Polynitrogen & High Nitrogen Chemistry: A New World of Challenges

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14. ABSTRACT
Polynitrogen compounds contain only nitrogen atoms and are expected to have unusual properties. Most important among these are High endothermicity šGreenŠ propellant šcombustionŠ product is only gaseous N2 High density High Isp values when compared to other monopropropellants or bipropellants High detonation velocity

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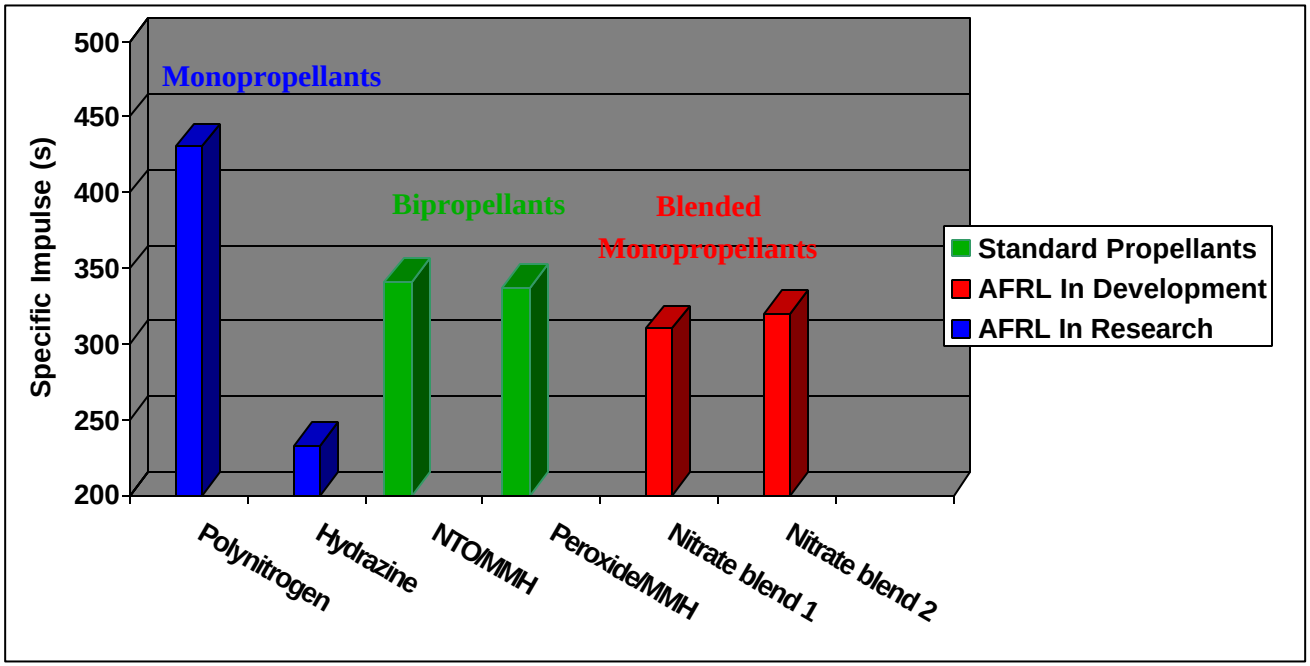
Why Polynitrogen Compounds ?

- Polynitrogen compounds contain only nitrogen atoms and are expected to have unusual properties. Most important among these are:
  - *High endothermicity*
  - *"Green" propellant*

    "combustion" product is only gaseous N_2
  - *High density*
  - *High* I_{sp} *values when compared to other monopropropellants or bipropellants*

High detonation velocity

Predicted Specific Impulse (s) Values for Neutral Polynitrogen Compounds

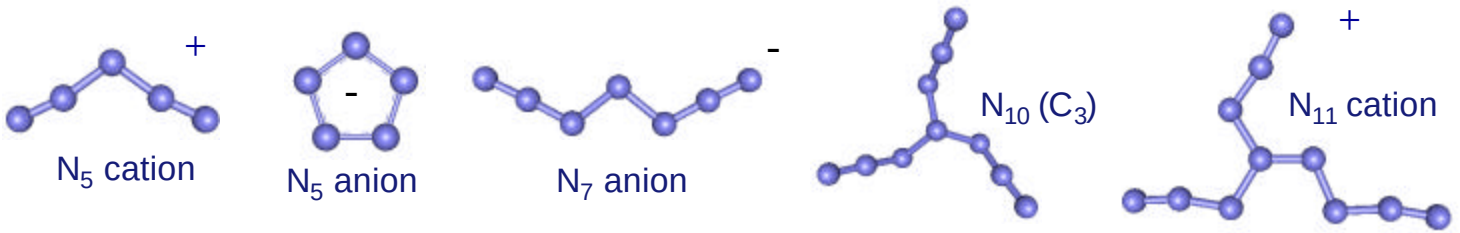


Polynitrogen Program Objectives

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

Technical Approach:

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



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≡C	194 kcal/mol

Nitrogen bond enthalpies	
N–N	38 kcal/mol
N=N	100 kcal/mol
N≡N	226 kcal/mol

$(–HC=CH)_n–$ +34 $HC\equiv CH$

85 + 143 ⟶ 194

stable polymers, unstable monomers

$(–N=N)_n–$ -88 $N\equiv N$

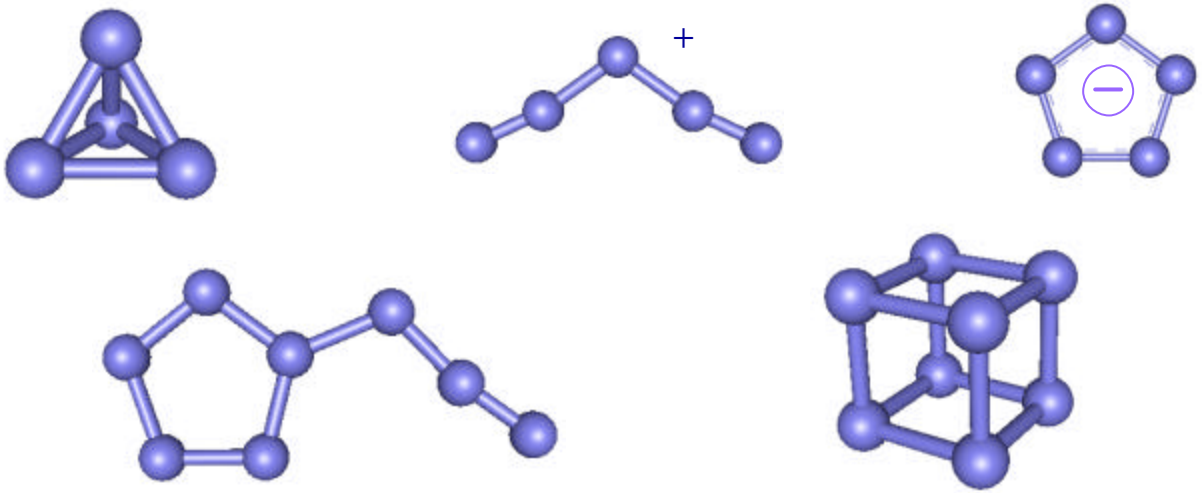
38 + 100 ⟶ 226

unstable polymers, stable monomer

This is the reason why N-N polymers

Research Philosophy and Technical Approach

Initially we preferred catenated over cyclic or polycyclic compounds



- Although polycyclic compounds are more energetic due to strain energy, and some of them have large barriers to decomposition (tetrahedral N_4), synthetic routes for their preparation are much more difficult

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

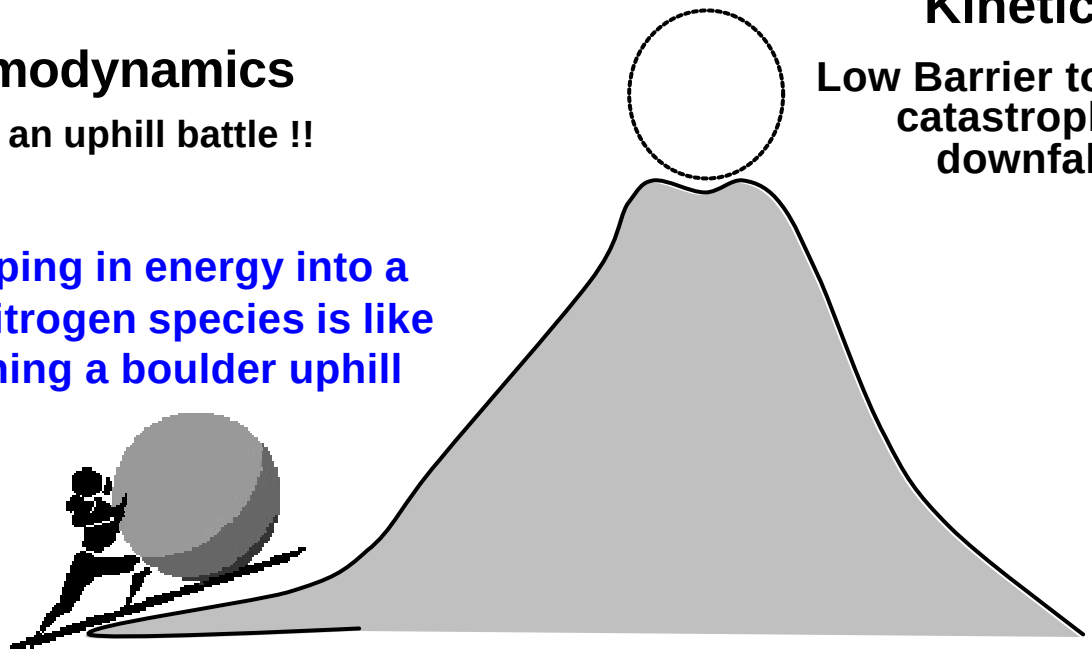
Thermodynamics

It is an uphill battle !!

Kinetics

Low Barrier towards catastrophic downfall

Pumping in energy into a polynitrogen species is like pushing a boulder uphill

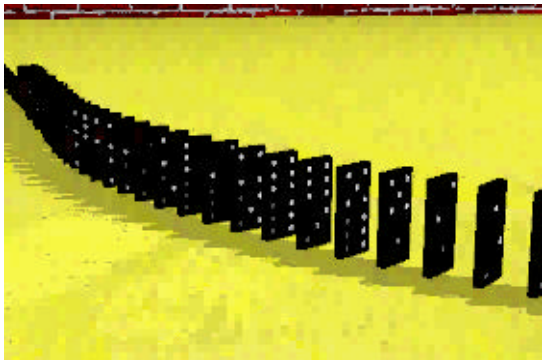


Polynitrogen for Dummies

- **Metastability requires a delicate balancing act !!**

Polynitrogen for Dummies

Avoid a domino effect !!!



Assembling a polynitrogen chain is like assembling metastable dominos with perfect spacing, without prematurely triggering an unwanted collapse

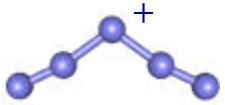
Recipe for Synthesizing Neutral Polynitrogen Compounds

- Combine a polynitrogen cation with a polynitrogen anion to form a neutral polynitrogen compound.

$$N_x^+ + N_y^- \longrightarrow N_{x+y}$$

ONLY TWO STABLE POLYNITOGEN IONS KNOWN TO EXIST IN BULK

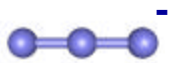
Cation



N_5^+ cation

(discovered in 1999, AFRL, Christe)

Anion



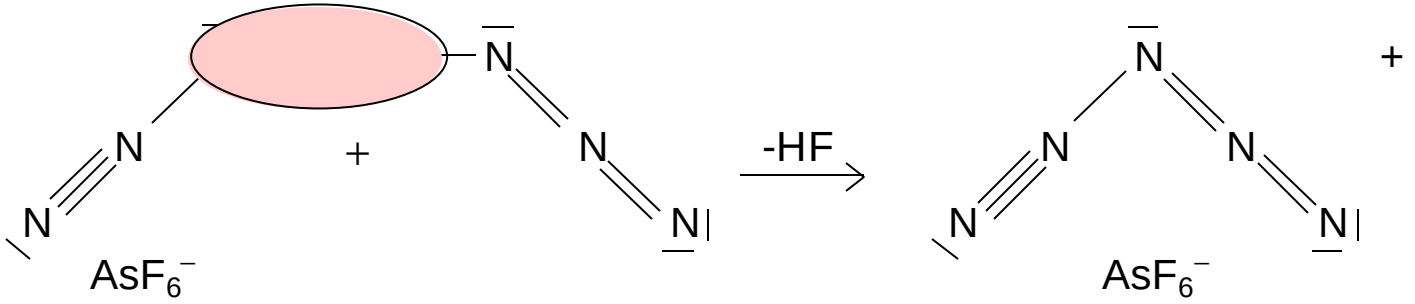
N_3^- anion

(discovered in 1890, Curtius)

Selection of Suitable Starting Materials for N_5^+ Synthesis

- Requirements:
  - Starting fragments must have relatively weak bonds
  - Must have formal positive charge (first IP of N2 = 359 kcal/mol)
  - Coupling reaction must be endothermic
  - Suitable solvent must be used as a heat sink and for stabilization

- Ideal candidate system:



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 $N_2F^+SbF_6^-$:

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

Aim: Can we cut any steps and decrease the synthesis time?

trans-cis Isomerization of N_2F_2

- ✓ Improved process (only ~10% SbF_5 needed as a catalyst)

$$\textit{trans}\text{-}N_2F_2 + SbF_5 \xrightarrow[4\ \text{days}]{\text{room temperature}} N_2F^+Sb_2F_{11}^- + \textit{cis}\text{-}N_2F_2$$

- ✓ Other process:

$$\textit{trans}\text{-}N_2F_2 \xrightarrow[15\ \text{hours}]{AlF_3,\,45\,^\circ C} \textit{cis}\text{-}N_2F_2$$

- ✓ Catalyst is not consumed and can be reused
- ✓ Gives pure *cis*-N_2F_2 in high yield.

Actual Synthesis of $N_5^+AsF_6^-$

- Reaction system worked as planned:

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

  - High yield
  - Only byproducts were 20-40% $H_2N_3^+AsF_6^-$
  - 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

Characterization of $N_5^+AsF_6^-$

- ^{14}N and ^{15}N NMR spectroscopy
- Low-temperature Raman and IR spectroscopy of normal and isotopically labeled N_5^+
- Normal coordinate analysis
- Mass spectrometry
- Calculations:
  - Electronic structure and geometry
  - Vibrational spectra, including isotopic shifts
  - NMR chemical shifts
  - Heat of formation

Vacuum Line Synthesis

Safer replacements for HN_3 in the N_5^+ synthesis

- HN_3 is very shock sensitive and frequently explodes in the presence of fluorinating agents (possible formation of FN_3)

- HN_3 can be replaced by insensitive, commercially available $(CH_3)_3SiN_3$ (TMS azide)

$$N_2F^+MF_6^- + (CH_3)_3SiN_3 \xrightarrow{SO_2} N_5^+MF_6^- + (CH_3)_3SiF \quad (M = As, Sb)$$

- HF solutions of HN_3 generated from NaN_3 and HF are another alternative to handling HN_3 directly

- Use of FEP-double U-tube apparatus to generate HN_3 *in situ. AVIOD METAL VALVES AND CONNECTORS*

- N_5^+ formation has been demonstrated for both systems in high yield, and N_5SbF_6 is now routinely prepared on a 5 g scale

Background in Nitrogen Chemistry

- $HN(SO_2F)_2$ and $HN(SO_2CF_3)_2$: Bis(fluorosulfonyl) and bis(trifluoromethylsulfonayl)imides and their derivatives (Electrophiles)
- Synthesis and reactivity of Perfluorovinylamines: R_fN-$CF=CF_2$ (fire retardants, surfactants etc.)
- Phosphonitrilic compounds: N_3P_3 monomers/prepolymers
- Triazenes, Mono- and Dicarbaphosphazenes: $N_3C_xP_{3-x}$ and P-C-N polymers
- Sappharenes, Sulfur/Selenium-Nitrogen macrocyclic ring systems.

Oxidizing Power of N_5^+

- The electron affinity of N_5^+ was determined by examining its ability to oxidize the following substrates:

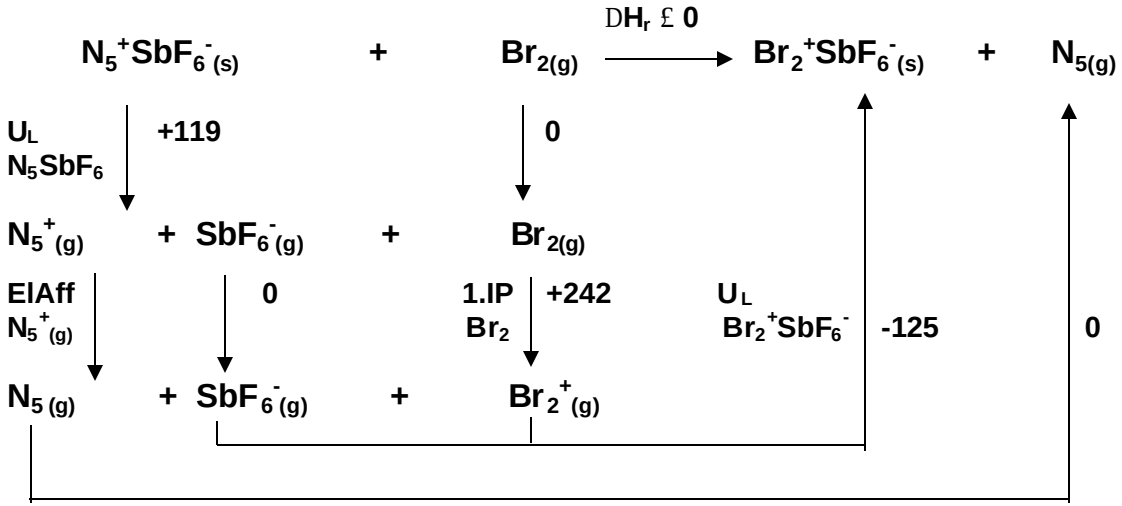
	First IP of substrate (eV)
$N_5^+SbF_6^- + NO \longrightarrow NO^+SbF_6^- + 2.5\ N_2$	9.26
$N_5^+SbF_6^- + NO_2 \longrightarrow NO_2^+SbF_6^- + 2.5\ N_2$	9.75
$N_5^+SbF_6^- + Br_2 \longrightarrow Br_2^+SbF_6^- + 2.5\ N_2$	10.52
$N_5^+SbF_6^- + Cl_2 \not\longrightarrow Cl_2^+SbF_6^- + 2.5\ N_2$	11.48
$N_5^+SbF_6^- + O_2 \not\longrightarrow O_2^+SbF_6^- + 2.5\ N_2$	12.07
$N_5^+SbF_6^- + 2\ Xe \not\longrightarrow Xe_2^+SbF_6^- + 2.5\ N_2$	12.13

- N_5^+ is a weaker oxidizer than PtF_6, which can oxidize O_2 to O_2^+. It is also a weaker oxidizer than O_2^+, which can oxidize Xe to Xe_2^+

Electron Affinity of N_5^+

- Electron affinity (EA) of N_5^+ needed for stability predictions of new N_5^+ salts using Born-Haber cycles

- EA of an oxidizer equals the IP of the substrate for gas-phase reactions; when solids are involved, lattice energy changes must be included



- The EA of N_5^+ falls between 236 and 255 kcal/mol (10.24 – 11.05 eV); it is a powerful one-electron oxidizer that neither fluorinates nor oxygenates

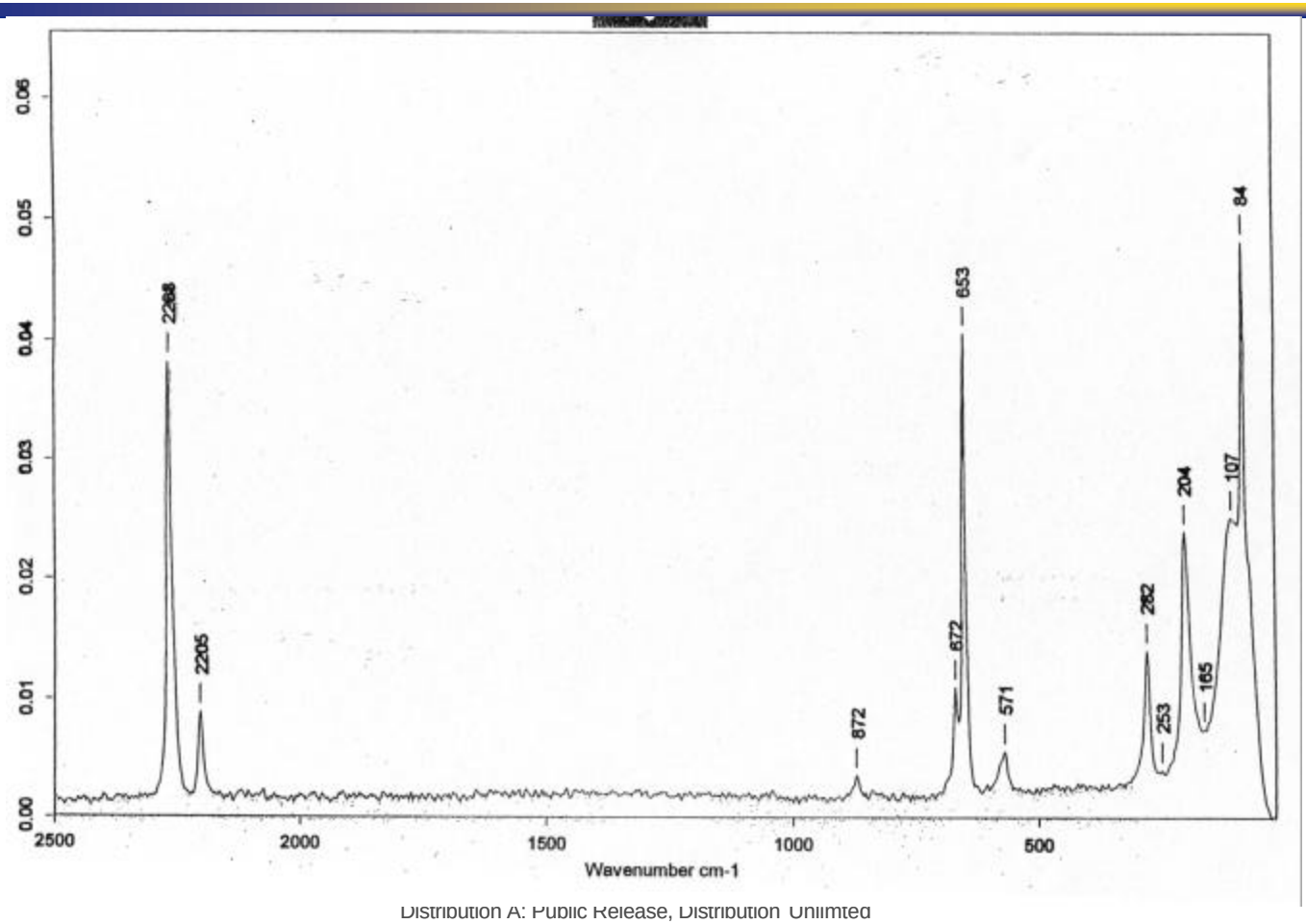
The Taming of $N_5^+SbF_6^-$

- Desired a more stable N_5^+ salt
- Prepared $N_5^+SbF_6^-$:

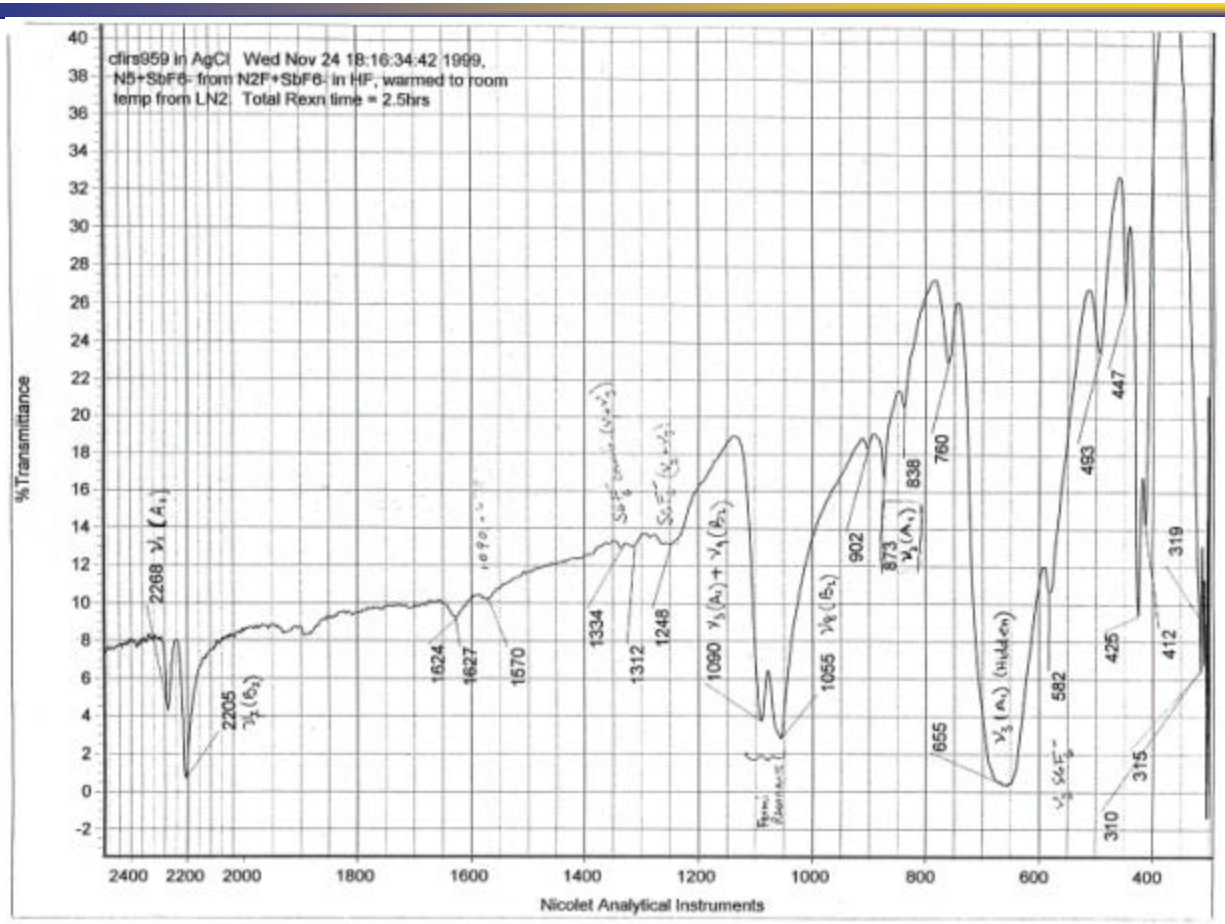
$$N_2F^+SbF_6^- + HN_3 \xrightarrow[-78°C \text{ to RT}]{HF} N_5^+SbF_6^- + HF$$

- Properties of $N_5^+SbF_6^-$:
  - White solid
  - Stable to 70°C
  - Obtained in high purity
  - Does not explode at 150 kg•cm (impact sensitivity test)
  - Exhibits all the still missing vibrational bands with the predicted frequencies
  - Soluble in SO_2, SO_2ClF, and HF
  - Are preparing it routinely on a 5 g scale

Raman Spectrum of $N_5^+SbF_6^-$



Infrared Spectrum of $N_5^+SbF_6^-$

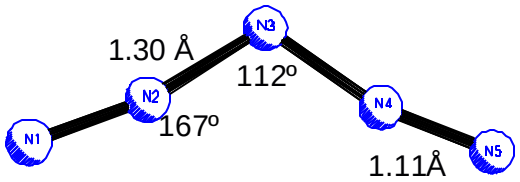


Vibrational Assignments for N_5^+

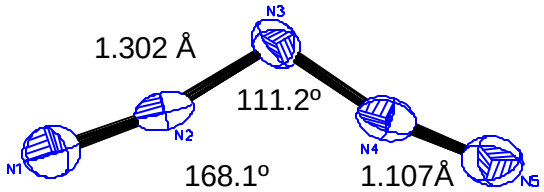
Observed		Calculated		
IR	Raman	B3LYP/ 6-311+G(2d)	CCSD(T)/ 6-311+G(2d)	Assignment
2268	2268	2236	2229	ν_1 (A_1)
2205	2205	2282	2175	ν_7 (B_1)
1090 (Fermi Resonance)		1167	1032	ν_3 (A_1) + ν_9 (B_2)
1055 (Fermi Resonance)				ν_8 (B_2)
873	872	850	818	ν_2 (A_1)
	672	678	644	ν_3 (A_1)
	478	502	475	ν_5 (A_2)
425		424	405	ν_6 (B_1)
412	414	436	399	ν_9 (B_2)
	204	193	181	ν_4 (A_1)

Geometry of the N_5^+ Cation

V-Shaped Geometry

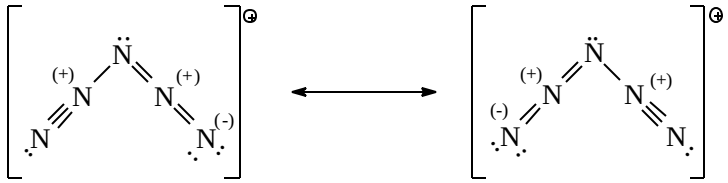


Calculated Structure

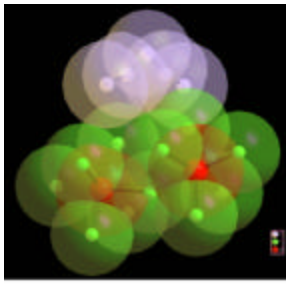


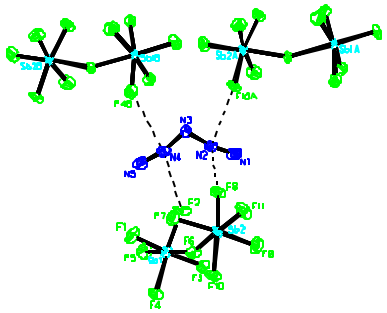
Experimental Structure

Vij, Wilson, Vij, Tham, Sheehy & Christe,
J. Am. Chem. Soc., **2001**,*123*, 6308-6313



Resonance Structure





N2 makes contacts at 2.723 and 2.768 Å
N4 contacts are at 2.887 and 2.814 Å

C&E News, **2000**, *78*, 41

Synthesis of New, More Energetic N_5^+ Salts

- Salts with Energetic Counterions – $N_5^+N_3^-$
  - Desired Metathesis:

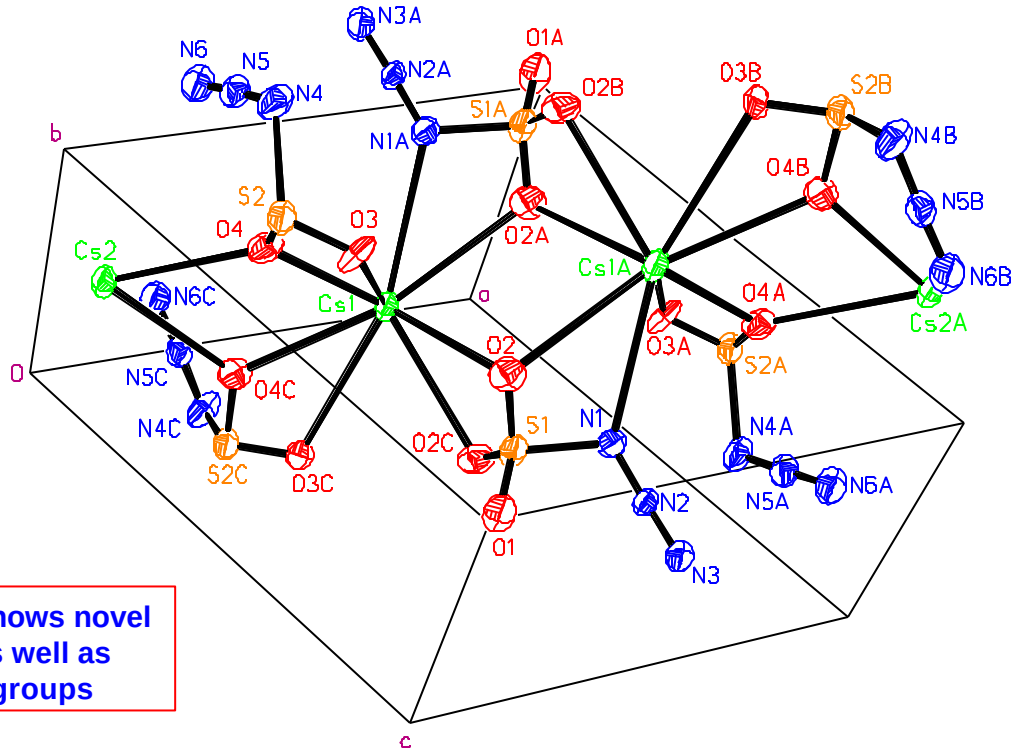
$$N_5SbF_6 + CsN_3 \xrightarrow[-64°C]{SO_2} N_5N_3 + CsSbF_6\downarrow$$

  - Obtained Products

$$CsSbF_6 + 4\,N_2 + \text{  }$$

  - Born-Haber Cycle Shows that Stabilization of $N_5^+N_3^-$ Requires a Minimum Lattice Energy of 183 ± 20 kcal/mol, but Estimated U_L for $N_5^+N_3^-$ Is only 130 kcal/mol

Unexpected complexation of SO_2 with the azide ion in CsN_3



Structure shows novel SO_2N_3 as well as SO_3N_3 groups

Synthesis of New, More Energetic N_5^+ Salts

- Salts with Energetic Counterions – $N_5^+NO_3^-$
  - 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_5NO_3 Is 129 kcal/mol

- Salts with Energetic Counterions – $N_5^+ClO_4^-$
  - 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_5ClO_4 Is 125 kcal/mol

Synthesis of more energetic N_5^+ salts, and 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 $N_5^+N_3^-$ ≈ 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

Synthesis of new N_5^+ salts $N_5B(CF_3)_4$

- N_5SbF_6 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 mass balance
  - Characterized by vibrational spectroscopy
  - Characterized by ^{14}N, ^{11}B, and ^{13}C NMR
  - Indefinitely stable in HF solution at room temperature with no decomposition products nor any unidentified species

(In)Compatability of N_5^+

Conclusion……Attempts to couple N_5^+ with energetic anions may result in explosive reactions !!!

$N_5^+N_3^-$

$N_5^+ClO_4^-$

$N_5^+NO_3^-$

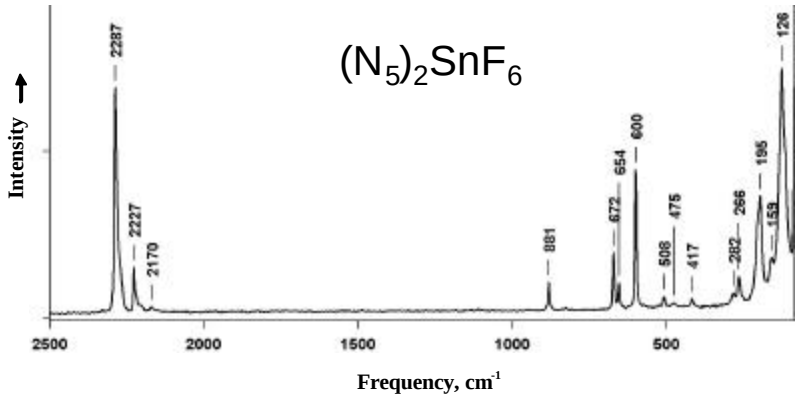
$N_5^+N(NO_2)_2^-$

Syntheses of new N_5^+ salts $(N_5)_2SnF_6$ and N_5SnF_5

- Salt with higher N_5^+ content (2:1 Cation/Anion Ratio)

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

- $(N_5)_2SnF_6$ marginally stable, but ***Friction Sensitive*** with explosive decomposition
  - White solid with double the N_5^+ content of N_5SbF_6
  - Important step toward synthesis of salts with "touching" Polynitrogen ions



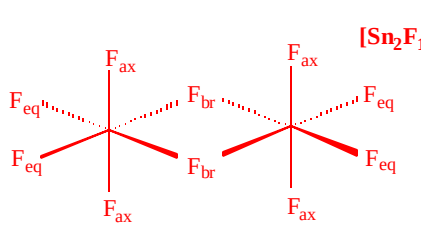
Thermal Generation of N_5SnF_5 from $(N_5)_2SnF_6$

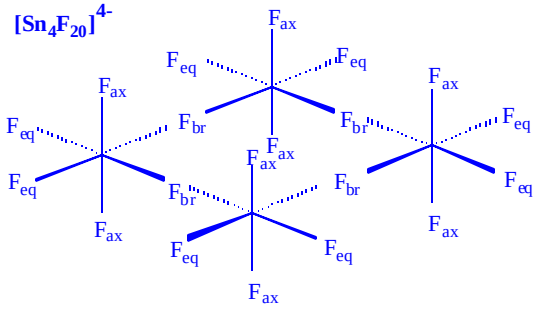
- Thermolysis of $(N_5)_2SnF_6$ above room temperature

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

- Properties of N_5SnF_5
  - White solid
  - Stable up to 50-60ºC
  - Characterized by vibrational and multi-Nuclear Magnetic Resonance spectroscopy
  - Contains $Sn_2F_{10}^{2-}$ and $Sn_4F_{20}^{4-}$ anions
- "N_5F" Unstable
  - Only decomposition products observed by FTIR and noncondensible measurements: N_2, *trans*-N_2F_2 and NF_3
  - J. Phys. Chem. **2003**, .

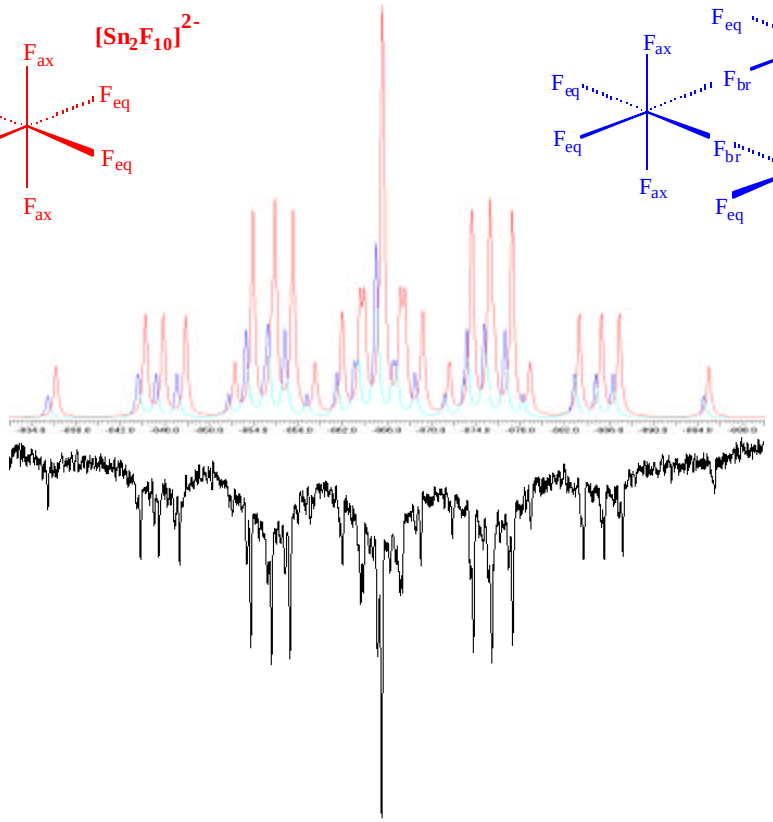
^{119} Sn NMR Spectrum of N_5SnF_5





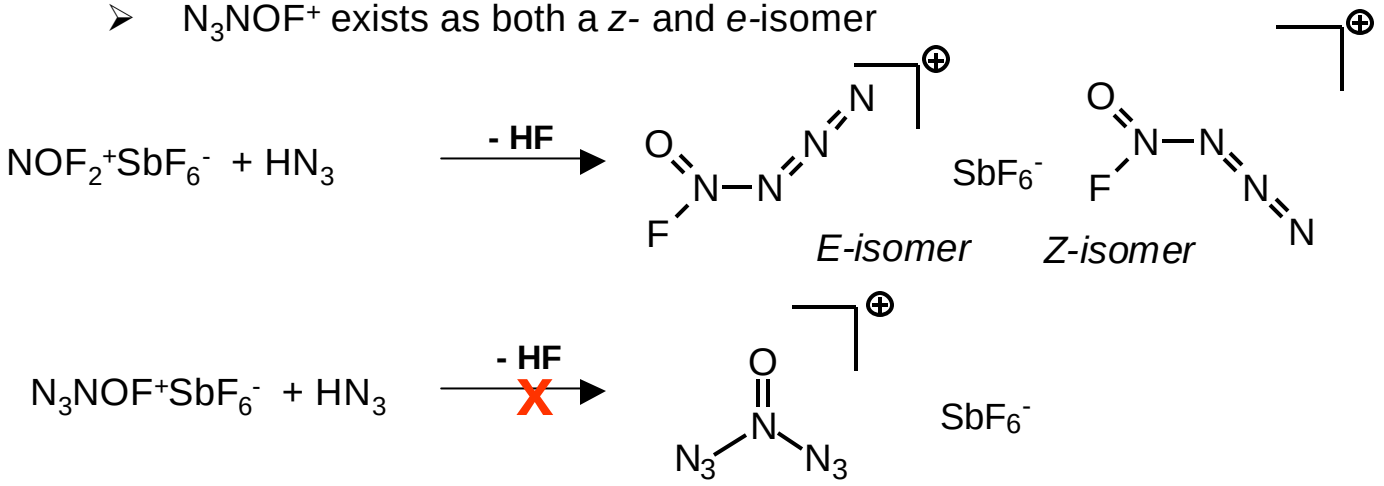
Simulated

Experimental



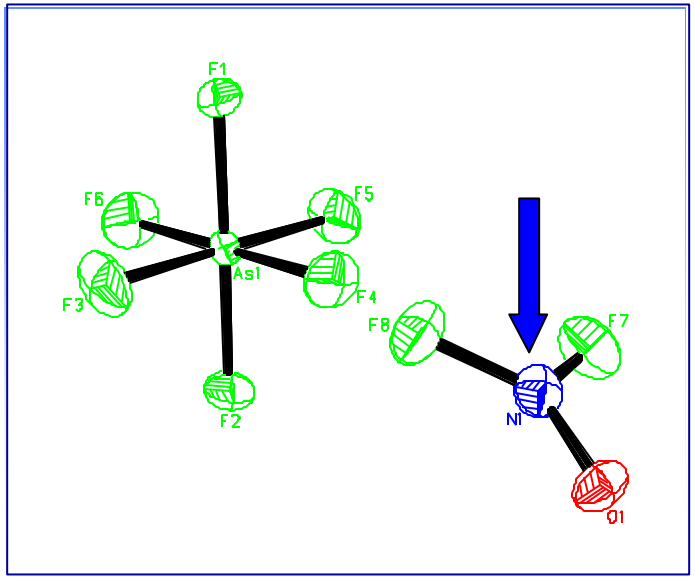
Attempted Preparation of the N_7O^+ Cation

- Another promising Polynitrogen target ion Is N_7O^+ cation.
  - Reaction of NOF_2SbF_6 with HN_3 studied in HF at –78 °C
  - $N_3NOF^+SbF_6^-$ isolated as white solid stable up to ~ -20 °C
  - N_3NOF^+ exists as both a *z*- and *e*-isomer



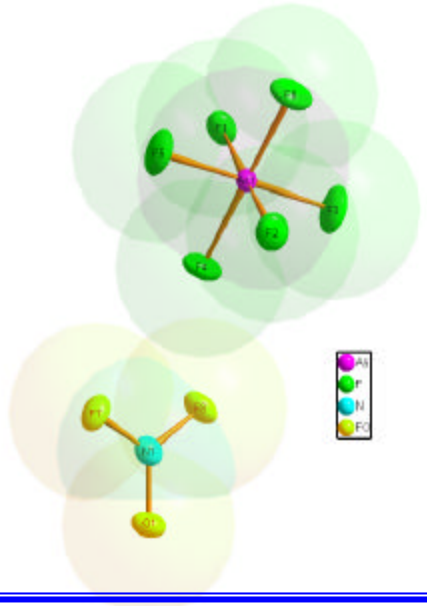
  - Characterized by vibrational and multi-nuclear resonance spectroscopy and calculations

The NOF_2^+ Cation Case



Due to their similar space requirements and electronic configurations, oxygen and fluorine ligands in oxofluorides are frequently disordered, particularly when the central atom lies on an intramolecular rotation axis.

The NOF_2^+ Cation Case….



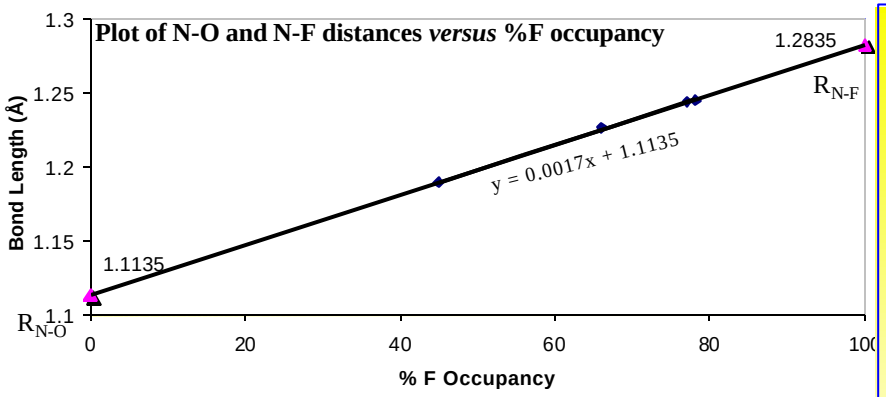
The Structure of $NOF_2^+AsF_6^-$

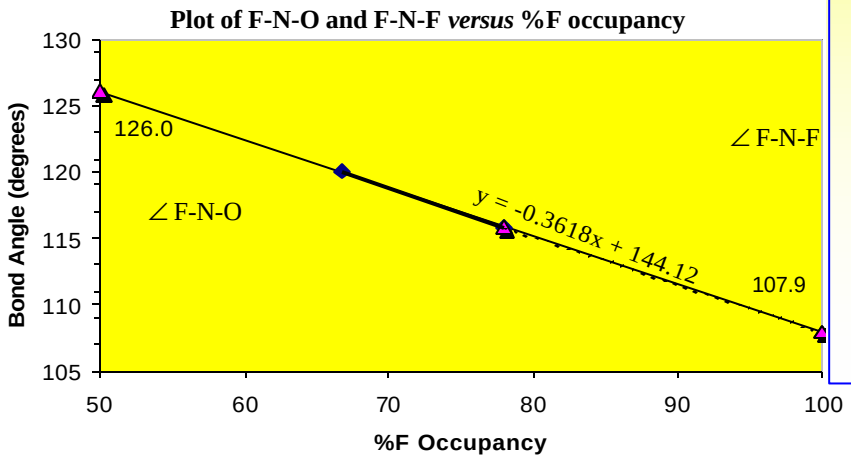
- ✓ The crystals grown from HF
- ✓ *Monoclinic* space group $P2_1/n$
- ✓ Cell constants: *a = 7.513(2) Å , b = 8.083(2) Å, c = 10.314(2) Å; b = 107.46(2)º*
- ✓ *Z = 4*
- ✓ *R = 0.0372*
- ✓ *Refined oxygen occupancy in NOF_2^+ cation is 55%*

What is wrong with this structure ??

N-O = 1.190(4) Å	…long!
N-F = 1.245(4), 1.246(4) Å	…short
Angle O-N-F = 122º	…wider
Angle F-N-F = 116º	…narrower

The disordered NOF_2^+ cation case…. Extracting the "true" geometry





Rules for refining occupancies

1. Sums of partial occupancies for O/F at any site is restricted to ONE.

2. The total O occupancy equals ONE and total F occupancies equals TWO.

Refined Occupancies

F/O = 77 and 78%

O/F = 45%

Results of Geometric "Extraction"

	Calculated		Experimental	
	B3YLP/ 631+G(2d)*,	CCSD(T)/ VTZ	"Apparent"	"Extraction" Method
N-O (Å)	1.129	1.137	1.190(4)	1.114
N-F (Å)	1.312	1.305	1.245(4), 1.246(4)	1.284
O-N-F (º)	125.8	125.6	122.0(3), 122.1(3)	126.0
F-N-F (º)	108.4	108.8	115.9(3)	107.9
R (*wR*2) (%)	-----		3.17, 7.33	3.03, 6.68

* Gillespie, R. J. *et al., Inorg. Chem.*, **1998**, *37*, 6884

The analysis demonstrates that the crystal structure of $F_2NO^+AsF_6^-$, extracted from an oxygen/fluorine disordered structure, is in very good agreement with the theoretical predictions

Factors influencing the stability of Polynitrogen compounds

Thermodynamic Factors

1. Electron Affinity of the Cation

   - *A fixed value, if we aim for a N_5^+ salt , i.e., 10.5-11.5 eV*

2. First Ionization Potential of the Anion

   - *The azide ion has a very low value of about 2.1 eV, which is the main reason for the instability of $N_5^+N_3^-$*
   - *New polynitrogen anions are needed with higher first IP values.* ***N_5^- and N_7^- anions are most promising candidates***

3. Lattice Energy of the Crystal

   - *U_L fixed by the molar volumes of cation and anion. Born-Haber cycle calculations for the lattice energy estimated for $N_5^+N_3^-$ are 50 kcal/mole lower than the requirement for the stabilization of an ionic salt*

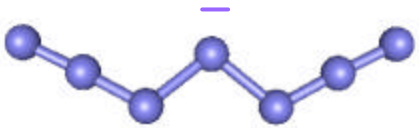
Kinetic Factors

- Low activation energy towards decomposition!

These energy values determine the stability of the individual ions

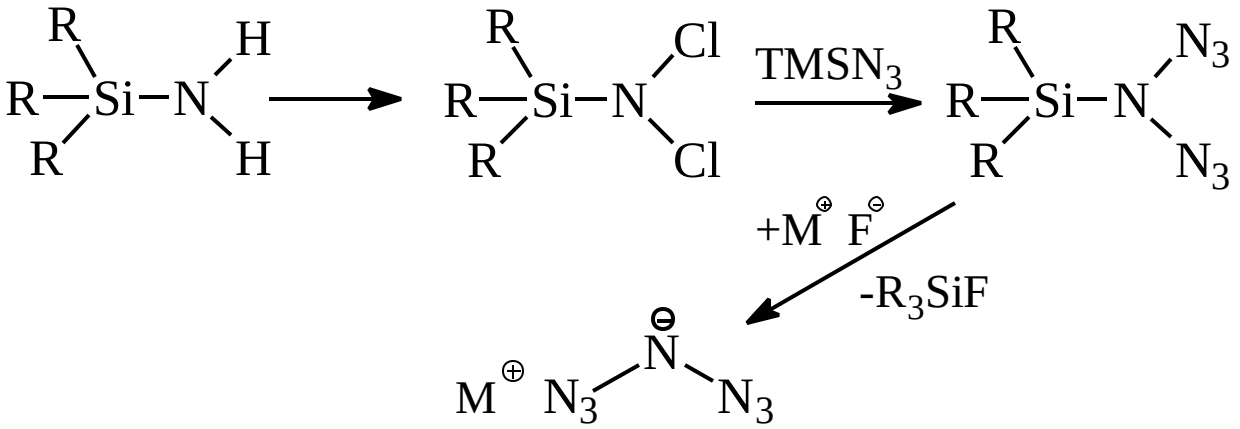
Identification and Synthesis of Polynitrogen Anions

New Polynitrogen Anions as Counterparts for N_5^+

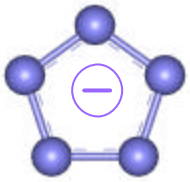


Heptanitrogen anion (N_7^-)

- *Theoreticians predict reasonable stability*
- *No reports have been published on attempts to prepare this anion. Work is in progess!*

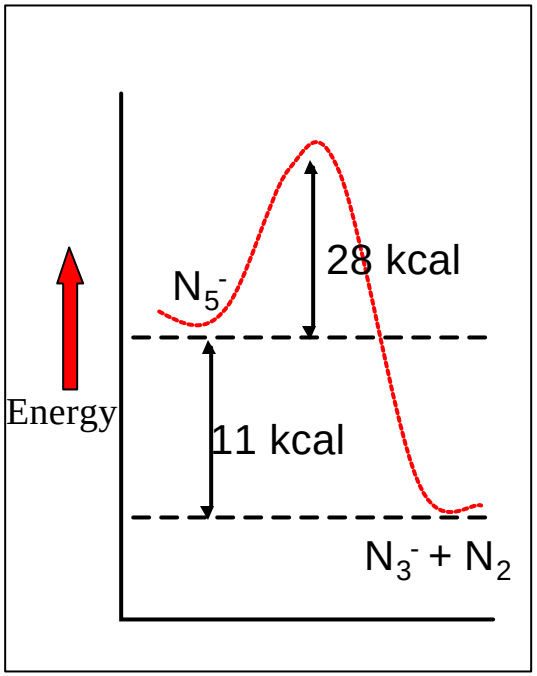


New Polynitrogen Anions as Counterparts for N_5^+



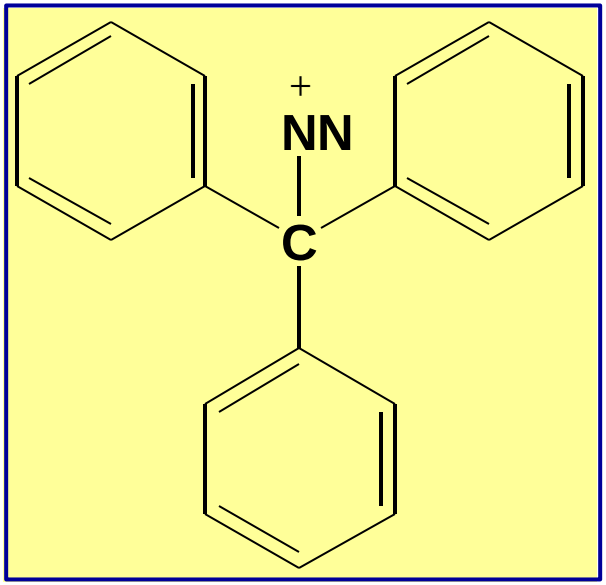
Pentazole anion (N_5^-)

- *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*
- *Free pentazole has not been isolated or characterized to date. Only aryl substituted pentazoles can be isolated and stabilized at low temperatures. These compounds rapidly decompose above 273K to form aryl azides and N_2 gas*

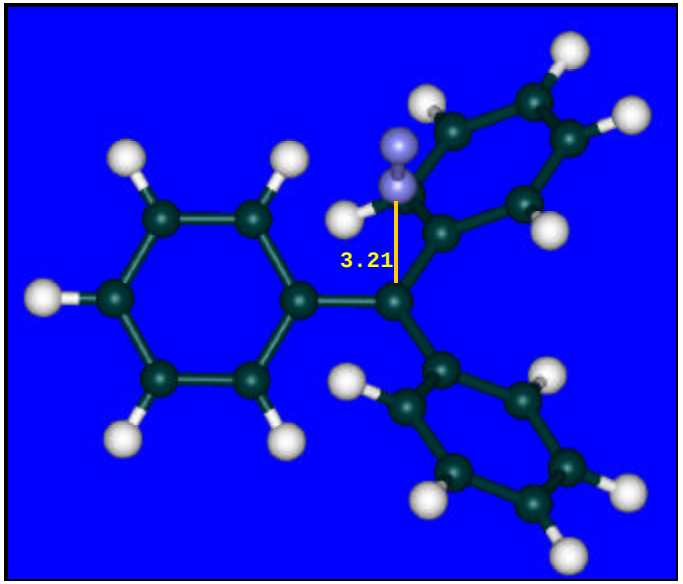


Identifying Potential Polynitrogen Precursors

This ion has been suggested as a useful precursor to new polynitrogen molecules...



... but calculations predict it to be unstable.

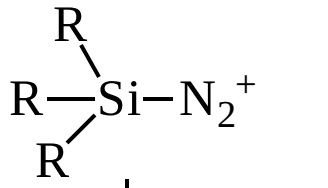


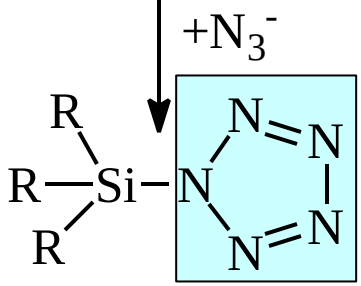
Synthetic Challenge – How do we make These New Anions??

Synthesis of Substituted Pentazoles

Sources for the Pentazole Anion (N_5^-)

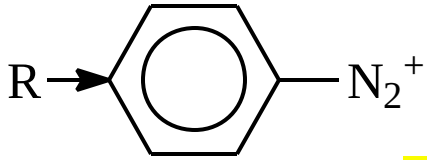
Silyl Diazonium Salts



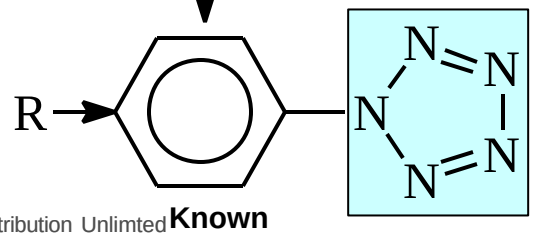


Unknown

Aryl Diazonium Salts



R = electron releasing group

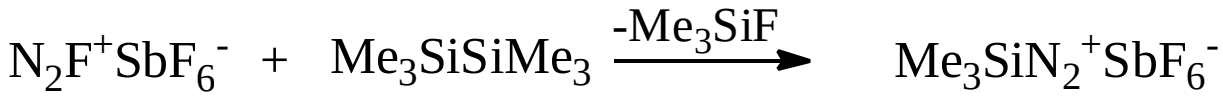


Known

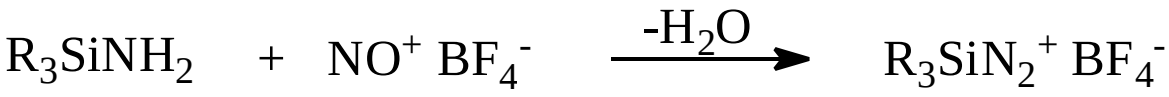
I. Ugi, *Angew Chem.*, **1961**, *73*, 172

Formation and Stability of Silyl Diazonium Salts

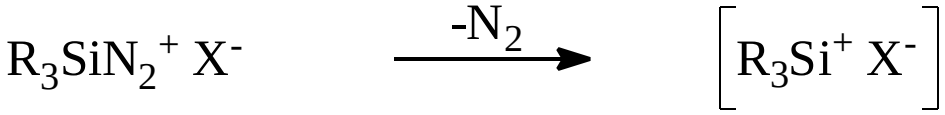
- Attempts to synthesize silyl diazonium salts



OR

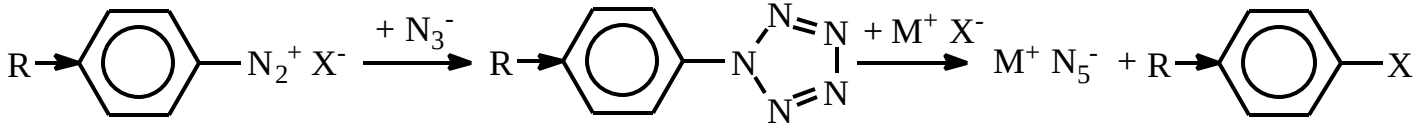


- $R_3SiN_2^+$ salts are unstable and spontaneously lose N_2



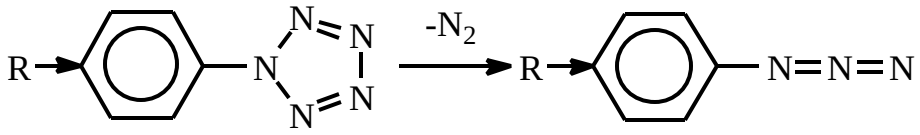
Theoretical calculations support this experimental observation

Use of Aryl Diazonium Salts – A Better Bet!



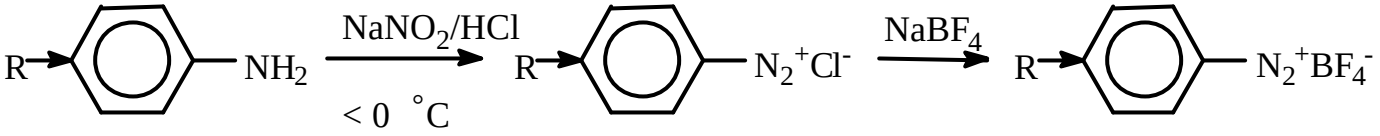
- R must be an electron releasing group, i.e., $-NMe_2$, -OH, $-OCH_3$, $-OC_6H_5$,$-O^-$, etc.
- Some of these substituted arylpentazoles have been known for about *four* decades but ***no success*** had been achieved to cleave the N_5 ring from the aryl group

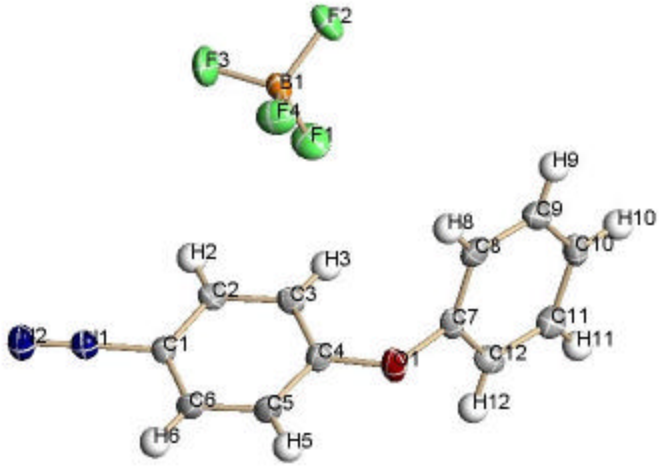
Aryl Pentazoles can rapidly lose N_2 at room temperature



Synthesis of Aryldiazonium Salts

Aqueous Media

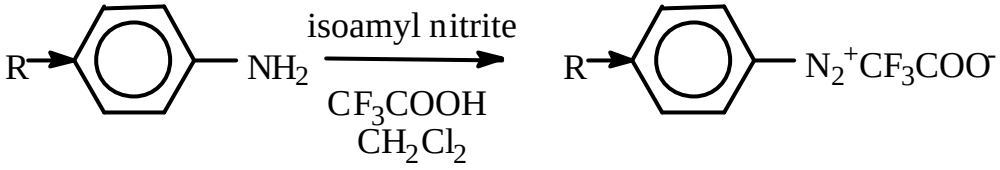




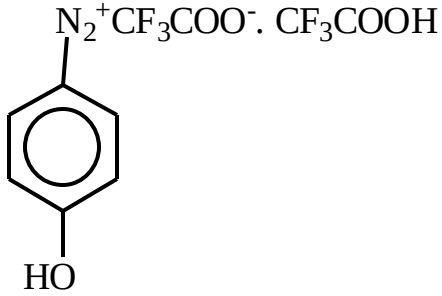
R = H, OH, OCH_3, OC_6H_5, $OC_6H_4N_2^+$, $N(CH_3)_2$

Synthesis of Aryldiazonium Salts…Non-aqueous synthesis

Non-aqueous Media



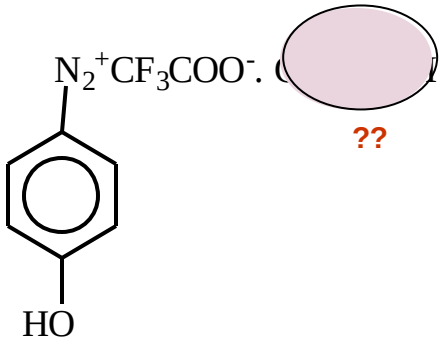
- Colas and Goeldner reported that the *p*-phenoxydiazonium trifluoroacetate to be a double salt. However, our results show no such behavior. In the case of a double salt, the –OH group can get protonated which prohibits pentazole formation!

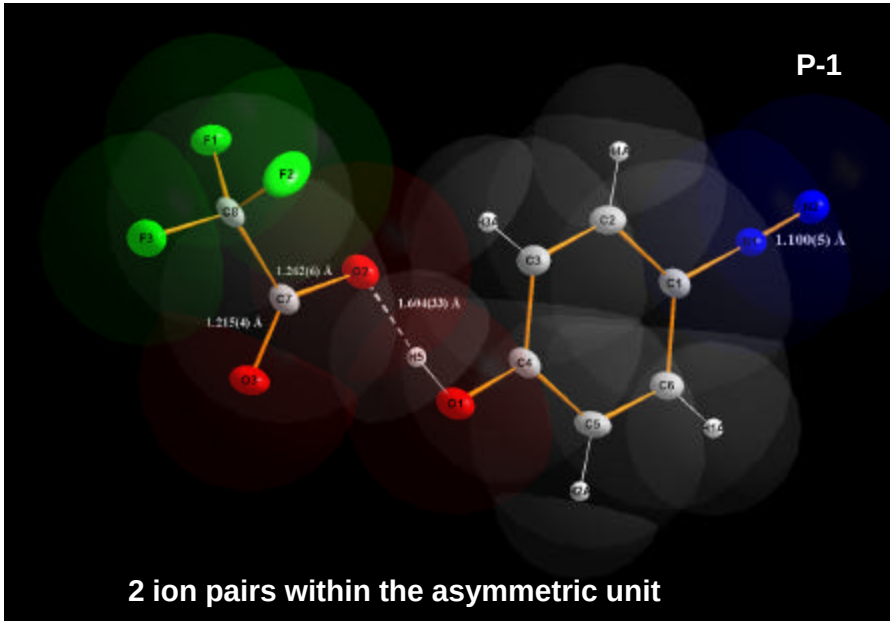


Colas and Goeldner, *Eur. J. Org. Chem.* **1999**, 1357-1366

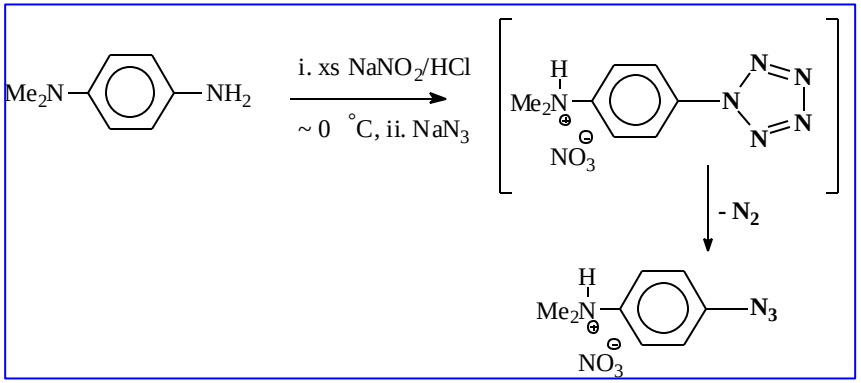
Single or Double Diazonium Salt ? Consequences of Lone Pair Occupation!

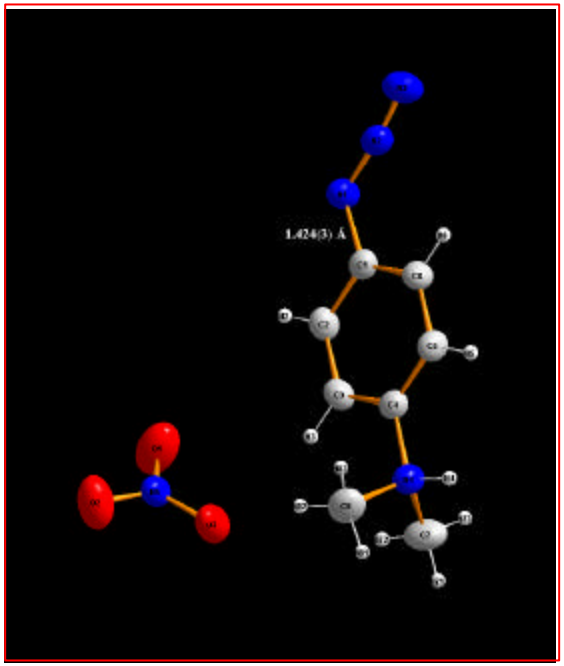
We DO NOT find any trifluoroacetic acid double salt. In fact, such a double salt would kill the pentazole formation





Pentazole Formation…
Role of the Substituent Electronic Effects





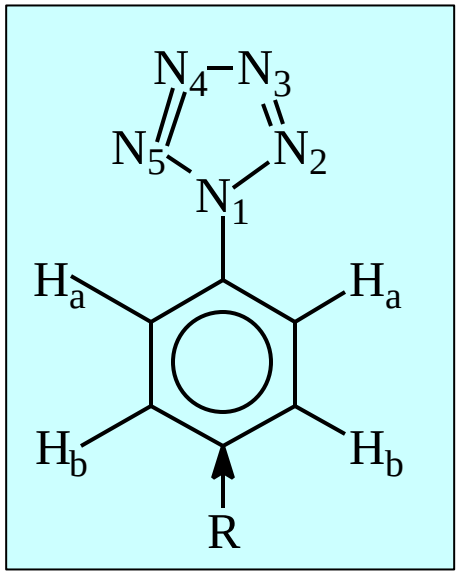
$$NaNO_2 + HCl \xrightarrow{< 0\ ^\circ C} NaCl + HONO$$

$$3\ HONO\ (aq) \rightleftharpoons H_3O^+ + NO_3^- + 2NO$$

Identification of Arylpentazoles

Pentazoles can be characterized by low temperature NMR spectral studies using ^{15}N labeled samples.

- **^{1}H NMR**: *AB*-type spectrum with H_a and H_b at 8.0 and 7.0 ppm
- **^{14}N NMR**: N_1 at ~ -80 ppm
- **^{15}N NMR**: N_2/N_5 at ~ -27 ppm and N_3/N_4 at ~4 ppm

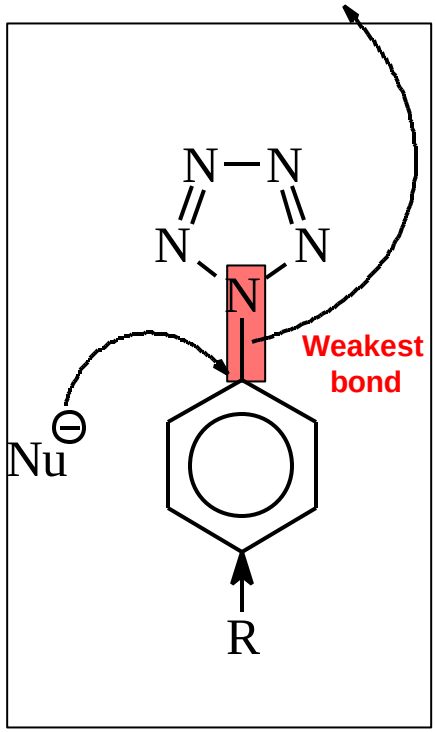


Note: Qualitative evidence for the presence of a pentazole ring: N_2 gas evolution in solution

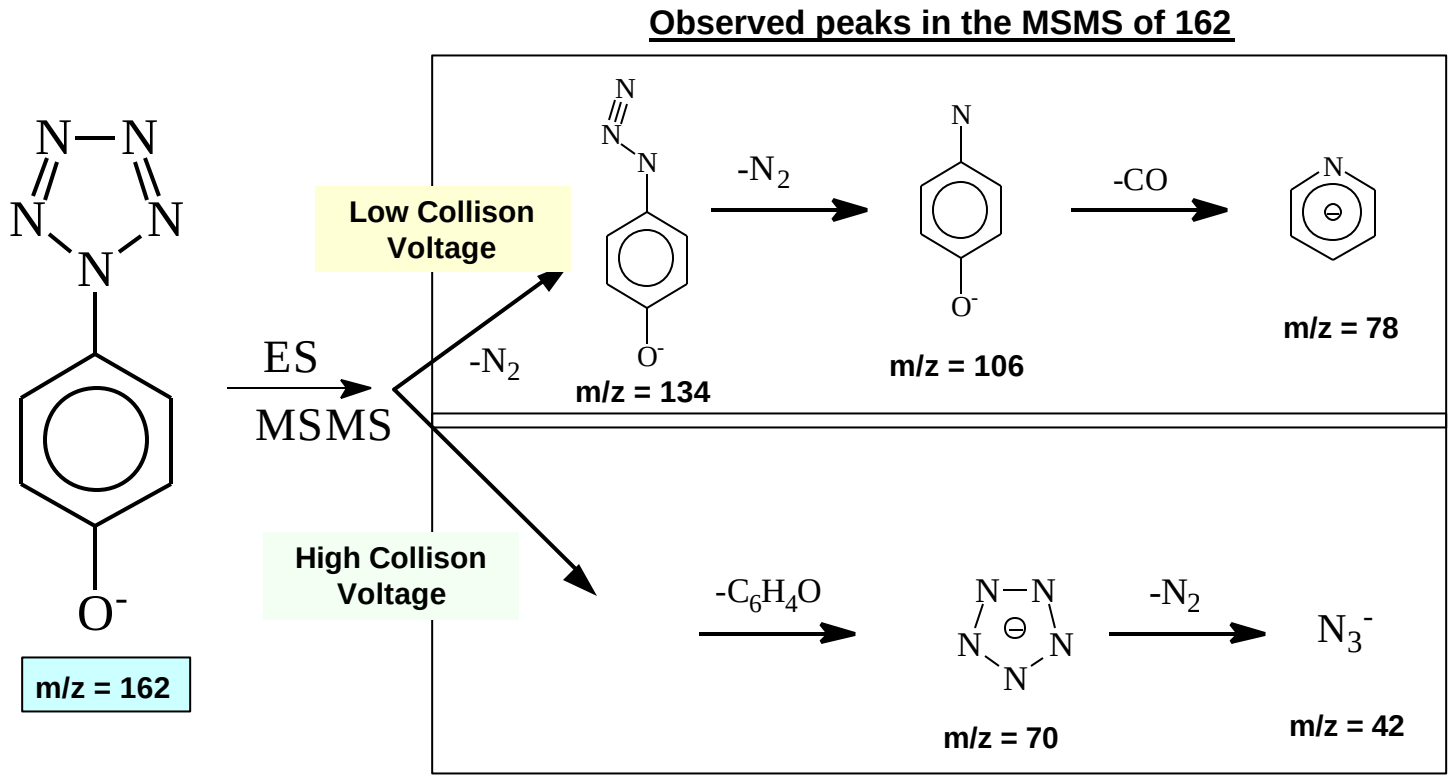
Cleavage of the Aryl-Pentazole Bond with Retention of the Pentazole Ring

- **Chemical Methods**
  - Ozonolysis does not work! (Ugi, Radziszewski)

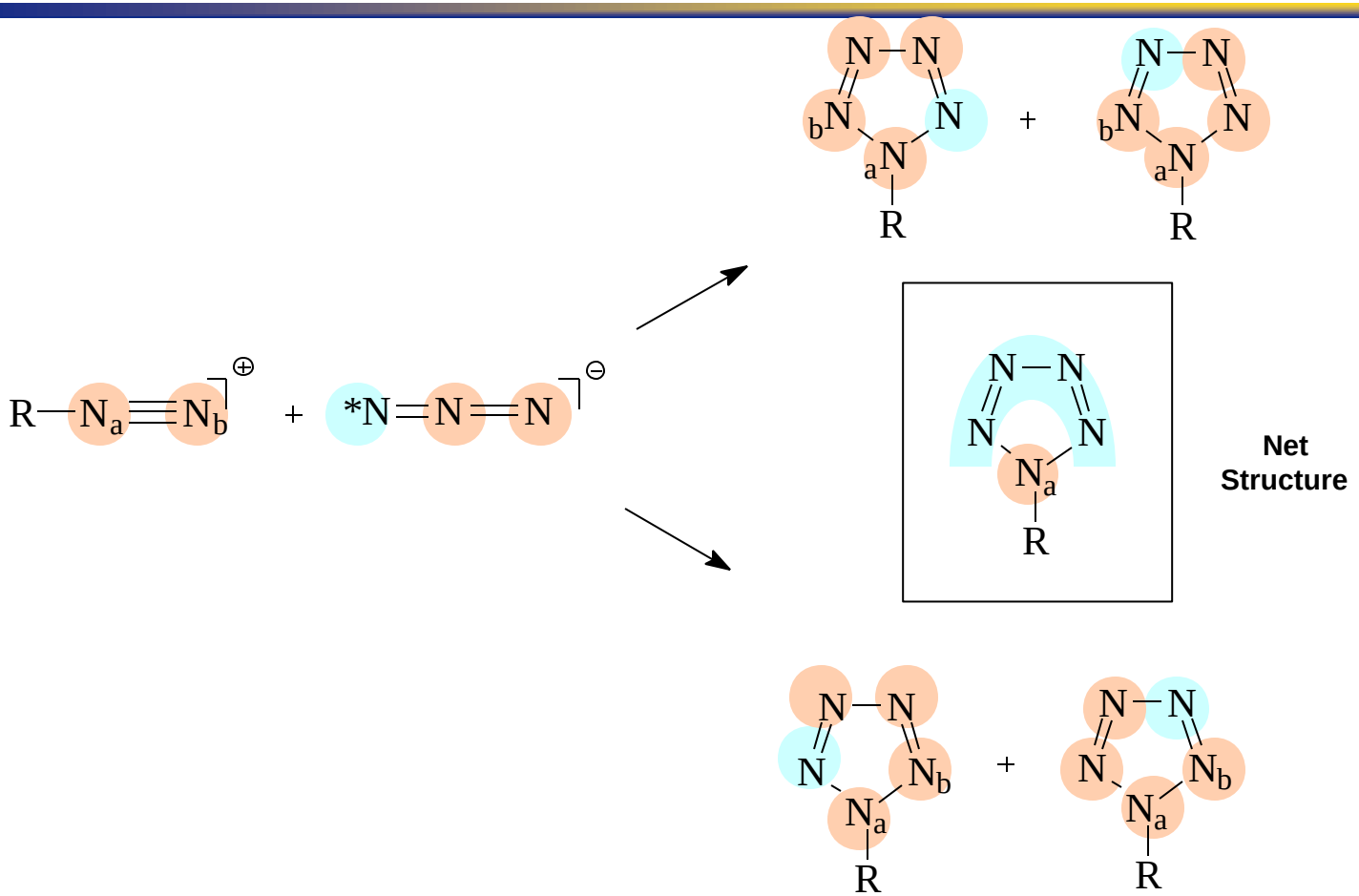
    V. Benin, P. Kszynski and G. J. Radziszewski, *J. Org. Chem.*, 2002, *67*, 1354
  - Nucleophilic substitution using strong nucleophiles such as the OH^-, OR^-, F^- etc.
- **Collisional Fragmentation (E**lectro**S**pray **I**on **M**ass **S**pectroscopy **– ESIMS)**
  - Electrospray is very gentle and produces high concentration of the parent anion which can be mass selected
  - Collisional fragmentation of the mass selected anions with variable collisional energies allow tailoring of fragmentation
  - Negative ion detection eliminates interference from neutral or positively charged species



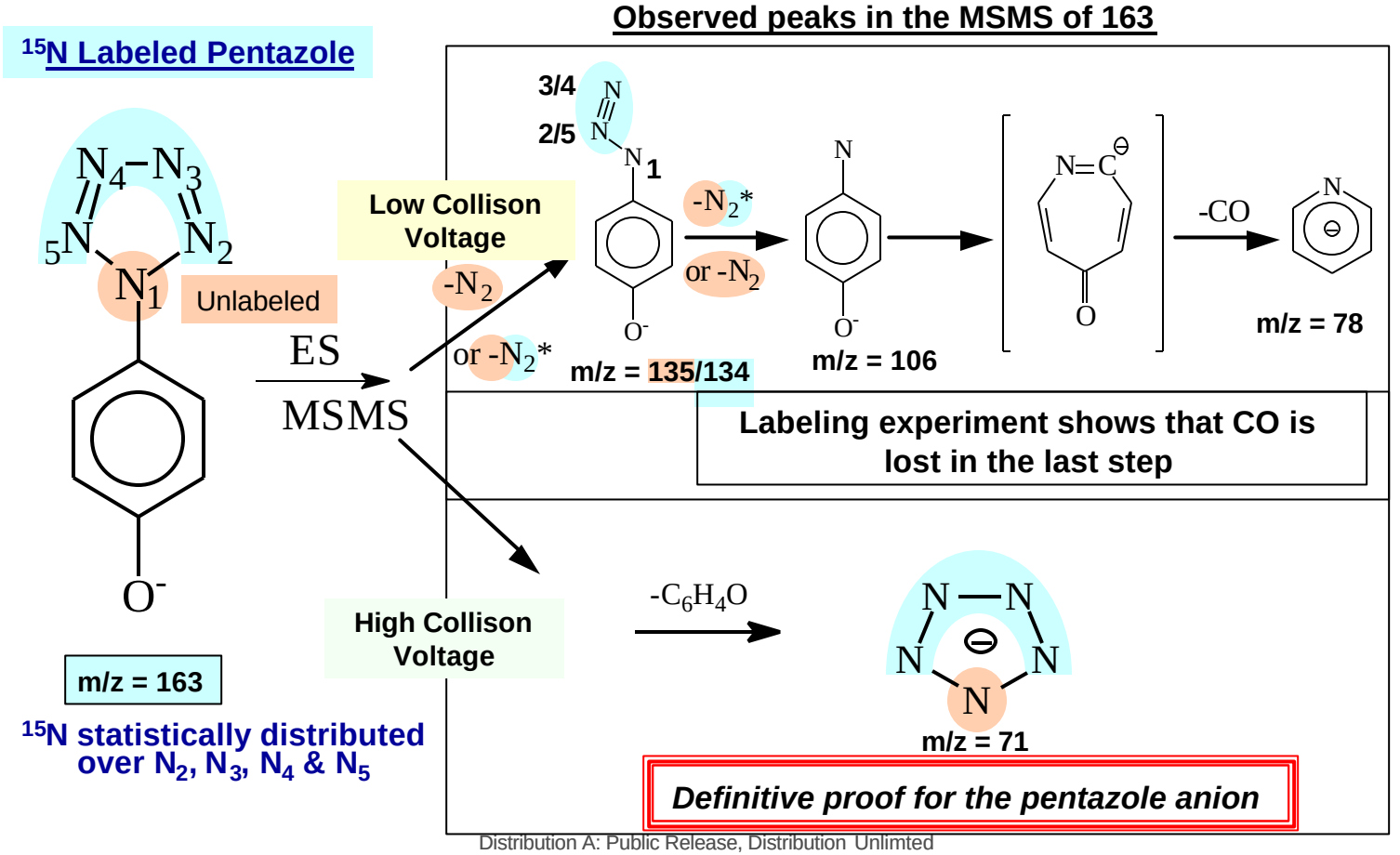
ESIMS of para-Phenoxypentazole



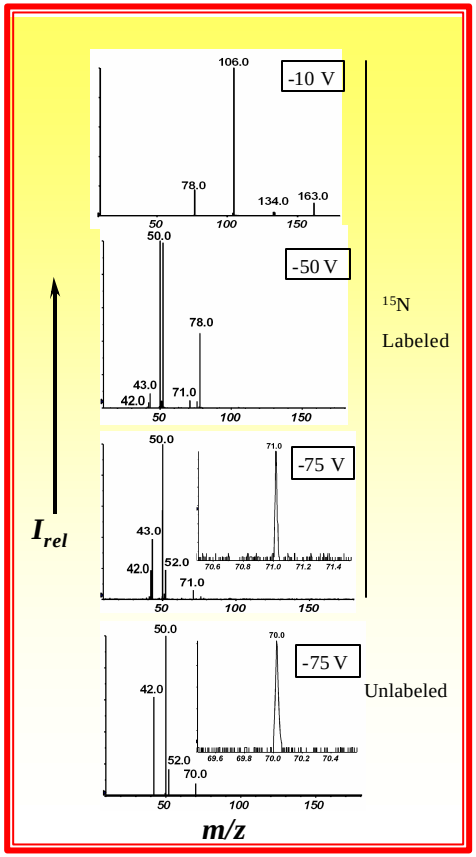
^{15}N Labeling of the Pentazole Ring



Is the Peak at m/z 70 indeed due to the Pentazole Anion?



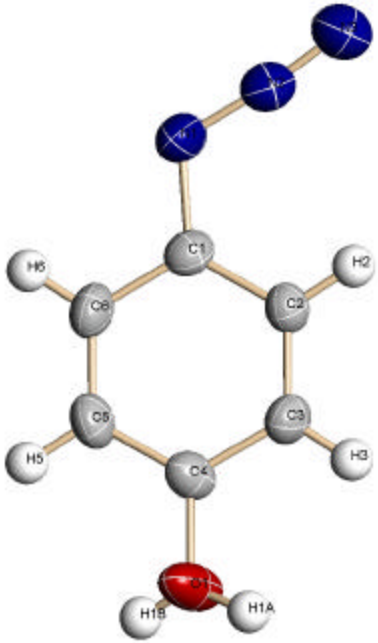
ESI-MS-MS fragmentation of 4-pentazolylphenolate anion at low and high collision voltages.



Negative ion, full-range CID mass spectra of the mass selected, 15N labeled (*m/z 163)* and unlabeled (*m/z* 162) peaks due to $[OC_6H_4N_5]^-$ recorded at collision voltages of –75, -50, and –10 Volts. All spectra are multi-channel spectra and the typical mass resolution and noise level are shown for the *m/z* 70 and 71 peaks in the inserts.

C&E News, **2002**, *80*, 8

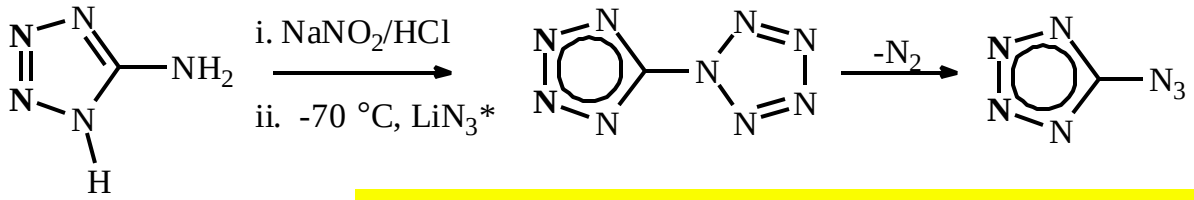
Crystal structure of 4-Hydroxyphenylazide



The thermal decomposition of 4-hydroxyphenylpentazole (4-HPP) results in the loss of N_2 gas and the formation of 4-hydroxyphenylazide. The "two" hydrogen atoms present on the *p*-oxygen atom are disordered.

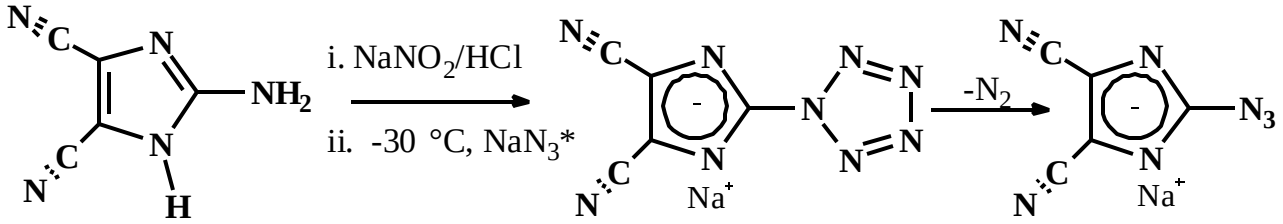
Pentazoles with Heterocyclic Substituents

- Tetrazolyl system is unstable above -70 °C and the pentazole ring rapidly decomposes to liberate N_2 gas.

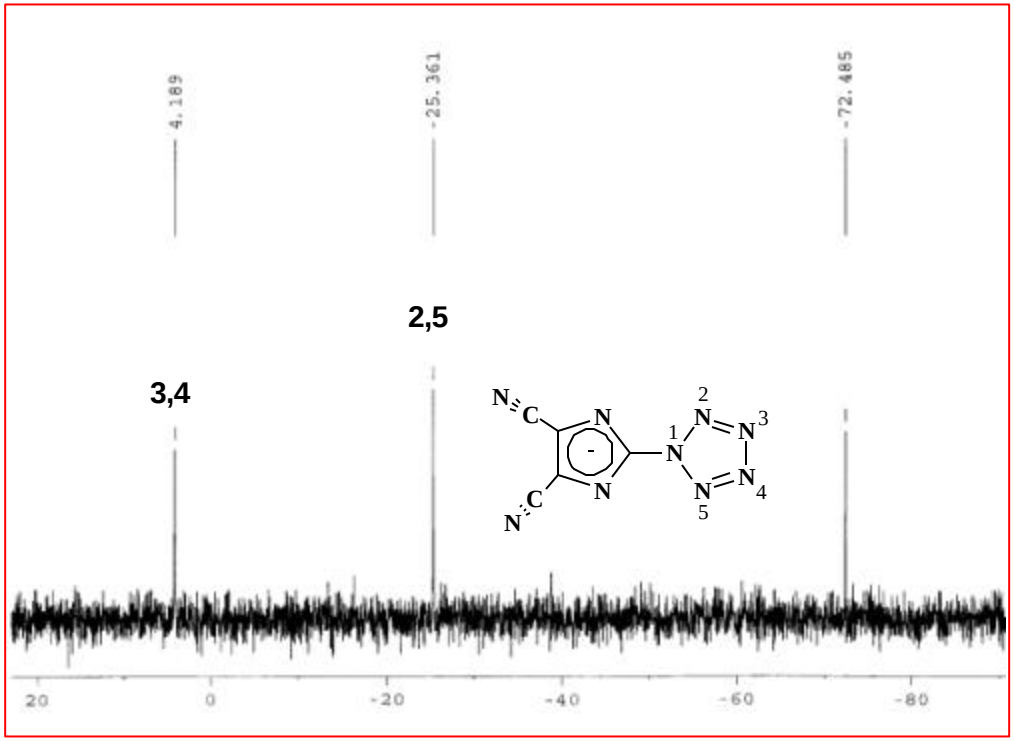


A. Hammerl and T. M. Klapoetke, *Inorg. Chem.* **2002**, *41*, 906-912

- In comparison, the pentazole ring derived from 2-amino-4,5-dicyanoimidazole shows higher thermal stability (-30 °C)

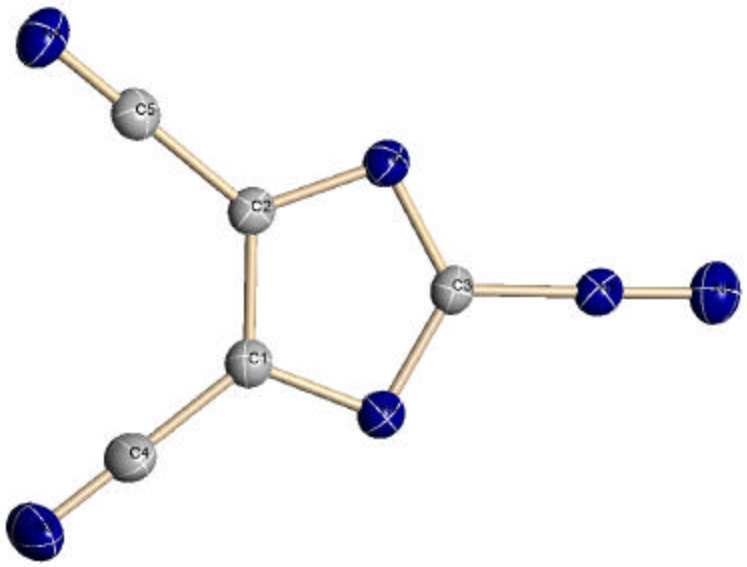


^{15}N NMR of 2-pentazolyl-4,5-dicyano-imidazole



^{15}N NMR recorded in a mixture of methanol and acetonitrile at -30 °C, nitromethane used as an external reference (0 ppm)

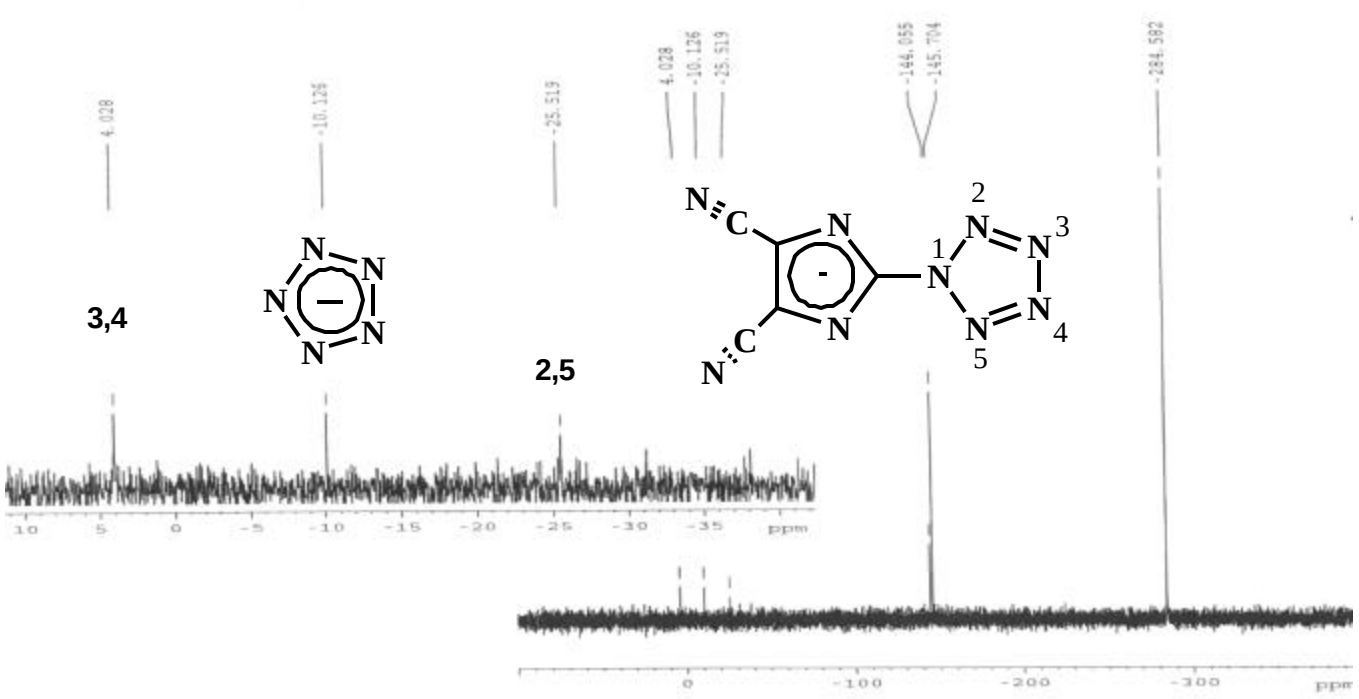
Crystal structure of 2-Diazo-4,5-dicyanoimidazole



N-N = 1.096 ?

C-N = 1.334, 1.336 ?

Does the Pentazolate Anion Exist in Solution ?



- ^{15}N NMR shows a peak at -10 ppm (-30 °C), which slowly decomposes to form N_2 and azide ion.
- This peak is also observed upon adding a base to the solution of arylpentazoles at -30 °C.

Synthesis, Mechanistic Studies and Structural Characterization of Binary Metal Azides

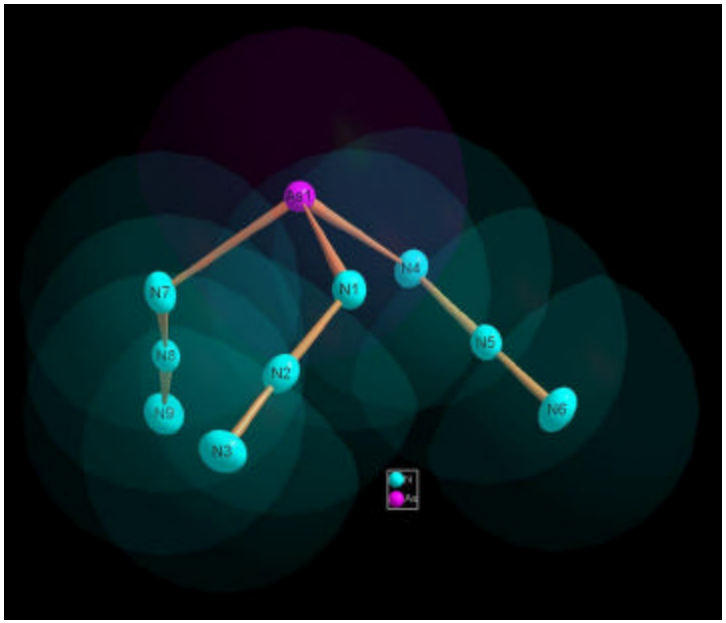
Reactions of Group 15 halides with Trimethylsilylazide

Crystalline binary metal azides were obtained upon reacting the corresponding metal fluorides with $TMSN_3$. These compounds were reported as either liquids or tacky solids by Klapoetke et al.

$$MF_3 + Me_3SiN_3 \xrightarrow{-Me_3SiF} M(N_3)_3$$

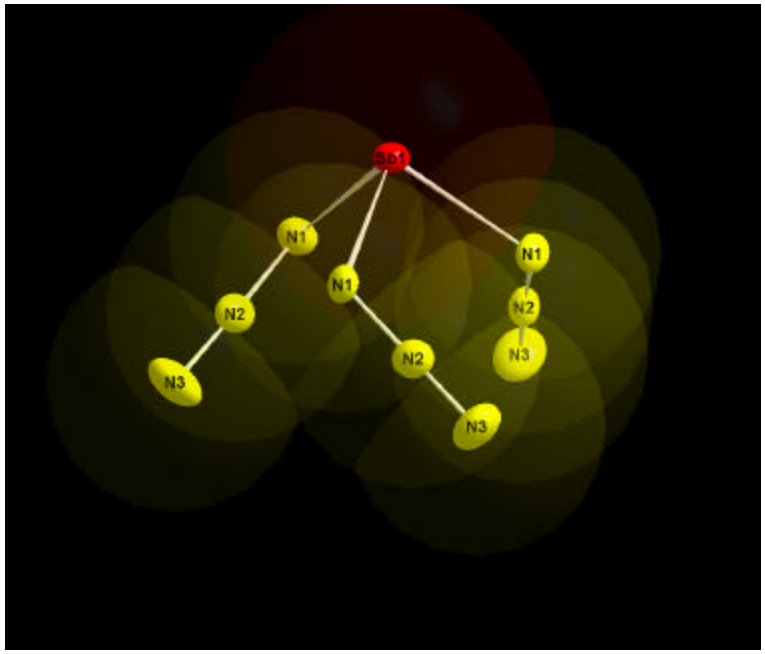
These solids could be sublimed under vacuum to yield colorless diffraction quality crystals with no incidents of explosion or thermal decomposition

Structure of $As(N_3)_3$



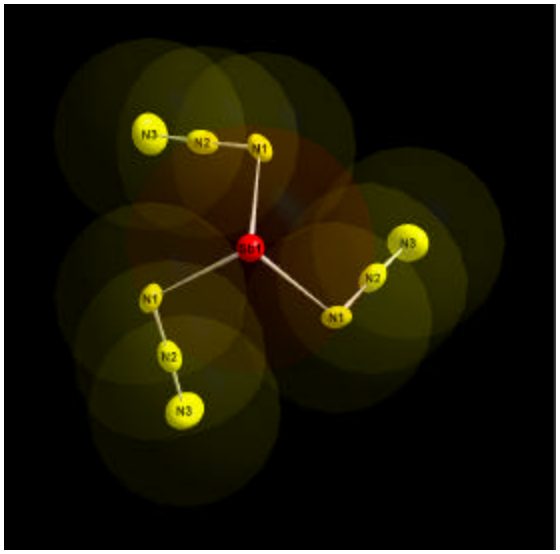
One of the azide groups N7-N8-N9 destroys the C_3 symmetry

Crystal Structure of $Sb(N_3)_3$



All azide groups oriented in a propeller-like fashion

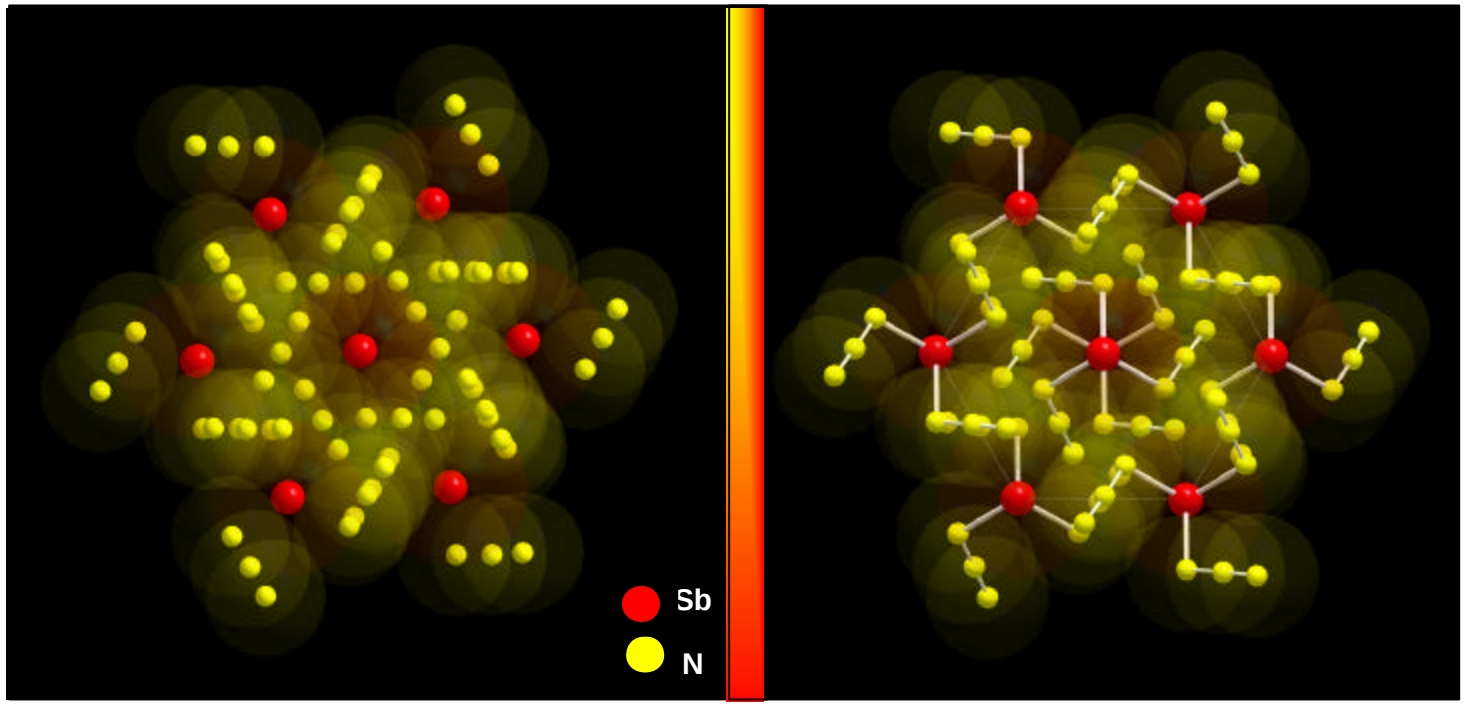
Crystal Structure of $Sb(N_3)_3$



View down the three-fold axis, all azide groups equivalent

Example of perfect C_3 symmetry

Crystal Structure of $Sb(N_3)_3$



“Star of David” Perspective

“Isle of Man” Perspective

Reactivity of hexachloroantimonate (VI) with Trimethylsilylazide

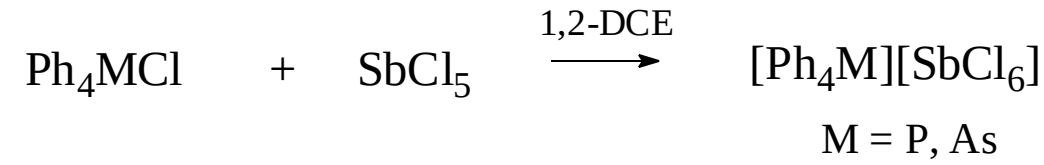
$$[Ph_4M][SbCl_6] + Me_3SiN_3 \xrightarrow[CH_3CN,\ 60\ ^oC]{-Me_3SiCl} [Ph_4M][SbCl_{6-x}(N_3)_x]$$

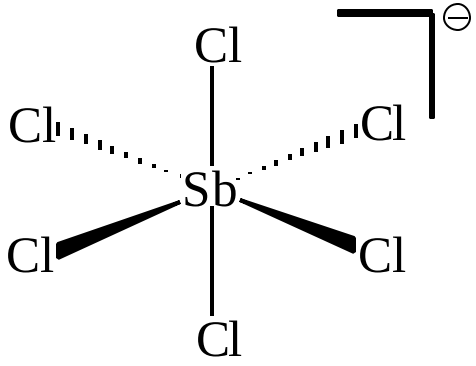
M = P, As; x = 2-6

✓The substitution of all the six chlorine atoms in $SbCl_6^-$ by the azide groups could not be accomplished in a single step, as reported in literature. The stepwise substitution gives a good insight into the substitution mechanism.

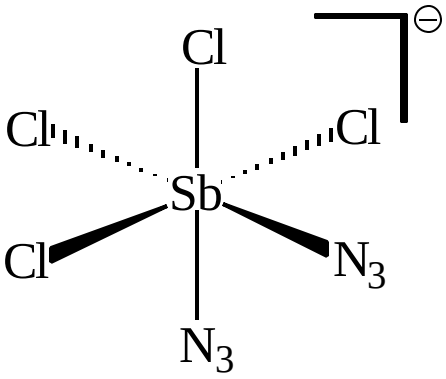
✓ Total substitution was achieved after four "refreshment" cycles of the reagents. During the intermediate cycles, the azide content gradually increased from two to five.

Episode I…Generation of the starting material

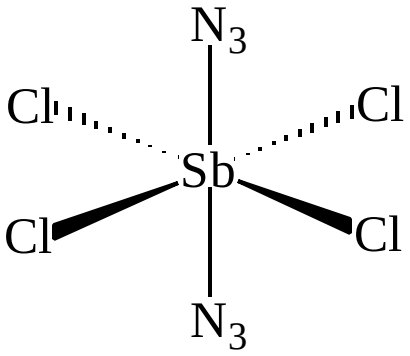




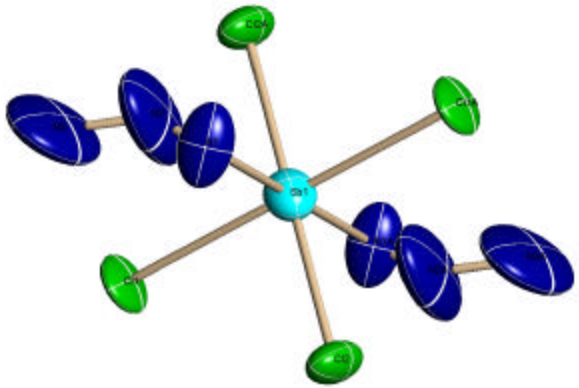
Episode II….cis- or trans- disubstitution with azide groups?



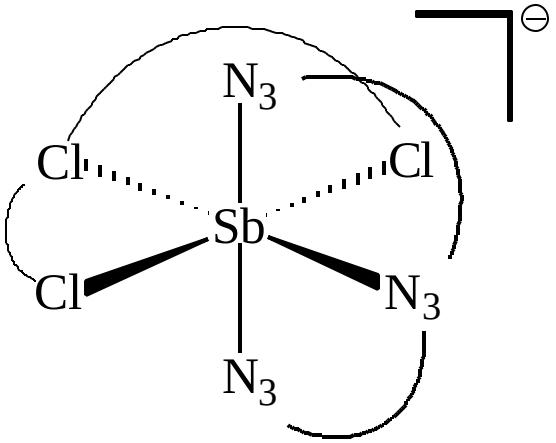
***cis*-isomer**

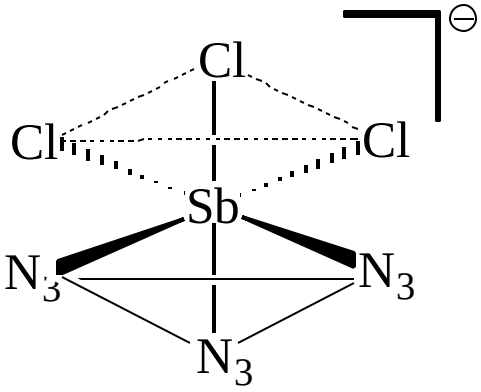


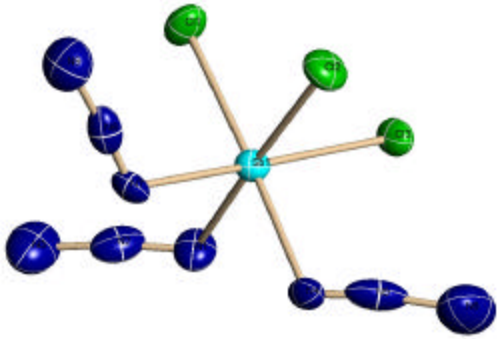
***trans*-isomer**



Episode III…Substitution of 3rd chlorine… fac- or mer- isomer ???



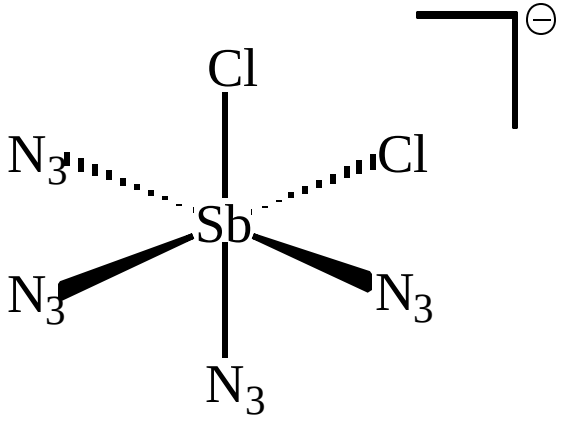


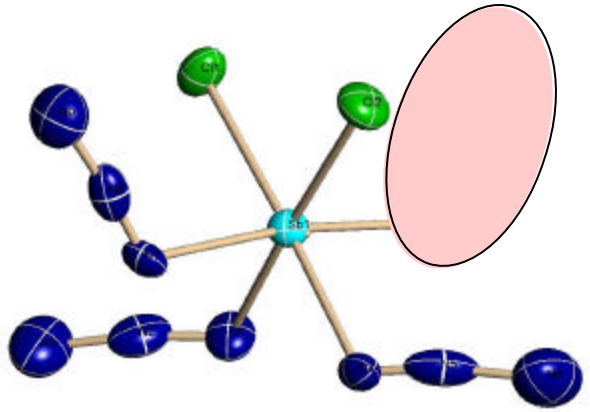


mer-SbCl$_3$(N$_3$)$_3$

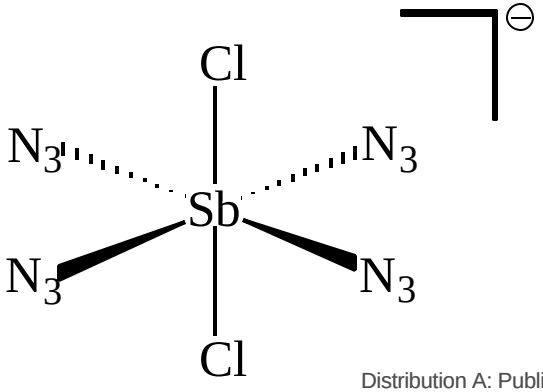
fac-SbCl$_3$(N$_3$)$_3$

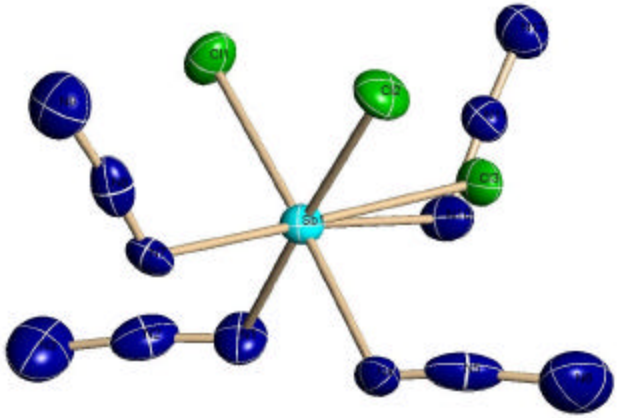
Episode IV…Capturing the "transition state" during the fourth substitution!



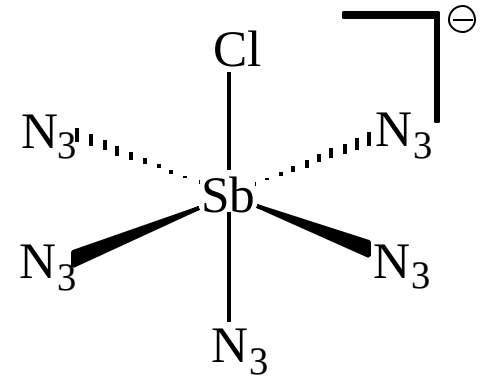


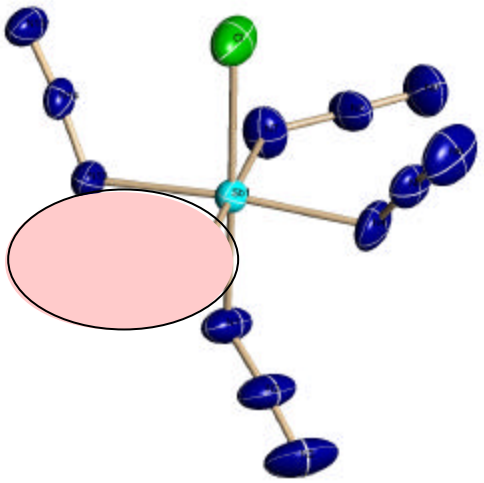
Cis- vs. trans- substitution





Chloropentaazidoantimonate(VI) Anion



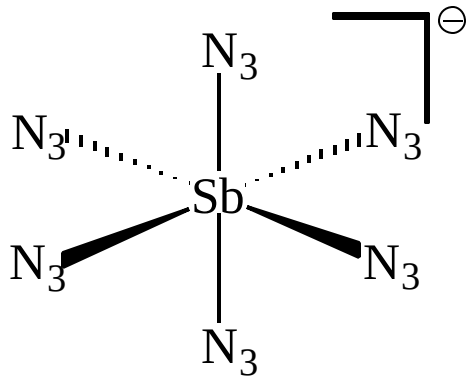


The Structure of $Ph_4PSbCl(N_3)_5$

- ✓ The crystals grown from CH_3CN
- ✓ *Triclinic* space group *P-1*
- ✓ Cell constants: *a = 11.134(3) Å , b = 11.663(3) Å, c = 13.754(4) Å; a = 104.314(5)º; b = 97.914(5)º; g = 115.807(4)º*
- ✓ *Z = 2*
- ✓ *R = 0.0762*
- ✓ *All azide distances "normal" except N10-N11-N12*

Episode VI…Complete substitution of chlorine atoms

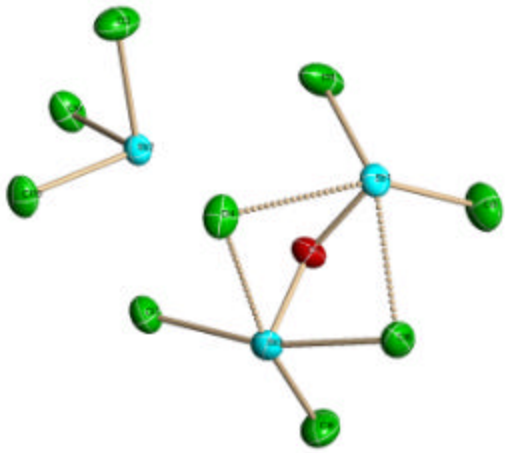
No crystal structure obtained yet. However, IR and Raman spectroscopy shows that Sb-Cl bonds are absent i.e., complete substitution by the azide groups.



Solvent effect in halide substitution reaction with $TMSN_3$

Using tetrahydrofuran (THF) in place of acetonitrile (AN) results in the formation of the $Sb_2OCl_6^{2-}$ anion. This probably results from the ring opening oxidation of THF.

$$[Ph_4P][SbCl_6] + Me_3SiN_3 \xrightarrow{THF} 2[Ph_4P]^+.[Sb_2OCl_6]^{2-}.SbCl_3$$



Summary – Polynitrogen Anions

- Synthesized aryl pentazoles: hydroxy group at the *para*-position on the aryl ring gives the best results as observed during this study.
- Demonstrated selective cleavage of C-N bond by ESIMS with retention of pentazole ring. Results confirmed studying ^{15}N labeled pentazoles.
- First experimental detection of pentazolate anion.
- Synthesis of pentazoles with a heterocylic substitutents
- Addition of OH^- ions to a solution of pentazole suggest C-N bond cleavage.
- Offers potential pathway for bulk synthesis of N_5^- salts

Summary- Polynitrogen Cations

- Use of AlF_3 as an efficient catalyst for the *trans-cis* isomerization of N_2F_2, which is a precursor for the synthesis of N_5AsF_6 and N_5SbF_6.
- Successfully demonstrated conversion of N_5SbF_6 into other salts, such as $N_5B(CF_3)_4$ and N_5SnF_5
- Prepared and characterized $(N_5)_2SnF_6$, thereby doubling the N_5^+ content of N_5SbF_6
- Obtained experimental and computational evidence for instability of N_5N_3, N_5NO_3, $N_5N(NO_2)_2$ and N_5ClO_4
- Prepared and characterized the N_3NOF^+ cation
- Attempted the preparation of $N_2(N_3)_3^+$ cation
- Attempted the preparation of $N(N_3)_4^+$ cation

Conclusions

- AlF_3 is the best catalyst for the isomerization of *trans*-N_2F_2
- N_5^+ cation can be stabilized with anions such as $B(CF_3)_4^-$, SnF_5^-, SnF_6^{2-}, SbF_6^- and $Sb_2F_{11}^{2-}$ but **NOT** with N_3^-, NO_3^-, ClO_4^- and $N(NO_2)^-$
- Only one fluorine atom in $N(O)F_2^+$ has been replaced with an azide ion to form the $N_3N(O)F^+$ cation
- The $N_2(N_3)_3^+$ cation could not be stabilized and isolated
- The $N(N_3)_4^+$ cation could not be stabilized and isolated
- Pentazoles with substituents other than the aryl group can be prepared and stabilized at low temperatures.
- 2-Pentazolyl-4,5-imidazole appears to undergo chemical C-N bond cleavage. Results are under investigation!

AFRL/USC/UC Coworkers and Collaborators

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University of Southern California
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University of California, Riverside
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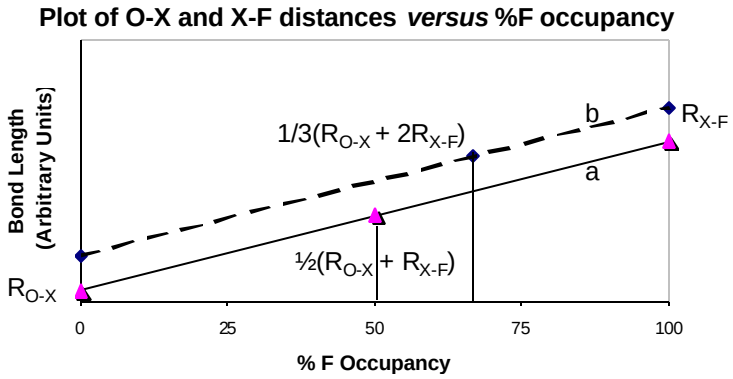
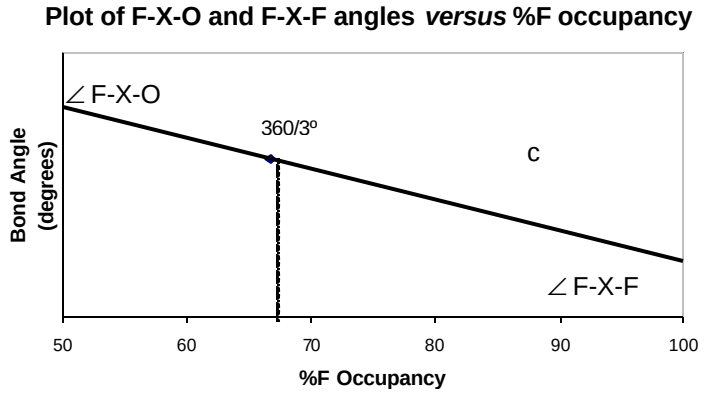
Dr. Don Woodbury
Dr. Arthur Morrish
Dr. Michael Berman
Dr. David Campbell

BACKUP

General approach for treating disorder



- For a linear $C_{\infty v}$ structure, FXO, midpoint is at 50% occupancy (plot a)
- For a trigonal C_{2v} species F_2XO, equilibrium point is weighted for the two types of atoms i.e., 2F and 1O (plot b)



- Plot c shows equilibrium bond angles for equal occupancies for two Fs (2/3) and O (1/3) i.e., 120 º. Also angle F-X-O = (1/2)(360-angle F-X-F)