B(DNT)_2]$ to the 5 g level.

Synthesis of $[NH_4][B(DNT)_4]$

$NH_4[B(DNT)_4]$ was prepared as an amorphous solid from the Na^+ salt by ion exchange in aqueous solution with Amberlyst 15 ion-exchange resin:

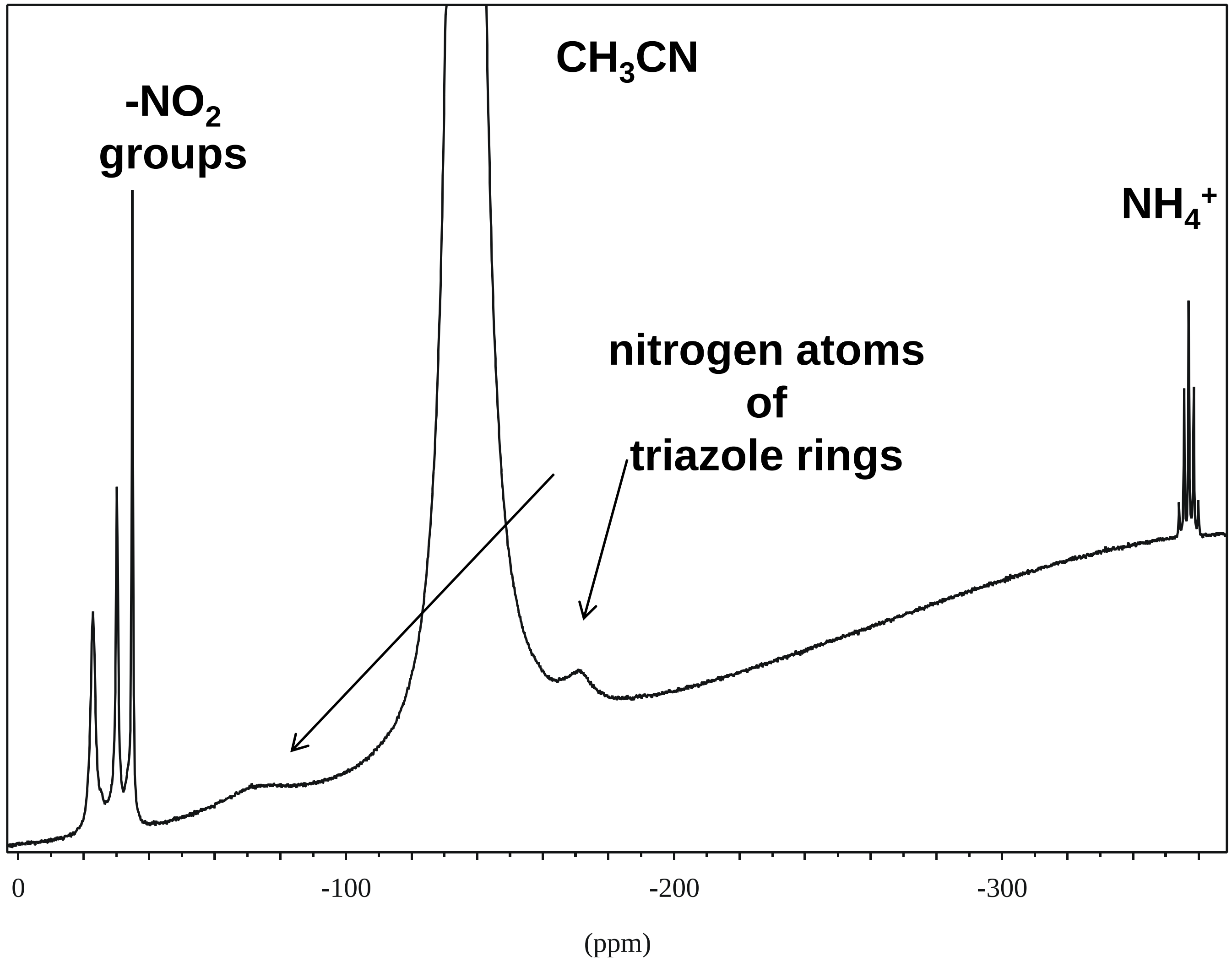
$$Na[B(DNT)_4] + NH_4^+\text{-resin} \xrightarrow{CH_3CN} NH_4[B(DNT)_4] + Na^+\text{-resin}$$

^{11}B NMR in CH_3CN:



$[NH_4][B(DNT)_4]$

^{14}N NMR in CH_3CN:



Status of $NH_4^+[B(DNT)_4]^-$

- Are working on improved HDNT process.
- Are working on growing single crystals of ABDNT.
- Have scaled up synthesis of ABDNT to 25 g level.
- Have verified its density experimentally.
- Have received funding from Cliff Bedford (ONR) to accelerate its process development for making larger amounts and better determine its properties.
- $NH_4^+[B(DNT)_4]^-$ is a very promising, high-performing, green replacement for AP.

Polyazide Chemistry

- Why are we interested in polyazides?
- One azido group contributes about 80 kcal/mol to the endothermicity of a compound.
- Polyazides are important for primary explosives, energetic binders, gas generators, high-nitrogen propellants.

General Method for Preparing Polyazides

$$\mathbf{MF_n + n\,Me_3SiN_3 \longrightarrow M(N_3)_n + n\,Me_3SiF}$$

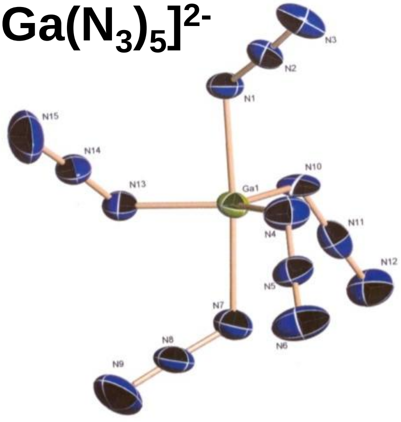
- Azides can be obtained by the reaction of the fluorides with Me_3SiN_3 in a suitable solvent, such as SO_2, CH_3CN, or excess Me_3SiN_3.

- Advantages of this method:
  - ➢ Rapid fluoride/azide exchange
  - ➢ Complete conversions in a single step
  - ➢ Highly pure products
  - ➢ Easy product separation

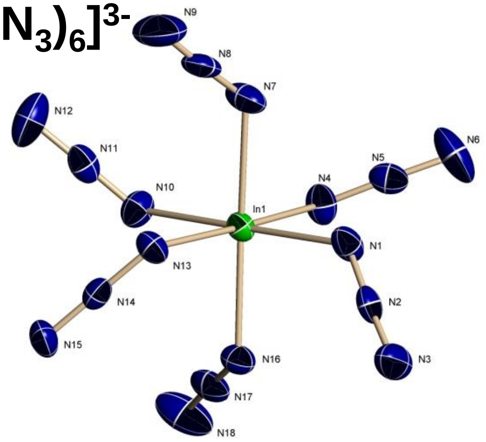
- Over 40 novel polyazides, oxo-azides, and nitrido-azides have been prepared by us using this method.

Examples of Novel Polyazides

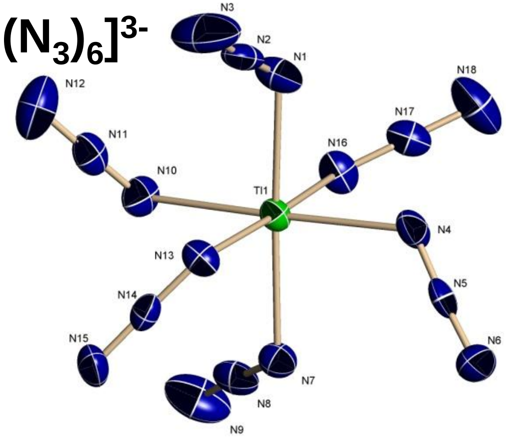
$[Ga(N_3)_5]^{2-}$



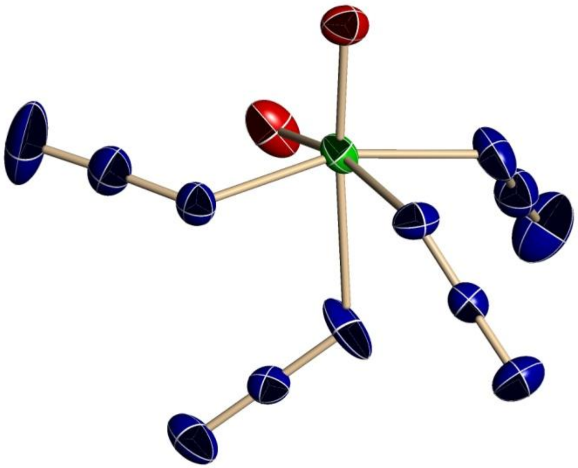
$[In(N_3)_6]^{3-}$



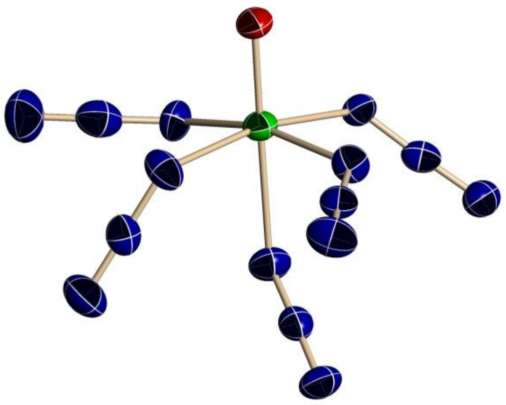
$[Tl(N_3)_6]^{3-}$



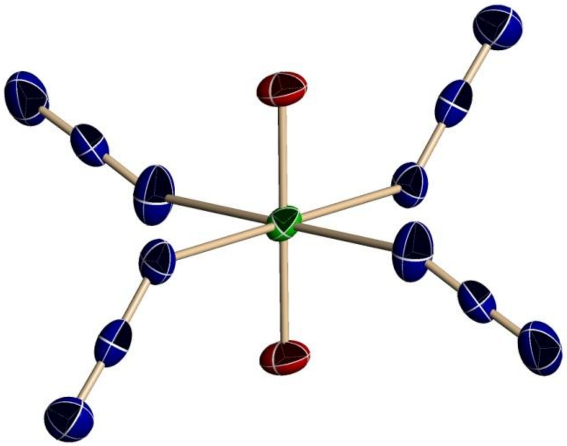
$[ReO_2(N_3)_4]^-$



$[OMo(N_3)_5]^{2-}$



$[O_2U(N_3)_4]^{2-}$



Stabilization of Polyazides

Neutral polyazides can generally be stabilized by anion-formation:

$$M(N_3)_x + n\,A^+[N_3]^- \longrightarrow [A^+]_n[M(N_3)_{x+n}]^{n-}$$

A = TMA, PPh_4, Ph_3PNPPh_3 (PNP)

- Anion formation increases ionicity of the azido groups.

- Increased ionicity enhances activation energy barrier toward catastrophic N_2 elimination.

Ionic N_3: $[N{=}N{=}N]^-$

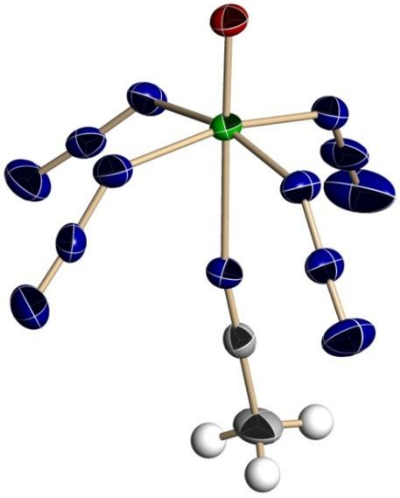
Covalent N_3: $-N{-}N{\equiv}N$

Other Methods for the Stabilization of Polyazides

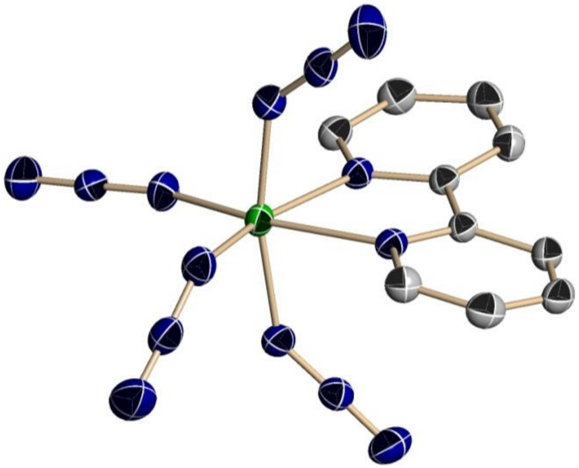
Polyazides can also be stabilized by adduct-formation with a donor ligand:

$$M(N_3)_x \quad + \quad D \longrightarrow [M(N_3)_x] \cdot D$$

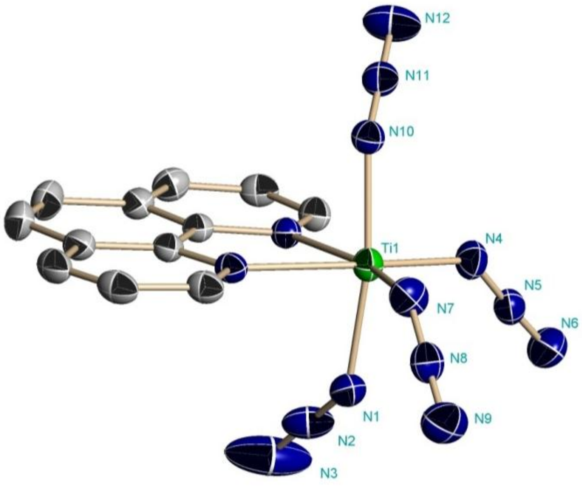
D = THF, CH_3CN, 1,10-Phenanthroline, 2,2’-Bipyridyl



$[OW(N_3)_4]\cdot CH_3CN$



$[Ti(N_3)_4]\cdot$Bipy



$[Ti(N_3)_4]\cdot$Phenanthroline

Bismuth azides, a Non-toxic Alternative for Lead Diazide

$$BiF_3 + 3\ Me_3SiN_3 \xrightarrow{CH_3CN} Bi(N_3)_3 + 3\ Me_3SiF$$

- Pale yellow solid
- Stable at room temperature
- Explodes on provocation (e.g. touching with metal spatula, fast heating, striking with a hammer)

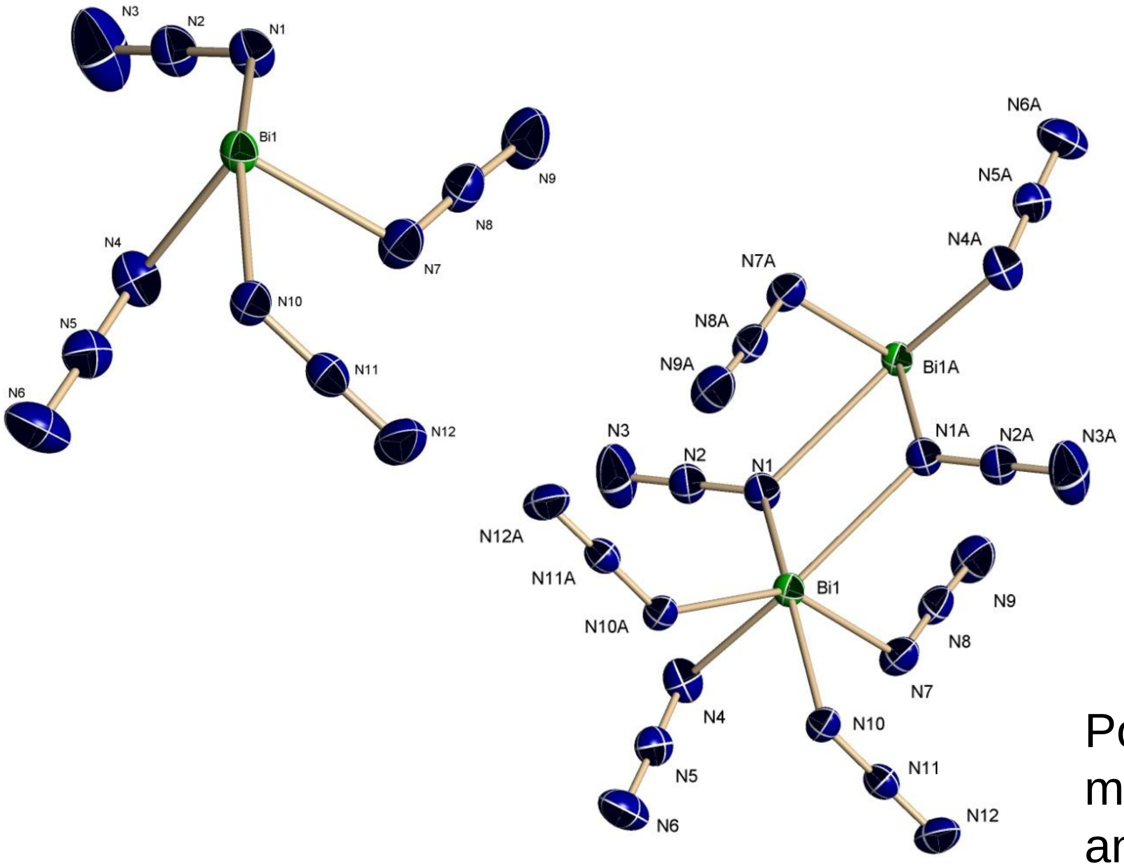
$$BiF_5 + 5\ Me_3SiN_3 \not\longrightarrow Bi(N_3)_5 + 5\ Me_3SiF$$

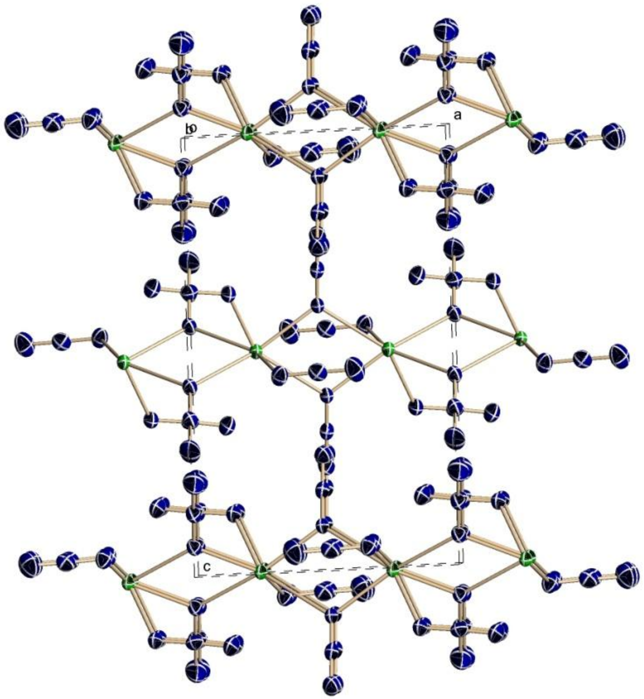
$$BiF_5 + 5\ Me_3SiN_3 \longrightarrow Bi(N_3)_3 + 5\ Me_3SiF + 3\ N_2$$

Some bismuth azides have recently also been reported:
A. Villinger , A. Schulz, *Angew. Chem. Int. Ed.* 2010, *49*, 8017

$[Bi(N_3)_4]^-$

$$Bi(N_3)_3 + PPh_4^+[N_3]^- \xrightarrow{CH_3CN} [PPh_4][Bi(N_3)_4]$$

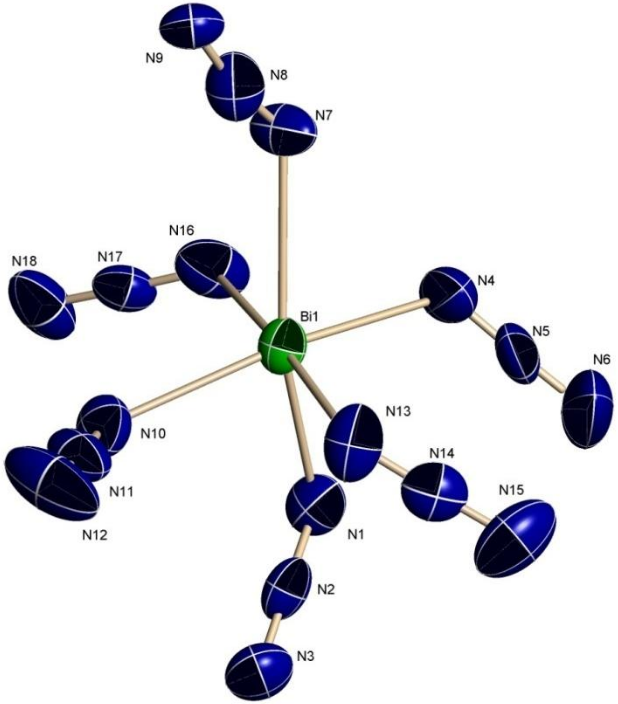




Polymeric anion chains of 4-membered rings with 2 terminal and 4 bridging azido ligands

$[Bi(N_3)_6]^{3-}$

$$Bi(N_3)_3 + 3\ PPh_4^+[N_3]^- \xrightarrow{CH_3CN} [PPh_4]_3[Bi(N_3)_6]$$



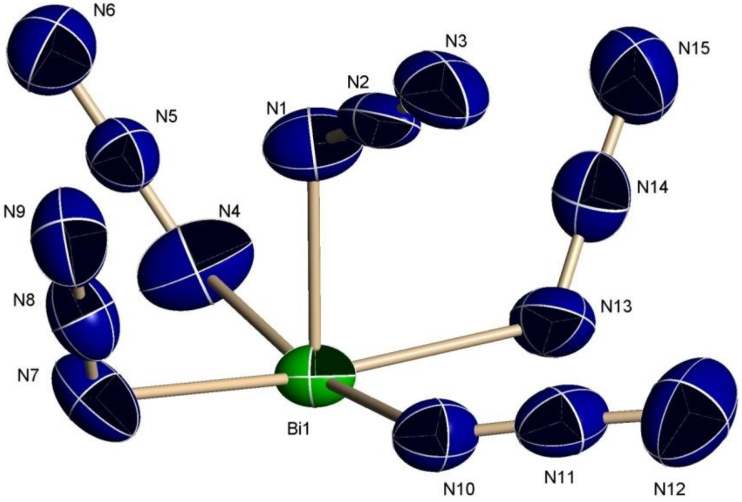
The triple negative charge increases the ionicity of the azido ligands, resulting in

- long Bi-N bonds of 2.4-2.6 Å.
- similar N-N bonds of about 1.2 Å.
- N-N-N angles of close to 180°.

BiN_6 skeleton is strongly distorted from octahedral geometry due to the presence of a sterically active free electron pair.

$[Bi(N_3)_5]^{2-}$

$$Bi(N_3)_3 + 3\ PNP^+N_3^- \xrightarrow{CH_3CN} [PNP]_2[Bi(N_3)_5] + PNP^+N_3^-$$



The azido ligands are less ionic than in $[Bi(N_3)_6]^{3-}$, resulting in

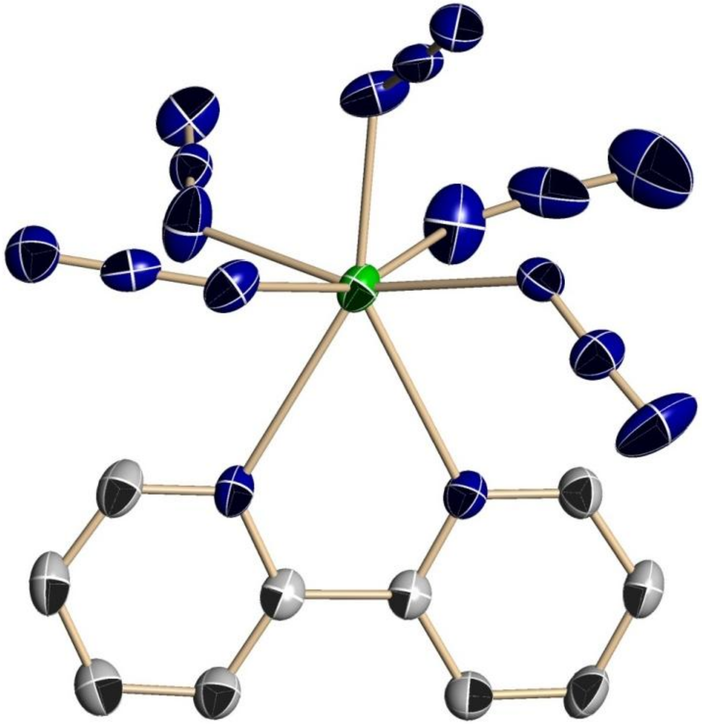
- shorter Bi-N bonds by about 0.2 Å.
- terminal N-N bonds that are shorter than the internal ones.
- N-N-N angles of less than 180°.

The BiN_5 skeleton has pseudo-octahedral geometry.
The sixth ligand is a free electron pair in the axial position.

Stabilization of Bismuth Polyazides by Adduct Formation

$Bi(N_3)_3$ + Bipy $\longrightarrow$ $Bi(N_3)_3 \cdot$ Bipy (no structure yet)

$[PPh_4]_2[Bi(N_3)_5]$ + Bipy $\longrightarrow$ $[PPh_4]_2[Bi(N_3)_5] \cdot$ Bipy



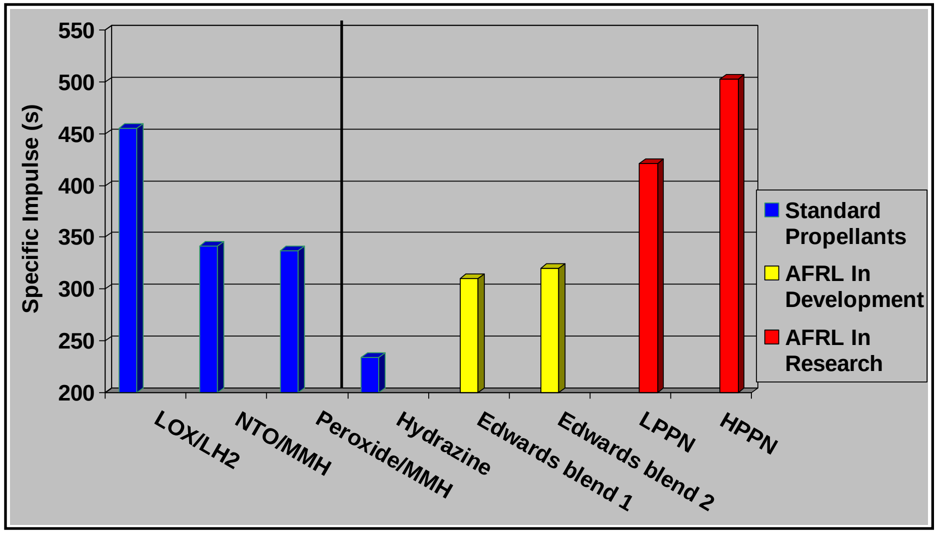
Bi-N_3 bonds of 2.3-2.5 Å are between the ones in $[Bi(N_3)_5]^{2-}$ and $[Bi(N_3)_6]^{3-}$.

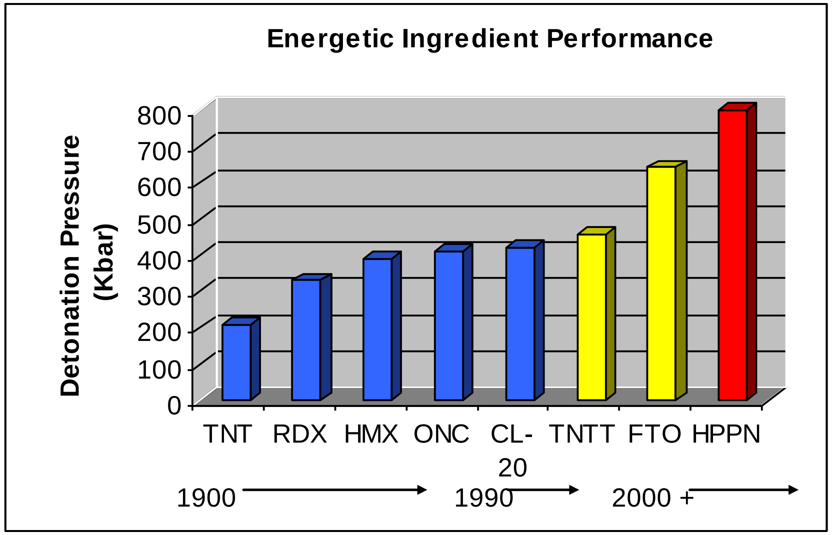
Status of Polyazide Program

- Metal azides can conveniently be prepared from the corresponding fluorides by reaction with trimethylsilyl azide and more than 40 novel polyazides, oxo-azides and nitrido-azides have been prepared and characterized.
- Metal polyazides can be stabilized by anion- and adduct-formation.
- Bismuth azides are a promising non-toxic alternative for lead(II) azide.

Polynitrogen Chemistry (AFOSR/DARPA)
Why are we interested in Polynitrogens?

The performance of polynitrogens as monopropellants would dwarf that of hydrazine, would greatly exceed even many bipropellants, and result in reduced signature





LPPN = Low performing polyN ($N_5^+N_3^-$);

HPPN = High performing polyN (cubic N_8)

Polynitrogens would also have great potential as high-performance explosives

Challenge of Polynitrogen HEDM Synthesis

- All the energy must come from endothermicity, and sensitivity typically increases with endothermicity
- Basis for high energy content is the large differences in bond energies

Carbon bond enthalpies	
$C{-}C$	85 kcal/mol
$C{=}C$	143 kcal/mol
$C{\equiv}C$	194 kcal/mol

Nitrogen bond enthalpies	
$N{-}N$	38 kcal/mol
$N{=}N$	100 kcal/mol
$N{\equiv}N$	226 kcal/mol

$(-HC{=}CH)_n-$ +34 $HC{\equiv}CH$
85 + 143 $\longrightarrow$ 194

stable polymers, unstable monomers

$(-N{=}N)_n-$ -88 $|N{\equiv}N|$
38 + 100 $\longrightarrow$ 226

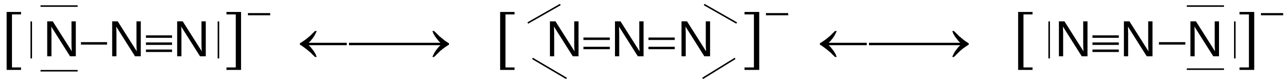
unstable polymers, stable monomer

General Concepts for Polynitrogen HEDM Synthesis

- All polynitrogens are thermodynamically unstable with respect to N_2 molecules and possess only kinetic stability.

- Their activation energy for N_2 elimination is largely determined by the weakest bond in the compound.

- Their kinetic stability is enhanced if suitable resonance structures exist:



$$[\,|\overline{\underline{N}}-N\equiv N|\,]^- \longleftrightarrow [\,N=N=N\,]^- \longleftrightarrow [\,|N\equiv N-\overline{\underline{N}}|\,]^-$$

- The double-bond character of the N—N bonds in the azide anion explains its exceptional stability.

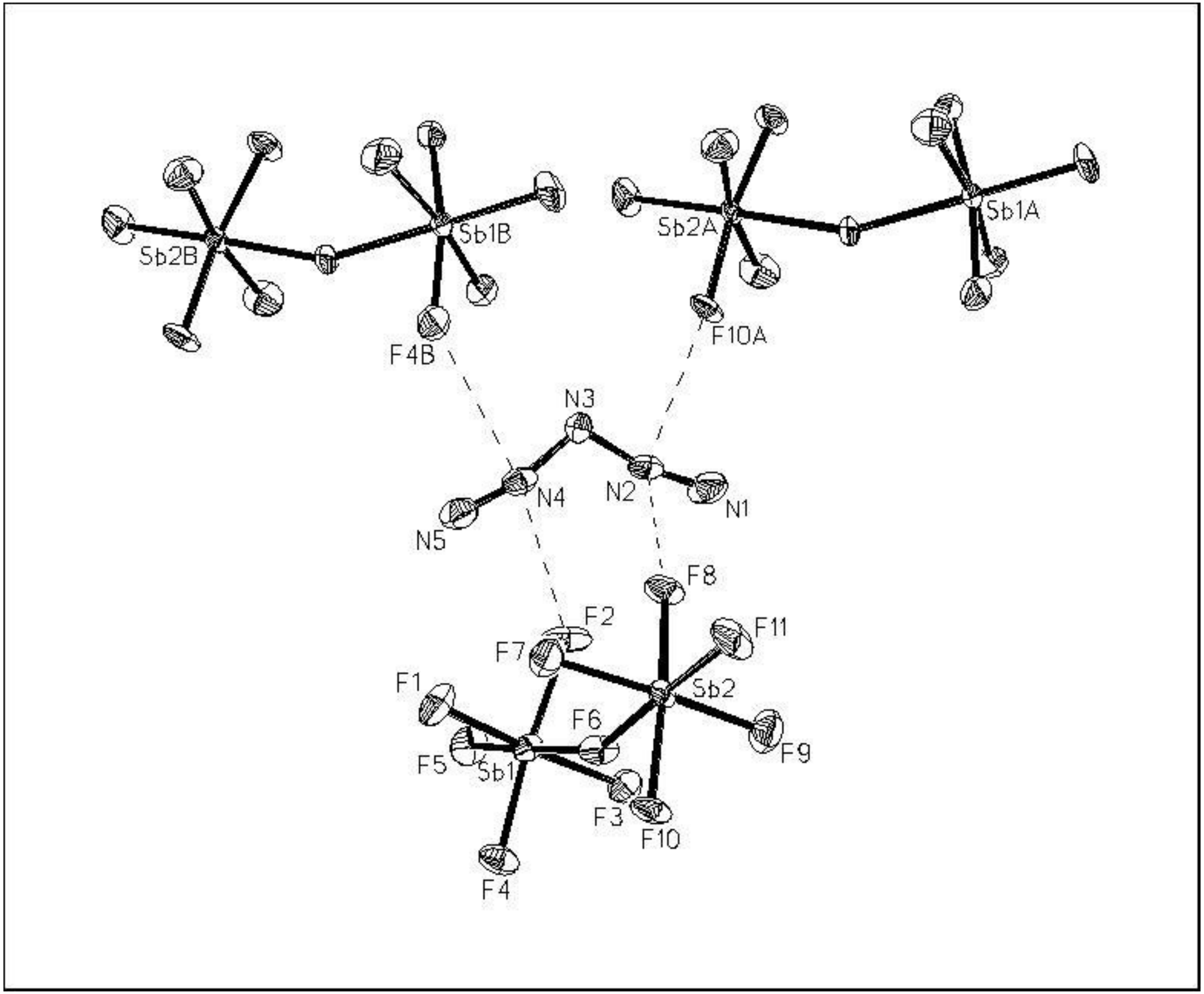
Synthesis and Characterization of $N_5^+SbF_6^-$

- Prepared $N_5^+SbF_6^-$:

$$N_2F^+SbF_6^- + HN_3 \xrightarrow[\text{-78°C to RT}]{\text{HF}} N_5^+SbF_6^- + HF$$

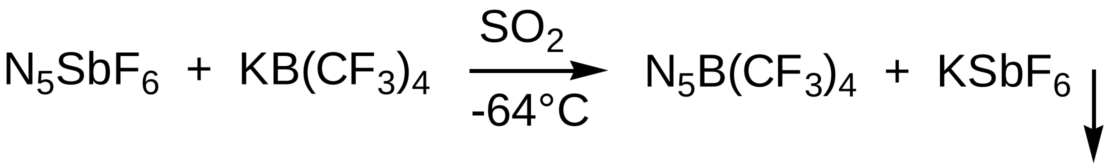
- Properties of $N_5^+SbF_6^-$:
  - White solid
  - Stable to 70 C
  - Obtained in high purity
  - Does not explode at 300 kg•cm (impact sensitivity test)
  - Exhibits all the vibrational bands with the predicted frequencies
  - Soluble in SO_2, SO_2ClF, and HF
  - Are preparing it routinely on a 5 g scale

Crystal Structure of $N_5^+Sb_2F_{11}^-$



Conversion of $N_5^+SbF_6^-$ into Other Salts

- N_5SbF_6 was successfully converted to $N_5B(CF_3)_4$ by metathesis in SO_2 solution



$$N_5SbF_6 + KB(CF_3)_4 \xrightarrow[-64°C]{SO_2} N_5B(CF_3)_4 + KSbF_6\downarrow$$

- $N_5B(CF_3)_4$ is a white solid, stable at room temperature
  - Characterized by vibrational spectroscopy

Syntheses of $N_5^+HF_2^-$, $N_5^+PF_6^-$, $N_5^+BF_4^-$ and $N_5^+SO_3F^-$

$$N_5^+SbF_6^- + Cs^+[N(CF_3)_2]^- + (n+2)HF \xrightarrow{HF} N_5HF_2 \cdot nHF + CsSbF_6\downarrow + HN(CF_3)_2$$

- $N_5^+HF_2^- \cdot nHF$ is a very useful reagent for the syntheses of other new stable N_5^+ salts:

$$N_5HF_2 \cdot nHF + PF_5 \longrightarrow N_5PF_6 + (n+1)\,HF$$

$$N_5HF_2 \cdot nHF + BF_3 \longrightarrow N_5BF_4 + (n+1)\,HF$$

$$N_5HF_2 \cdot nHF + HSO_3F \longrightarrow N_5SO_3F + (n+2)\,HF$$

Combination of N_5^+ with $P(N_3)_6^-$ and $B(N_3)_4^-$

- First successful combinations of N_5^+ with highly energetic anions:

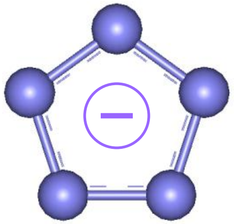
$$N_5SbF_6 + NaP(N_3)_6 \xrightarrow{SO_2,\ -64°C} N_5P(N_3)_6 + NaSbF_6\downarrow$$

$$N_5SbF_6 + NaB(N_3)_4 \xrightarrow{SO_2,\ -64°C} N_5B(N_3)_4 + NaSbF_6\downarrow$$

- $NaP(N_3)_6$ and $NaB(N_3)_4$ are already extremely shock-sensitive and their N_5^+ salts are even more vicious.
- $N_5B(N_3)_4$ contains 96 weight % of energetic nitrogen.

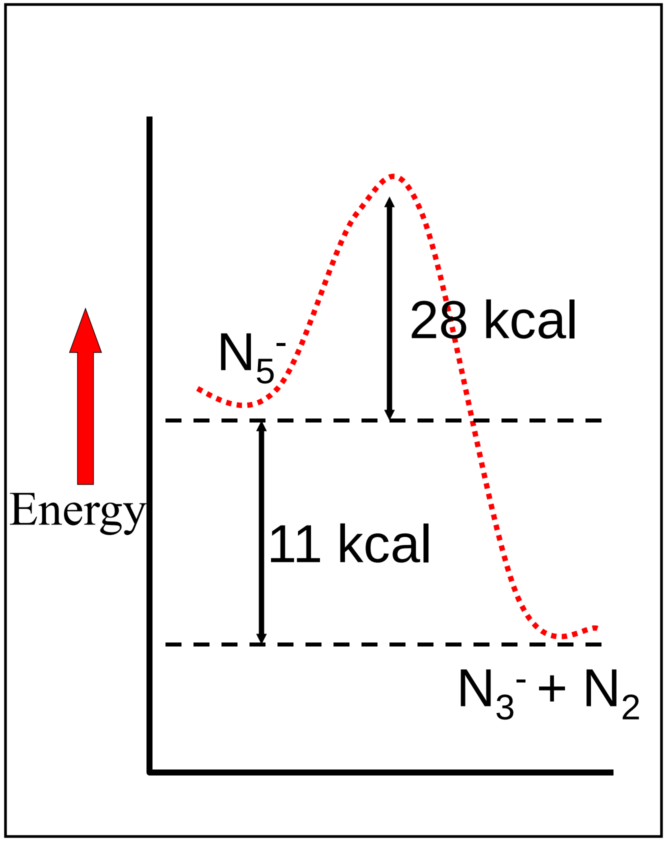
How much damage can 100 mg of $N_5^+[P(N_3)_6]^-$ cause ?

Search for New Polynitrogen Anions



Pentazolate 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*
- *Free pentazole, HN_5, has not been isolated to date. Only aryl substituted pentazoles, RN_5, were known for 40 years. These compounds decompose at room temperature to form aryl azides and N_2 gas*



Discovery of the cyclo–N_5^- Anion

- The N_5^- anion was discovered by us in 2002 at AFRL using Electro Spray negative Ion Mass Spectroscopy (ESIMS) and published in 2002 in Angewandte Chemie.
- The AFRL results were confirmed by Oestmark et al. in 2003.
- A bulk synthesis of the zinc salt of N_5^- has been claimed by Butler et al. in 2003, based upon nitrogen-NMR spectra.
- We have repeated Butler’s work and have shown that his NMR signal attributed to N_5^- is due to the nitrate anion (Chem. Commun. 2005).
- The bulk synthesis of N_5^- is still being pursued at USC and elsewhere.

Syntheses of N_3NOF^+ and N_7O^+

- Our successful synthesis of N_5^+

$$N_2F^+ + HN_3 \longrightarrow N_5^+ + HF$$

implied that a similar approach might also work for other cations, such as NOF_2^+

$$NF_2O^+ + HN_3 \longrightarrow N_3NFO^+ + HF$$

$$N_3NFO^+ + HN_3 \longrightarrow N_3N(O)N_3^+ + HF$$

Reactions of NOF_2^+ with HN_3

- 1:1 Reaction

$N_3NOF^+SbF_6^-$ was successfully prepared in HF solution between -45 °C and room temperature.

$$NOF_2^+SbF_6^- + HN_3 \longrightarrow N_3NOF^+SbF_6^- + HF$$

- 1:2 Reaction

$$NOF_2^+SbF_6^- + 2\,HN_3 \longrightarrow N_5^+SbF_6^- + 2\,HF + N_2O$$

N_5^+ formation was observed at temperatures as low as -64 °C, and the replacement of HN_3 by $(CH_3)_3SiN_3$ and of HF solvent by $(CF_3)_2CFH$ did not change the course of the reaction.

Status of Polynitrogen Program

- We have successfully characterized the novel N_5^+, *cyclo*-N_5^-, N_3NOF^+ and N_7O^+ ions.
- We have shown that the syntheses of ionic pure polynitrogen compounds, such as $N_5^+N_3^-$ or $N_5^+N_5^-$, is impossible.
- The bulk synthesis of a kinetically stable nitrogen allotrope must be focused on neutral covalent polynitrogens.
- We are presently working on the synthesis of such neutral polynitrogens.

DTRA Program for CBA Defeat

- Objective
  - Synthesize and characterize novel, powerful, high-density halogen oxidizers, capable of destroying biologically active materials
- Requirements for the novel oxidizer
  - Must be a powerful oxidizer
  - Must be capable of generating positive halogen atoms
  - Must have a high density for maximum target penetration
  - Must carry excess oxygen to give over-oxidized formulations
- Unique Approaches
  - Prepare new, high-density, halogen-based oxygen carriers
  - Formulate these new oxygen carriers with metal fuels or standard explosives, such as HMX or RDX, to produce a reactive oxidizing fire ball

Status of DTRA Program

- The new iodine (VII) oxide, I_2O_7, was successfully prepared and identified.

- Although I_2O_7 is thermally not stable enough, I_2O_6 is an excellent high-oxygen carrier and was fully characterized. It has an outstanding heat of formation (-90.2 kJ/mol), density (5.40 g/cm^3), is thermally stable, has excellent explosives properties in aluminized formulations with a bootstrap, and can deliver the desired halogen atoms for the potential destruction of the biologically active materials.

- An improved, one-step, high-yield synthesis for I_2O_6 from cheap, commercially available starting materials was developed and scaled up to the 100g level.

- Several hundred gram of I_2O_6 were prepared and distributed to collaborators for neutron diffraction and neutron inelastic scattering, explosives testing, and biological activity studies.

- Continuation funding is in limbo.

Key Challenges

- The key challenges are not
  - the generation of new ideas
  - the availability of qualified manpower
  - lacking enthusiasm
- The major problems are
  - insufficient funding
  - no continuity of funding
  - small size of the programs
  - lack of funds for the purchase of major pieces of required equipment
  - hiring discrimination against non-US citizen in Gov. Labs

Thank You for Your Attention

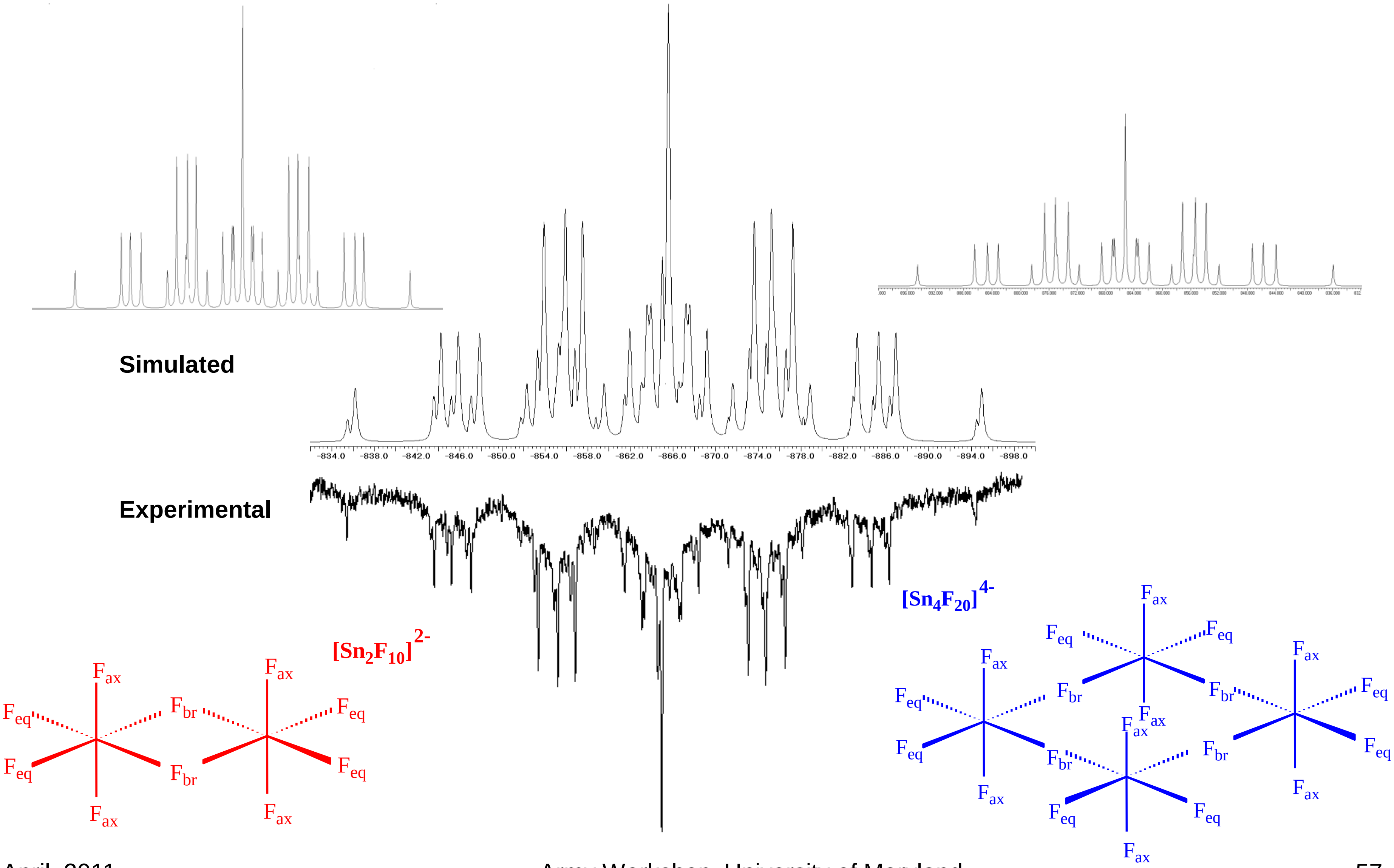
Vibrational Spectrum of z-N_3NFO^+

	observed freq, cm^{-1}, rel int				calcd freq, (IR)[Ra] int[b]	
mode	Ra, HF sol, 20 °C	Ra, solid, 20 °C	IR,[c] solid, 20 °C	$\Delta\nu$ $^{14}N/^{15}N$[d]	CCSD(T)/6-31G(d) ^{14}N[d]	$\Delta\nu$ $^{14}N/^{15}N$[d,e]
a’ ν_1	2253 [10]	2252 [10]	[f]	32	2246 (27)[114]	33.2
ν_2	1771 [1.1]	1771 [.8]	1765 s	0	1810(387)[6.2]	0
ν_3	1159 [1.7]	1162 [1.8]	1156 vs	12-20[g]	1201 (285)[49]	20.5
ν_4	979 [1]	980 sh, vw	994 ms		991(71)[.40]	13.3
ν_5	[h]	733 [.8]	732 m		750 (58)[8.3]	4.4
ν_6	680 sh	683 [1]	[i]		669 (1.7)[9.3]	0.7
ν_7	546 [1.3]	548 [.6]	545 w		538 (6.7)[5.6]	1.3
ν_8	443 [0.6]	447 [0+]			436 (0.7)[.87]	0.6
ν_9	204 [4.4]	210 [1.5]			191 (1.1)[2.9]	2.4
a’’ ν_{10}	[k]	683 [1]	[i]		656 (9.3)[.77]	3.0
ν_{11}	461 [0.4]	465 [.3]			451 (3.8)[.59]	0
ν_{12}	140 sh	140 sh			142(0.37)[.24]	0.8

Vibrational Spectrum of e-N_3NFO^+

	observed freq, cm^{-1}, rel int				calcd freq, (IR)[Ra] int[b]	
mode	Ra, HF sol, 20 °C	Ra, solid, 20 °C	IR,[c] solid, 20 °C	$\Delta\nu$ $^{14}N/^{15}N$[d]	CCSD(T)/6-31G(d) ^{14}N[c]	$\Delta\nu$ $^{14}N/^{15}N$[d,e]
a’ ν_1	2253 [10]	2252 [10]	[f]	32	2249 (16)[126]	33.4
ν_2	1705 [0.7]	1704 [0.6]	1704 ms	0	1739 (273)[8.9]	0.5
ν_3	1159 [1.7]	1162 [1.8]	1156 vs	12-20[g]	1210 (413)[44]	12.0
ν_4	991 [.9]	995 [1.3]	994 ms	10	1009 (12)[5.6]	9.8
ν_5	[h]	901 [0.4]	903 m	18.7	885 (24)[7.2]	18.5
ν_6	668 [1]	672 [0+]	[i]		658 (14)[6.6]	0.8
ν_7	516 [.7]	519 [.6]	518 w		504 (5.3)[3.9]	1.8
ν_8	465 [0+]	465 [.4]	463 w		451 (1.7)[.95]	0.9
ν_9	180 sh	193 sh			177 (1.1)[4.2]	2.0
a’’ ν_{10}	[k]		[i]		675 (10)[.86]	1.5
ν_{11}		480 [0+]	477 vw		473 (1.5)[.39]	0.4
ν_{12}	140 sh	140 sh			159 (0.00)[.39]	0.8

^{119}Sn NMR Spectrum of N_5SnF_5



FN_5 (J. Phys. Chem. A, 107, 6638 (2003) Netzloff, Gordon, Christe, Wilson, Vij, Vij, Boatz)

- Controlled decomposition of $(N_5^+)_2SnF_6^{2-}$ to $N_5^+SnF_5^-$ and “FN_5” allowed us to search for FN_5 by dynamic FT-IR spectroscopy

- Observed only FN_3 and its decomposition products (N_2F_2 and NF_3)

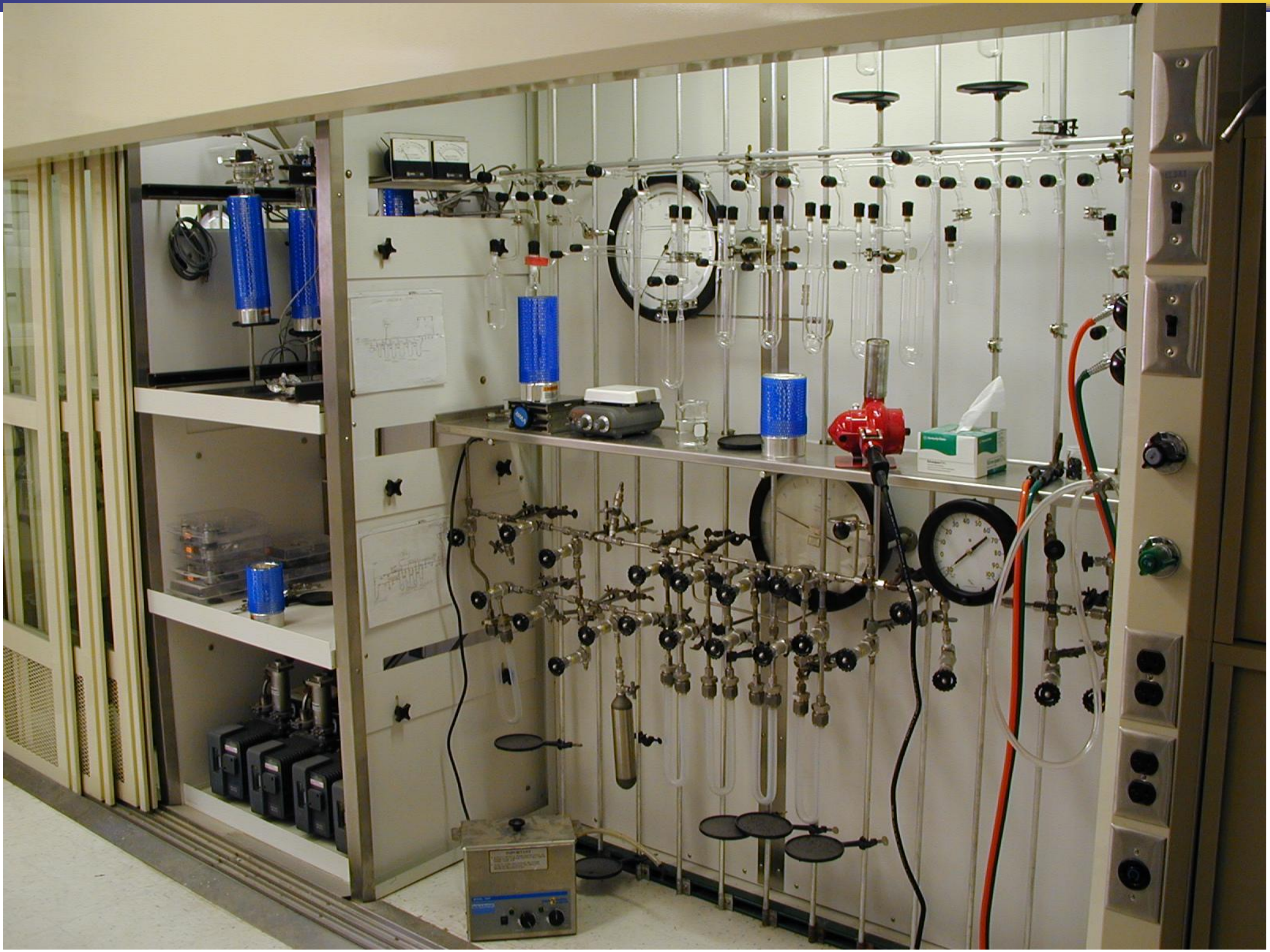
- Theoretical study was carried out showing six stable isomers differing by about 6 (MP2) and 10 (CCSD(T)) kcal/mol in energy

- Intrinsic reaction coordinate and dynamic reaction path calculations were used to study the isomerization and decomposition of FN_5

- Based on a Rice-Ramsperger-Kassel-Marcus analysis, the lifetime of FN_5 was estimated to be in the nanosecond range explaining our failure to observe FN_5 experimentally

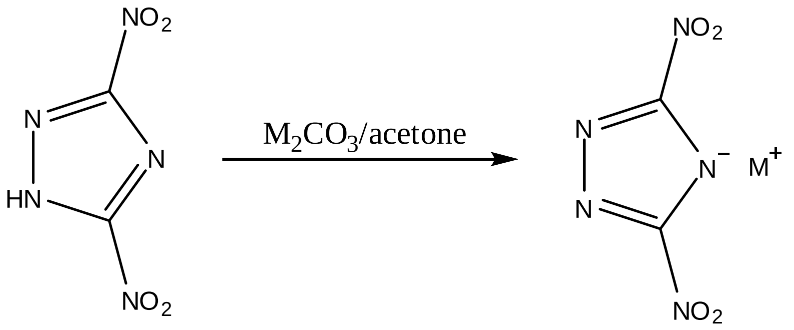
Polyazides can be Dangerous!!

USC Facilities



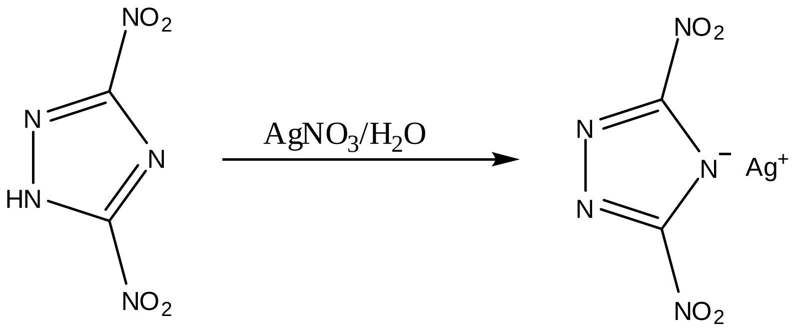
M^+DNT^- Salts of Interest for Pyrotechnics

- **Reaction of HDNT with alkali metal carbonates**



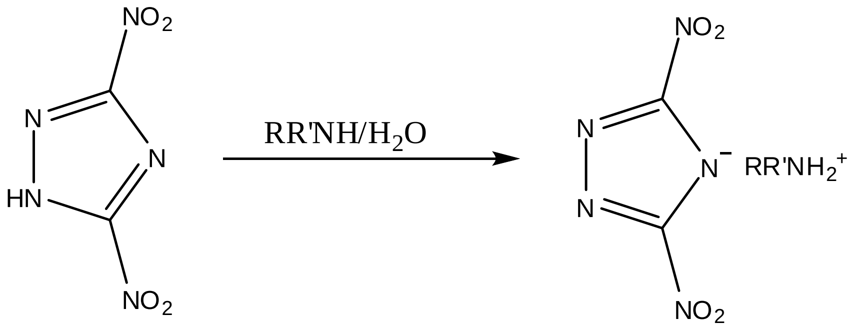
M = Li, Na, K, Rb, Cs

- **Reaction of HDNT with $AgNO_3$**



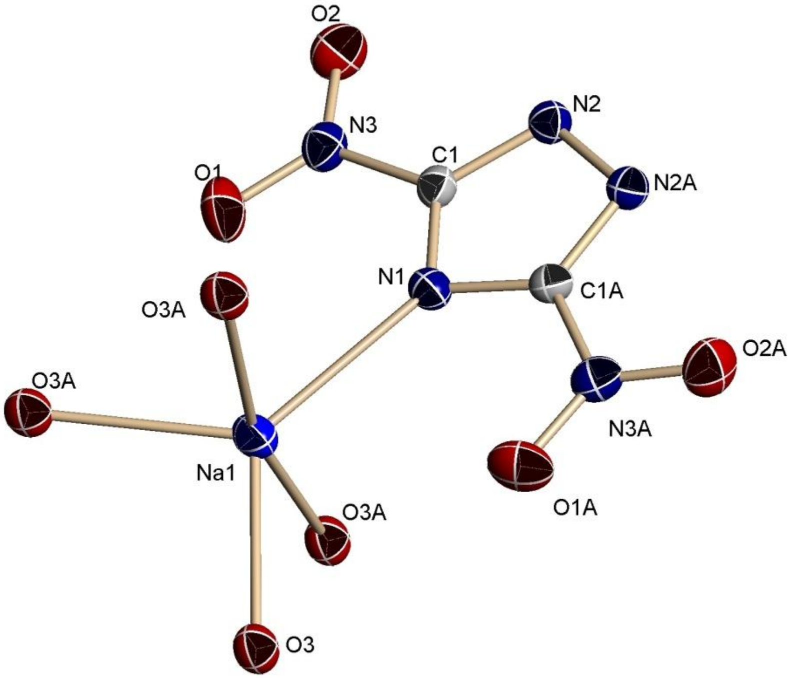
M^+DNT^- Salts of Interest for Pyrotechnics

- **Reaction of HDNT with amines**

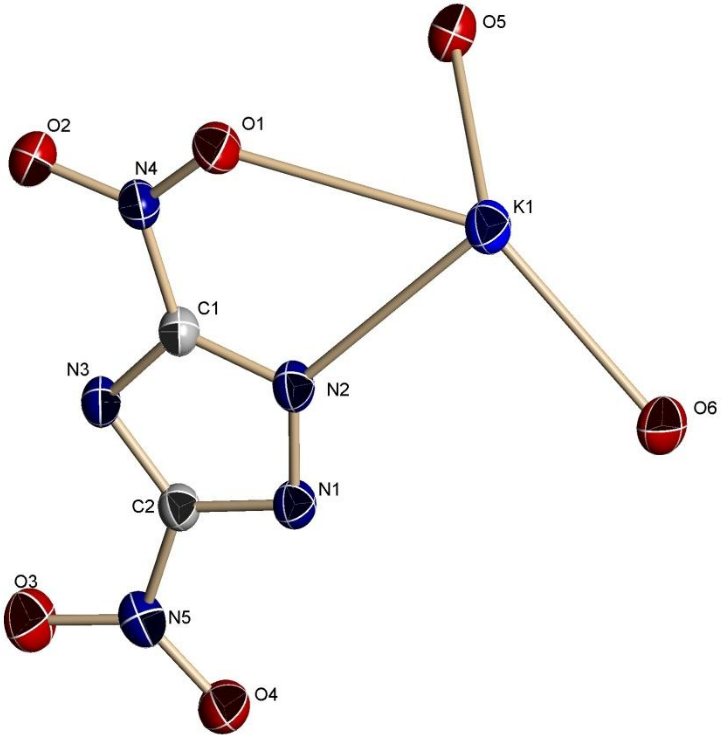


RR’NH = NH_3, tetrazole, 2-amino tetrazole

Alkali metal [DNT]$^-$ salts

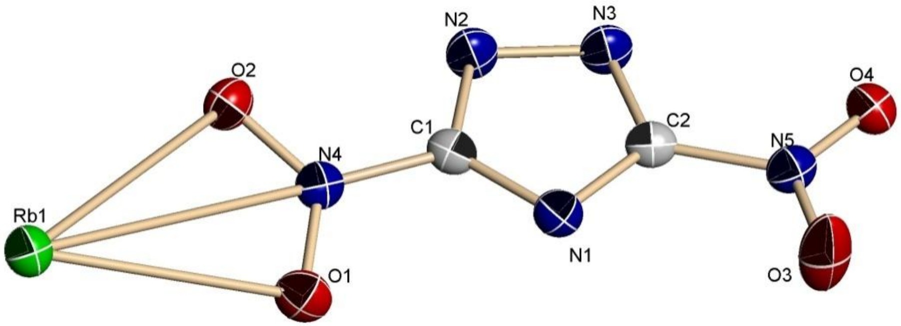


NaDNT·2 H_2O
ρ = 1.746 g/cm^3



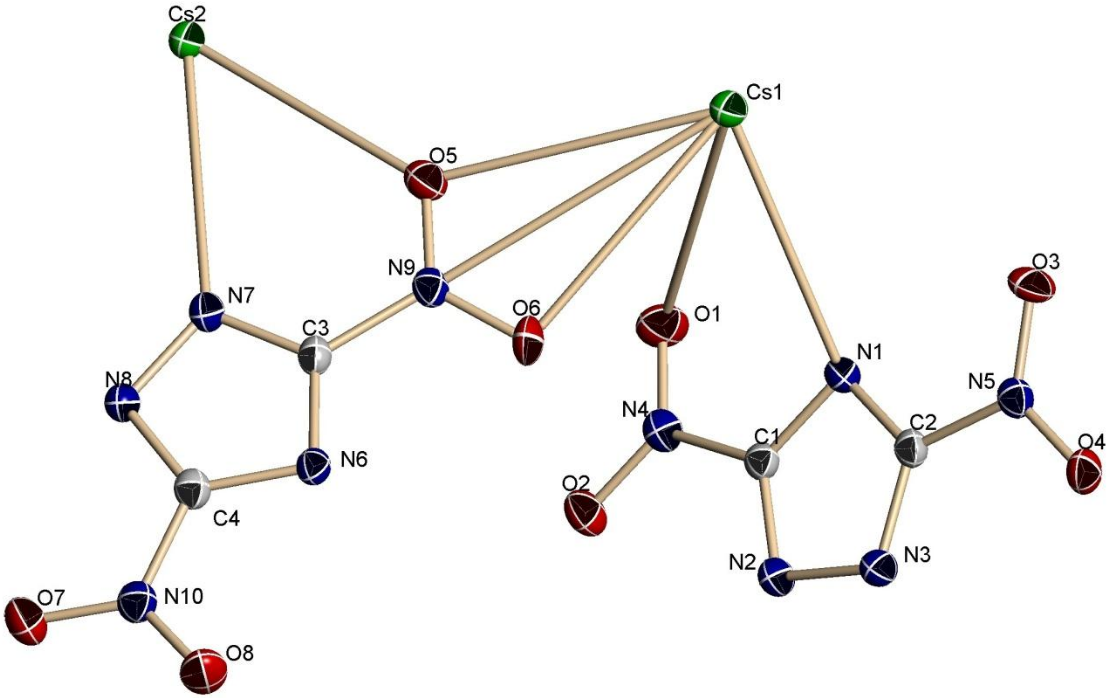
KDNT·2 H_2O
ρ = 1.846 g/cm^3
Water loss: 40 - 120°C (TGA)
Decomp: 270°C (TGA)

Alkali metal [DNT]$^-$ salts (cont.)



RbDNT

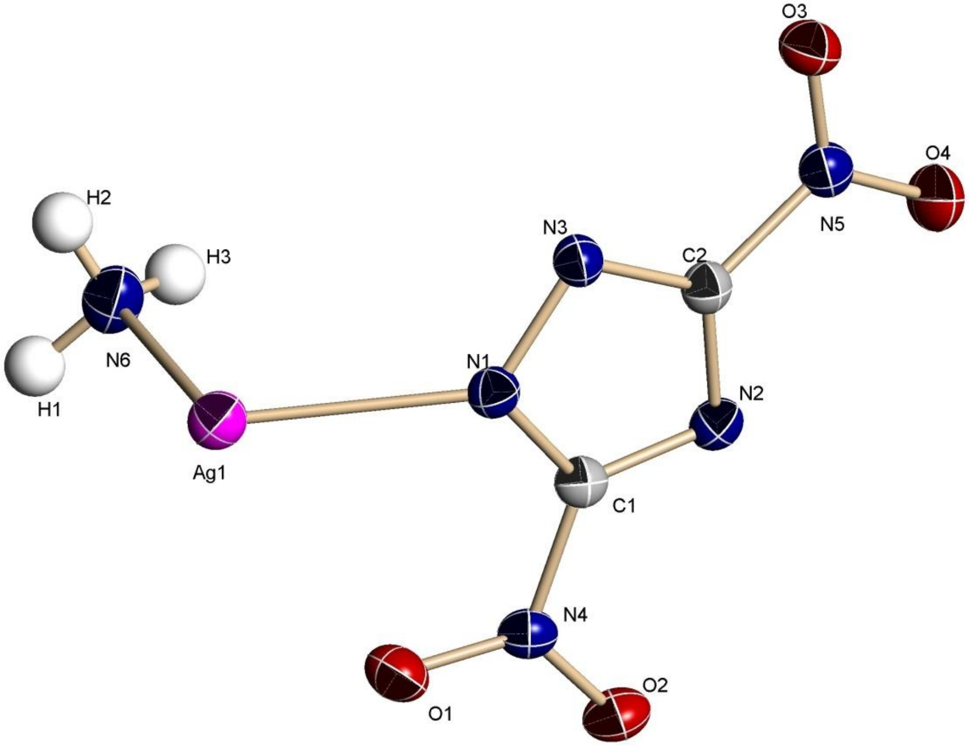
$\rho = 2.436\ \mathrm{g/cm^3}$



CsDNT

$\rho = 2.766\ \mathrm{g/cm^3}$

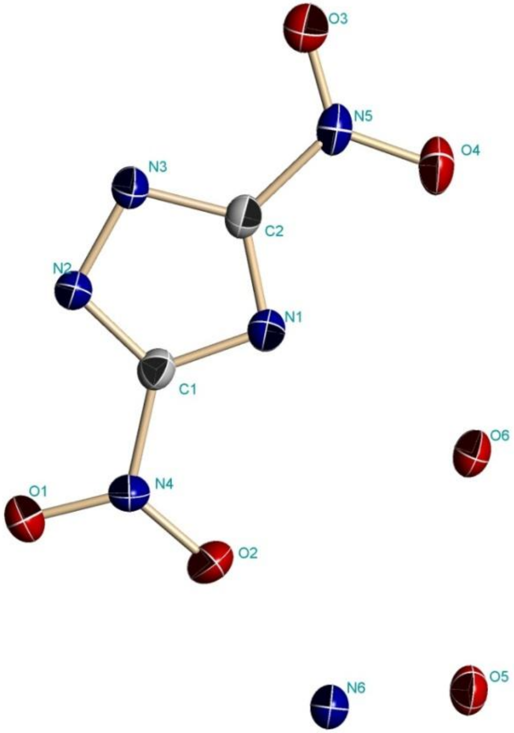
AgDNT



AgDNT·NH_3

$\rho = 2.594\ g/cm^3$

Ammonium [DNT]$^-$ salts

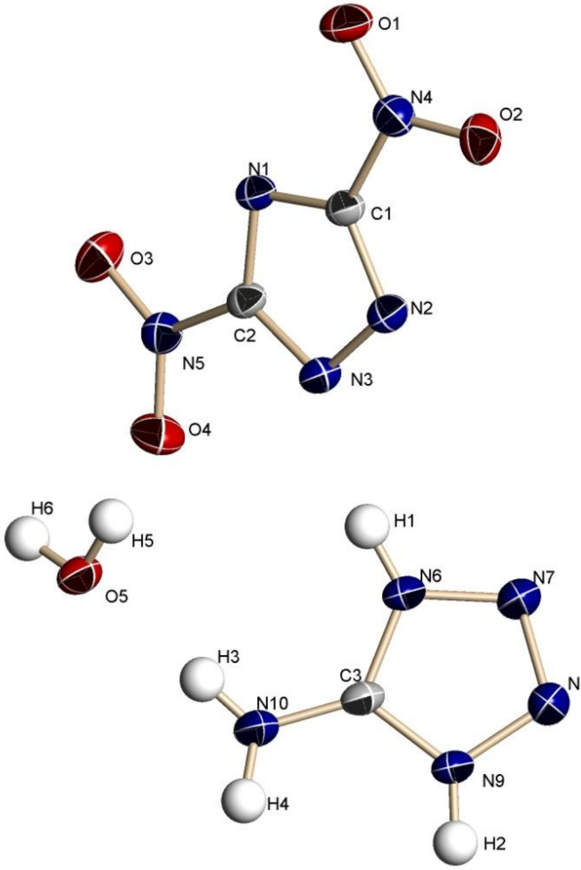


$NH_4DNT \cdot 2\ H_2O$

ρ = 1.564 g/cm^3

Water loss: 40 - 150°C (DSC)

Decomp: 182°C (DSC)

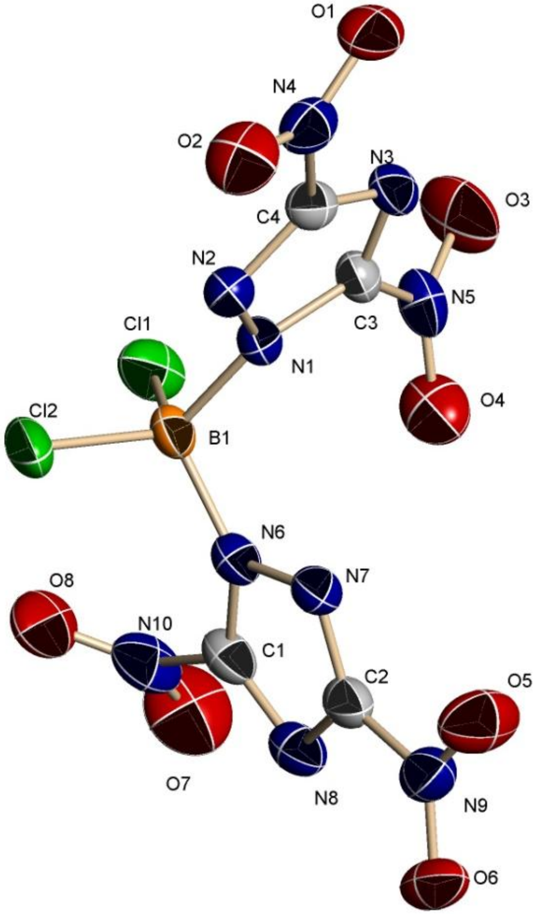


$CH_4N_5DNT \cdot H_2O$

ρ = 1.669 g/cm^3

Alternate Approach to DNT Borate Salts

$$\mathbf{N(CH_3)_4Cl + BCl_3 + 4\,KDNT \xrightarrow{SO_2} 2\,KCl + [N(CH_3)_4]^+[Cl_2B(DNT)_2]^- + 2\,KDNT}$$



- Only partial ligand exchange (even at 100 C under autogenous pressure in a steel cylinder)
- $[N(CH_3)_4]^+[Cl_2B(DNT)_2]^-$ was characterized by its X-ray crystal structure, is hydrolytically stable and has a density of $\rho = 1.60$ g/cm^3 .

Outline

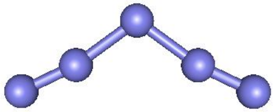
- Green Replacement for AP (ONR)
- Polyazide Chemistry (NSF)
- Polynitrogen Chemistry (AFOSR)
- Dense High-Energy Oxygen Carriers for Agent Defeat (DTRA)

Program Objectives

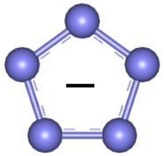
Discover, synthesize, characterize, and scale-up novel, highly energetic nitrogen-rich compounds

Technical Approach:

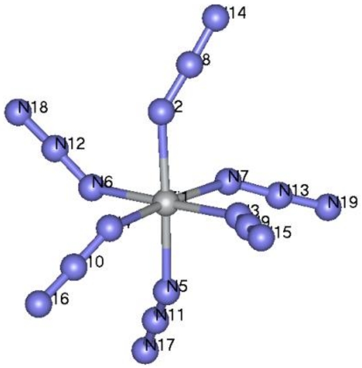
- Exploit synergism between theory and synthesis
  - Use calculations to identify the most promising candidates and predict their properties
  - Use experimental expertise to design synthesis approaches, prepare novel compounds, and characterize products



N_5^+ cation



N_5^- anion

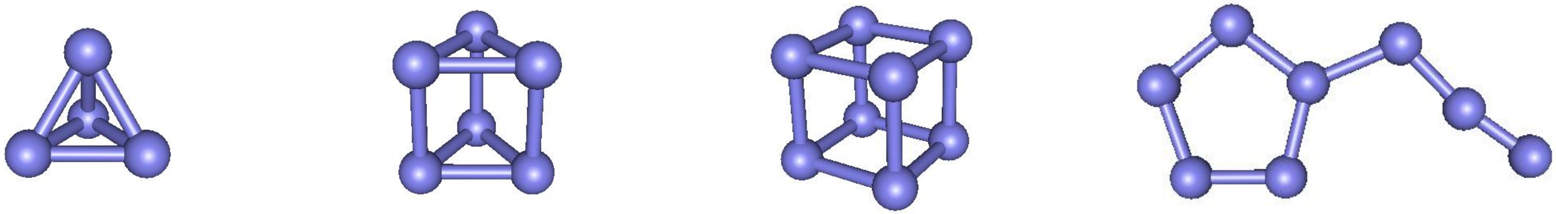


Polyazido Compounds

State of the Art Circa 1998

- Only two all-nitrogen species had ever been isolated in bulk quantities:
  - N_2 was extracted from air in 1772 (Scheele, Cavendish, Rutherford)
  - The azide ion, N_3^-, was synthesized in 1890 (Curtius)

- Calculations over the past 20 years have suggested that other polynitrogens might exist, but none had ever been isolated in bulk



Publicity for N_5^+ Synthesis

The New York Times
ON THE WEB

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February 2, 1999

New Nitrogen Ion Carries Warning: Handle With Care

By MALCOLM W. BROWNE

For a century, chemists doubted that such a substance could exist, but scientists at an Air Force laboratory have created a freakish form of **nitrogen** believed to be one of th most violently explosive substances ever made.

To the acclaim of many other scientists, a team of chemists headed by Dr. Karl O. Christe
and D
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ociety.

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news of the week

N_5^+ CATION MAKES EXPLOSIVE DEBUT

High-energy ion is first new all-nitrogen species in 100 years

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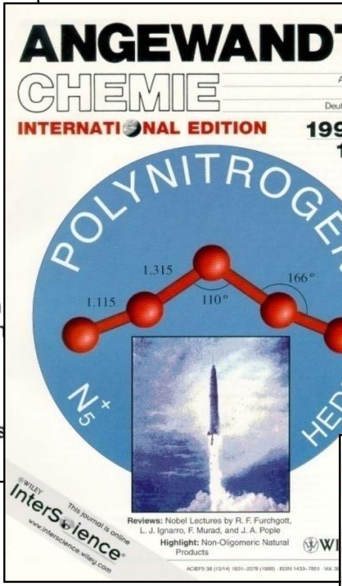
1946 CPIA 1999
A DTIC-Sponsored DoD Information Analysis Center
The Johns Hopkins University
Chemical Propulsion Information Agency
Bulletin
Vol. 25, No. 2, March 1999

Breakthrough In Polynitrogen Chemistry



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A Journal of the Gesellschaft Deutscher Chemiker
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Reviews: Nobel Lectures by R. F. Furchgott, L. J. Ignarro, F. Murad, and J. A. Pople
Highlight: Non-Oligomeric Natural Products

THE TIMES

The next big bang: explosive the size of salt grains

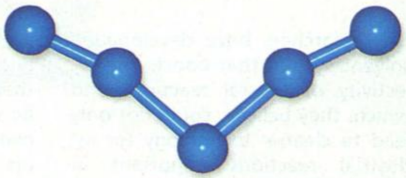
The creation of N_5, an atomic freak of nature, has stunned the world of chemistry. **Nicholas Booth** reports

---

science insights

Chemistry's top five achievements in 1999

Exploding onto the scene

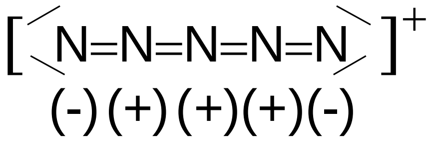


It may not be the safest compound to work with, but chemists from the Air Force Research Laboratory's propulsion directorate, based at Edwards Air Force Base in California, US, have recently managed to synthesise the first new all-nitrogen species for more than 100 years – a salt containing an N_5^+ cation.

propellants, and the N_5^+ cation is reportedly a more powerful oxidiser than O_2^+ and reacts explosively

Extension of the Azide Structure Principle to Higher Polynitrogens by Adding N^+ Units to N_3^-

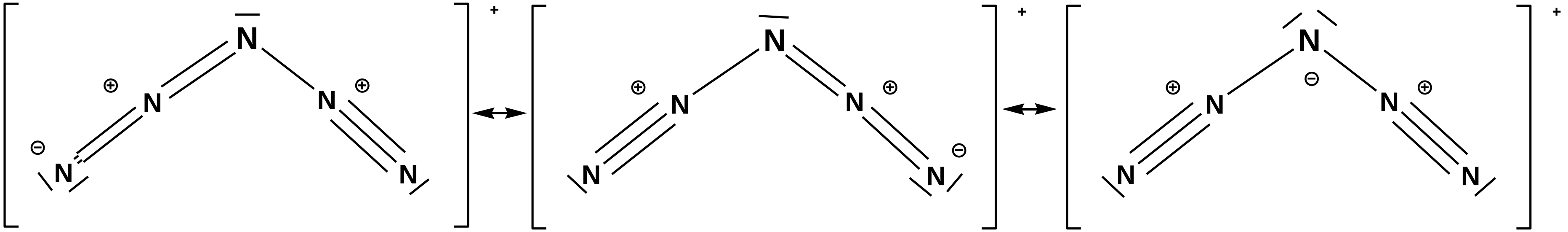
- Although at first glance linear N_4 and N_5^+ look like ideal targets with nothing but double bonds, theoretical calculations show these structures to be vibrationally unstable because of neighboring positive charges:



$$[\mathrm{N{=}N{=}N{=}N{=}N}]^+$$

(-) (+) (+) (+) (-)

- However, if one allows N_5^+ to be bent, resonance structures can be written that avoid neighboring positive charges:

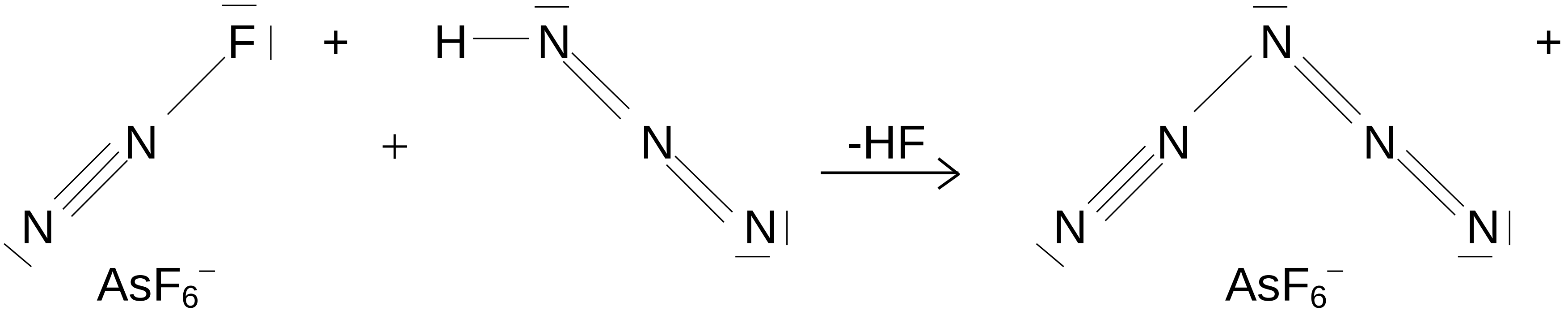


- *Ab initio* calculations confirm the stability of this C_{2v} structure

Selection of Suitable Starting Materials for N_5^+ Synthesis

- Requirements:
  - Starting fragments must contain already high energy (relatively weak bonds)
  - Must have formal positive charge (first IP of N_2 = 359 kcal/mol)
  - Coupling reaction must be exothermic
  - Suitable solvent must be used as a heat sink and for stabilization

- Ideal candidate system:



Actual Synthesis of $N_5^+AsF_6^-$

Angew. Chem., 38 (1999) 2004

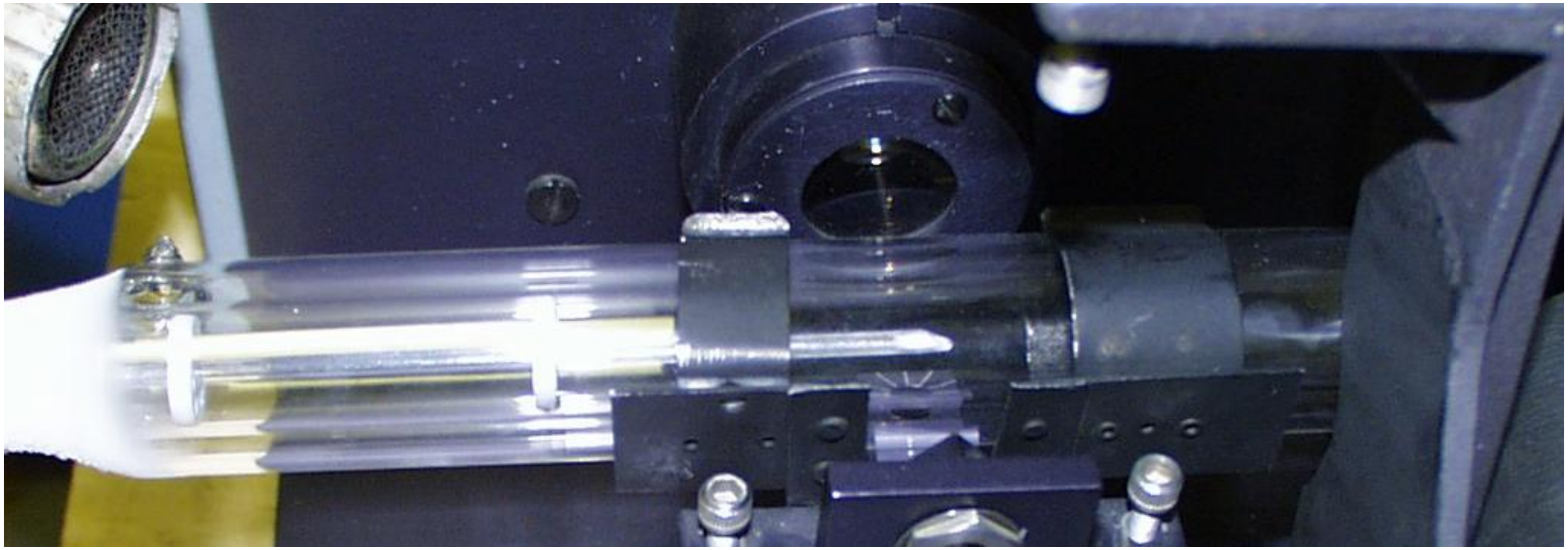
- Reaction system worked as planned:

$$\mathrm{N_2F^+AsF_6^-} + \mathrm{HN_3} \xrightarrow[-78^\circ\mathrm{C}]{\mathrm{HF}} \mathrm{N_5^+AsF_6^-} + \mathrm{HF}$$

  - ➢ High yield
  - ➢ 2 mmol (0.5 g) scale

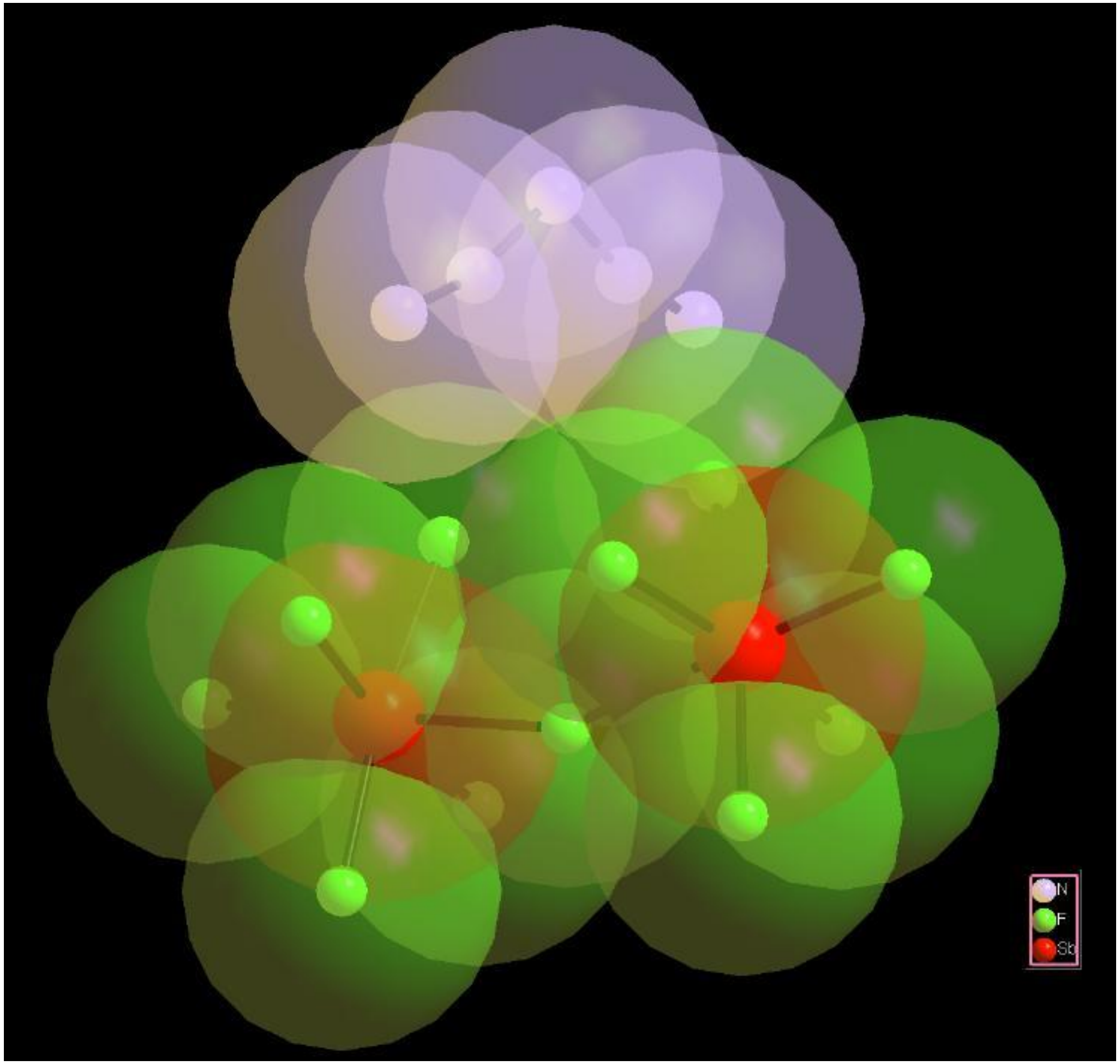
- Properties of $N_5^+AsF_6^-$:
  - ➢ White solid
  - ➢ Sparingly soluble in HF
  - ➢ Marginally stable at 22 C
  - ➢ Highly energetic
  - ➢ Reacts violently with water and organics
  - ➢ Calculated ΔH_f (298 C) = 351 kcal/mol

$N_5^+AsF_6^-$ in Low-Temperature Raman Spectrometer



Crystal Structure of $N_5^+Sb_2F_{11}^-$

Crystal structure of N_5^+ was in perfect agreement with our calculated predictions



Synthesis of the $N_2F^+SbF_6^-$ Precursor

- Reduction of N_2F_4 to N_2F_2

$$\text{Graphite} + AsF_5 \longrightarrow C_{12}{\cdot}AsF_5$$

$$C_{12}{\cdot}AsF_5 + N_2F_4 \longrightarrow 2\,C_{12}^{+}AsF_6^{-} + \textit{trans}\text{-}N_2F_2$$

- *trans-cis* isomerization of N_2F_2:

$$\textit{trans}\text{-}N_2F_2 + AsF_5 \xrightarrow{T/P} N_2F^{+}AsF_6^{-}$$

$$N_2F^{+}AsF_6^{-} + NaF \xrightarrow{HF} NaAsF_6 + \textit{cis}\text{-}N_2F_2$$

- Formation of $N_2F^+SbF_6^-$:

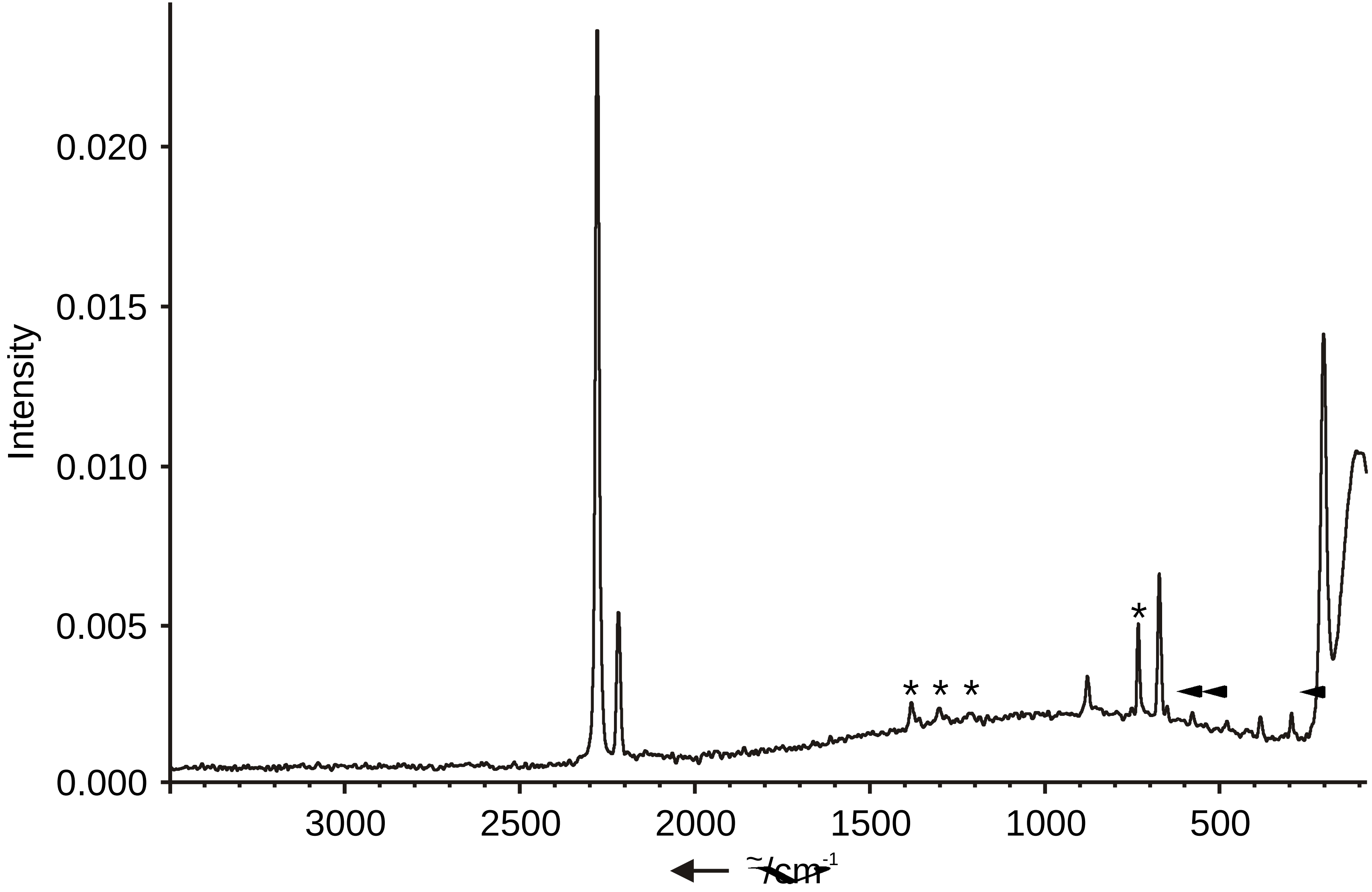
$$\textit{cis}\text{-}N_2F_2 + SbF_5 \xrightarrow{HF} N_2F^{+}SbF_6^{-}$$

- If N_2F_4 is not available, add:

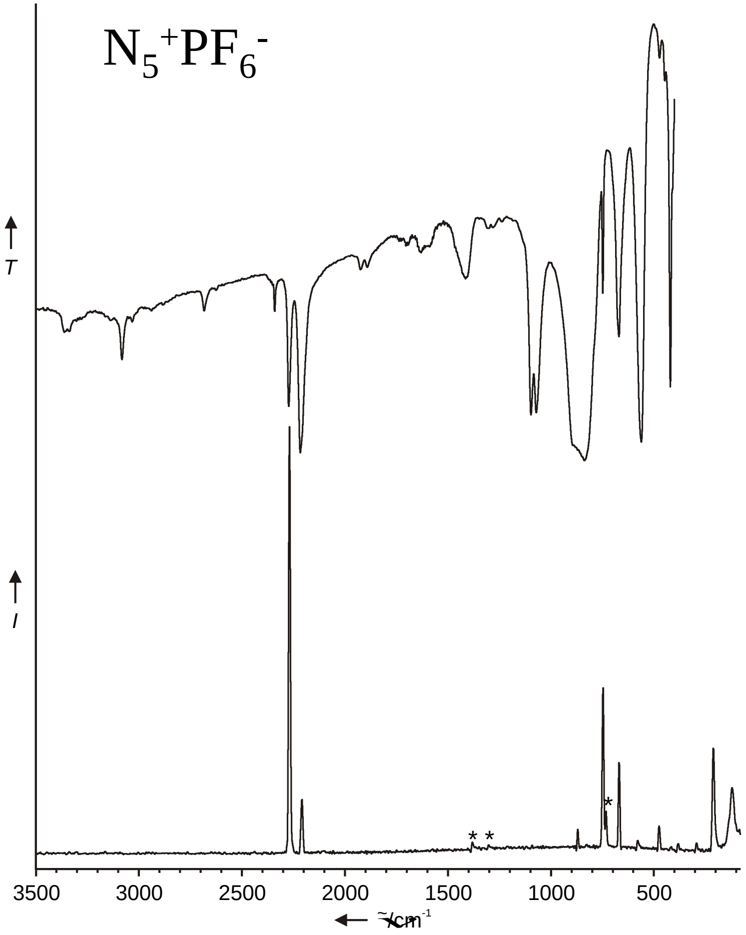
$$H_2NCONH_2 \longrightarrow F_2NCONH_2 \longrightarrow NHF_2 \longrightarrow N_2F_4$$

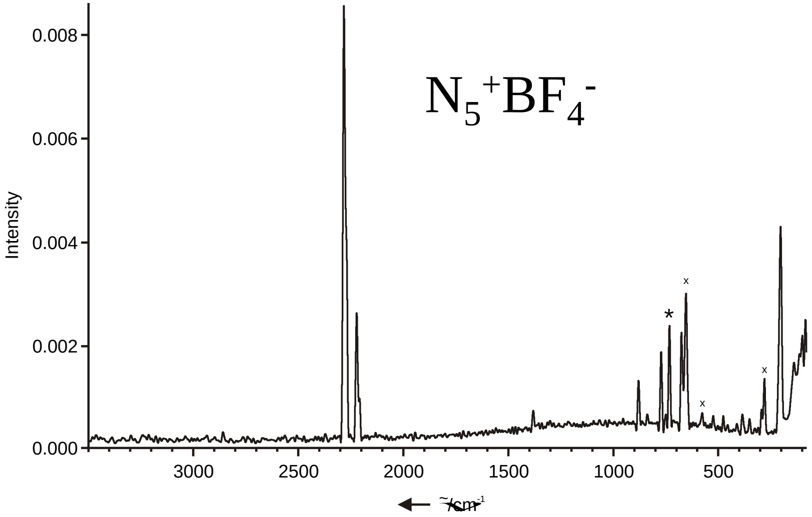
Typical Vacuum Line and Safety Equipment

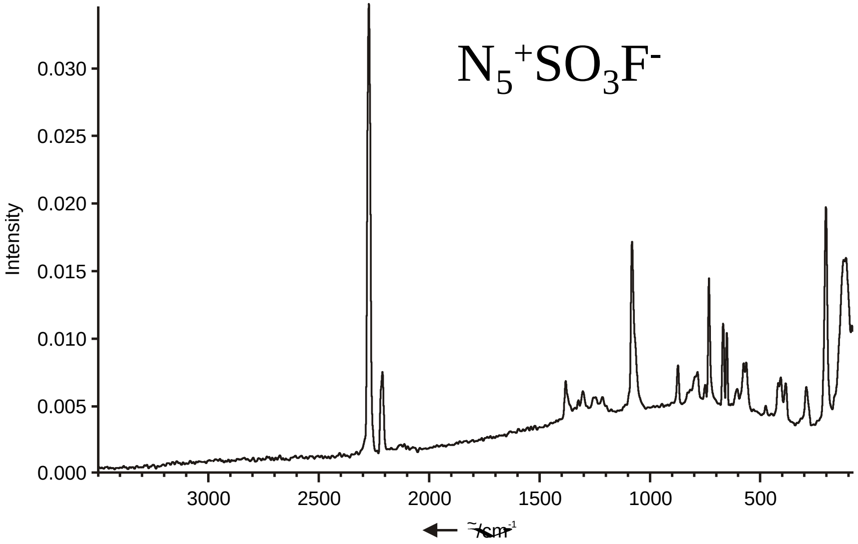
Raman Spectrum of $N_5^+HF_2^-\cdot nHF$



Vibrational Spectra of the New N_5^+ Salts

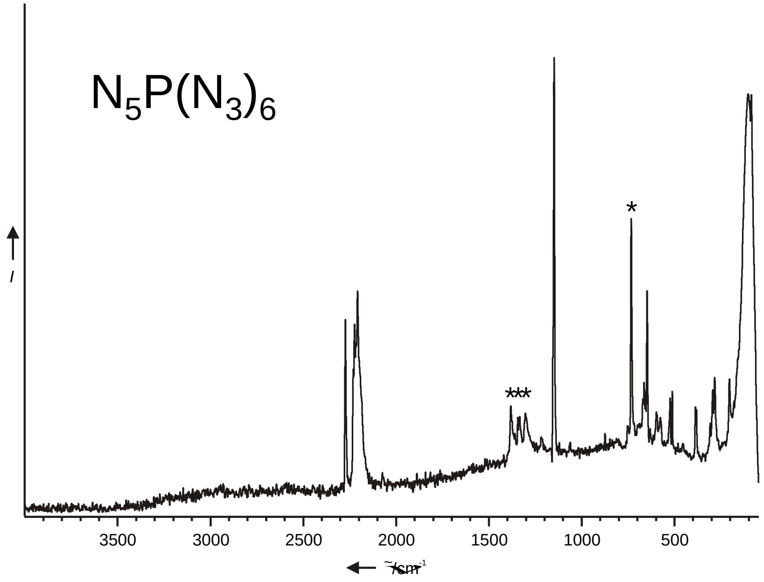


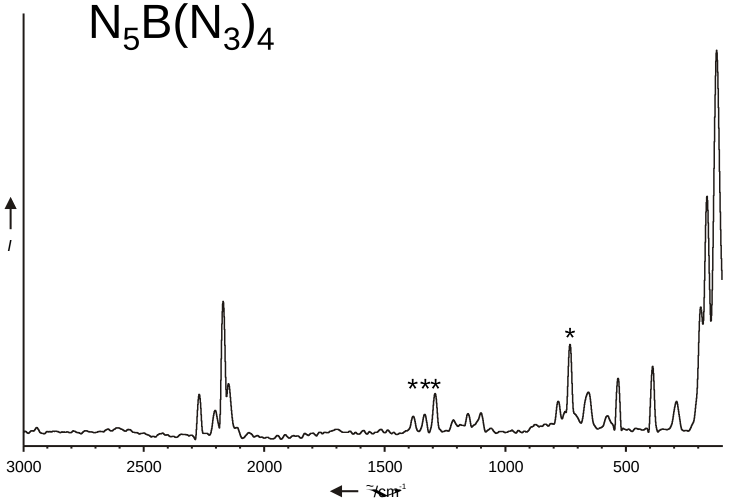




Characterization of $N_5P(N_3)_6$ and $N_5B(N_3)_4$

- Low-temperature Raman spectra





- Material balances

- Compounds are stable at -64 C, but explode violently on warm-up toward room temperature

Synthesis of More Energetic N_5^+ Salts

Chem. Eur. J. ***2003,*** *9, 2840*

- Doubling of the N_5^+ content:

$$2\ N_5SbF_6 + Cs_2SnF_6 \xrightarrow[-78°C]{HF} (N_5)_2SnF_6 + 2\ CsSbF_6 \downarrow$$

- Successful synthesis of $(N_5)_2SnF_6$ demonstrates that polynitrogen salts with touching polynitrogen ions can be prepared

- The salt is friction sensitive and can decompose explosively, but under carefully controlled conditions, stepwise decomposition is possible

$$(N_5)_2SnF_6 \xrightarrow[20°C]{} N_5SnF_5 + \text{"}N_5F\text{"}$$

- N_5SnF_5 is a white solid, stable at room temperature
  - ➢ N_5SnF_5 was characterized by vibrational and NMR spectroscopy, but

    N_5F is too short-lived for experimental observation (J. Phys. Chem. A, 107, 6638 (2003))

Synthesis of More Energetic N_5^+ Salts

- **$N_5^+NO_3^-$**
  - ➢ Desired metathesis:

$$N_5SbF_6 + CsNO_3 \xrightarrow[-64 \text{ to } 20°C]{SO_2} N_5NO_3 + CsSbF_6\downarrow$$

  - ➢ Did not proceed because $CsNO_3$ is less soluble in SO_2 than $CsSbF_6$
  - ➢ U_L required for stabilization is 154 kcal/mol; estimate for $N_5^+NO_3^-$ is 129 kcal/mol

- **$N_5^+ClO_4^-$**
  - ➢ Desired metathesis resulted in:

$$N_5SbF_6 + CsClO_4 \xrightarrow[-78°C]{HF} NO^+ClO_4^- + CsSbF_6\downarrow + N_2$$

  - ➢ U_L required for stabilization is 138 kcal/mol; estimate for $N_5^+ClO_4^-$ is 125 kcal/mol

Synthesis of More Energetic N_5^+ Salts. Estimated Energy Content of $N_5^+N_3^-$

- Heat of formation of $N_5^+N_3^-$
  - ΔH_f (298) of $N_5^+{}_{(g)}$ = 351 kcal/mol   (calculated value)
  - ΔH_f (298) of $N_3^-{}_{(g)}$ = 43.2 kcal/mol   (NBS tables)
  - Lattice energy of $N_5^+N_3^- \approx 130$ 20 kcal/mol   (Christe estimate)

So ΔH_f (298) of $N_5^+N_3^-$ = 351 + 43 – 130 = 264   25 kcal/mol

- Energy density of $N_5^+N_3^-{}_{(s)}$ = 2.36 kcal/g

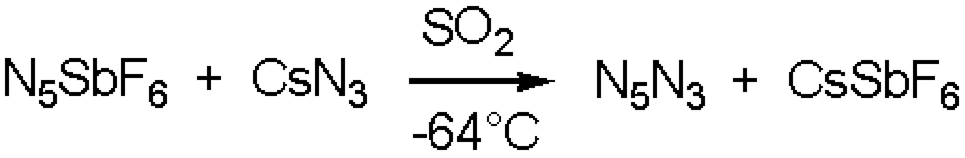
- Comparison with other molecular systems (kcal/g):

O_3	$C(N_3)_3^+N(NO_2)_2^-$	HN_3	$N_5^+N_3^-$	H_2/O_2
0.71	1.42	1.63	2.36	3.21

Can $N_5^+N_3^-$ and $N_5^+N_5^-$ exist?

(J. Am. Chem. Soc. 2004, 126, 834)

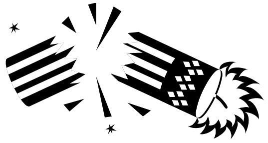
- Our theoretical calculations and Born-Haber cycles show that, contrary to a literature claim, both $N_5^+N_5^-$ and $N_5^+N_3^-$ are unstable by large margins.
- The use of vertical instead of adiabatic potentials and the assumption of vibrationally stable N_5 radicals as the decomposition products caused huge errors of about 100 kcal/mol per N_5 unit in the previous stability predictions.
- Our conclusion that $N_5^+N_3^-$ and $N_5^+N_5^-$ are unstable and decompose spontaneously with N_2 evolution was experimentally confirmed in our laboratory for $N_5^+N_3^-$
  - Desired metathesis:



$$N_5SbF_6 + CsN_3 \xrightarrow[-64°C]{SO_2} N_5N_3 + CsSbF_6$$

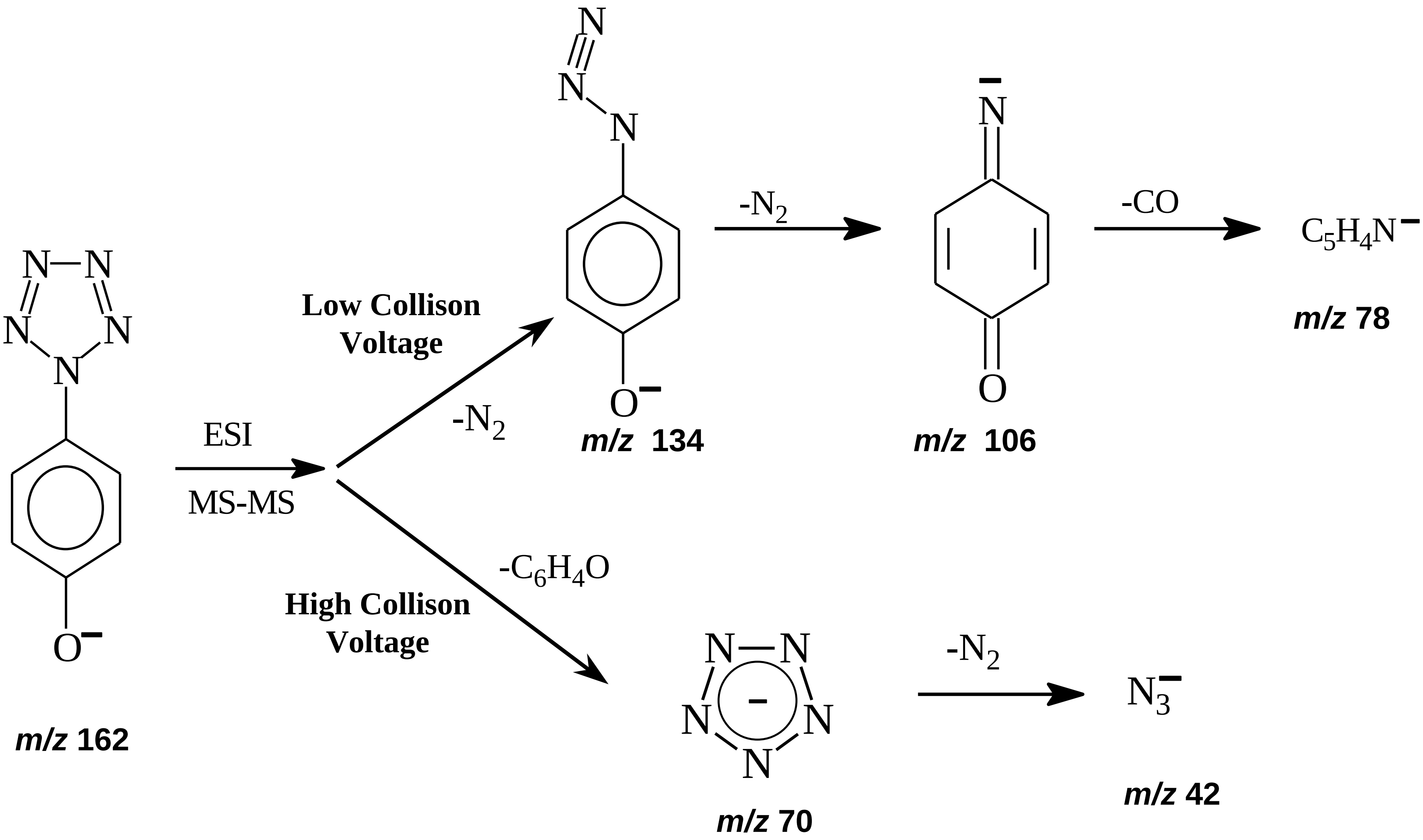
Obtained products:

$4\ N_2\ +\ CsSbF_6\ +$

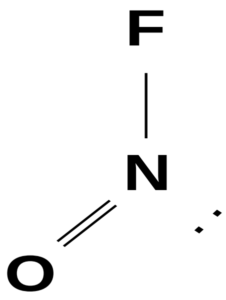


ES-IMS of para-Pentazolylphenolate

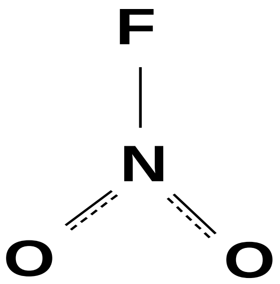
Angew. Chem. 41, 3051 (2002), and C&E News, Aug 19, 2002



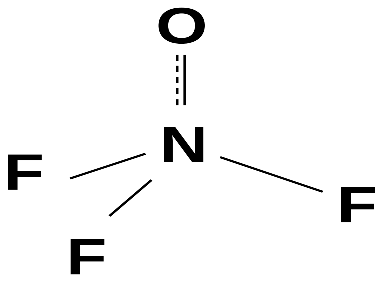
Presently Known, Stable Nitrogen Fluoride Oxides



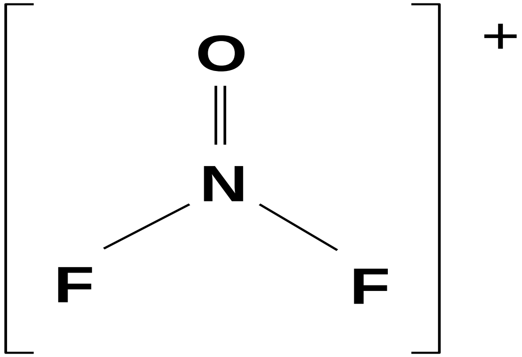
FNO



FNO_2



NF_3O



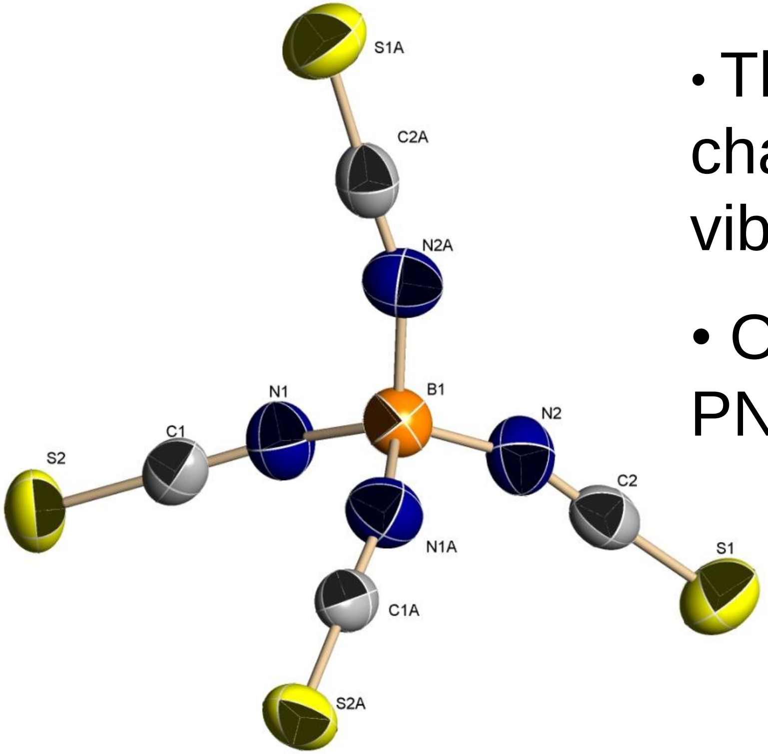
NF_2O^+

Coworkers *(wishful thinking)*

The Tetraisothiocyanato Borate Anion

- The new $B(NX)_4^-$ skeleton was synthesized from KSCN and BCl_3:

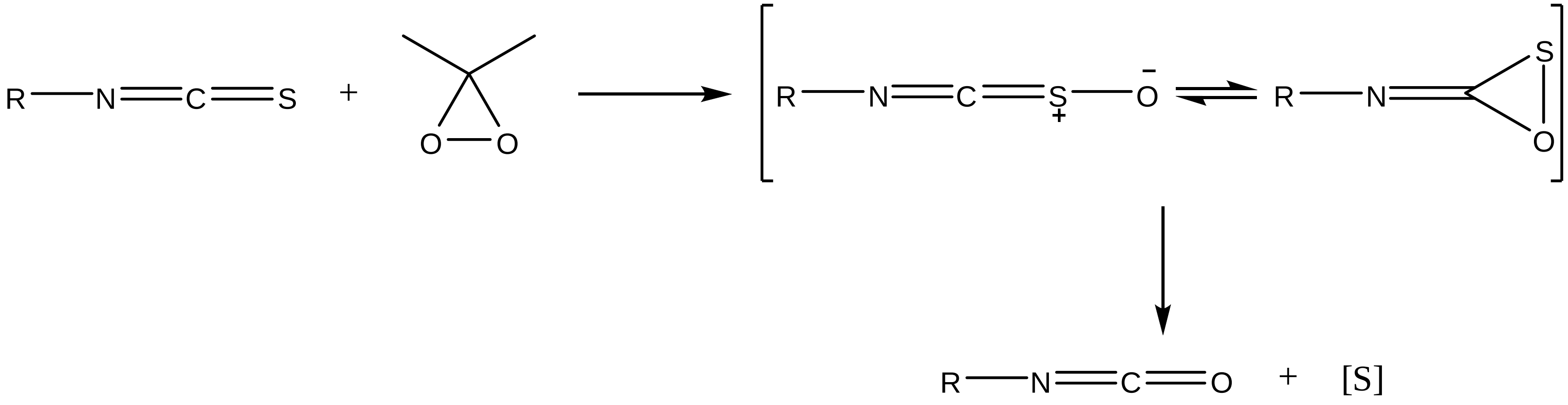
$$4\,KSCN + BCl_3 \xrightarrow{CH_3CN} K[B(NCS)_4] + 3\,KCl$$



- The compound was characterized by NMR and vibrational spectroscopy.
- Obtained crystal structure as $PNP^+[B(NCS)_4]^-$.

Oxidative Cleavage of $[B(NCS)_4]^-$

- Isothiocyanates can be converted into isocyanates by treatment with dimethyldioxirane:



- The isocyanate can then be further oxidized to the nitro compound:

$$R{-}N{=}C{=}O \xrightarrow{[O]} R{-}NO_2$$

The $[B(N(SiMe_3)_2)_4]^-$ Anion

- Another promising $B(NX)_4^-$ skeleton is $[B(N(SiMe_3)_2)_4]^-$
- Synthesis

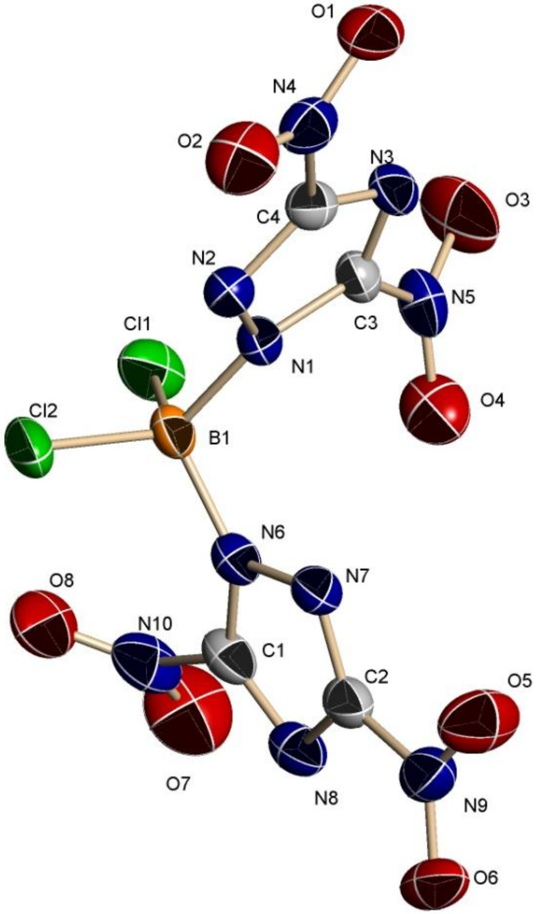
$$4\ KN(SiMe_3)_2 \quad + \quad BCl_3 \xrightarrow{CH_3CN} K[B(N(SiMe_3)_2)_4] \quad + \quad 3\ KCl$$

- Proposed conversions to $[B(NO_2)_4]^-$

$$K[B(N(SiMe_3)_2)_4] \xrightarrow{[O]} K[B(NO_2)_4] \quad + \quad 2\ Me_3SiOSiMe_3$$

Alternate Approach to DNT Borate Salts

$$N(CH_3)_4Cl + BCl_3 + 4\ KDNT \xrightarrow{SO_2} 2\ KCl + [N(CH_3)_4]^+[Cl_2B(DNT)_2]^- + 2\ KDNT$$

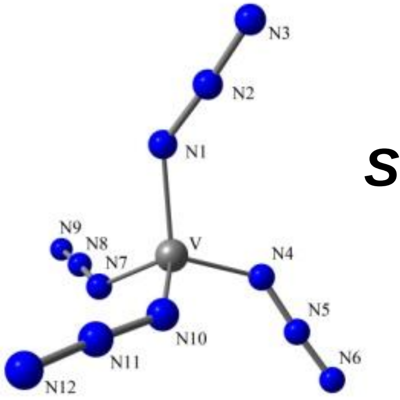


- Only partial ligand exchange (even at 100 C under autogenous pressure in a steel cylinder)
- $[N(CH_3)_4]^+[Cl_2B(DNT)_2]^-$ was characterized by its X-ray crystal structure, is hydrolytically stable and has a density of $\rho = 1.60\ g/cm^3$

Reaction of Vanadium(IV) Fluoride

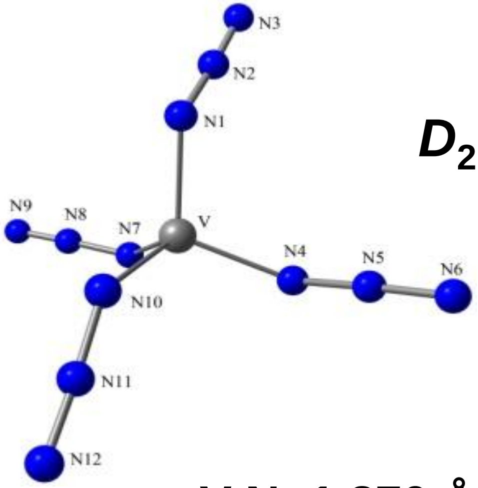
$$\mathbf{VF_4 \; + \; 4\,Me_3SiN_3 \xrightarrow{CH_3CN} V(N_3)_4 \; + \; 4\,Me_3SiF}$$

- Solid appears black, dilute solutions are dark red
- Stable at room temperature
- Very sensitive and explodes violently upon provocation
- MP2/MCP-TZP calculation results in S_4 structure, B3LYP/MCP-TZP calculation favors D_{2d} isomer.



$\boldsymbol{S_4}$

V-N: 1.841 Å



$\boldsymbol{D_{2d}}$

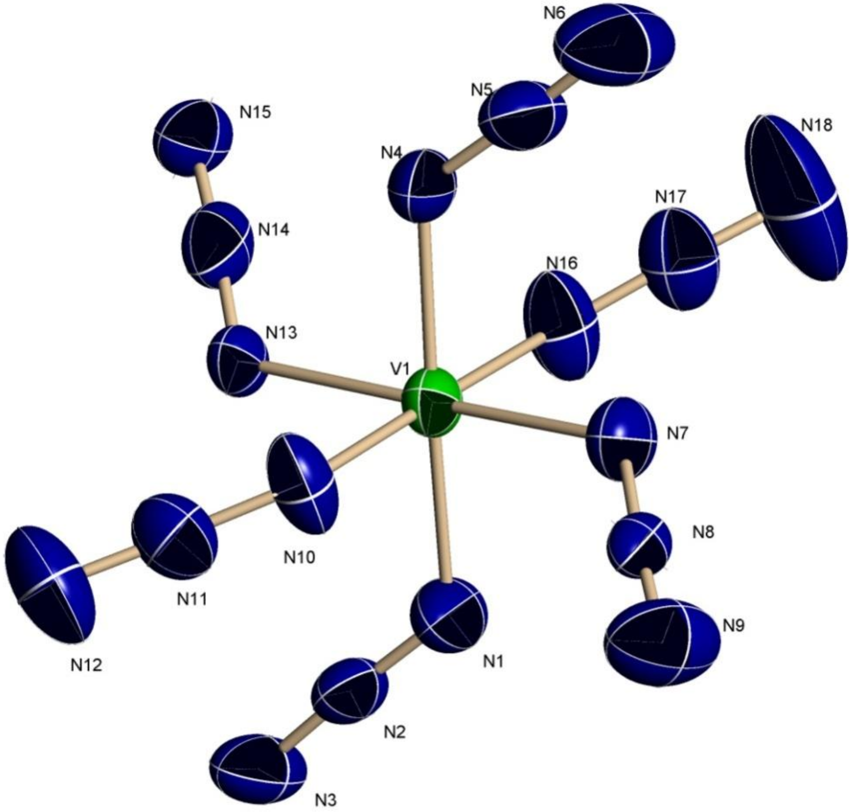
V-N: 1.870 Å

R. Haiges, J.A. Boatz, K.O. Christe, *Angew. Chem. Int. Ed.* 2010, *49*, 8008

Hexaazidovanadate(IV)

$V(N_3)_4 + 2\, A^+[N_3]^- \xrightarrow{CH_3CN} A_2[V(N_3)_6]$ A = PPh_4, PNP

- dark maroon to nearly black solids
- stable at room temperature
- melting point (decomp.):
  PPh_4^+ salt: 175 - 177°C
  PNP^+ salt: 169 - 172°C



Reaction of Vanadium(V) Fluorides

Reaction of VF_5 with Me_3SiN_3 did not result in the isolation of $V(N_3)_5$:

$$VF_5 \quad + \quad 5\ Me_3SiN_3 \xrightarrow{\qquad \mathbf{X} \qquad} V(N_3)_5 \quad + \quad 5\ Me_3SiF$$

Even at temperatures of -35°C, dinitrogen is released and $V(N_3)_4$ obtained:

$$2\ VF_5 \quad + \quad 10\ Me_3SiN_3 \xrightarrow{\qquad\qquad} 2\ V(N_3)_4 \quad + \quad 10\ Me_3SiF \ + \ 3\ N_2$$

Reaction of Vanadium(V) Fluorides contd.

A vanadium(V) azide was obtained by the following sequence:

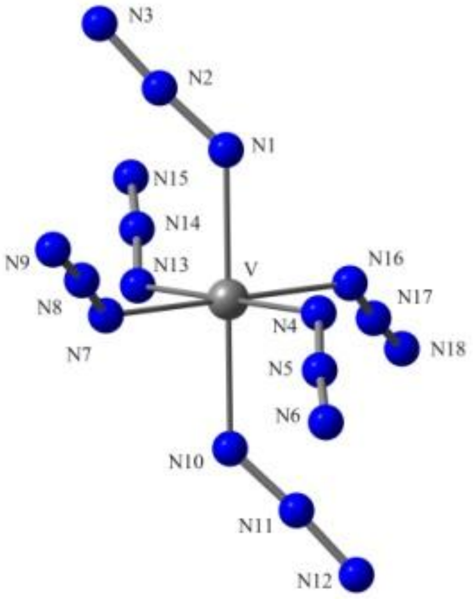
$$VF_5 \ + \ [NMe_4][F] \xrightarrow{\qquad\qquad} [NMe_4][VF_6]$$

$$[NMe_4][VF_6] \ + \ 6\ Me_3SiN_3 \xrightarrow{\qquad\qquad} [NMe_4][V(N_3)_6]$$

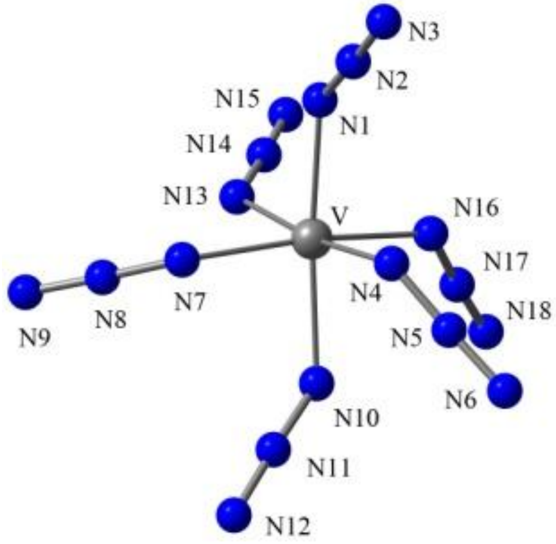
- dark maroon to nearly black amorphous solid
- thermally stable at room temperature
- highly shock-sensitive
- Only three other binary vanadium(V) species known: VF_5, VF_6^-, V_2O_5

Structures of Hexaazidovanadates

Predicted structures (MP2/MCP-TZP and B3LYP/MCP-TZP):



$[V(N_3)_6]^{2-}$: D_{3d}
octahedral VN_6 skeleton with
six similar V-N bonds
-N_3 groups are more ionic
V-N: 2.03 Å (B3LYP)
Exp: 2.00 Å



$[V(N_3)_6]^{-}$: C_1
distorted VN_6 skeleton with three
short and three long V-N bonds
-N_3 groups are more covalent
V-N: 1.96 Å (B3LYP)

Stabilized Vanadium Azide

$$V(N_3)_4 + 2\ \text{Bipy} \xrightarrow{CH_3CN} V(N_3)_4 \cdot 2\ \text{Bipy}$$

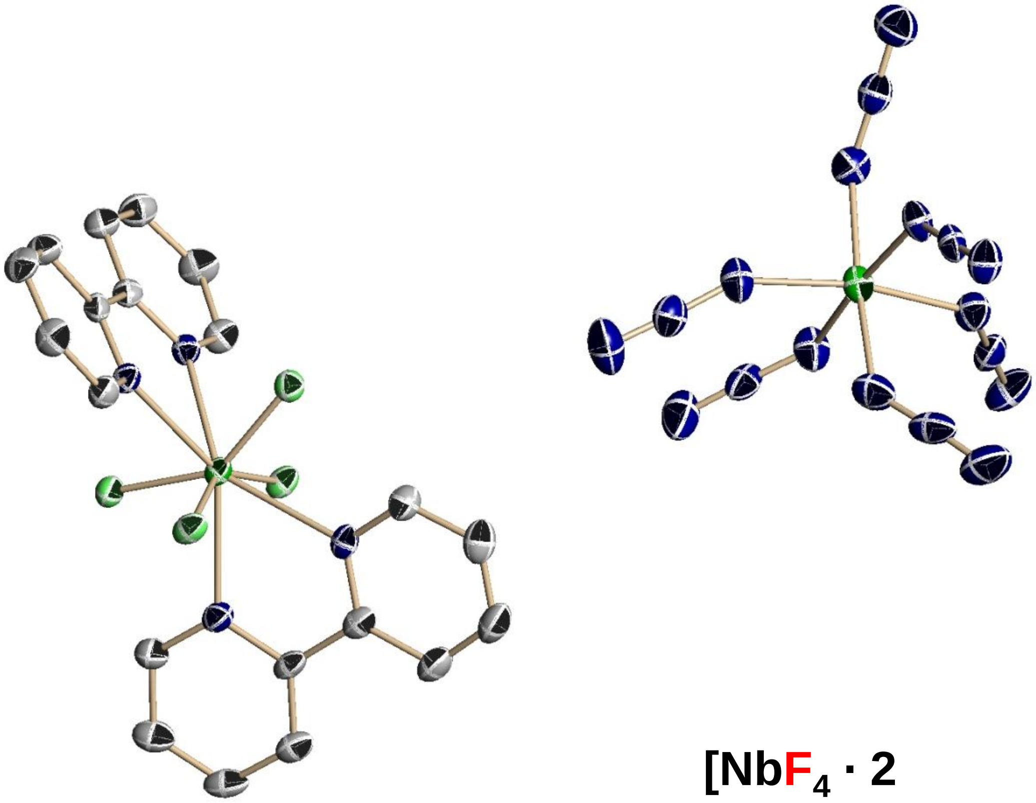
- dark maroon to nearly black solid
- thermally stable at room temperature
- much less shock-sensitive than parent compound
- only spectroscopy data
- no crystal structure so far

Niobium and Tantalum Fluorides

(Using only 3 Moles of TMSA per MF_5)

$$2\ MF_5 + 2\ Bipy + 6\ Me_3SiN_3 \longrightarrow [MF_4 \cdot 2\ Bipy][M(N_3)_6] + 6\ Me_3SiF$$

(M = Nb, Ta)



Only Anion exchanges Ligands

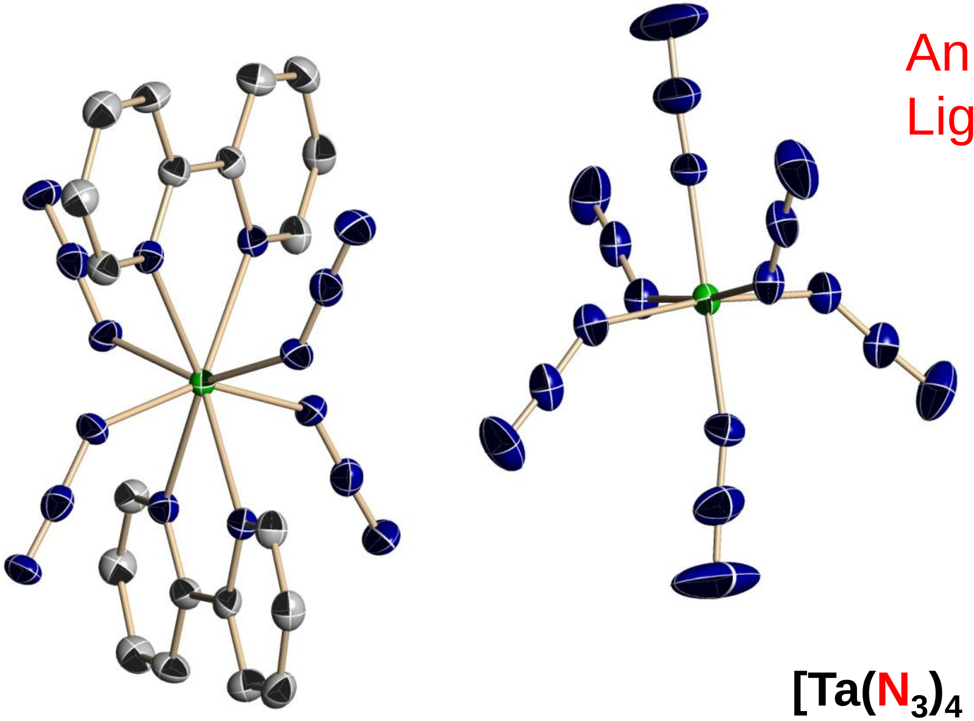
$[NbF_4 \cdot 2\ Bipy][Nb(N_3)_6]$

Niobium and Tantalum Fluorides

(Using an Excess of TMSA)

$$[MF_4{\cdot}2\ Bipy][M(N_3)_6] + 4\ Me_3SiN_3 \longrightarrow [M(N_3)_4{\cdot}2\ Bipy][M(N_3)_6] + 4\ Me_3SiF$$

(M = Nb, Ta)

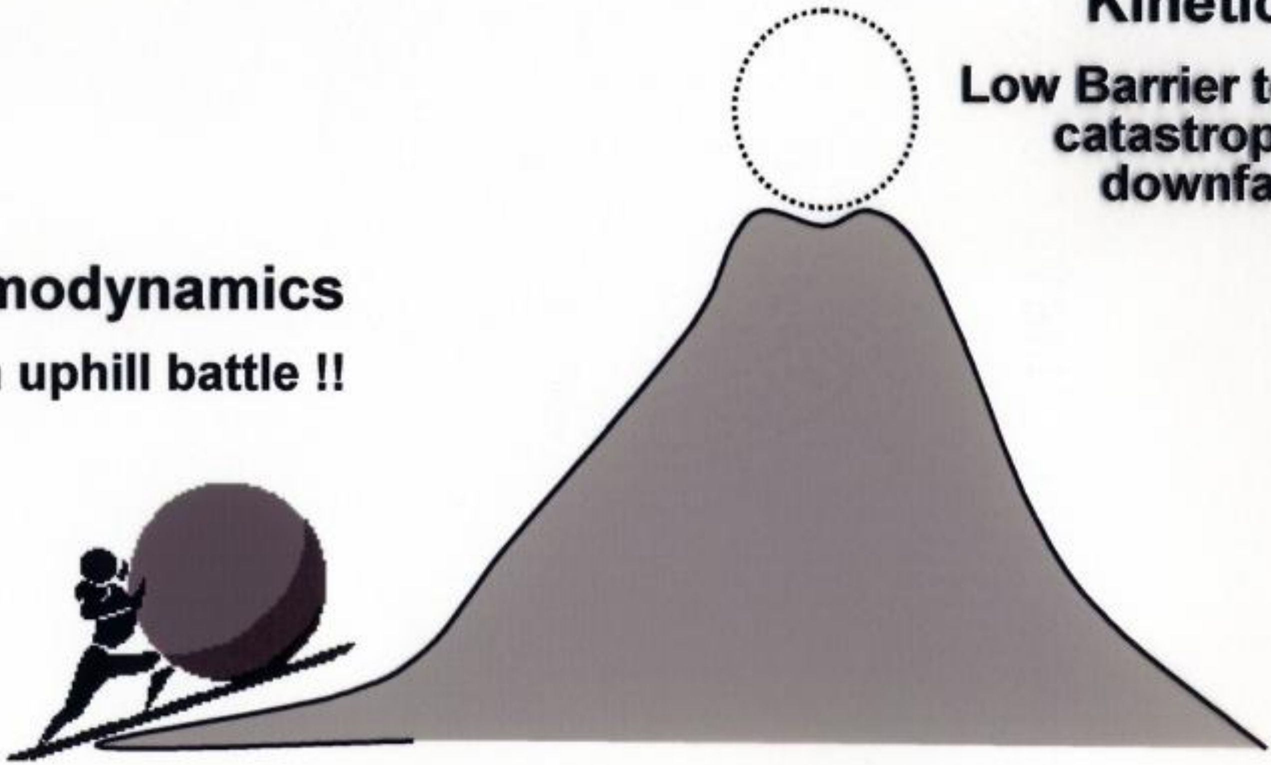


Anion *and* Cation undergo Ligand Exchange

$[Ta(N_3)_4 \cdot 2\ Bipy][Ta(N_3)_6]$

Polynitrogen for *Dummies I*

What has Thermodynamics and Kinetics got to do with it ??



Kinetics

Low Barrier towards catastrophic downfall

Thermodynamics

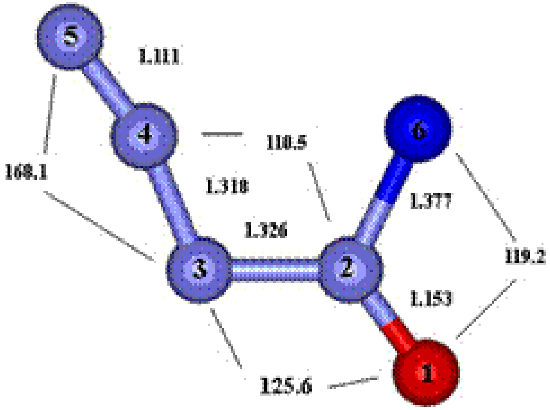
It is an uphill battle !!

Characterization of $N_3NFO^+SbF_6^-$

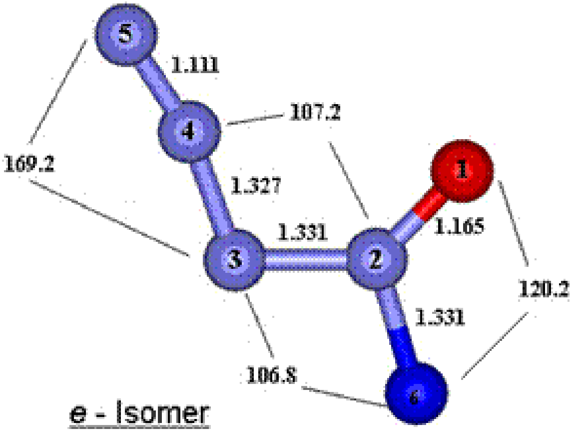
- $^{14/15}N$ and ^{19}F NMR and vibrational spectra show the presence of 2 isomers which we could not separate.

- Theoretical calculations at the B3LYP, MP2 and CCSD(T) levels showed two minimum energy structures (*z*- and *e*-isomers) of very similar energies ($\Delta E \leq 0.6$kcal/mol) and one cyclic isomer (5-membered N_4O-ring with F in α-position to O) which is 34.9 kcal/mol higher in energy.

- Calculated CCSD(T) structures (planar, C_s symmetry)

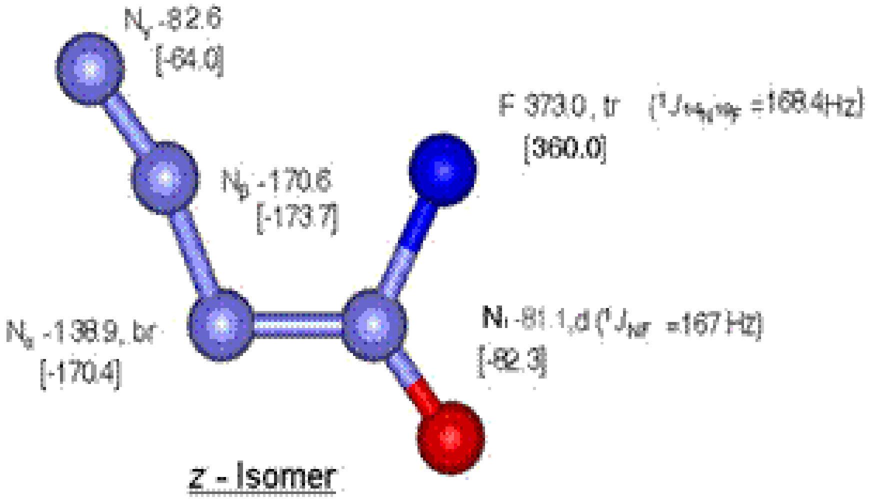


z - Isomer

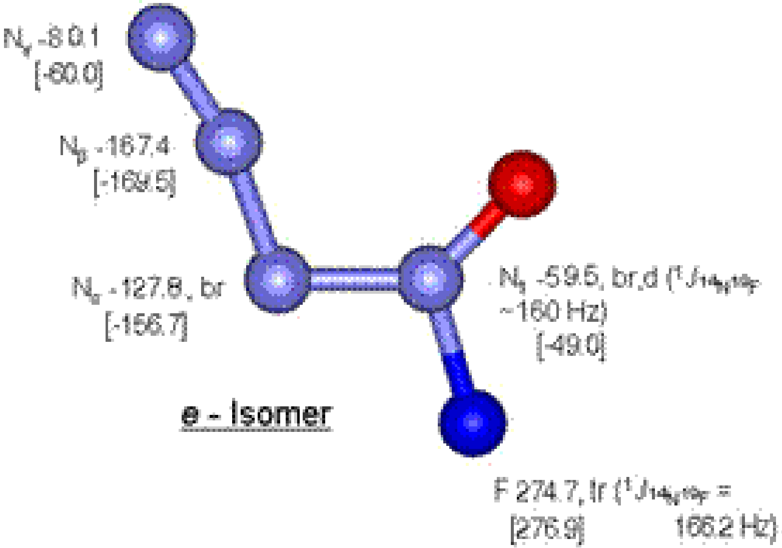


e - Isomer

NMR Parameters for the two N_3NFO^+ Isomers
(values calcd at B3LYP level in [ ])



z - Isomer



e - Isomer

Ratio of z- to *e*-isomer = 1:1.45

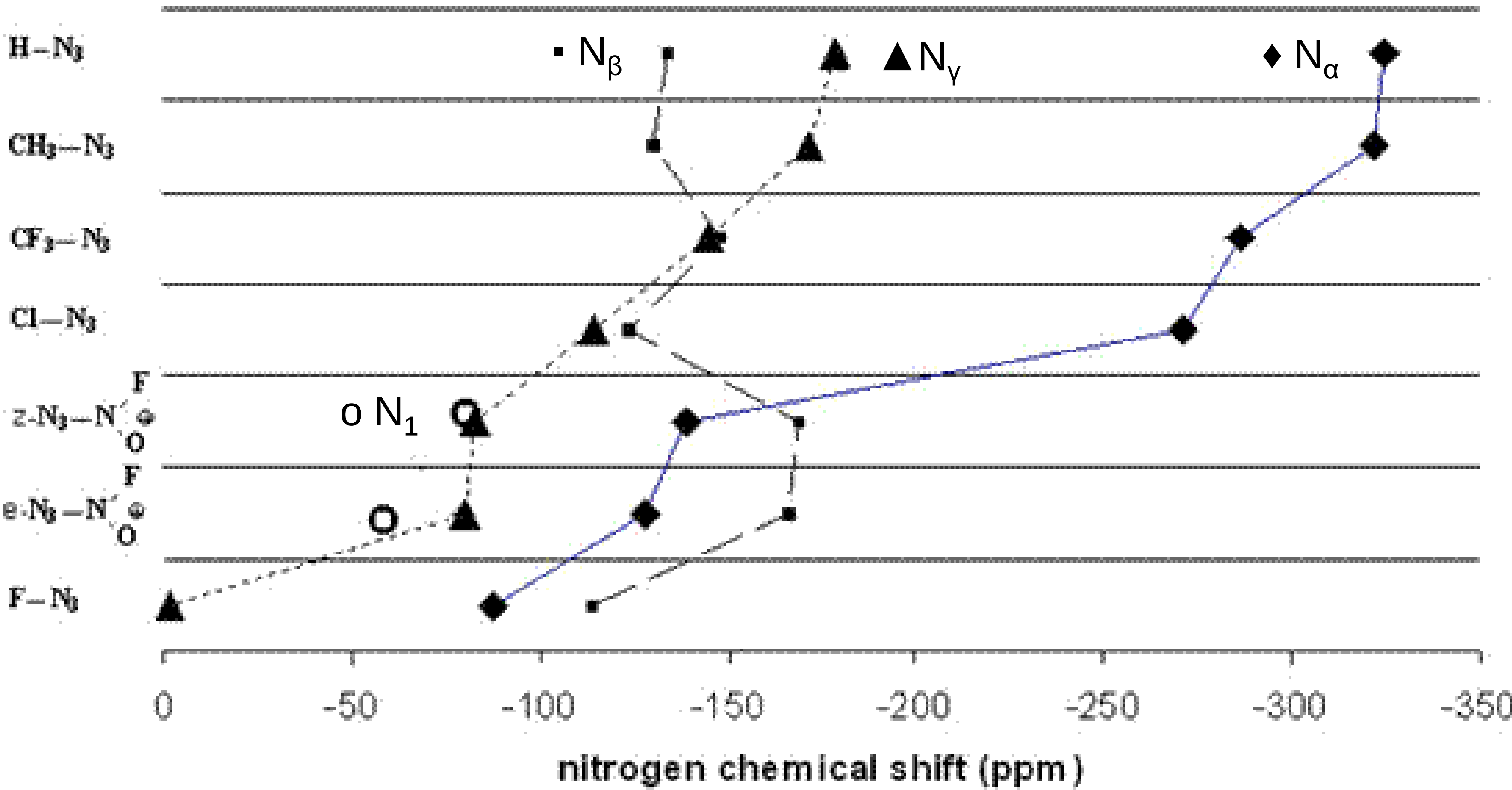
Properties of $N_3NFO^+SbF_6^-$

- $N_3NOF^+SbF_6^-$ is a white solid that is stable at room temperature.
- It thermally decomposes at 60 °C

$$3\ N_3NFO^+SbF_6^- \longrightarrow 3\ NO^+SbF_6^- + 4\ N_2 + NF_3$$

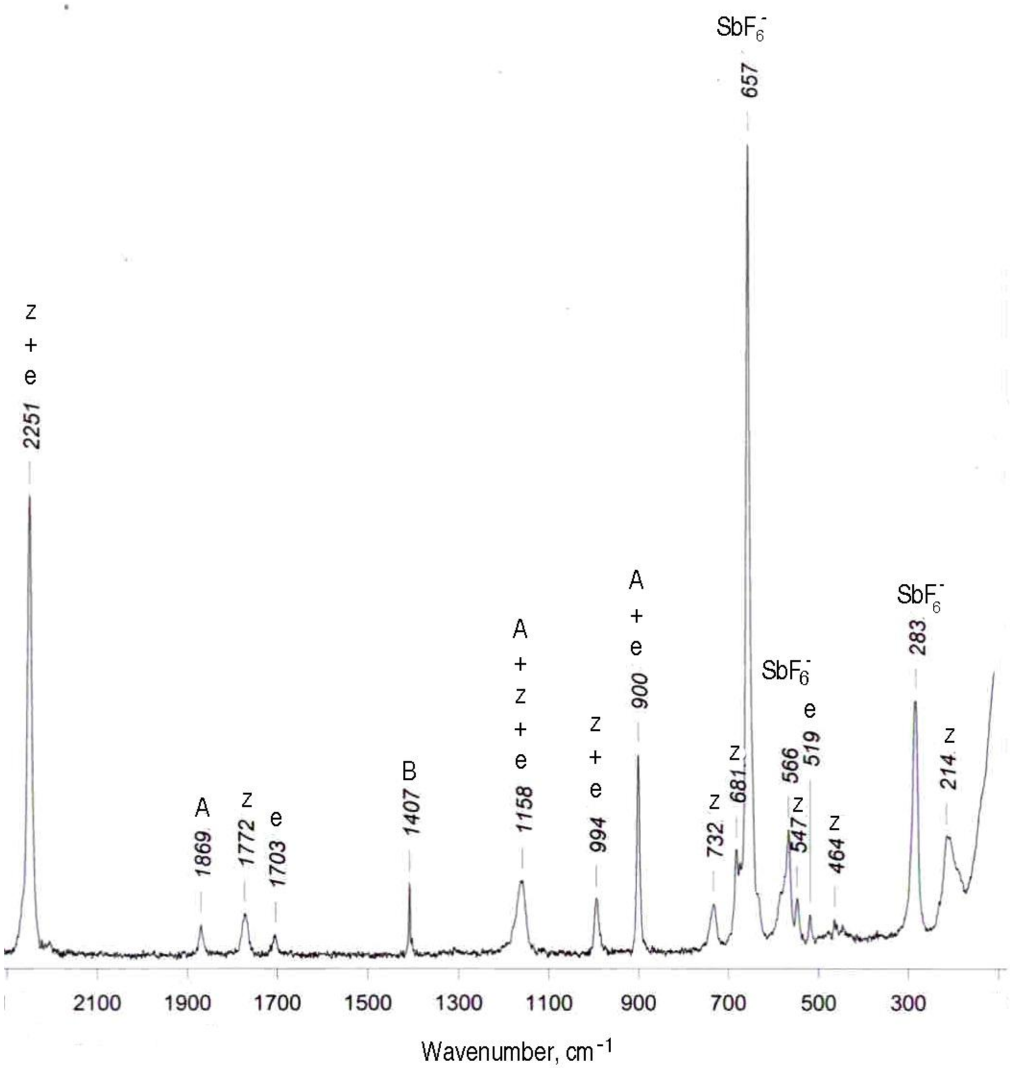
- It is
    - ➢ soluble in HF
    - ➢ does not detonate when struck with a hammer or scraped with a spatula
    - ➢ deflagrates when heated in an open flame
    - ➢ ignites ethanol and reacts violently with water

Comparison of NMR Parameters with Those of Related Covalent Azides



- With increasing electron withdrawing power of the ligand, N_α and N_γ become deshielded

Typical Raman Spectrum of $N_3NFO^+SbF_6^-$



A = NF_2O^+

B = NO_2^+

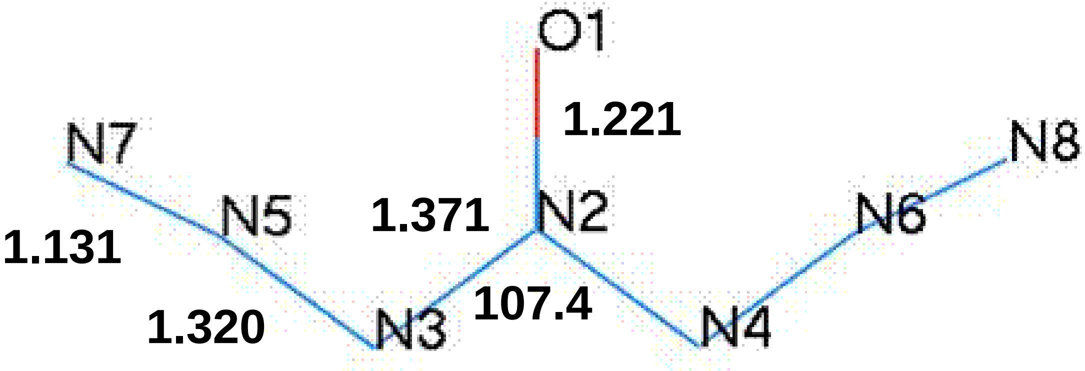
1:2 Reactions

- We were not able to observe directly the postulated N_7O^+ cation
- Obtained very strong experimental and computational support for the formation of N_7O^+ as an intermediate that rapidly loses N_2O at its formation temperatures.

$$NF_2O^+ + 2\ HN_3 \longrightarrow N_3N(O)N_3^+ + 2\ HF$$

$$N_3N(O)N_3^+ \longrightarrow N_5^+ + N_2O$$

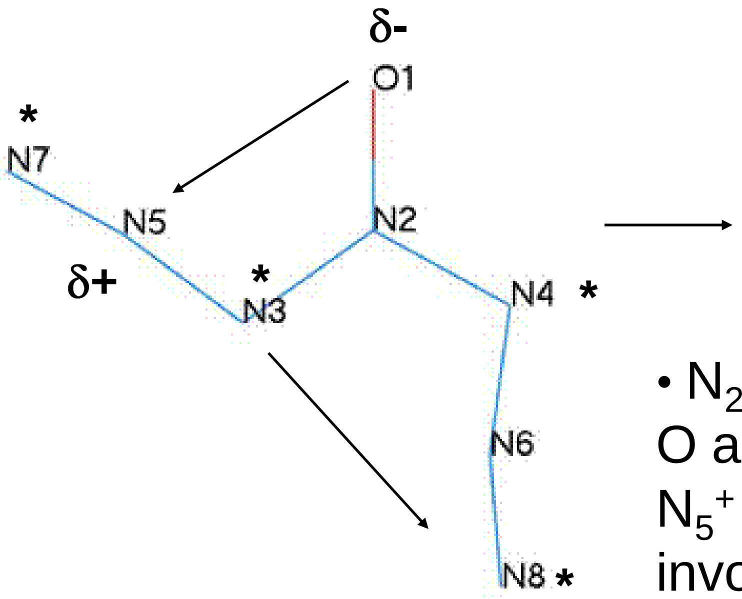
- Predicted Structure (C_{2v}) at the CCSD(T)/6-31G(d) level:



N_7O^+

- The azido arms in N_7O^+ are very floppy and a C_s isomer is only 2.7 kcal/mol higher in energy than the C_{2v} isomer.

- The mechanism of the N_2O elimination was established by isotopic labeling experiments and multinuclear NMR analysis of the decomposition products.



$N^*_7{=}N_5{=}O_1$ + $N_5^+(C_{2v})$ equally labeled in all 5 positions

- N_2O labels suggest that negatively charged O attacks the positively charged N5, and the N_5^+ labels show that the N_2O elimination involves the C_s isomer and a cyclic intermediate.

Formation Mechanism of N_7O^+ and Improved Synthesis of N_5^+

- The mechanism of the N_2O elimination was also supported by preliminary theoretical calculations of the barriers. The N_2O elimination from C_s N_7O^+ has a barrier of less than 43 kcal/mol, while the N_2O elimination from N_3NFO^+ has a barrier of about 80 kcal/mol, explaining why N_7O^+ is thermally much less stable than N_3NFO^+.
- The synthesis of N_5^+ from NF_2O^+ and excess HN_3 offers the following advantages over our previous synthesis from N_2F^+.
  - $NF_2O^+Sb_2F_{11}^-$ can be readily prepared in one-step and quantitative yield from commercially available NF_3, N_2O and SbF_5.

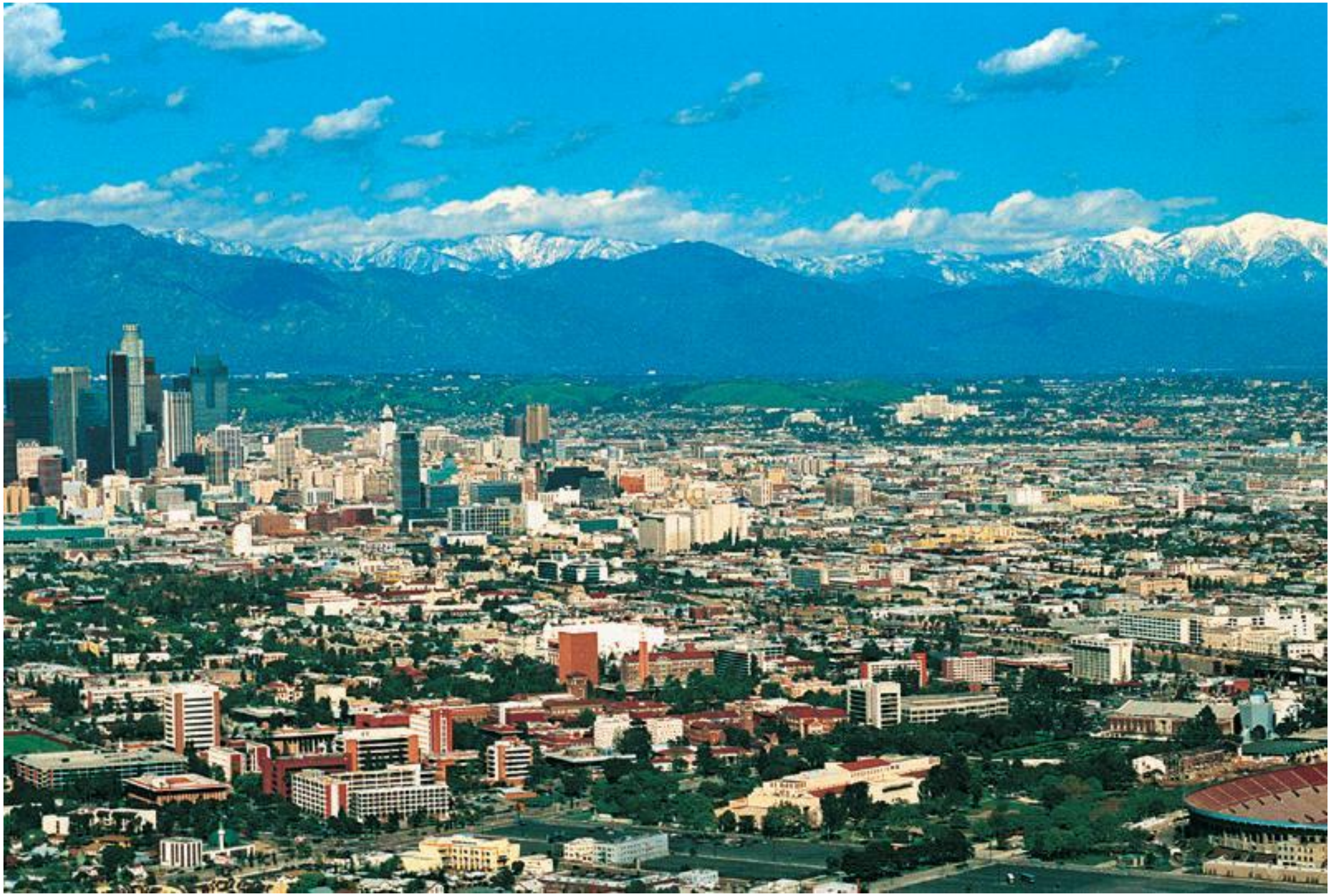
$$NF_3 + N_2O + 2\,SbF_5 \xrightarrow{150\text{ C}} NF_2O^+Sb_2F_{11}^- + N_2$$

Christe, JACS, **117**, 6136 (1995)

  - N_5^+ with ^{15}N labels in all 5 positions can be obtained from singly labeled N_3^-.

Magic Chemistry at Loker

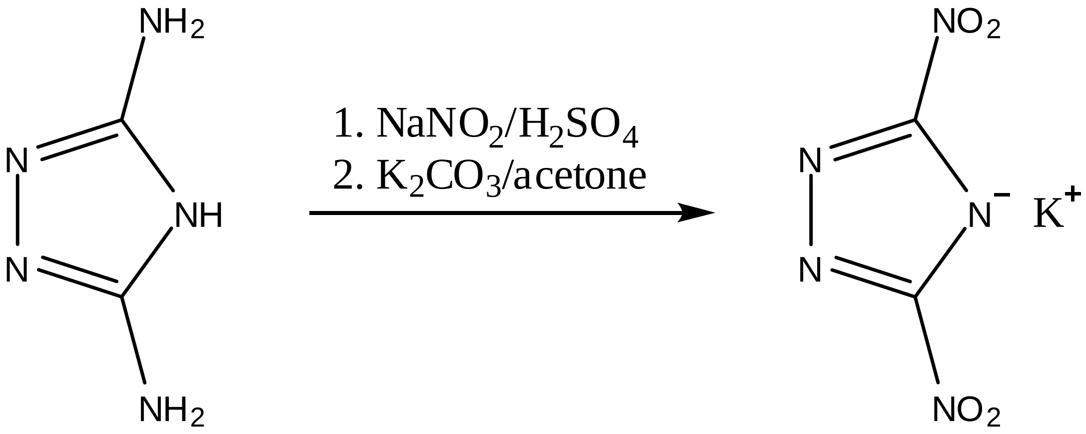
Wintertime in LA



Plans for Future Research

- Scale up the synthesis of $[NH_4][B(DNT)_4]$ and fully characterize it (we really need our own test equipment! Can you help?).
- File patents for $[NH_4][B(DNT)_4]$.
- Grow single crystals of $B(DNT)_4^-$ salts for structure determinations.
- Synthesize ionic liquids by replacement of NH_4^+ or Na^+ by energetic N-heterocyclic cations.
- If everything looks promising, transition the technology to NAVY laboratories for further testing and formulating.
- Continue to pursue the syntheses of the $[B(NO_2)_4]^-$ and $[B(DN)_4]^-$ anions.

Literature Synthesis of KDNT



KDNT

V. M. Chernyshev, N.D. Zemlyakov, V. B. Il’in, V. A. Taranushich, *Russ. J. Appl. Chem.* 2000, 73, 839.