HISTORY OF THE AFRL/USC DARPA PROGRAM ON POLYNITROGEN CHEMISTRY

K. Christe
Principal Investigator
University of Southern California,
and AFRL, Edwards AFB
and
A. Vij
Program Manager
AFRL, Edwards AFB

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14. ABSTRACT

In 1986, Air Force started the High Energy Density Matter (HEDM) Program. Original focus: CBES (Chemically Bound Excited States), meta-stable helium, cryo-solids, and among other things, theoretical studies on polynitrogens and polyoxygens. In 1998, Henric Oestmark approached DARPA to fund an experimental study in polynitrogen chemistry. HenricŸs proposal was reviewed at AFRL, and DARPA was convinced to sponsor a broad program in polynitrogen chemistry involving 8 research groups, including AFRL.

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Outline of Presentation

Christe
- Background
- Objectives
- Technical challenges and general concepts
- Syntheses of $N_5^+AsF_6^-$ and $N_5^+SbF_6^-$
- Program expansion to USC
- Azidamines, N_3NOF^+, and N_5^-
- N_5^+ Chemistry
- FN_5
- $N_5^+N_3^-$ and $N_5^+N_5^-$
- Polyazide Chemistry

Vij
- Polyazides and mixed chloro-azidoantimonates
- Characterization of N_5^-

Summary, Conclusions and Recommendations (Vij & Christe)

Areas not covered in this talk

- Results from many theoretical studies, new methods for simulating infinite chains, and concept of attracting points on a sphere
- Numerous crystal structures (NF_4^+, NOF_2^+, N_2F^+, ClF_4^+, BrF_4^+, IF_4^+, ClF_6^+, BrF_6^+, IF_6^+, ClF_3O, NH_3F^+, N_2F_3+, $NH_2F_2^+$) and general methods for solving disordered crystal structures
- Development of a quantitative scale for Lewis acidity
- Reaction chemistry of $(CH_3)_3SiN_3$ and NMR studies
- Development of a new reagent for the introduction of NF_2-groups
- Recent work on FN_3 and N_3^+
- Collaborations (Dave Dixon, Dave Feller, Mark Gordon, Gary Schrobilgen, Konrad Seppelt, Bob Bau, Fook Tham, Russ Hemley, George Olah, Surya Prakash, Josh Telser, Don Jenkins, Jim Pavlovich, Eduard Bernhardt)

Background

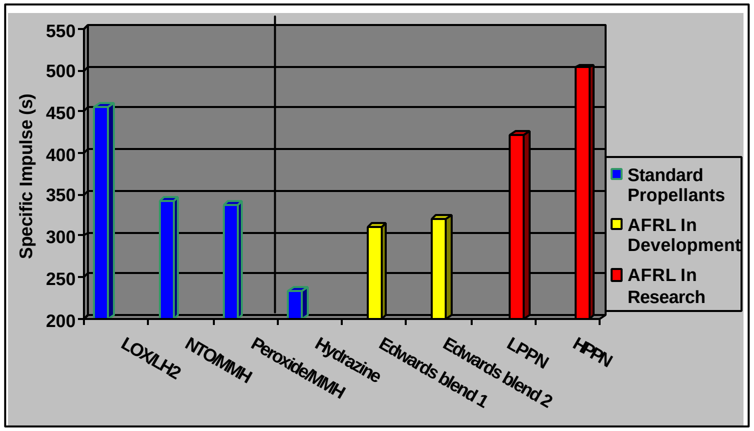
- In 1986, Air Force started the High Energy Density Matter (HEDM) Program. Original focus: CBES (Chemically Bound Excited States), meta-stable helium, cryo-solids, and among other things, *theoretical studies on polynitrogens and polyoxygens*.

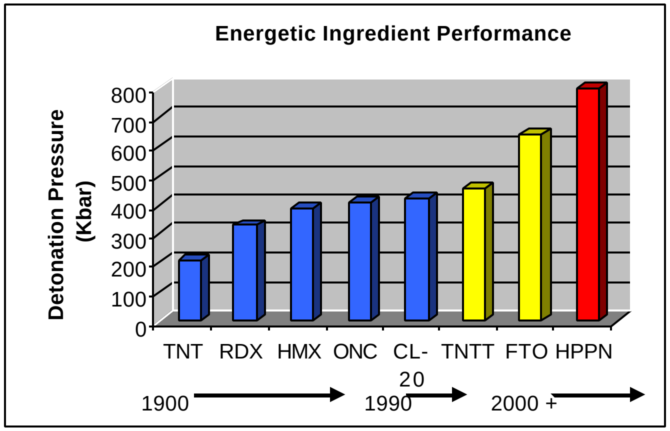
- In 1998, Henric Oestmark approached DARPA to fund an experimental study in polynitrogen chemistry.

- Henric's proposal was reviewed at AFRL, and DARPA was convinced to sponsor a broad program in polynitrogen chemistry involving 8 research groups, including AFRL.

Performance of polynitrogens as monopropellants and explosives

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





LPPN = Low performing polyN ($N_5^+N_3^-$); HPPN = High performing polyN (cubic N_8)

Condition: P_c = 1000 psi, e = 40, vacuum expansion

In addition to propellant applications, polynitrogens would also have great potential as high-performance explosives

AFRL Program

- Program started in 1998 with

  Karl Christe (Principal Investigator)

  William Wilson (Senior Scientist)

  Jerry Boatz and Jeff Sheehy (Computational Chemistry)

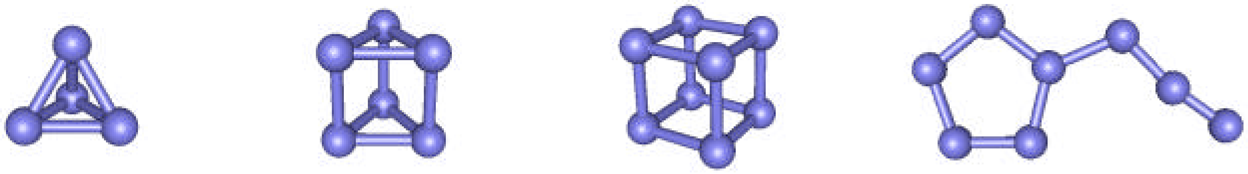
  Pat Carrick (Government Program Manager)

  Art Morrish (DARPA Program Manager)

State of the Art in 1998

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

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

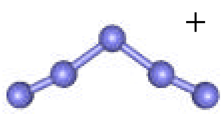


Objectives of AFRL Program

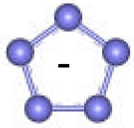
Discover, synthesize, characterize, and scale-up novel, highly energetic polynitrogen compounds

Technical Approach:

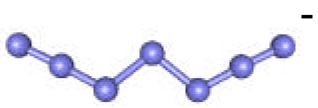
- Exploit synergism between theory and synthesis
  - Use calculations to identify the most promising candidates and predict their properties
  - Use experimental expertise to design synthesis approaches, prepare novel compounds, and characterize products



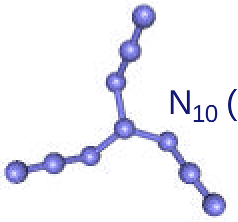
N_5 cation



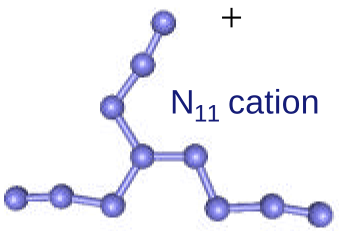
N_5 anion



N_7 anion



N_{10} (C_3)



N_{11} cation

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

$$\underset{85 + 143}{(-HC{=}CH)_{n}-} \xrightarrow{+34} \underset{194}{HC{\equiv}CH}$$

stable polymers,
unstable monomers

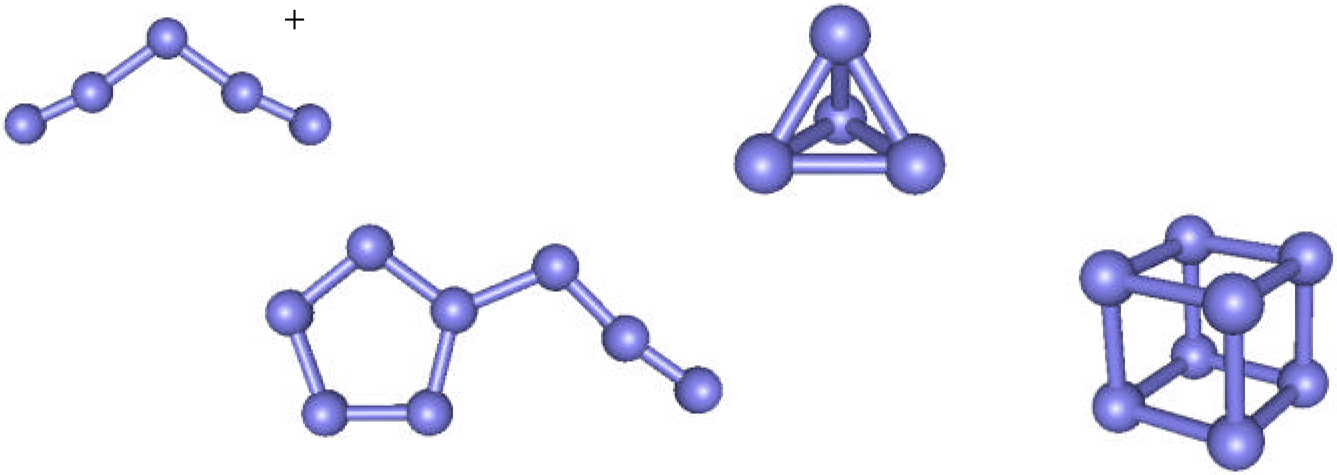
$$\underset{38 + 100}{(-N{=}N)_{n}-} \xrightarrow{-88} \underset{226}{|N{\equiv}N|}$$

unstable polymers,
stable monomer

Or, why the atmosphere is made of gas and we aren't

Our Research Philosophy and Technical Approach

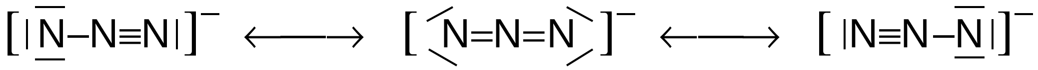
Initially we preferred catenated over cyclic or polycyclic compounds



- Although polycyclic compounds can be 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

General Concepts for Polynitrogen HEDM Synthesis

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

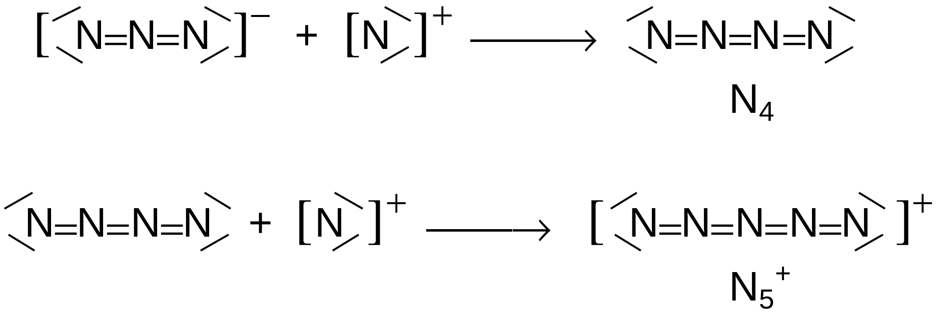


$$[|\overline{\underline{N}}-N\equiv N|]^- \longleftrightarrow [N=N=N]^- \longleftrightarrow [|N\equiv N-\overline{\underline{N}}|]^-$$

- The double-bond character of the N—N bonds in the azide anion explains its exceptional stability
- How can this stabilization effect be used to our advantage in preparing new compounds?

Expansion of the Azide Structure

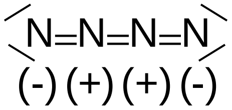
- Addition of $[N]^+$ units to N_3^-:



N_4

N_5^+

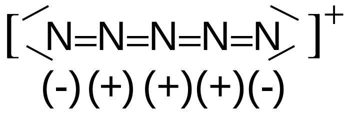
- However, theory and calculations show that linear N_4 is not stable; neighboring charges of equal sign must be avoided



- No plausible resonance structure can be written for N_4 that retain double-bond character while avoiding neighboring charges of equal sign

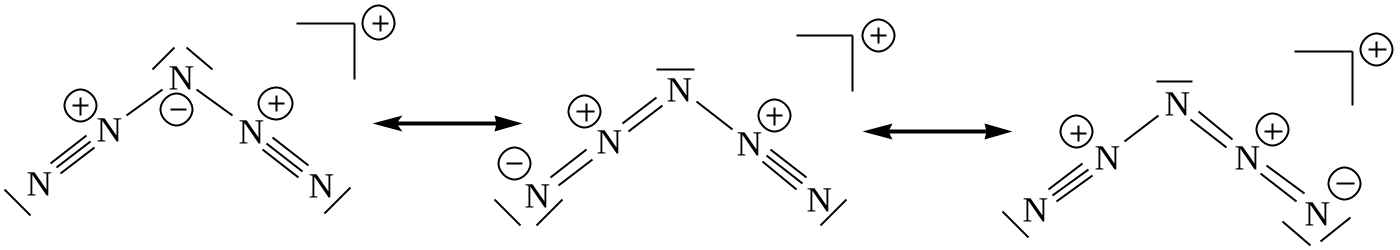
Expansion of the Azide Structure to N_5^+

- The same problem of neighboring positive charges exists for the linear N_5^+ structure:



$$[\overset{(-)}{N}=\overset{(+)}{N}=\overset{(+)}{N}=\overset{(+)}{N}=\overset{(-)}{N}]^+$$

- Resonance structures can be written, however, that avoid this problem:

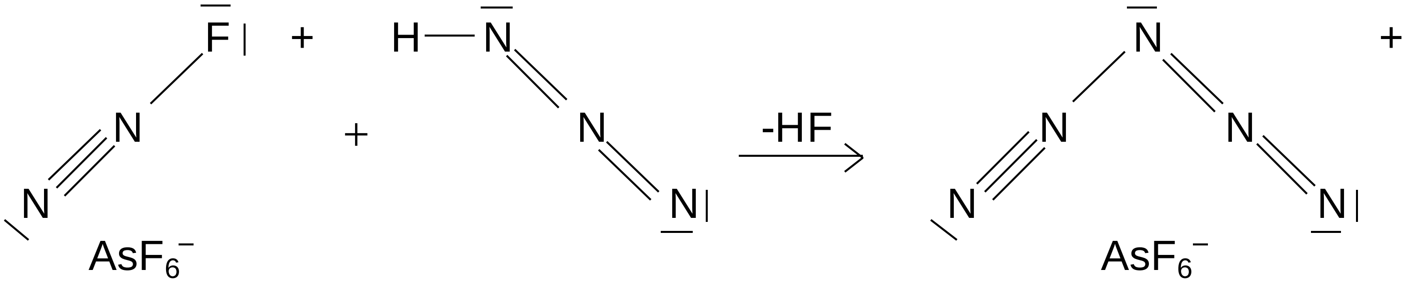


- *Ab initio* calculations confirm the stability of this C_{2v} structure

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 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 $N_5^+AsF_6^-$

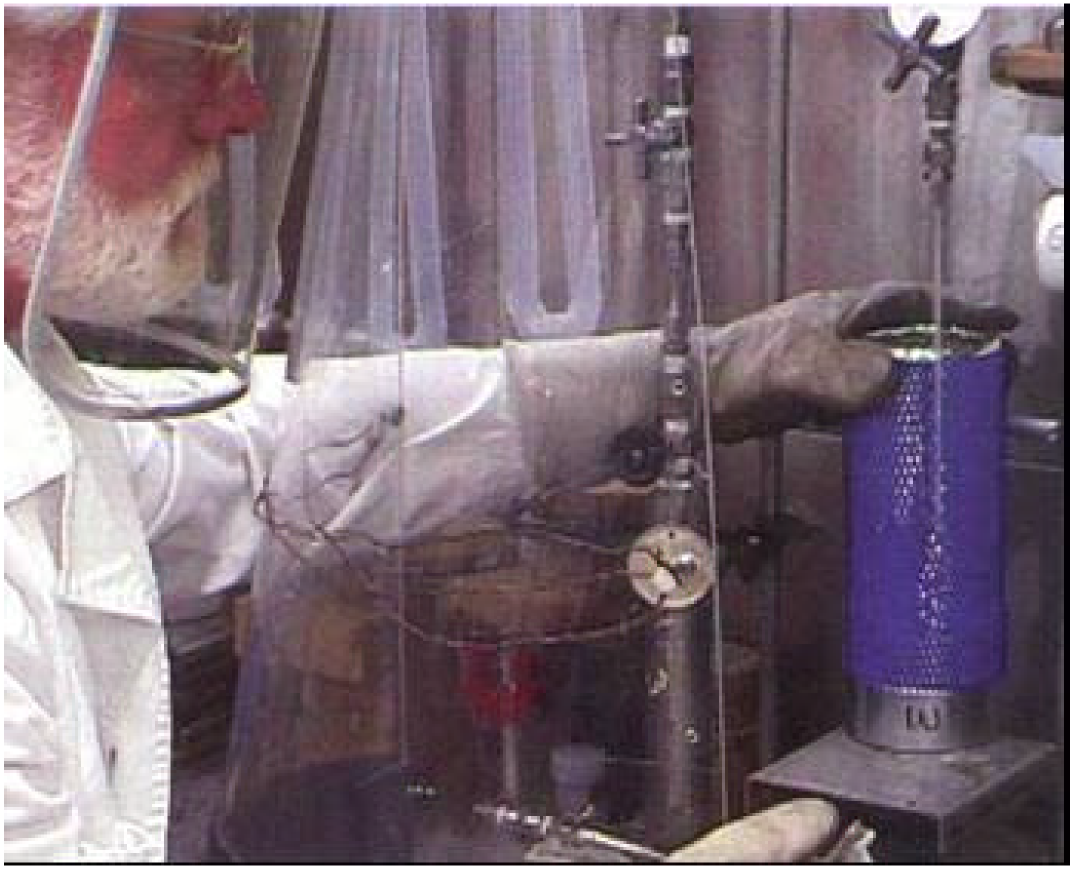
- Reaction system worked as planned:

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

  - 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

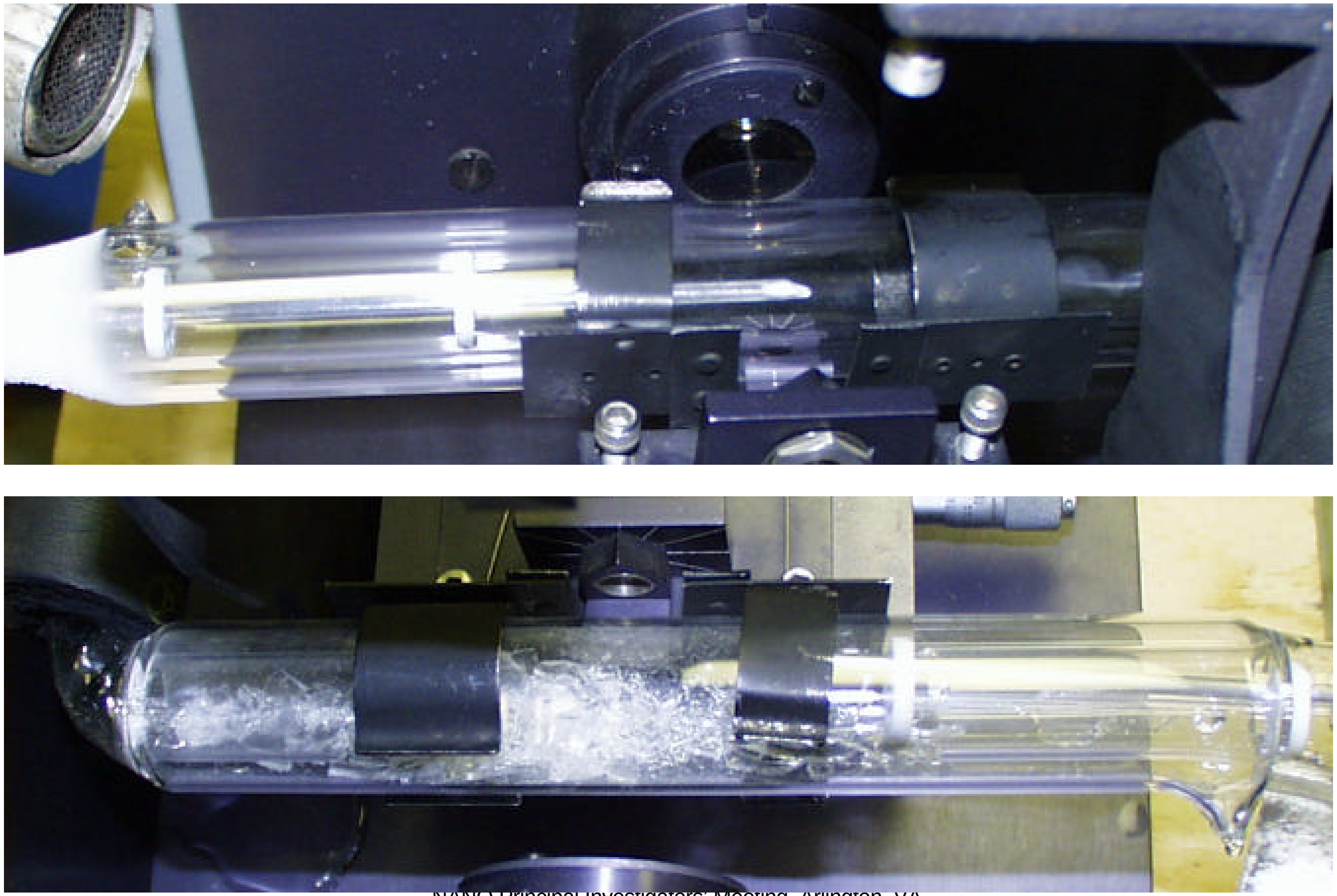
Dr. Wilson preparing $N_5^+AsF_6^-$



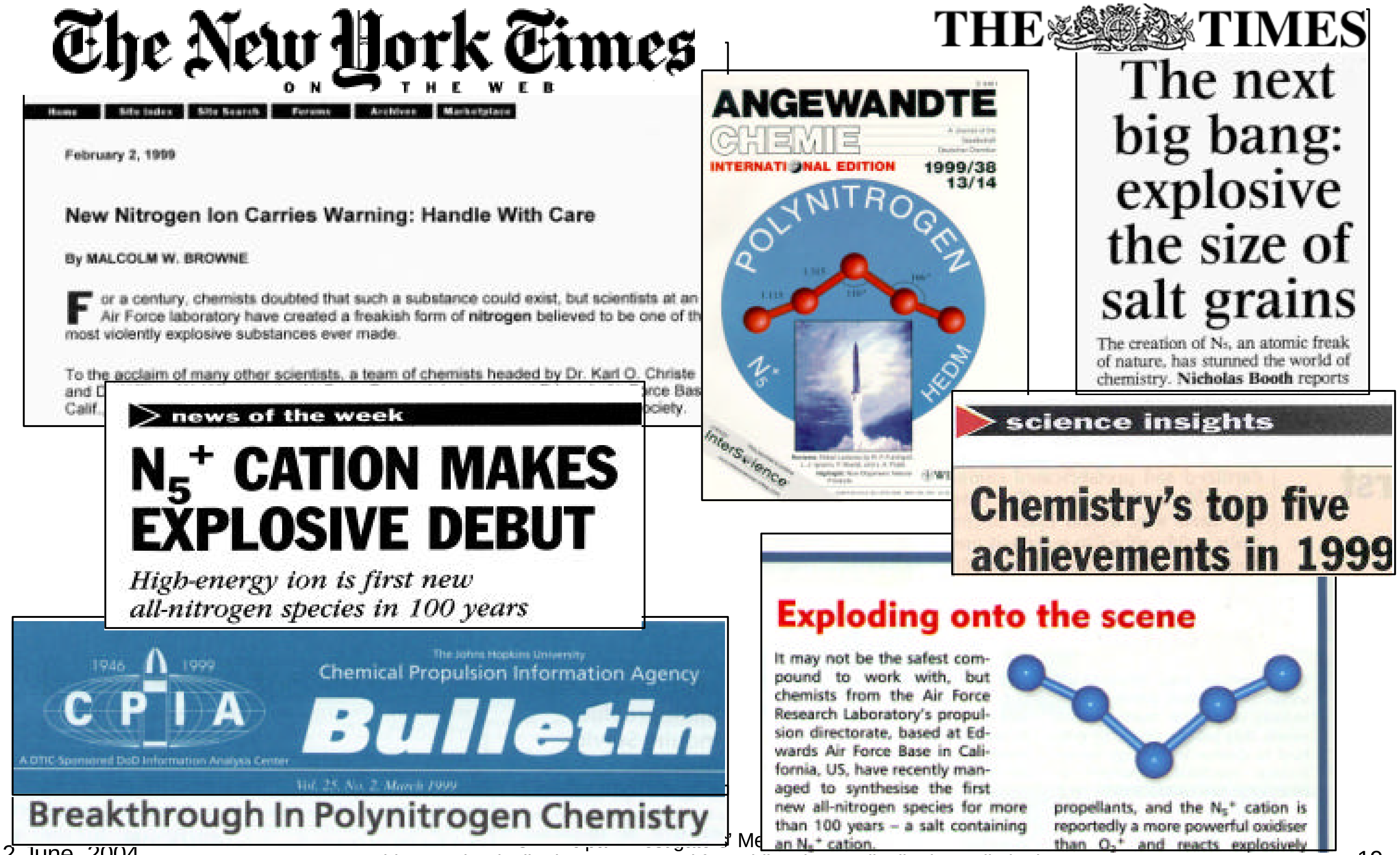
Characterization of $N_5^+AsF_6^-$

- ^{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

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



Publicity for N_5^+ Synthesis



The New York Times
ON THE WEB

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 rce Bas Calif. ociety.

news of the week

N_5^+ CATION MAKES EXPLOSIVE DEBUT

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

ANGEWANDTE CHEMIE
INTERNATIONAL EDITION
1999/38
13/14

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

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

Breakthrough In Polynitrogen Chemistry

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

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Expansion of AFRL Program

- Successful synthesis of N_5^+ cation provided the first stable polynitrogen species in more than a century and only the second stable polynitrogen, ever prepared.

- In view of this success, DARPA allowed us to hire two additional chemists (Ashwani and Tini Vij) at AFRL and to start an independent support program at USC. Pat Carrick was succeeded by Jessica Harper and later by Jeff Sheehy, Robert Corley, and Ashwani Vij as government program managers at AFRL.

- Two laboratories were constructed at USC and four post-docs (Thorsten Schroer, Stefan Schneider, Michael Gerken, and Ralf Haiges) were assigned to this program under the direction of Karl Christe.

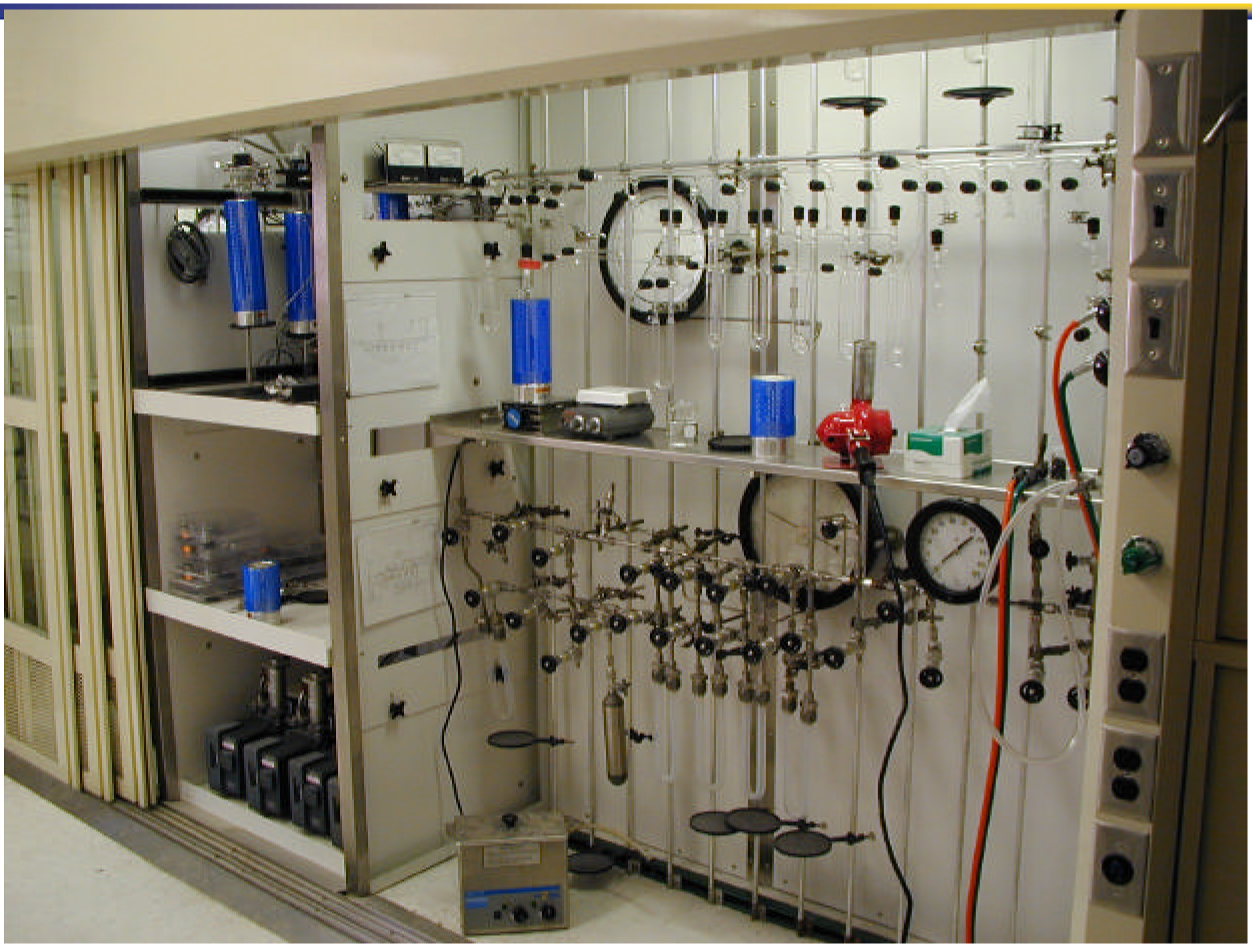
AFRL Group

From left to right: Jerry Boatz, Ashwani Vij, Vandana Vij, Karl Christe, William Wilson, and Jeff Sheehy

USC Group

From left to right: Ralf Haiges, Thorsten Schroer, Ross Wagner, Stefan Schneider, Karl Christe, and Michael Gerken.

New USC facilities



The Taming of N_5^+

J. Am. Chem. Soc. 2001, 123, 6308

- Desired a N_5^+ salt more stable than $N_5^+AsF_6^-$

- Prepared $N_5^+SbF_6^-$:

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

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

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:

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

Vacuum Line Synthesis

The Perils of Polynitrogen 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)

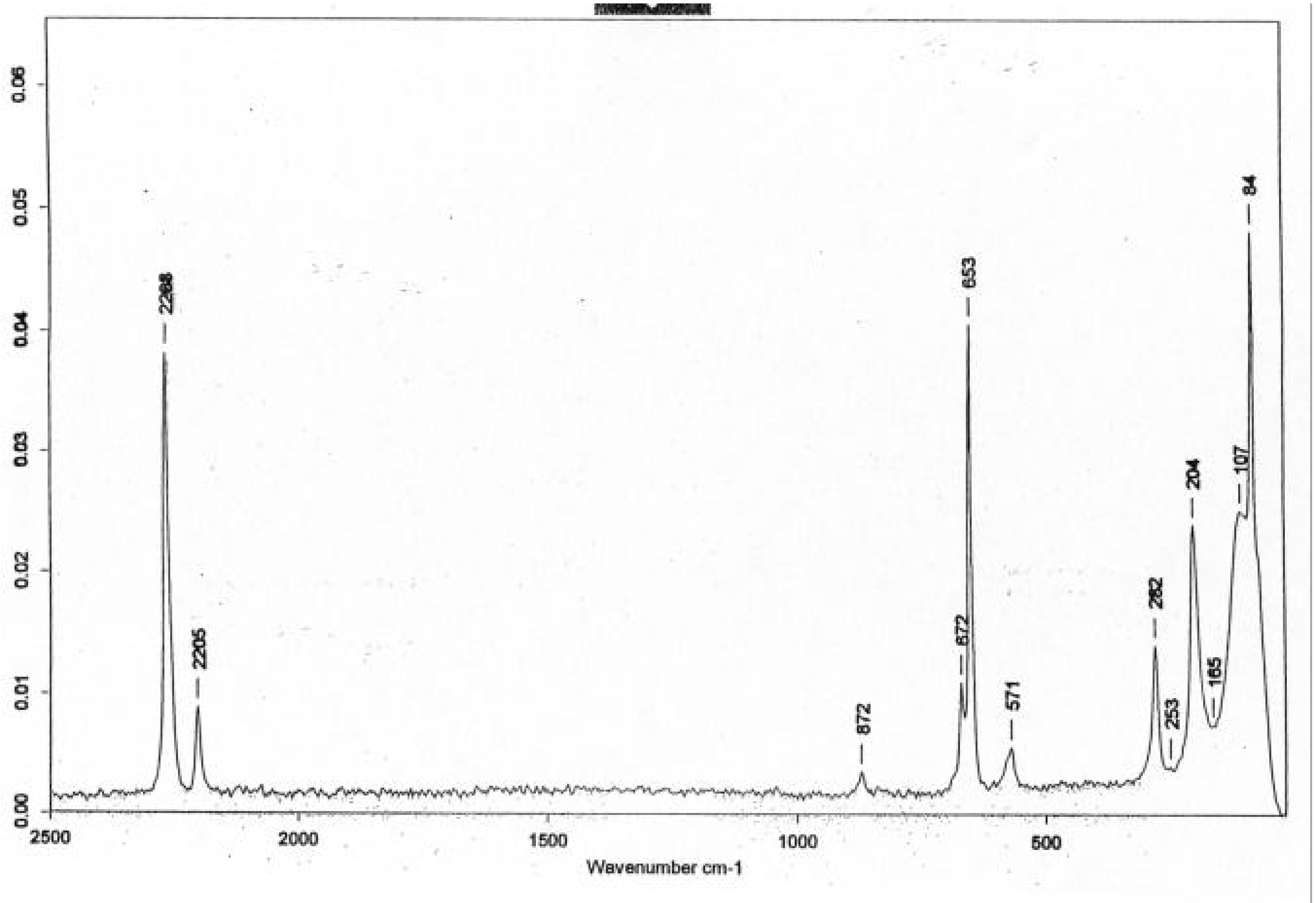
- HN_3 can be replaced by insensitive, commercially available $(CH_3)_3SiN_3$ (TMS azide)

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

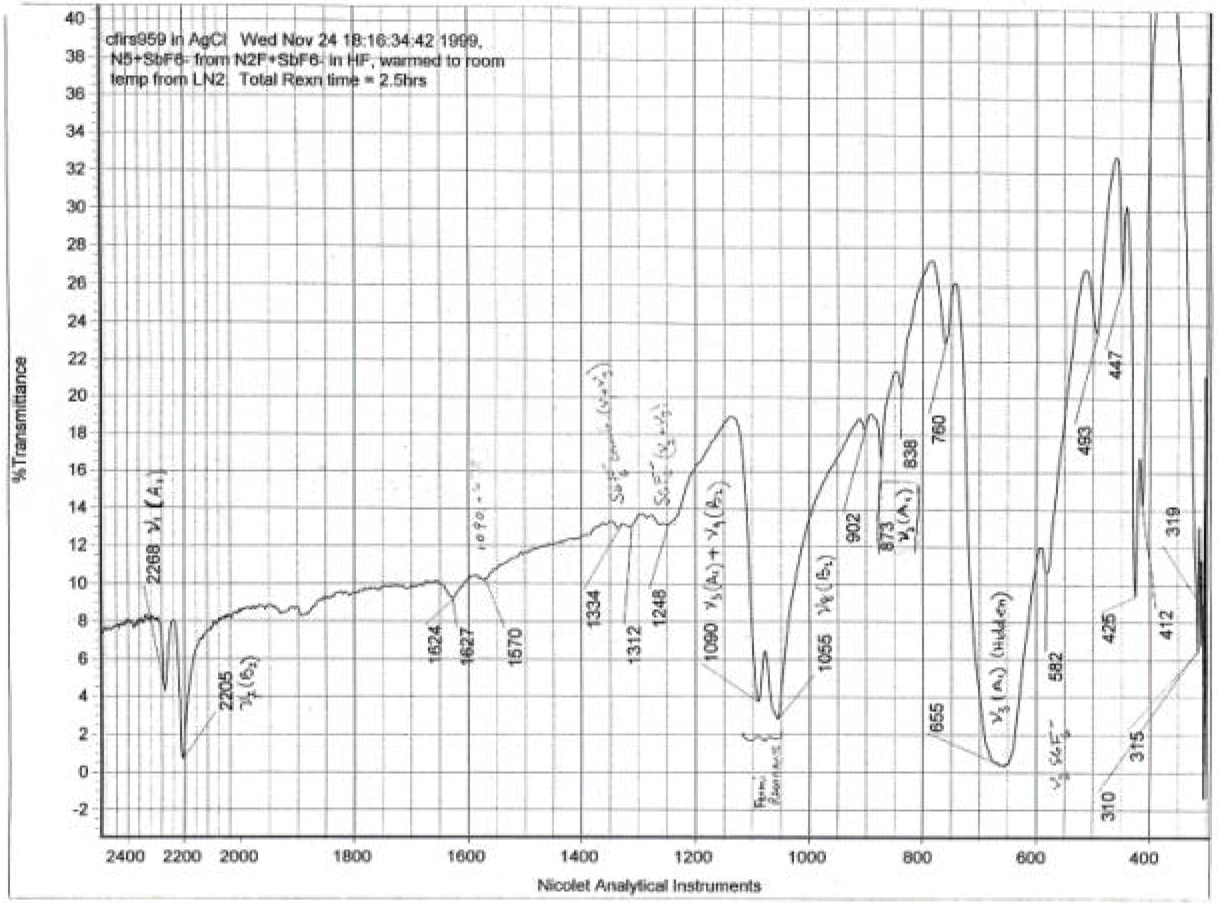
- HF solutions of HN_3 generated from NaN_3 and HF are another alternative to handling HN_3 directly

- N_5SbF_6 can be routinely prepared in a safe manner on a 5 g scale

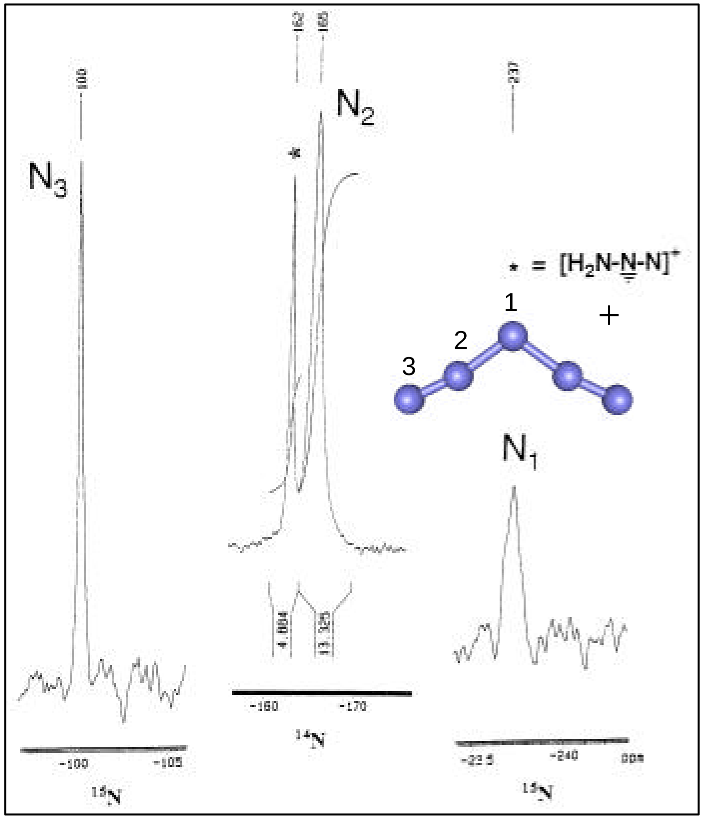
Raman Spectrum of $N_5^+SbF_6^-$



Infrared Spectrum of $N_5^+SbF_6^-$



NMR Spectra



Accurate calculations of nitrogen NMR shifts had been nearly infeasible for N_5^+ and impossible for anything larger

Our new method of obtaining accurate results with less demanding calculations:

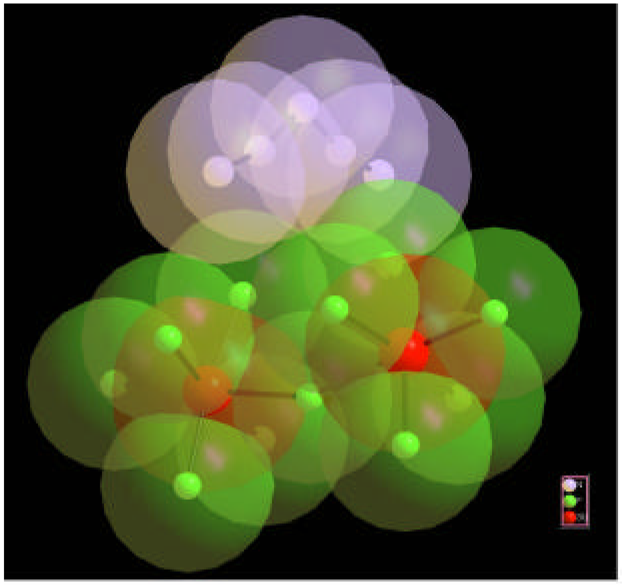
$$\delta[\text{calc}] = \delta[\text{MP2/pz3}d\text{1}f] - \delta[\text{MP2/qzp}] + \delta[\text{CCSD(T)/qzp}]$$

NMR Chemical Shifts (ppm)†

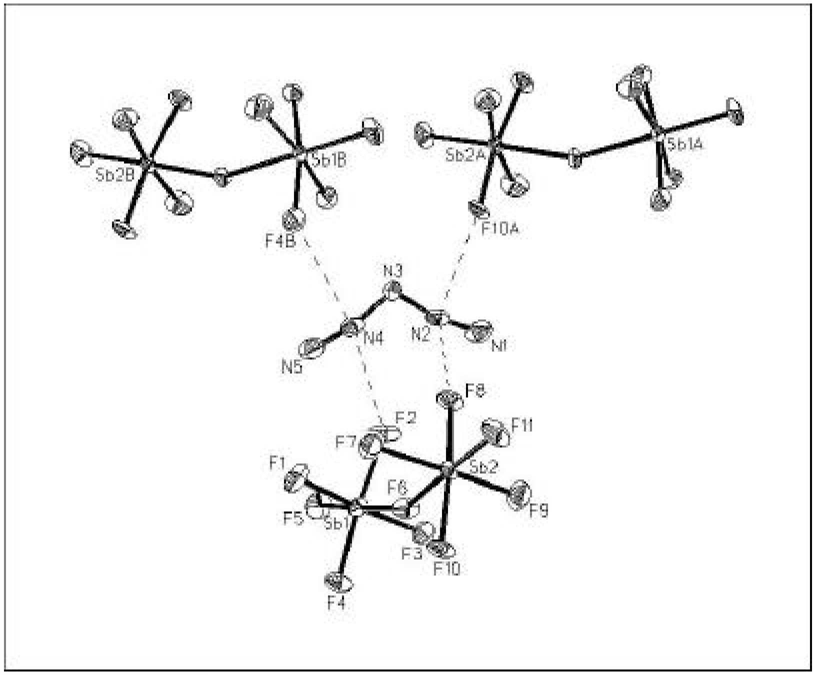
Atom	Obs.	MP2‡	CCSD(T)‡	δ[calc]
N_1	-237.3	-180	-215	-236
N_2	-165.3	-85	-146	-167
N_3	-100.4	-80	-75	-88

† Relative to CH_3NO_2 ‡ qzp basis set

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



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



Oxidizing Power of N_5^+

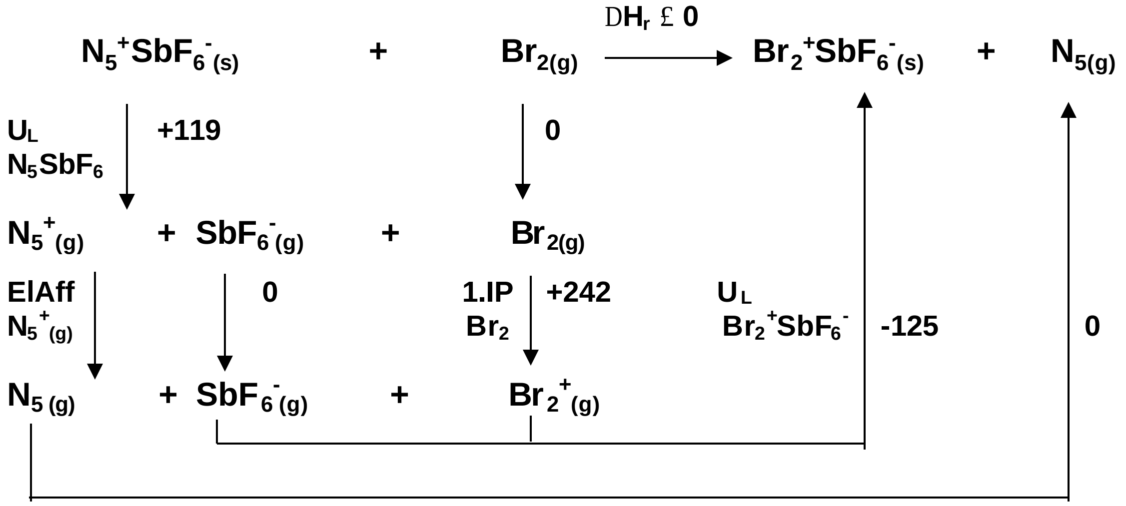
- Electron affinity (EA) of N_5^+ needed for stability predictions of new N_5^+ salts using Born-Haber cycles. The electron affinity of N_5^+ was determined by examining its ability to oxidize the following substrates:

	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
$N_5^+SbF_6^- + Cl_2 \xcancel{\longrightarrow} Cl_2^+SbF_6^- + 2.5\ N_2$	11.48
$N_5^+SbF_6^- + O_2 \xcancel{\longrightarrow} O_2^+SbF_6^- + 2.5\ N_2$	12.07
$N_5^+SbF_6^- + 2\ Xe \xcancel{\longrightarrow} Xe_2^+SbF_6^- + 2.5\ N_2$	12.13

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



$N_5^+SbF_6^-{}_{(s)}$ + $Br_{2(g)}$ $\xrightarrow{\Delta H_r \leq 0}$ $Br_2^+SbF_6^-{}_{(s)}$ + $N_{5(g)}$

U_L N_5SbF_6 +119

0

$N_5^+{}_{(g)}$ + $SbF_6^-{}_{(g)}$ + $Br_{2(g)}$

ElAff $N_5^+{}_{(g)}$

0

1.IP Br_2 +242

U_L $Br_2^+SbF_6^-$ -125

0

$N_{5\,(g)}$ + $SbF_6^-{}_{(g)}$ + $Br_2^+{}_{(g)}$

- 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

Attempted Syntheses of Azidamines

- Only three azidamines have been reported in the literature:

$(CH_3)_2N\text{-}N_3$ thermally stable (Bock and Kompa, 1962)

$[(CH_3)_3Si]_2N\text{-}N_3$ stable up to 100 °C (Wiberg 1962)

$(FSO_2)_2N\text{-}N_3$ thermally unstable (Klapoetke, 1996)

- Attempts to repeat the Bock and Kompa work failed. The

$$(CH_3)_2NCl + NaN_3 \xrightarrow{CH_2Cl_2} (CH_3)_2N\text{-}N_3 + NaCl$$

reaction gave $CH_2(N_3)_2$ as the only covalent azide.

Attempted Syntheses of Azidamines

- Attempts to repeat the Wiberg work also failed, but resulted in an interesting spin-off discovery of the first stable, simple, inorganic ammonium cation with an N-Cl bond (Angew. Chem. in press).

$$[(CH_3)_3Si]_2NCl + HF + AsF_5 \longrightarrow NH_3Cl^+AsF_6^- + 2\,(CH_3)_3SiF$$

- Several NH_3Cl^+ salts were prepared and characterized. They are all stable salts and react slowly with water to give NH_2Cl.

$$NH_3Cl^+AsF_6^- + H_2O \longrightarrow OH_3^+AsF_6^- + NH_2Cl$$

- NH_2Cl is an effective spore killer, and salts could serve as a solid NH_2Cl gas generator.

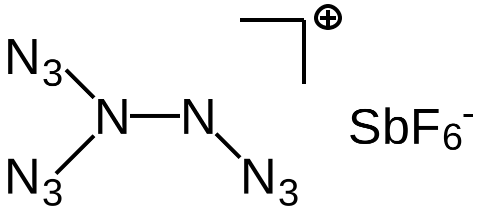
Pursuit of Azidamines

- Desired product $(N_3)_2NN(N_3)SbF_6$

HF

$N_2F_3SbF_6$? 3 HN_3 ? ?

-78?C

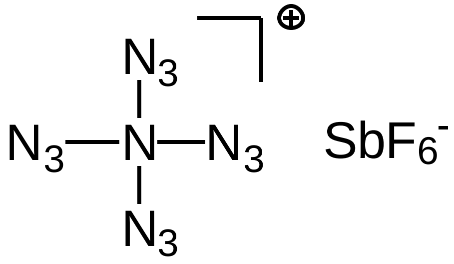


- Desired product $N(N_3)_4SbF_6$

HF

NF_4SbF_6 ? 4 HN_3 ? ?

-78?C to -20?C



Reaction of NF_4^+ with HN_3

- Reaction of NF_4^+

$$NF_4SbF_6 + HN_3 \xrightarrow{HF/-78\ C} NF_3 + HF + FN_3 + SbF_5$$

$$2\ FN_3 \longrightarrow 2\ N_2 + trans\text{-}N_2F_2$$

$$HN_3 + HF + SbF_5 \longrightarrow H_2N_3SbF_6$$

$$3\ trans\text{-}N_2F_2 \longrightarrow 2\ N_2 + 2\ NF_3$$

- NF_4^+ acts as a fluorinating agent, fluorinating HN_3 to FN_3

Reaction of $N_2F_3^+$ with HN_3

- Reaction of F_2NNF^+

$$F_2NNF^+SbF_6^- + HN_3 \xrightarrow{\text{HF/ -78 C}} [F_2NNN_3^+SbF_6^-] + HF$$

$$[F_2NNN_3^+SbF_6^-] \longrightarrow [F_2NNN^+SbF_6^-] + N_2$$

$$[F_2NNN^+SbF_6^-] \longrightarrow [F_2N^+SbF_6^-] + N_2$$

$$[F_2N^+SbF_6^-] \longrightarrow NF_3 + SbF_5$$

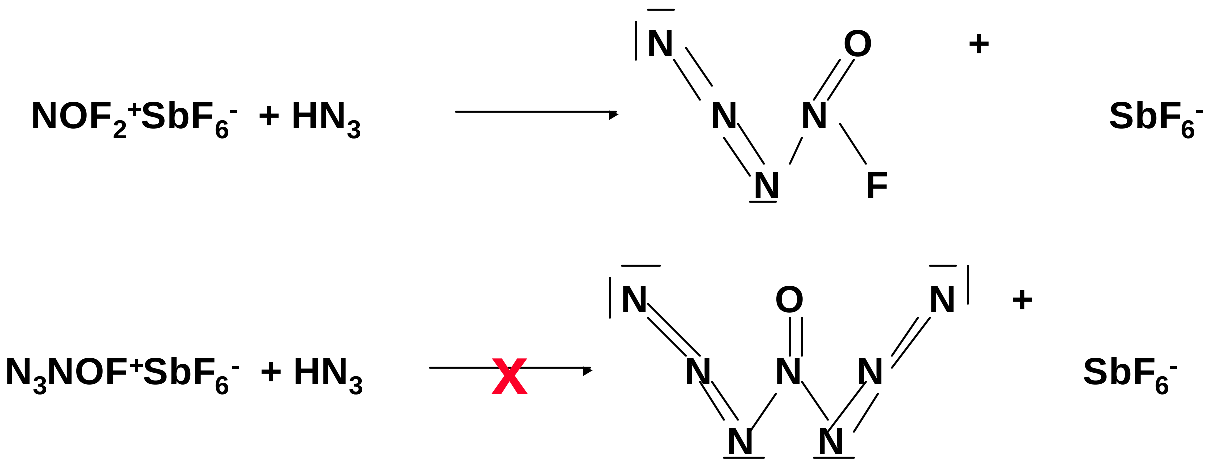
$$HN_3 + HF + SbF_5 \longrightarrow H_2N_3^+SbF_6^-$$

- The absence of $N_2F^+SbF_6^-$ or $N_5^+SbF_6^-$ in the product favors this substitution mechanism over an oxidation reaction with N_2F_2 formation

Synthesis and Characterization of N_3NOF^+

- **Another promising polynitrogen target ion is the N_7O^+ cation**

- **Reaction of $NOF_2^+SbF_6^-$ with HN_3 was studied in HF at –78 °C, and $N_3NOF^+SbF_6^-$ was isolated as a white solid stable up to ~ -20 °C. N_3NOF^+ exists as both, a *cis-* and *trans*-isomer**



Metathetical Conversions of N_5^+ Salts

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

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

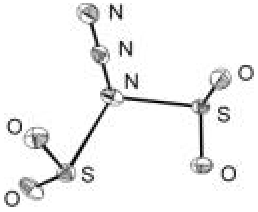
$$N_5SbF_6 + KB(CF_3)_4 \xrightarrow[-64°C]{SO_2} N_5B(CF_3)_4 + KSbF_6 \downarrow$$

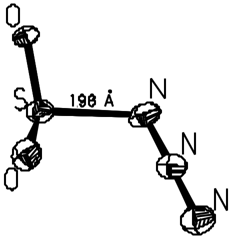
- $N_5B(CF_3)_4$ is a white solid, stable at room temperature
  - ➢ Characterized by vibrational spectroscopy

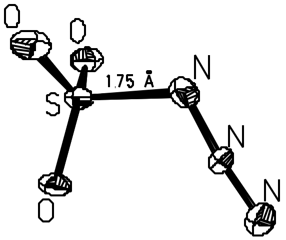
INTERACTION OF SO_2 WITH N_3^-

Inorg. Chem. **2002, *41*, 4275 and 2003, *42*, 416**

- **Colorless N_3^- and colorless SO_2 form a bright *yellow* solution.**
- **yellow solution contains a covalent azide**
  - **Raman: strong band at 2016 cm^{-1}**
  - **^{14}NMR: deshielding of terminal N by 79 ppm relative to N_3^-**
- **Removal of SO_2 produces**
  - **at –64 °C: a yellow 1:2 adduct, $[N_3{\cdot}2SO_2]^-$**
  - **at –50 to 20 °C: a white 1:1 adduct, $[N_3{\cdot}SO_2]^-$**
  - **above 20 °C: white N_3^-**
- **Products were characterized by**
  - **material balances**
  - **vibrational spectra**
  - **theoretical calculations**
  - **crystal structures**







Synthesis of More Energetic N_5^+ Salts

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

- Salts with higher N_5^+ content:

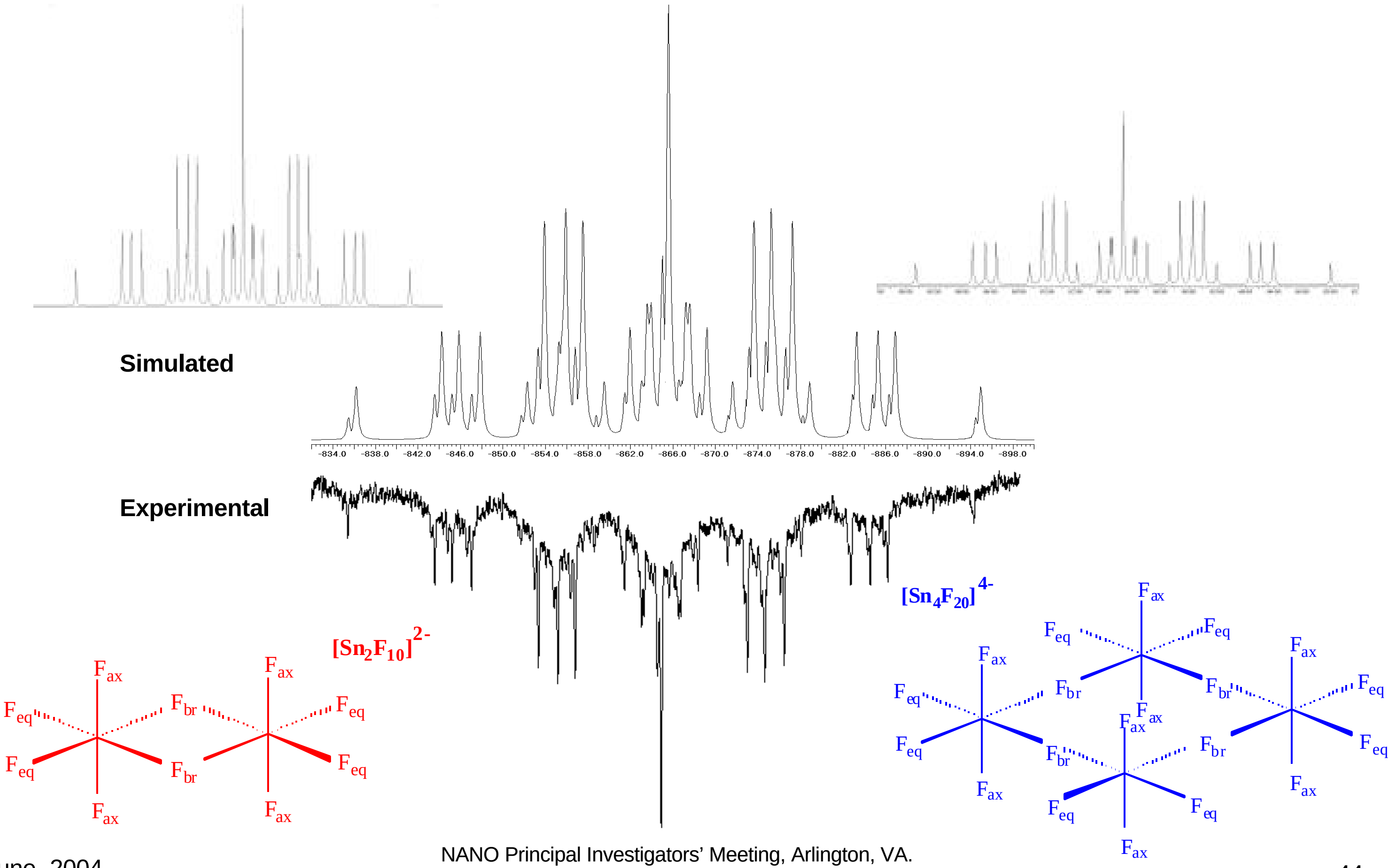
$$2\ N_5SbF_6 + Cs_2SnF_6 \xrightarrow[-78°C]{HF} (N_5)_2SnF_6 + 2\ CsSbF_6 \downarrow$$

- $(N_5)_2SnF_6$ is friction sensitive and can decompose explosively
  - ➢ Double the N_5^+ content of N_5SbF_6
  - ➢ Important step toward synthesis of salts containing touching polynitrogen ions
  - ➢ Under carefully controlled conditions, stepwise decomposition

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

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

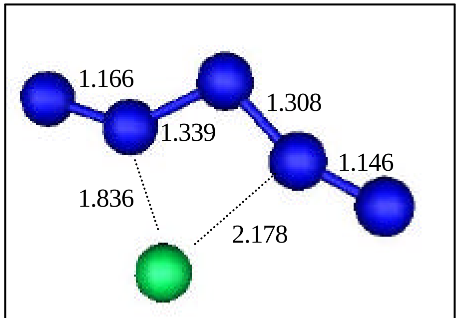
^{119}Sn NMR Spectrum of N_5SnF_5



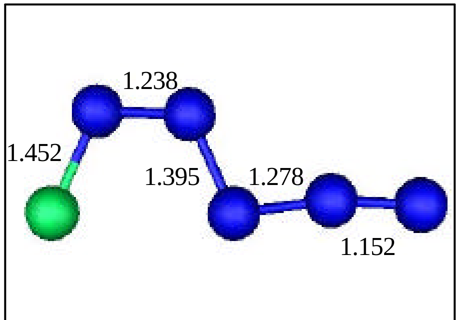
FN_5 (*J. Phys. Chem. A* 2003, 107, 6638)

- 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

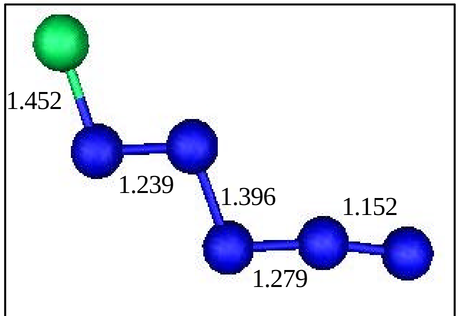
Six FN_5 Isomers *(MP2/6-31++G(d,p))*



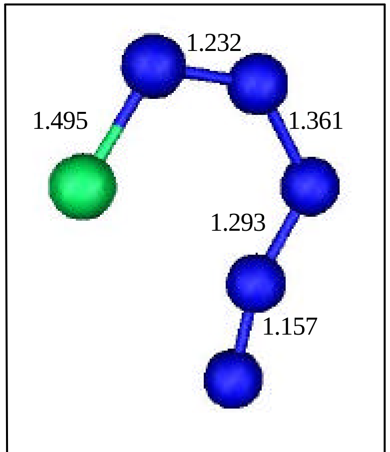
bifurcated (1)



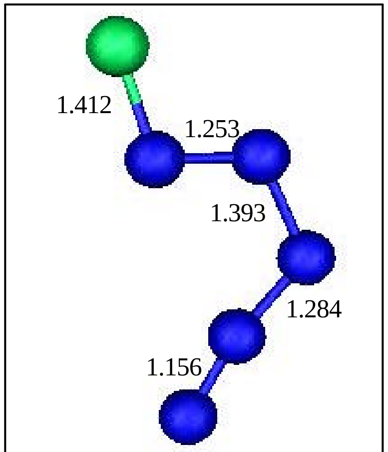
cis (2)



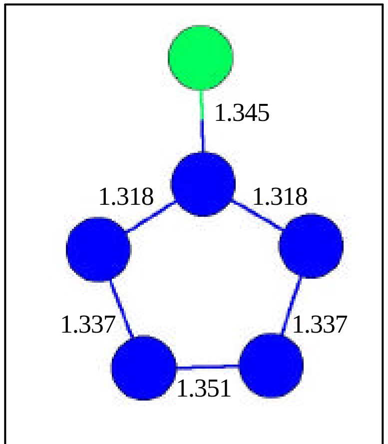
3 (trans)



harp (4)

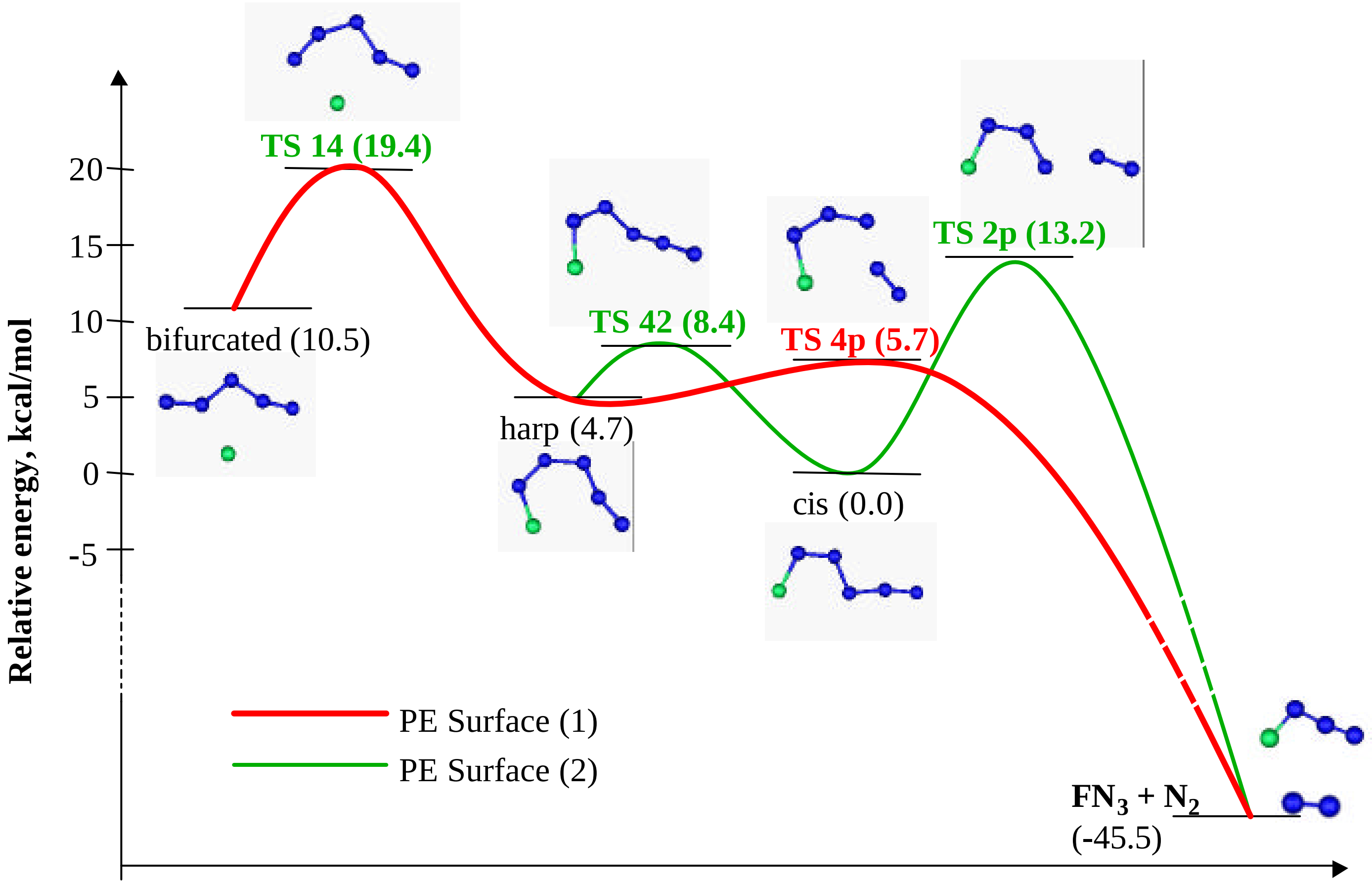


wag (5)



cyclic (6)

Relative isomerization/decomposition PESs with FN_5 isomers (reference = cis isomer)



*Energies: CCSD(T)/aug-cc-pVDZ with ZPE

Synthesis of $N_5^+HF_2^-$,

Angewandte Chemie in press

- Desired reaction was:

$$N_5SbF_6 + Cs[N(CF_3)_2] \xrightarrow{HF} N_5[N(CF_3)_2] + CsSbF_6?$$

- Obtained at -64 °C a clear colorless liquid whose Raman spectrum showed only bands due to N_5^+:

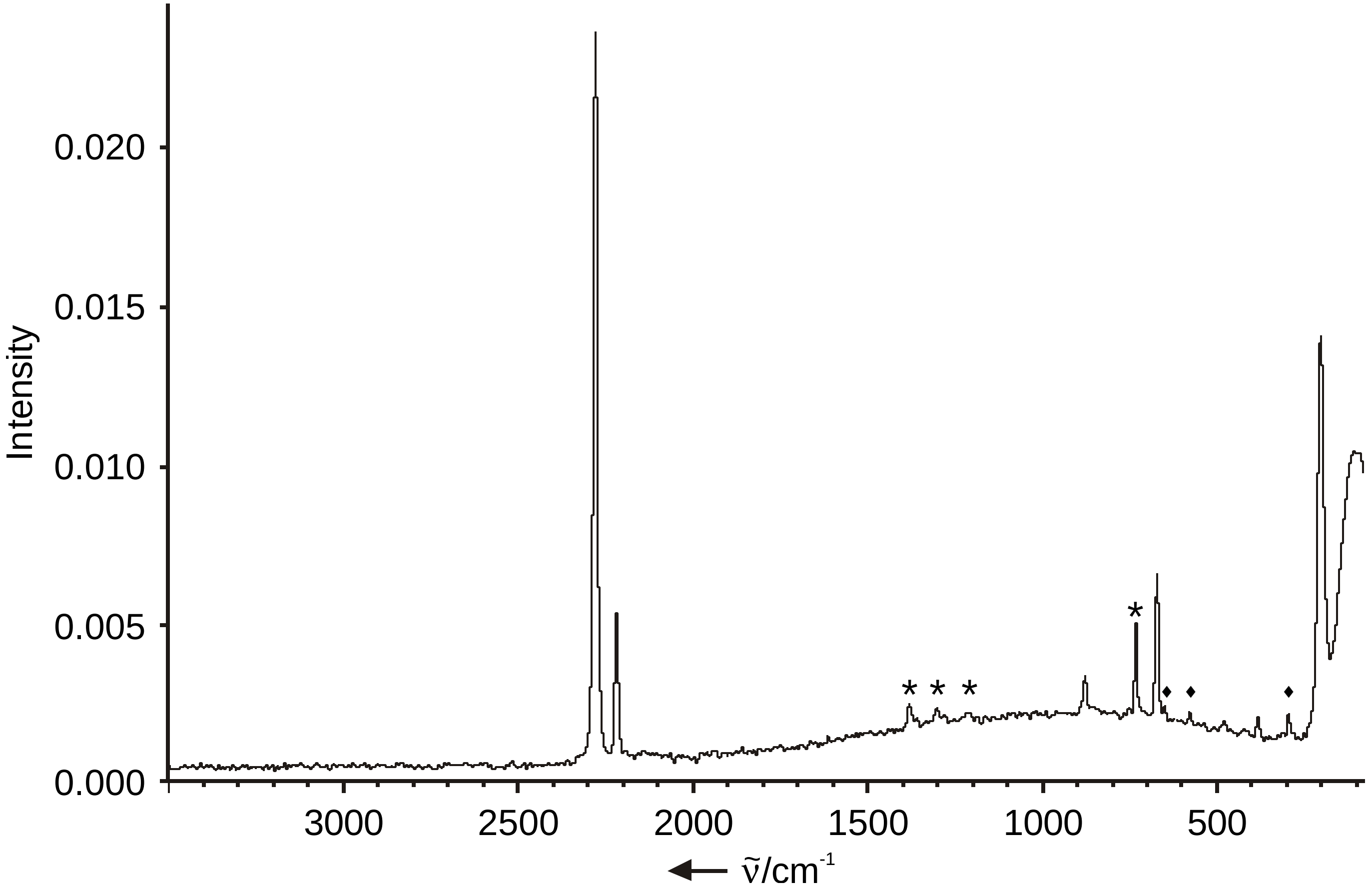
- Actual reaction:

$$Cs^+[N(CF_3)_2]^- + 2\ HF \longrightarrow Cs^+HF_2^- + HN(CF_3)_2$$

$$Cs^+HF_2^- + n\ HF + N_5^+SbF_6^- \longrightarrow N_5HF_2 \cdot nHF + CsSbF_6?$$

- Observed chemistry is analogous to that observed by us 24 years ago for $NF_4^+HF_2^-$ (*Inorg. Chem.* **1980**, *19*, 1494).

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



$N_5^+HF_2^-\cdot nHF$, a General Reagent for the Syntheses of Other N_5^+ Salts

- Because HF is a relatively weak Lewis acid, it can be displaced from its $N_5^+HF_2^-\cdot nHF$ salt by any stronger Lewis acid. This principle was successfully demonstrated for the syntheses of the following new N_5^+ salts from HF solution at -64°C:

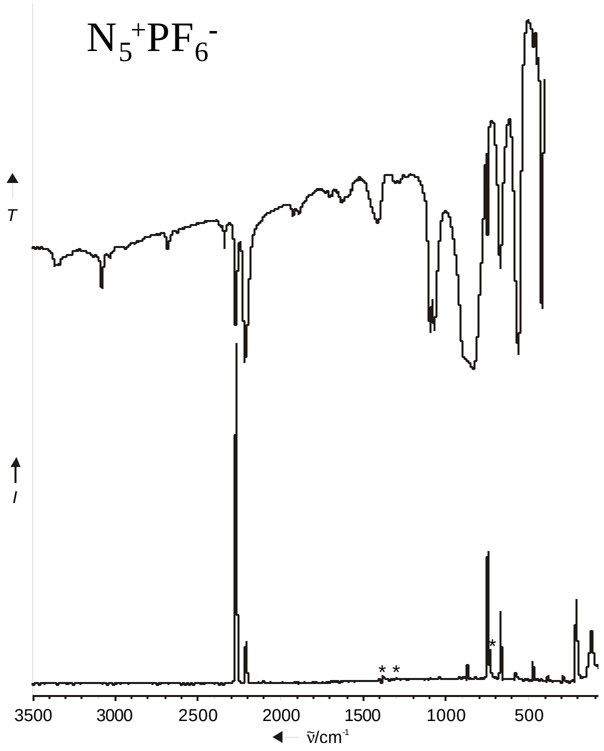
$$N_5HF_2\cdot nHF \quad + \quad PF_5 \longrightarrow N_5PF_6 \quad + \quad (n+1)\ HF$$

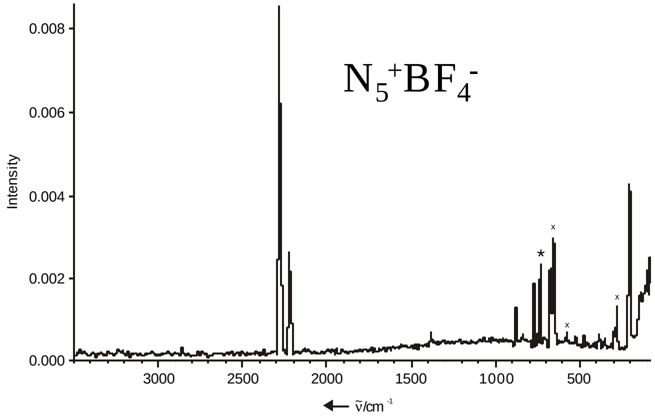
$$N_5HF_2\cdot nHF \quad + \quad BF_3 \longrightarrow N_5BF_4 \quad + \quad (n+1)\ HF$$

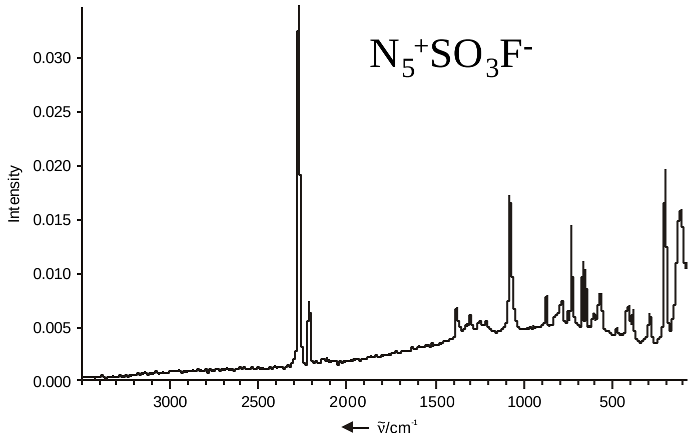
$$N_5HF_2\cdot nHF \quad + \quad HSO_3F \longrightarrow N_5SO_3F \quad + \quad (n+2)\ HF$$

- All three salts are white solids that are marginally stable at room temperature. They were characterized by vibrational and multi-nuclear NMR spectroscopy.

Vibrational Spectra of the New N_5^+ Salts







Synthesis of New, More Energetic N_5^+ Salts

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

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

  - 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:

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

  - 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 $N_5^+N_3^- \approx 130 \pm 20$ kcal/mol (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

- Using theoretical calculations and Born-Haber cycles based on adiabatic electron affinity and ionization potentials, we have shown that both $N_5^+N_5^-$ and $N_5^+N_3^-$ are unstable toward decomposition to N_3 + N_2 by large margins. Because there is no kinetic barrier towards electron transfer from an anion to a cation, the process

$$A^+B^-_{(s)} \quad ? \quad A_{(g)} + B_{(g)}$$

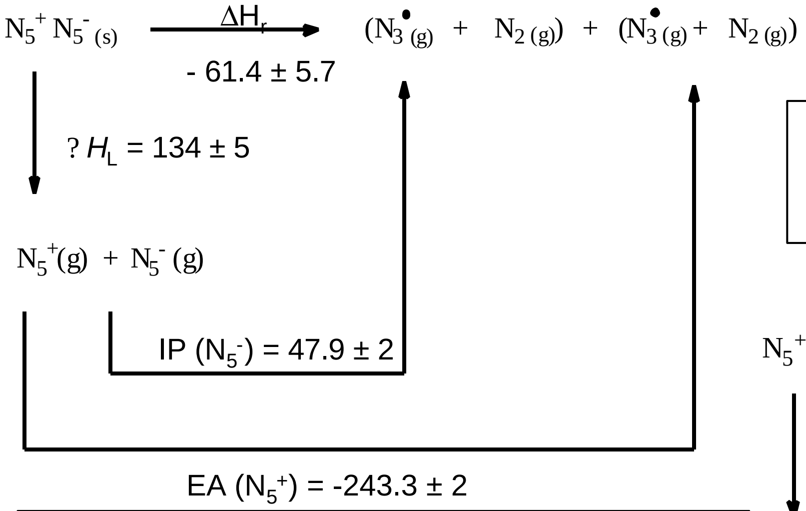
is only thermodynamically controlled (change in ?G).

- Because both catenated and cyclic N_5 radicals are vibrationally unstable and decompose with little or no barrier spontaneously to the first vibrationally stable species, i.e., N_3 + N_2, the energy of this highly exothermic process must be added to the above given decomposition process.
- The use of vertical instead of adiabatic potentials and the assumption of N_5 radicals as the decomposition products can cause huge errors of about 100 kcal/mol per N_5 unit in stability predictions.

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

- The correctness of our approach was demonstrated by experimentally bracketing the electron affinity of N_5^+ (10.52-11.48 eV) which agrees well with our calculated adiabatic value of 10.55 eV, but not with the vertical value of 6.04 eV.
- We have calculated highly accurate enthalpies of formation and adiabatic electron affinities and ionization potentials for N_3, N_3^-, N_5^+ and N_5^- from total atomization energies.
- The stability of an ionic solid is governed by the sum of the adiabatic first ionization potential of the anion, the adiabatic electron affinity of the cation, and the lattice energy, as shown by the following Born-Haber cycles.

Born-Haber Cycles for $N_5^+N_3^-$ and $N_5^+N_5^-$



$N_5^+N_5^-{}_{(s)} \xrightarrow{\Delta H_r} (N_3^{\bullet}{}_{(g)} + N_{2\,(g)}) + (N_3^{\bullet}{}_{(g)} + N_{2\,(g)})$

- 61.4 ± 5.7

? H_L = 134 ± 5

$N_5^+(g) + N_5^-(g)$

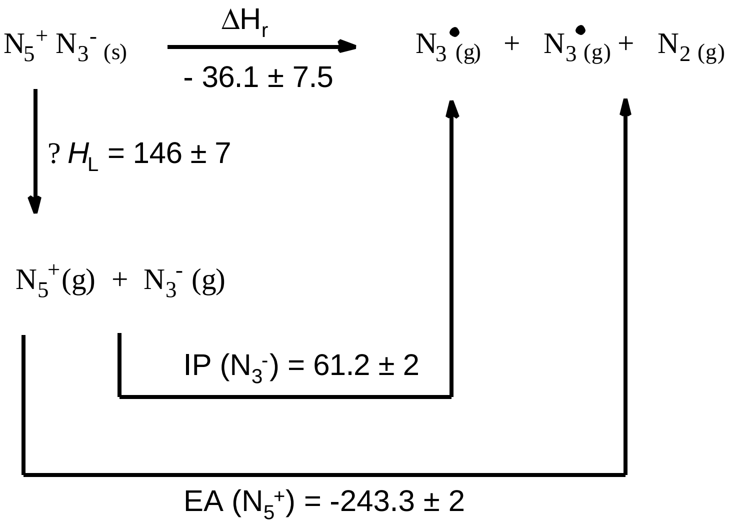
IP (N_5^-) = 47.9 ± 2

EA (N_5^+) = -243.3 ± 2

- For a salt to be stable, ? Hr must be zero or positive

- Problem with the N_5 ions:

 Both, cyclic and catenated N_5 radicals are vibrationally unstable and decompose without barrier to N_3. Because N_3 has a barrier, $N_5^+N_3^-$ is less unstable than $N_5^+N_5^-$



$N_5^+N_3^-{}_{(s)} \xrightarrow{\Delta H_r} N_3^{\bullet}{}_{(g)} + N_3^{\bullet}{}_{(g)} + N_{2\,(g)}$

- 36.1 ± 7.5

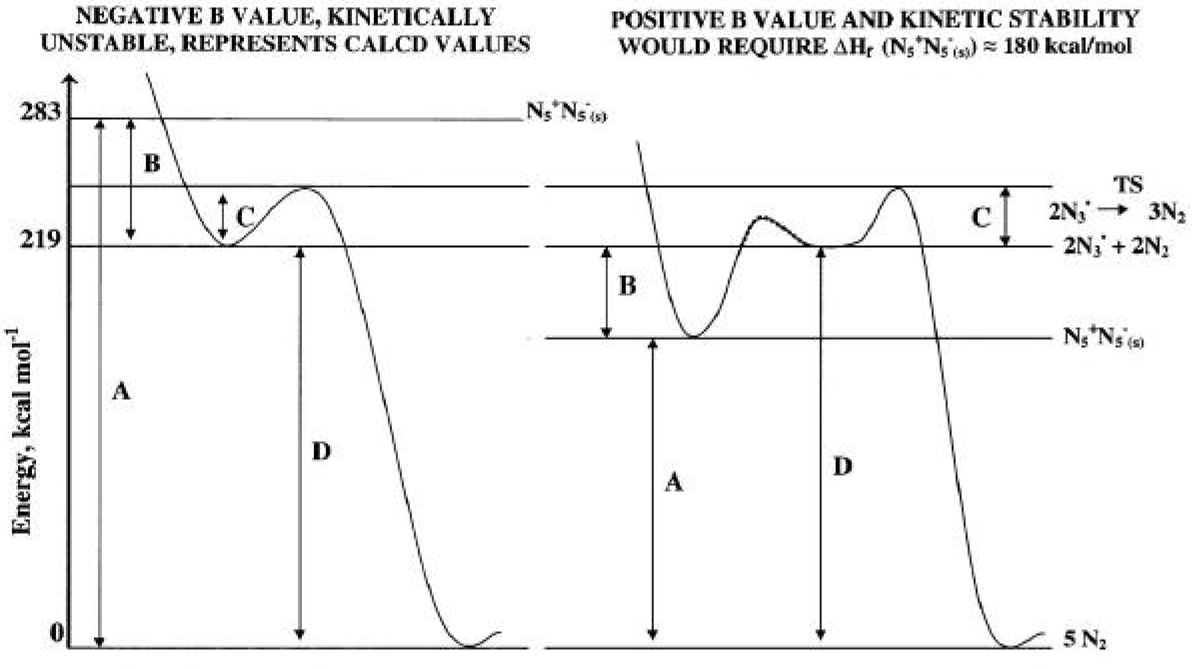
? H_L = 146 ± 7

$N_5^+(g) + N_3^-(g)$

IP (N_3^-) = 61.2 ± 2

EA (N_5^+) = -243.3 ± 2

Potential energy curves for $N_5^+N_5^-$


NEGATIVE B VALUE, KINETICALLY UNSTABLE, REPRESENTS CALCD VALUES

POSITIVE B VALUE AND KINETIC STABILITY WOULD REQUIRE ΔH_f $(N_5^+N_5^-{}_{(s)}) \approx 180$ kcal/mol

A = ΔH_f $(N_5^+N_5^-{}_{(s)})$

B = ΔH_r $(N_5^+N_5^-{}_{(s)} \longrightarrow 2N_3^{\bullet}{}_{(g)} + 2\ N_{2\,(g)}) = U_L\ (N_5^+N_5^-{}_{(s)}) + 2\ RT + IP\ (N_5^-{}_{(g)})\ -\ EA\ (N_5^+{}_{(g)})$

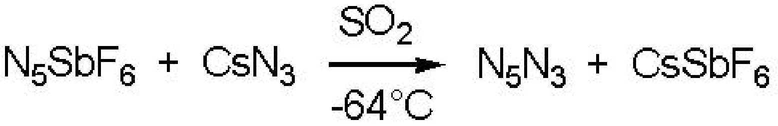
C = Activation energy barrier for decomposition of $2N_3^{\bullet}{}_{(g)} \longrightarrow 3N_{2\,(g)}$

D = ΔH_r $(\ 2N_3^{\bullet}{}_{(g)} \longrightarrow 3N_{2\,(g)})$

Experimental confirmation of instability of $N_5^+N_3^-$

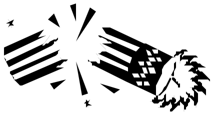
- Our conclusion that $N_5^+N_3^-$ and $N_5^+N_5^-$ are unstable and decompose spontaneously with N_2 evolution was experimentally confirmed in our laboratory for $N_5^+N_3^-$

  - Desired metathesis:



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

Obtained products:

$4\ N_2 + CsSbF_6 +$ 

Requirements for the synthesis of a stable all-nitrogen compound

- The synthesis of a stable nitrogen allotrope requires either:
  - an N_5^+ salt that is lower in energy than (N_3 + N_2), which is very unlikely
  - a new polynitrogen cation, such as N_3^+, that is derived from a stable radical
  - or the direct synthesis of a neutral polynitrogen.

Polyazide Chemistry

- Complex azides have great potential for energetic high-nitrogen ingredients and as potential counter-ions for N_5^+.
- Typical examples of compounds previously prepared by us:

  $C(N_3)_3^+ClO_4^-$, $C(N_3)_3^+N(NO_2)_2^-$, and $C(N_3)_3^+NO_3^-$
- Some polyazides had been known, but often their structures had not been determined because of handling problems.
- Most of these compounds are very sensitive, but some can be safely handled, particularly when combined with large counter-ions.
- For their syntheses we have used at USC the reactions of the corresponding fluorides with $(CH_3)_3SiN_3$ in suitable solvents, such as SO_2 or CH_3CN. This results in the rapid and complete replacement of all fluorines by azides.

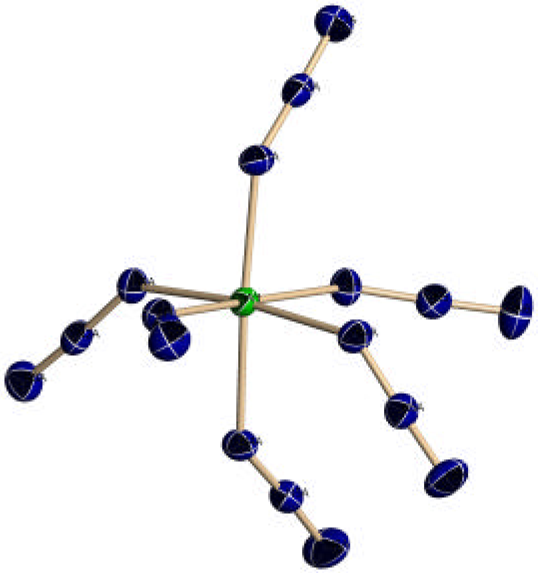
Highlights of Polyazide Chemistry

- Compounds studied so far under this program include:

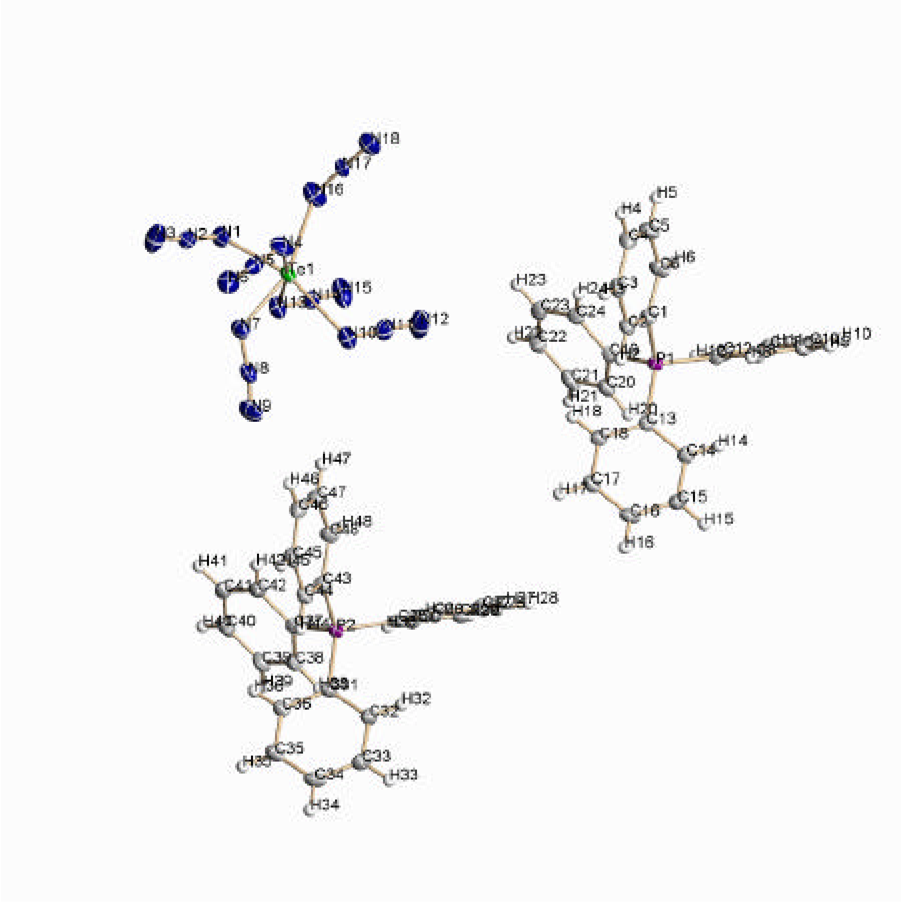
  $W(N_3)_6$, $Mo(N_3)_6$, $W(N_3)_7^-$, $WO(N_3)_4$, $Ta(N_3)_5$, $Ti(N_3)_4$, $Ti(N_3)_5^-$, $Ti(N_3)_6^{2-}$, $Te(N_3)_4$, $Te(N_3)_5^-$, $Te(N_3)_6^{2-}$, $Sb(N_3)_5$, $As(N_3)_5$, $Sb(N_3)_6^-$, $As(N_3)_3$, $Sb(N_3)_3$, $B(N_3)_4^-$, and $P(N_3)_6^-$

- Tellurium azide paper was published in Angewandte as a "Hot Paper" (*Angew. Chem. Int. Ed.* **2003**, *42*, 5847) and highlighted in Chem. & Eng. News.
- $As(N_3)_3$ and $Sb(N_3)_3$ were published in Chemistry – A European Journal" (*Chem. Eur. J.* **2004**, *10*, 508).
- Titanium azide work was accepted by Angewandte as a "Very Important Paper" and has appeared on line.

Crystal Structure of $W(N_3)_6$

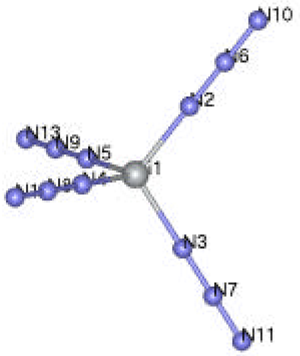


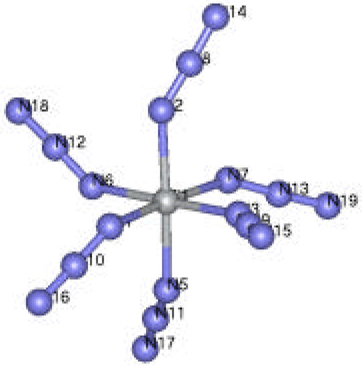
Structure of $[(C_6H_5)_4P^+]_2[Te(N_3)_6]^{2-}$



Novel type of covalent azides with linear M-N-N bonds

- Based on quantum chemical calculations, Gagliardi and Pyykkoe have recently predicted, (*Inorg. Chem*. **2003**, *42*, 3074), for $Ti(N_3)_4$, $Zr(N_3)_4$, $Hf(N_3)_4$, and $Th(N_3)_4$ a novel type of bonding involving linear M-N-N bonds.
- We have confirmed these calculations for $Ti(N_3)_4$ and also predict that other azides, such as $Fe(N_3)_2$ (Melanie Teichert), can form linear M-N-N bonds. Based on our calculations, we also expect that the $Ti(N_3)_6^{2-}$ anion possesses the usual bent M-N-N bonds.





Synthesis and Characterization of $Ti(N_3)_4$

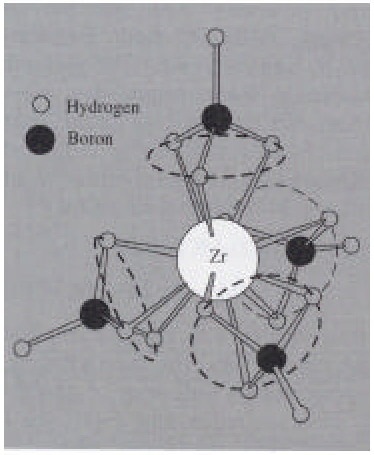
- Synthesis

  TiF_4 + exc. $TMSN_3$? $Ti(N_3)_4$ + 4 TMSF

- Properties
  - ➢Yellow-orange solid
  - ➢Very shock-sensitive
  - ➢Very low volatility, decomposes on sublimation
  - ➢Could not get single crystals for structure determination, but Raman spectrum and comparison with calculated spectra suggest that CN is higher than 4 and the Ti-N-N angle is bent.
  - ➢Need a gas-phase structure of free $Ti(N_3)_4$

Possible explanations for linear M-N-N bonds

- Gagliardi and Pyykkoe invoke conjugation.
- We prefer the following interpretation because the calculated Ti-N bond distances are relatively long and are similar to single bonds. Also, the $N_{ß}$-$N_{?}$ bonds are quite short, and the Ti-N-N bonds in $Ti(N_3)_6^{2-}$ are strongly bent.
  - ➢ The N_a atom of the $–N_3$ ligand has three free valence electron pairs which can act as a tridentate ligand and, in a tetrahedron, can perfectly overlap with three of the lobes of the Ti 3*d*-orbitals. This scheme is analogous to the structure of $Zr(BH_4)_4$ which possesses 4 trihapto BH_4 groups. In the usual covalent azides, the azide ligands utilize only one electron pair of the N_a atom for the bonding, and the presence of two additional, sterically active free valence electron pairs results in a pyramidal configuration with an M-N-N angle of about 120 °.

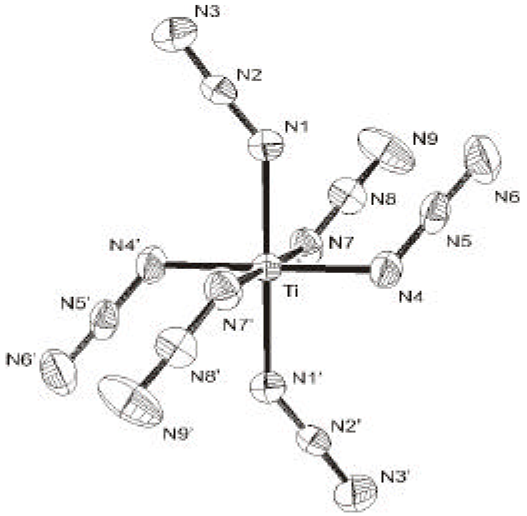


Crystal Structure of $[Ti(N_3)_6]^{2-}$

- Synthesized the $[Ti(N_3)_6]^{2-}$ anion according to

$$Ti(N_3)_4 + 2\,P(Ph)_4^+N_3^- \longrightarrow [P(Ph)_4]_2[Ti(N_3)_6]$$

and determined its crystal structure.



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

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

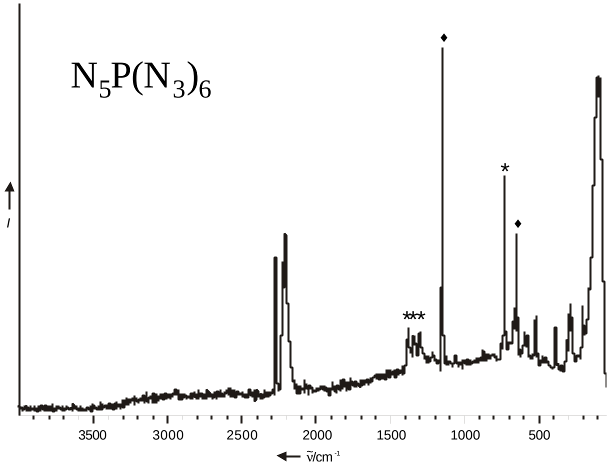
$$N_5SbF_6 + NaP(N_3)_6 \xrightarrow{SO_2,\ -64\ C} N_5P(N_3)_6 + NaSbF_6\bullet$$

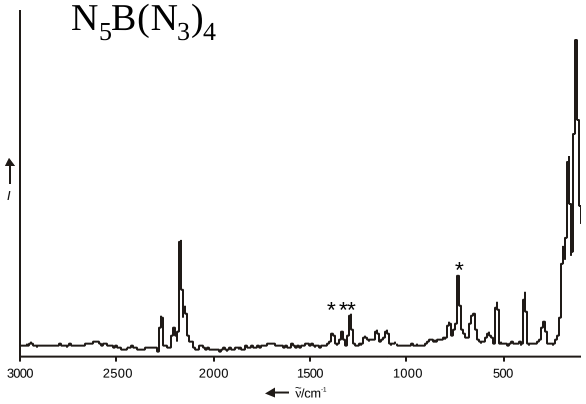
$$N_5SbF_6 + NaB(N_3)_4 \xrightarrow{SO_2,\ -64\ C} N_5B(N_3)_4 + NaSbF_6\bullet$$

- $NaP(N_3)_6$ 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.

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

- Low-temperature Raman spectra





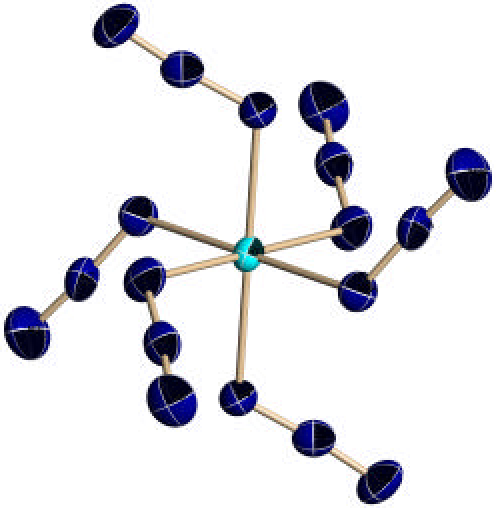
- Material balances
- Stable at -64 °C, explode on warm-up toward room temperature

How much damage can ½ mmol of $N_5^+[P(N_3)_6]^-$ cause ?

Ralf Haiges

Syntheses of free $Sb(N_3)_5$ and $As(N_3)_5$

- Although the $As(N_3)_6^-$ and $Sb(N_3)_6^-$ ions had been isolated before, the free parent molecules had not been obtained because of their high explosiveness.
- We successfully prepared free $Sb(N_3)_5$ and $As(N_3)_5$ and characterized them by vibrational spectroscopy.
- Furthermore, we have obtained the crystal structure $Sb(N_3)_6^-$.



Pentazole & High Nitrogen Anions

DARPA NANO WORKSHOP

Arlington, VA

June 2, 2004

Ashwani Vij
Research Scientist
AFRL/PRSP
Air Force Research Laboratory

Reactions of Group 15 halides with Trimethylsilylazide

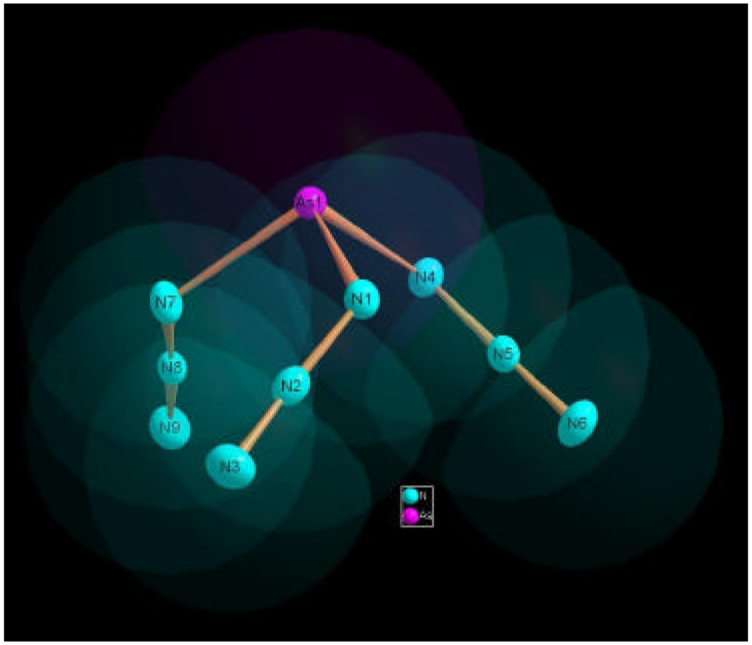
Crystalline binary metal azides were obtained upon reacting the corresponding metal fluorides with $TMSN_3$. These compounds were reported as either liquids or tacky solids by Klapoetke et al.

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

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

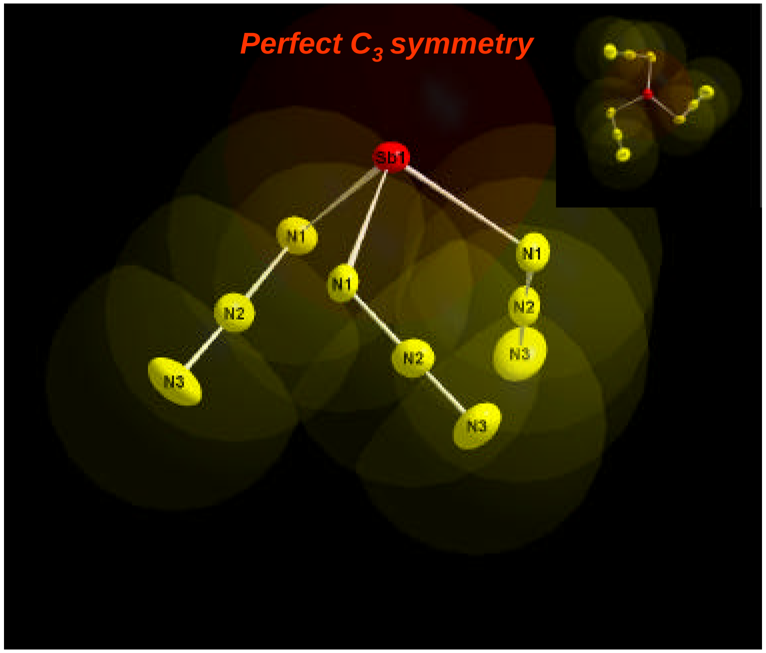
Structures of $As(N_3)_3$ and $Sb(N_3)_3$

Arsenic trizaide



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

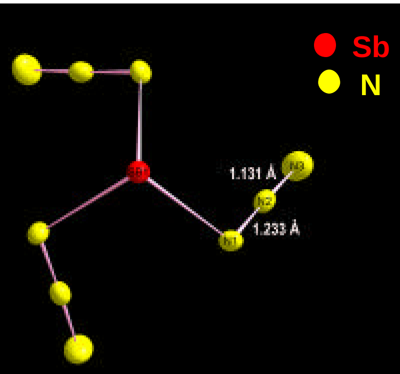
Antimony trizaide



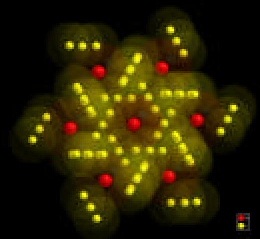
Perfect C_3 symmetry

All azide groups oriented in a propeller-like fashion

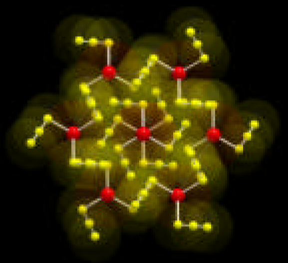
What are "normal" N-N distances in azides?



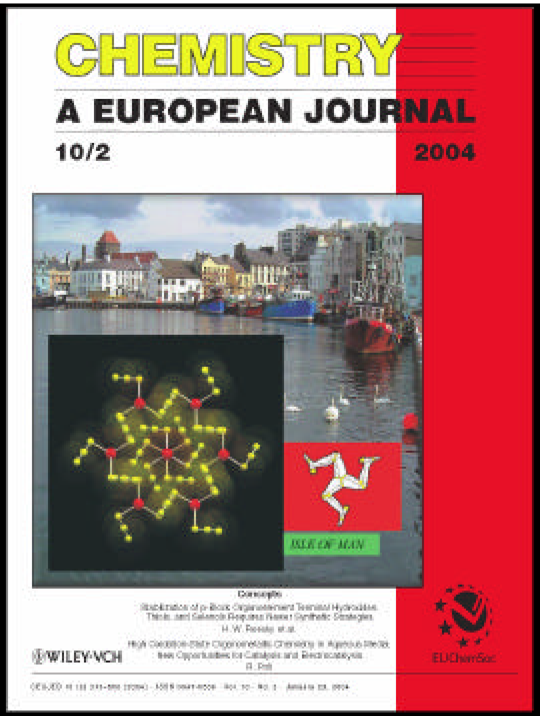
Chloride free synthesis



"Star of David" Perspective



"Isle of Man" Perspective



CHEMISTRY

A EUROPEAN JOURNAL

10/2 2004

Concepts

WILEY-VCH

EUChemSoc

Haiges, Vij, Christe *et al.* *Chemistry Eur. J.*, **2004,** *10*, 508**.**

Reactivity of hexachloroantimonate (VI) with trimethylsilylazide

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

M = P, As; x = 2-6

- ✓ Six chlorine atoms in $SbCl_6^-$ can't be substituted by azide groups in a single step, as reported in literature (Klapoetke *et al.* Inorg. Chem. 2002, *41*, 170).
- ✓ The stepwise substitution gives a good insight into the substitution mechanism.
- ✓ Total substitution was achieved after four "refreshment" cycles of the reagents. Intermediates had azide content from two to five.

Abnormalities in azide distances: An acceptable “abnormal” behavior

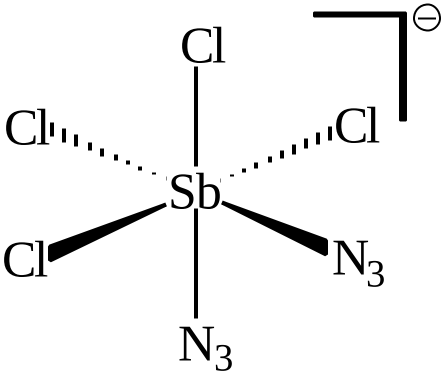
$M\text{-}N_{a}\text{-}N_{ß}\text{-}N_{?}$

- ✓ For covalent metal azides VB theory says N_{a}-$N_{ß}$ > $N_{ß}$=$N_{?}$: However a large number reported structures have unusually short N_{a}-$N_{ß}$ (0.8- 1.0 ?) and long $N_{ß}$-$N_{?}$ (1.2-1.4 ?) distances.

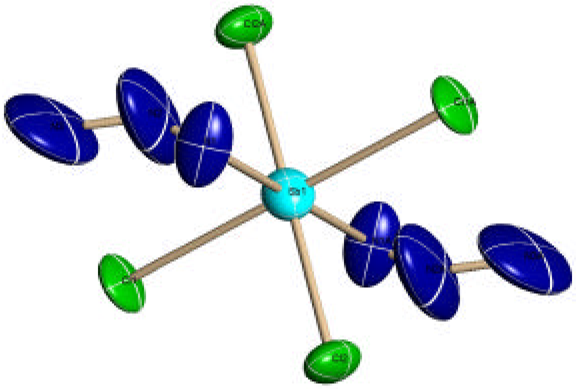
Wolfgang, F. and Klapoetke, T. In Inorganic Chemistry Highlights; Meyer, G.; Naumann, D. and Wesemann, L. Eds.; Wiley-VCH: Weinheim, 2002, Chapter 16 ***and references therein***

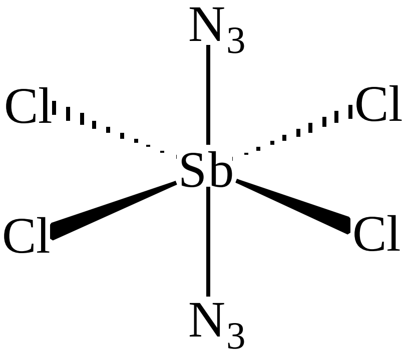
- ✓ In most cases, these derivatives were prepared from metal chloride salts and/or recrystallized from chlorinated solvents – identifying the culprit.

Bis substitution: Cis- or trans- ?



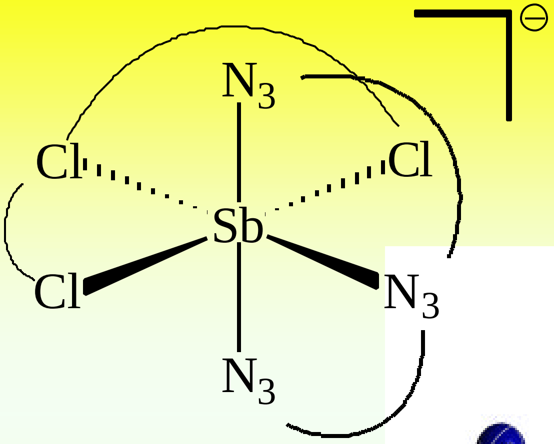
***cis*-isomer**



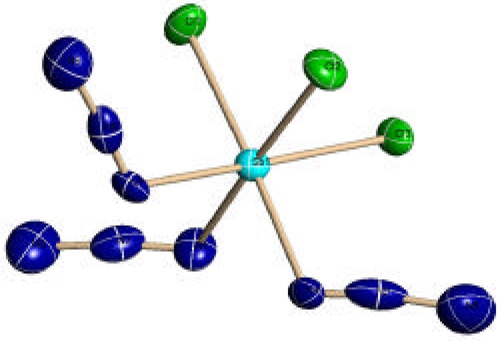


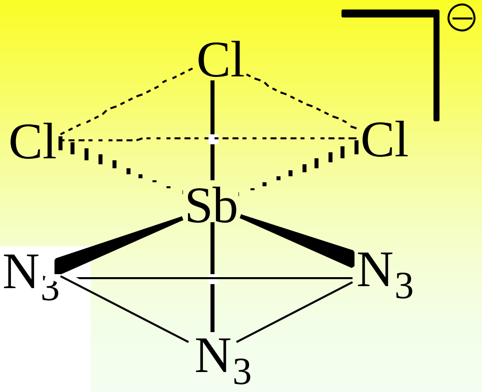
***trans*-isomer**

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



mer-$SbCl_3(N_3)_3$

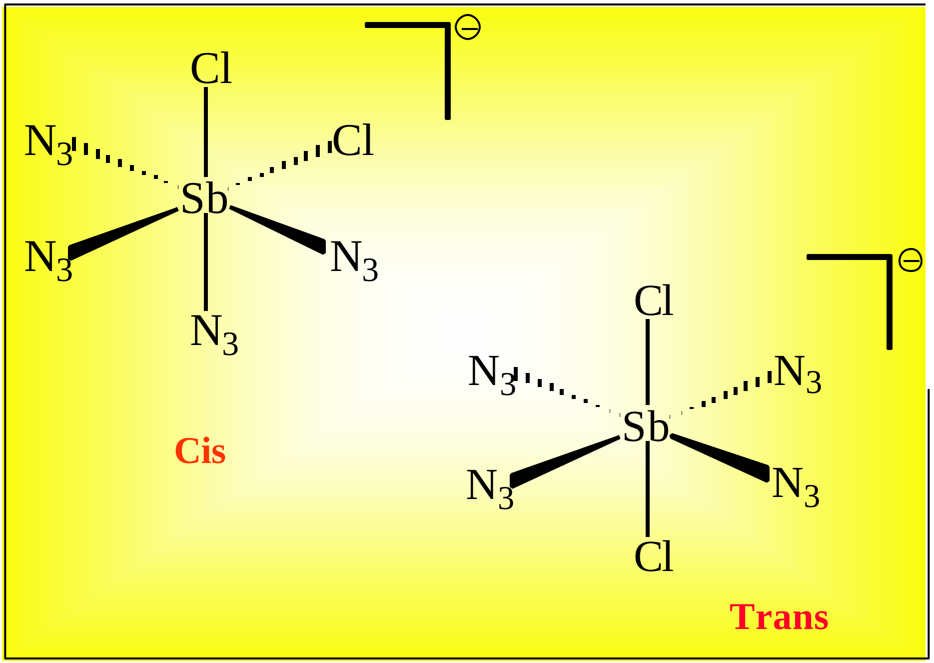


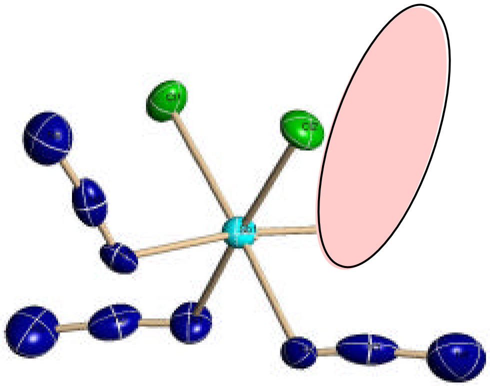


fac-$SbCl_3(N_3)_3$

Substitution of fourth chlorine: Opening a can of worms!

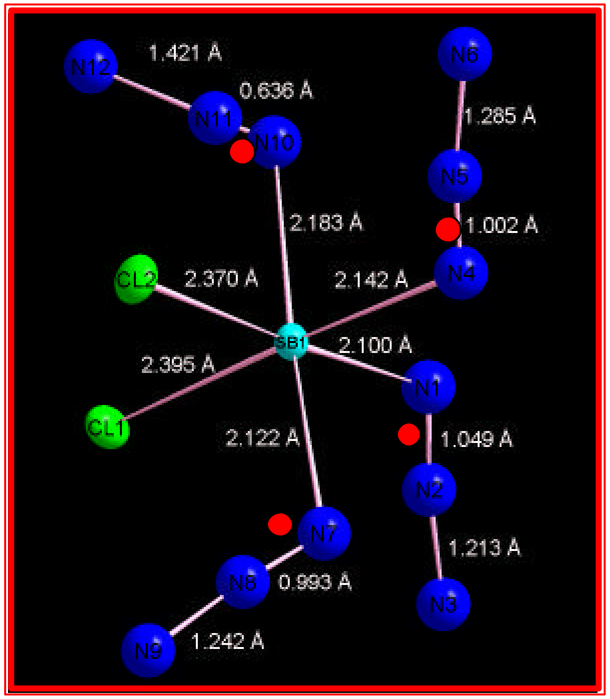
Cis- vs. trans- substitution





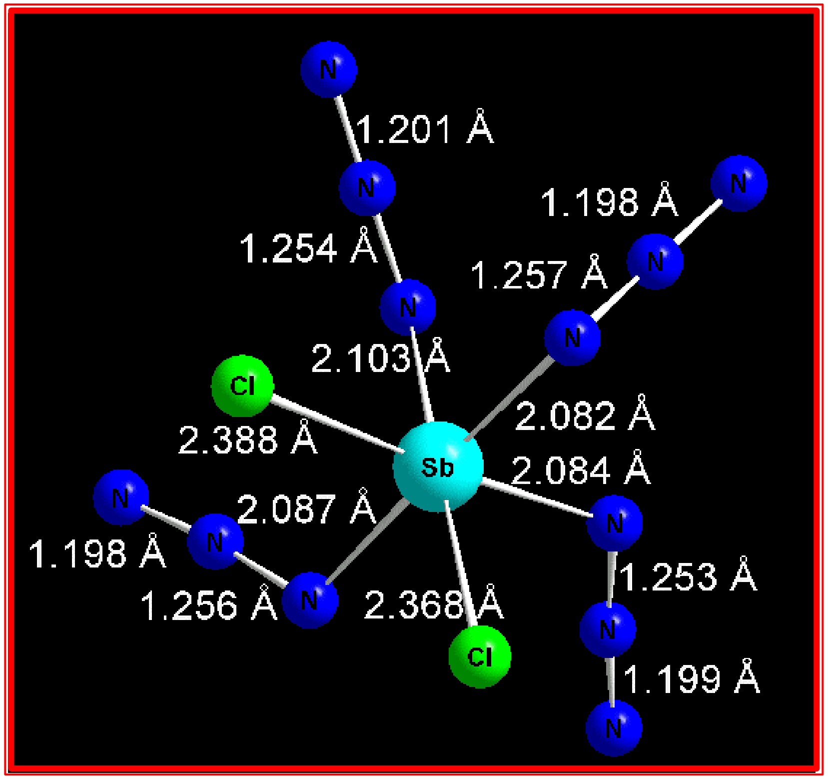
Na-Nß < Nß-N?

Normalizing the "abnormal" behavior-respecting the "residuals ?"



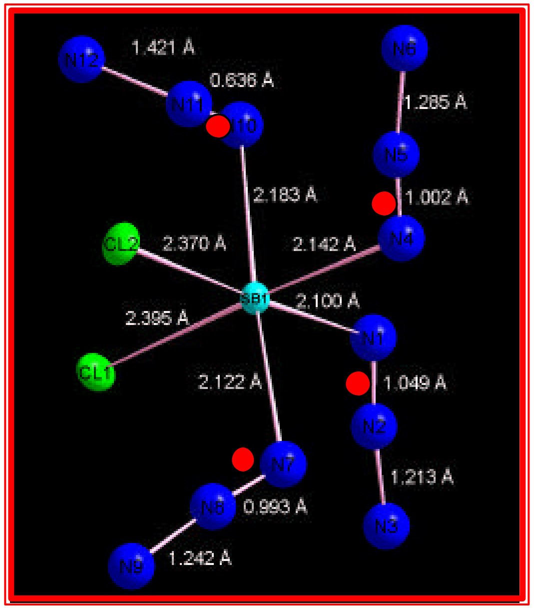
Orthorhombic, $P2_12_12_1$

R = 3.19%, S = 1.084, highest peak = 0.58 e/?^{3}; Flack's parameter = 0.03(1)



Calculated structure

Normalizing the "abnormal" behavior- Canning the worms!

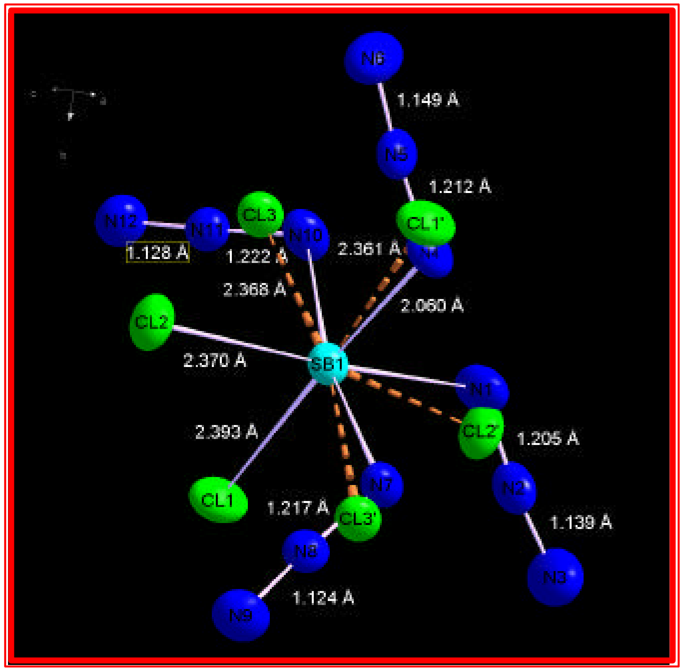


Orthorhombic, $P2_12_12_1$

a, b, c (?) =7.7744(14), 13.610(3), 27.094(5)

V = 2866.8(10), Z = 4

R = 3.19%, S = 1.084, highest peak = 0.58 e/?^{3}; Flack's parameter = 0.03(1)



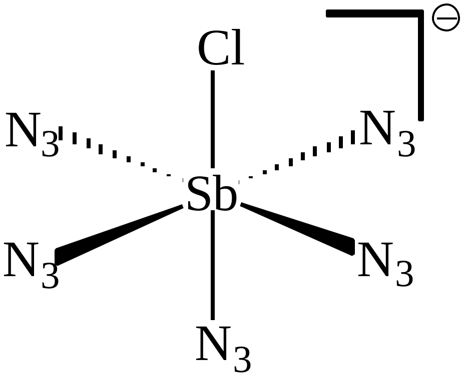
Chloride contamination (%)

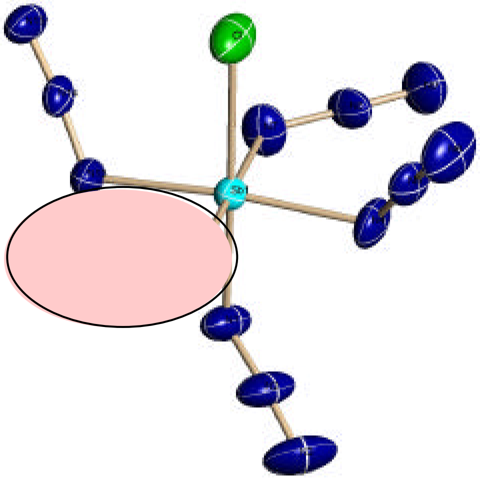
N1-N3 = 10; N4-N6 = 18; N7-N9 = 16; N10-N12 = 37

R = 3.00%, S = 1.003, highest peak = 0.57 e/?^{3}

Flack's parameter = 0.02(1)

Synthesis of Chloropentaazido antimonate(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)°; b = 97.914(5)°; g = 115.807(4)°*
- ✓ *Z = 2*
- ✓ *R = 0.0762*
- ✓ *All azide distances "normal" except N10-N11-N12*

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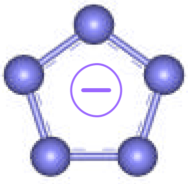
Summary – metal azides

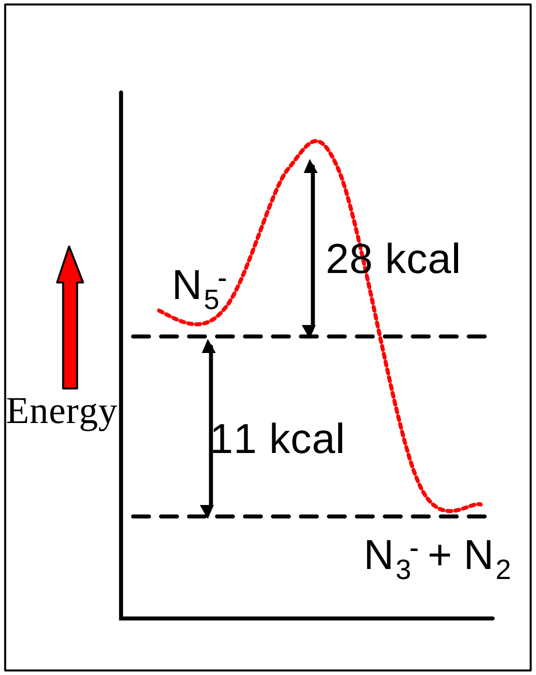
- For binary metal azides, we found that chloride ion contamination causes abnormalities in N-N bonds in azides.
- This observation clarifies the ambiguity created by “bond-stretch isomer” theory.
- Chlorine abstraction from CH_2Cl_2 also observed in Te azide case. All recrystallization process for metal azides should be performed in non-halogenated solvents.
- Reacting metal fluorides with trimethylsilylazide is the best and the cleanest method to prepare metal azides.

New Polynitrogen Anions as Counterparts for N_5^+

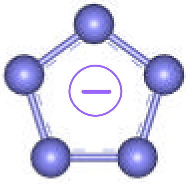


Pentazole anion (N_5^-)

- *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 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*

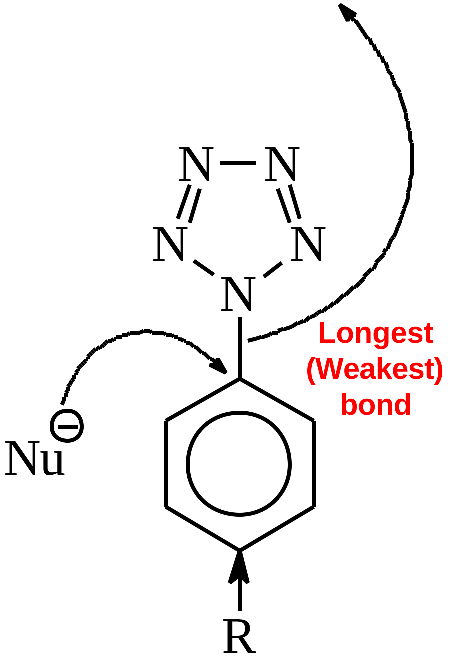


Polynitrogen anion – N_5^-



Pentazole anion (N_5^-)

- *First discovered by AFRL researchers in 2002 (Vij, Christe) using gas-phase mass spectroscopy*
- *AFRL results were reproduced and published by Oestmark et al. in late 2003.*
- *Chemical cleavage reported in 2003 – no hard evidence!*
- ***Free pentazole has not been isolated to date.***

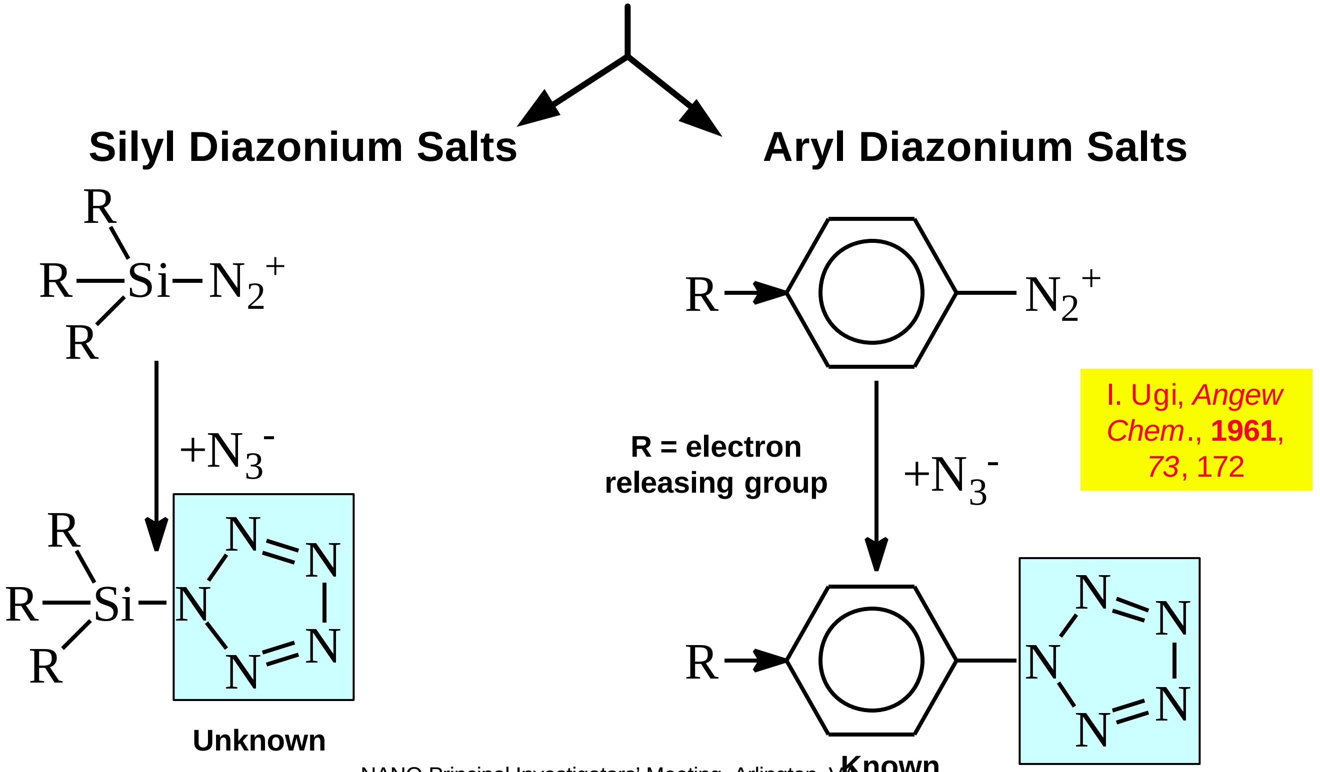


Longest (Weakest) bond

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

Synthesis of Substituted Pentazoles

Sources for the Pentazole Anion (N_5^-)



Silyl Diazonium Salts

Aryl Diazonium Salts

Unknown

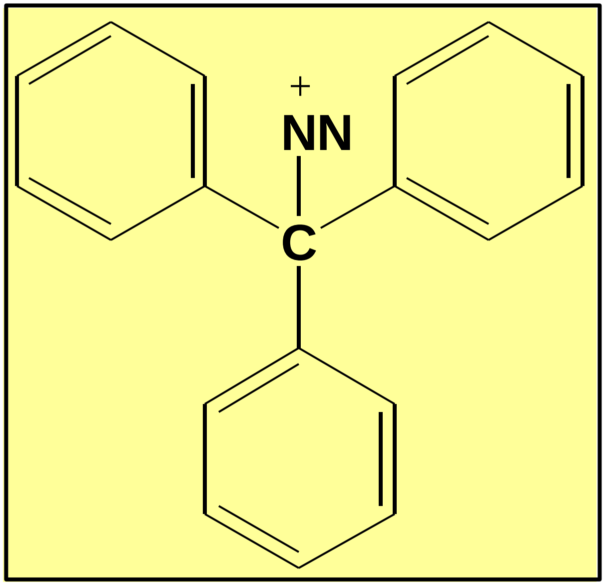
R = electron releasing group

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

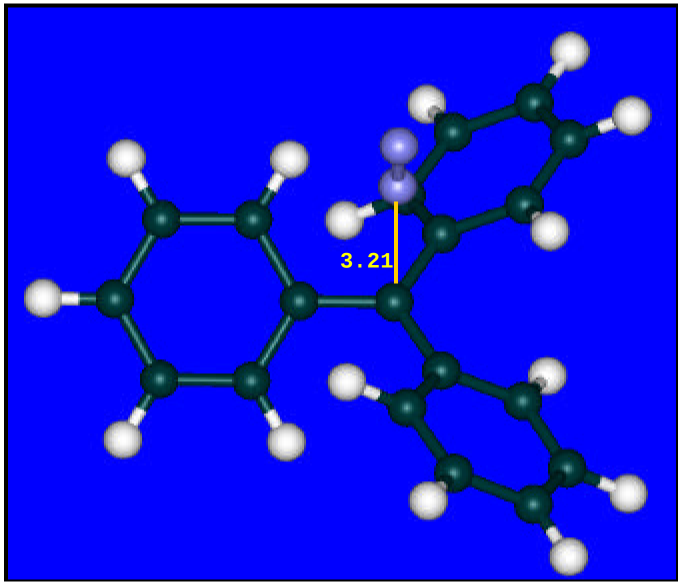
Known

Identifying Potential Polynitrogen Precursors

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



... but calculations predict it to be unstable.



Formation and Stability of Silyl Diazonium Salts

- Failed attempts to synthesize silyl diazonium salts

$$N_2F^+SbF_6^- \; + \; Me_3SiSiMe_3 \xrightarrow{-Me_3SiF} Me_3SiN_2^+SbF_6^-$$

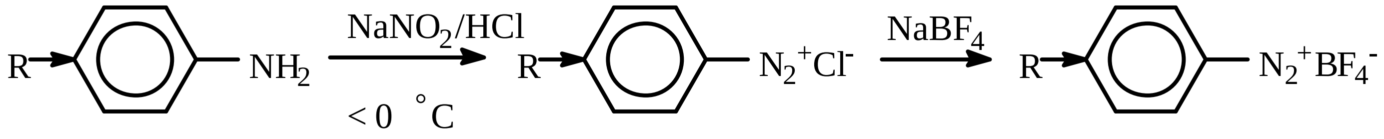
- $R_3SiN_2^+$ salts are unstable and spontaneously lose N_2

$$R_3SiN_2^+\,X^- \xrightarrow{-N_2} \left[R_3Si^+\,X^- \right]$$

Theoretical calculations support this experimental observation

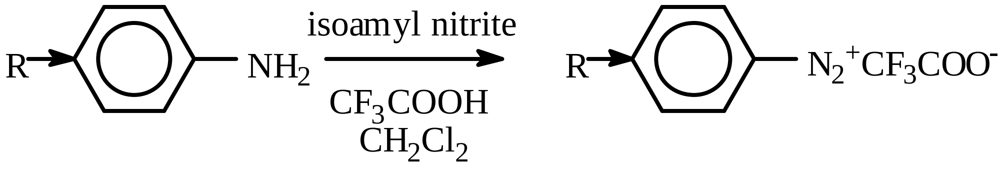
Synthesis of Aryldiazonium Salts

Aqueous Media



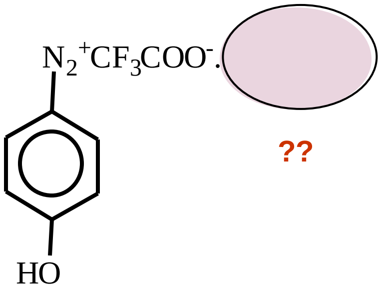
R = H, OH, OCH$_3$, OC$_6$H$_5$, OC$_6$H$_4$N$_2^+$, N(CH$_3$)$_2$

Non-aqueous Media

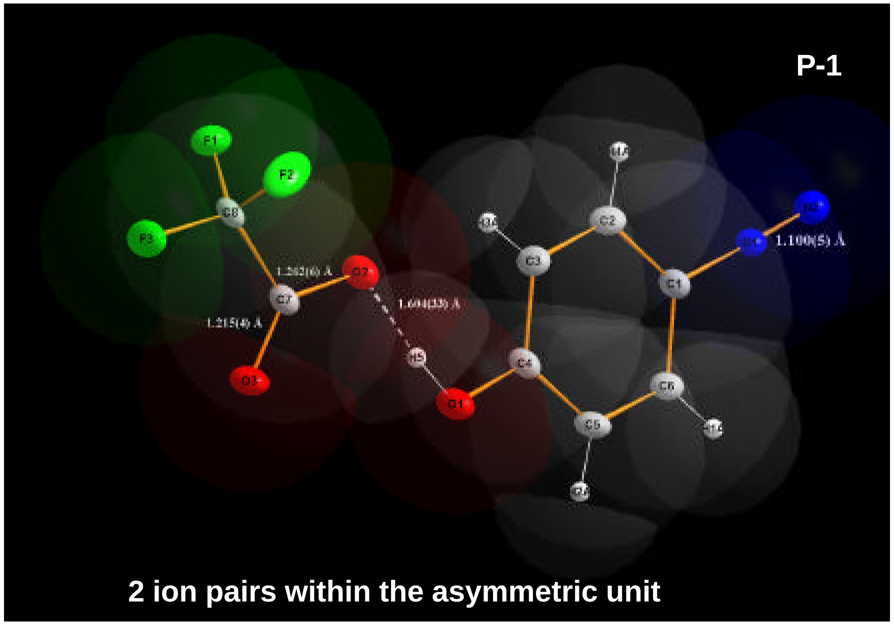


Single or Double Diazonium Salt ?
Consequences of Lone Pair Occupation!

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 is a kiss of death!

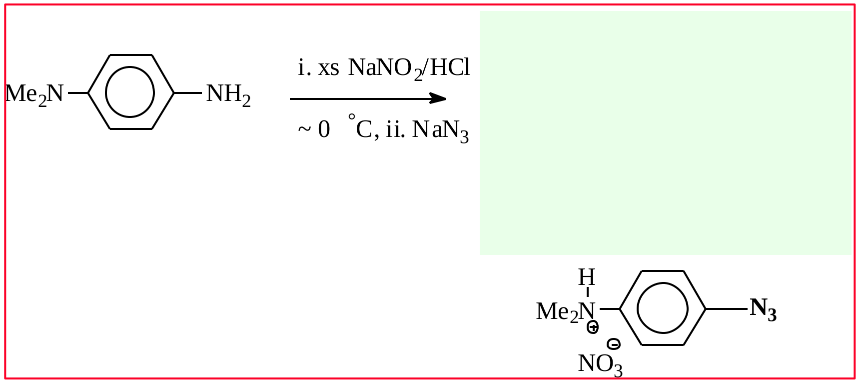


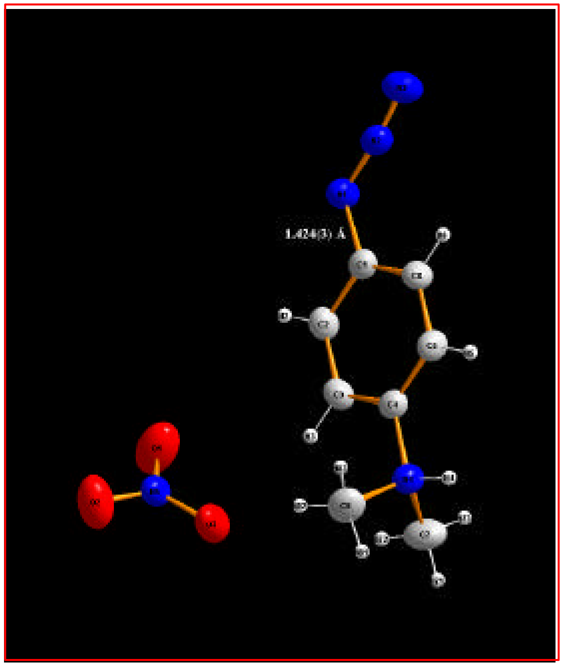
Colas and Goeldner, *Eur. J. Org. Chem.* **1999**, 1357-1366



2 ion pairs within the asymmetric unit

Pentazole Formation… Not a Trivial Chore !!!

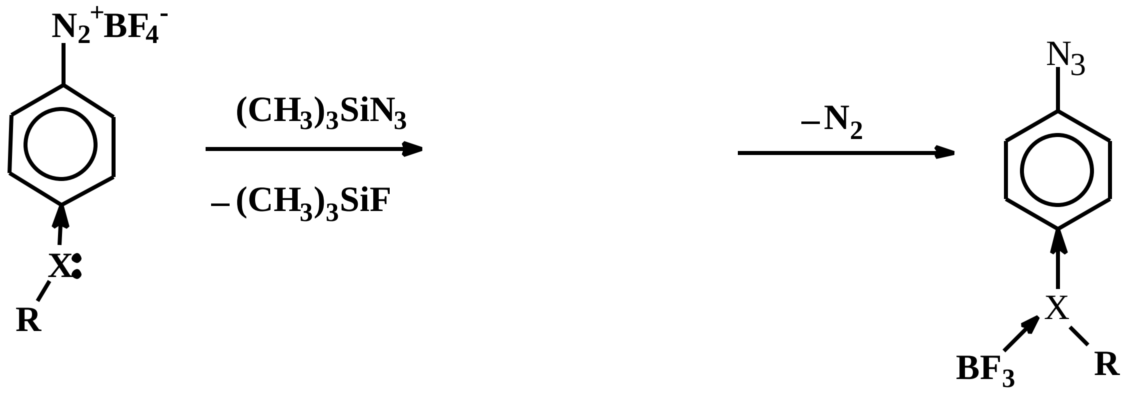




$$\mathbf{NaNO_2 + HCl \xrightarrow{<0\ ^\circ C} NaCl + HONO}$$

$$\mathbf{3\,HONO\,(aq) \rightleftharpoons H_3O^+ + NO_3^- + 2NO}$$

Reaction with Trimethylsilyl Azide



X= N, O

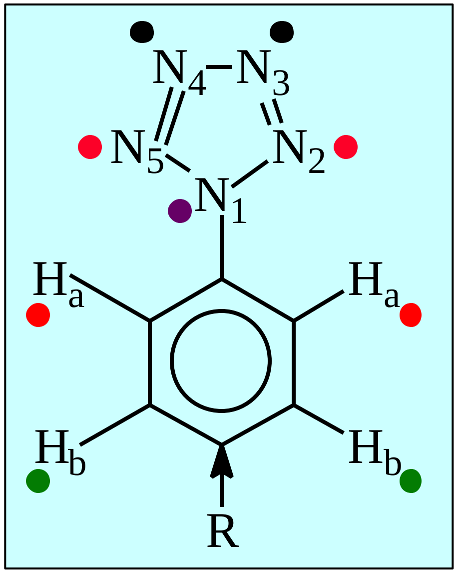
No pentazoles were isolated !!!

Reactions carried out in acetonitrile at -30 ℃

Identification of Arylpentazoles

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

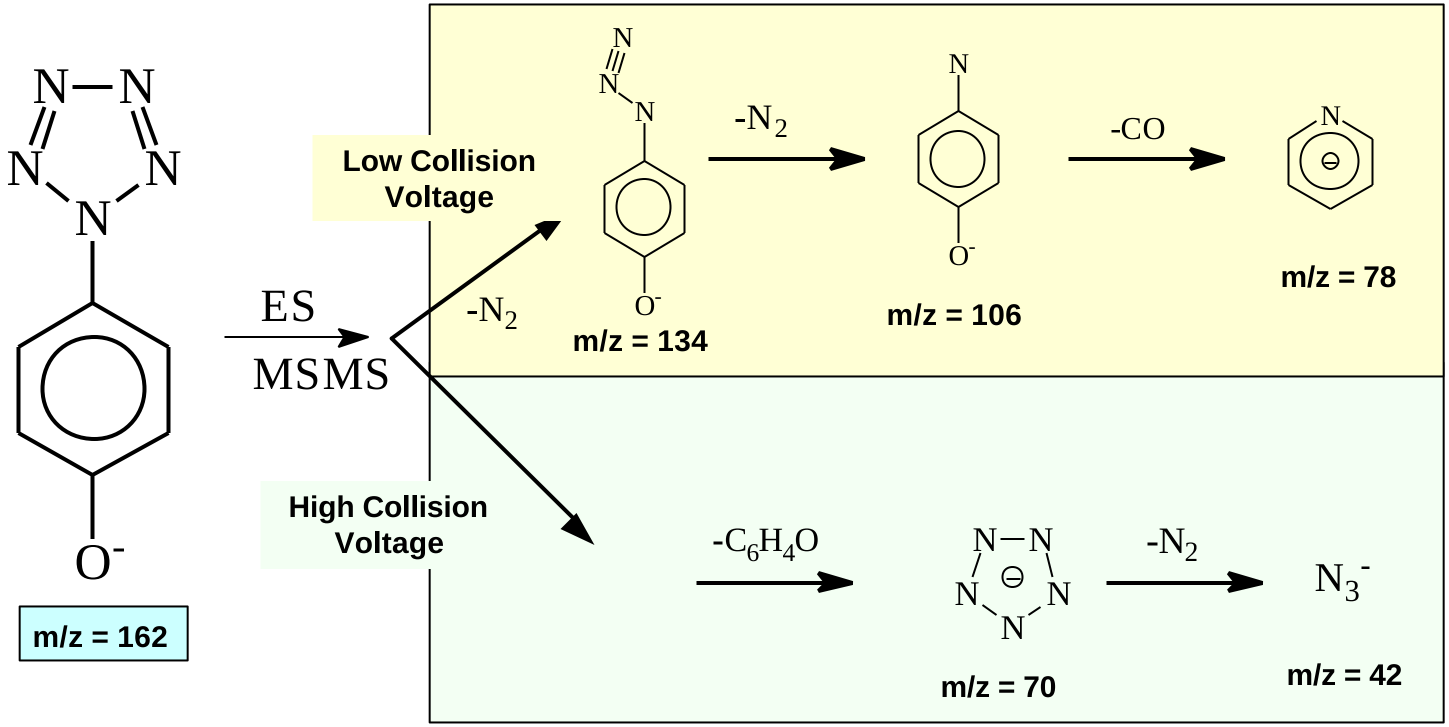
- **^{1}H NMR**: *AB*-type spectrum with H_a and H_b at 8.0 and 7.0 ppm
- **^{14}N NMR**: N_1 at ~ -80 ppm
- **^{15}N NMR**: N_2/N_5 at ~ -27 ppm and N_3/N_4 at ~4 ppm



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

ESIMS of para-Phenoxypentazole

Observed peaks in the MSMS of 162

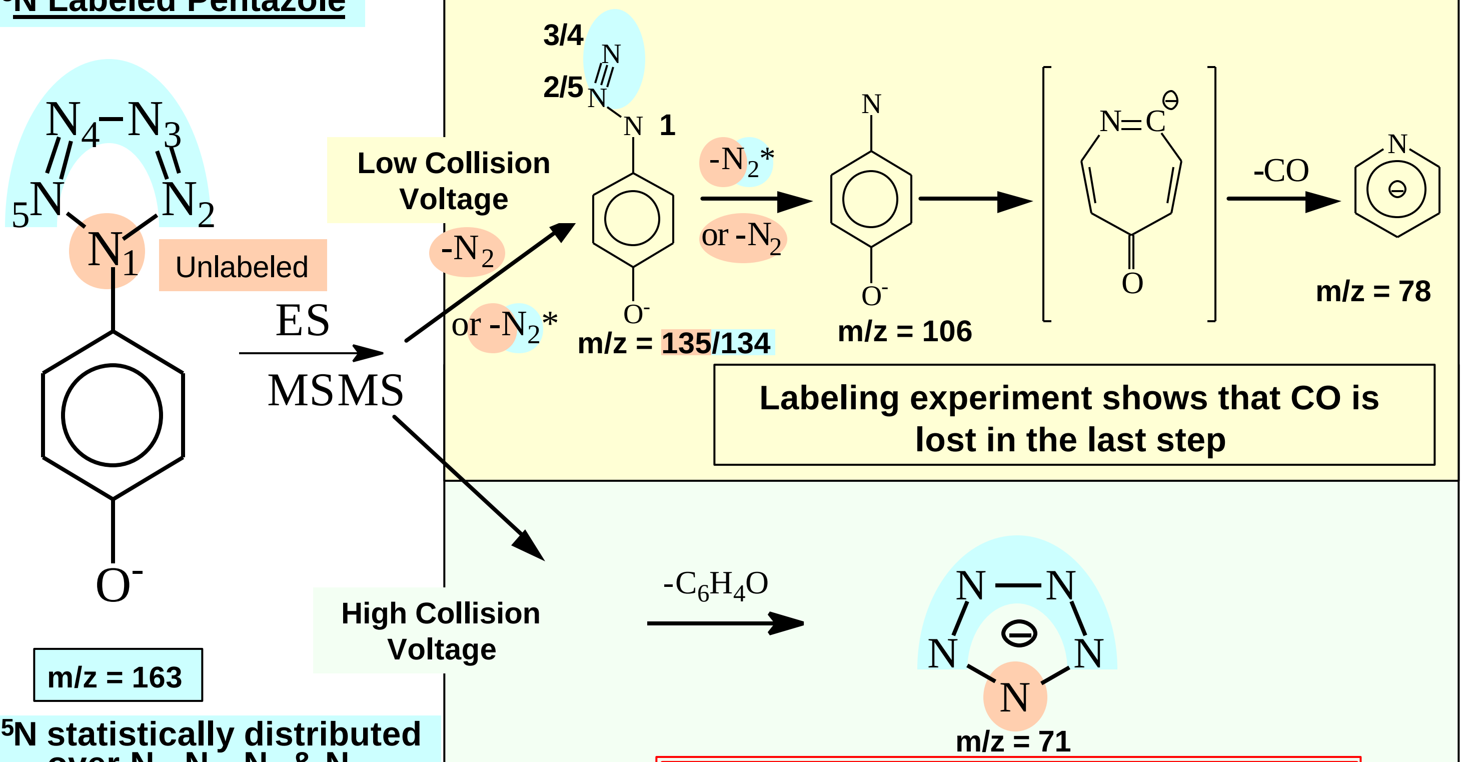


Vij, Pavlovich, Wilson, Vij & Christe, *Angew. Chem. Int. Ed.*, **2002**, *41*, 3051-3054

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

Observed peaks in the MSMS of 163

^{15}N Labeled Pentazole

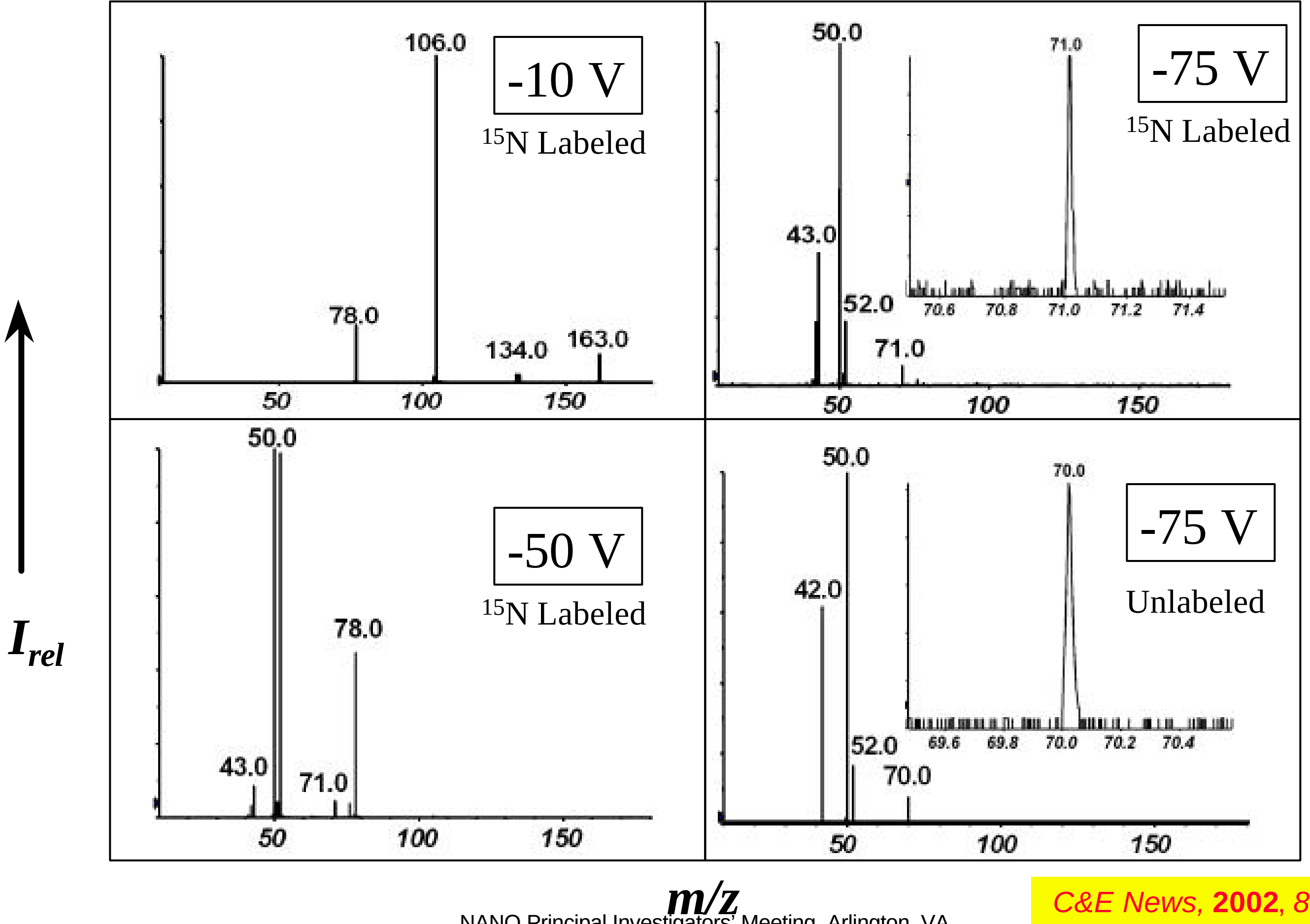


Labeling experiment shows that CO is lost in the last step

^{15}N statistically distributed over N_2, N_3, N_4 & N_5

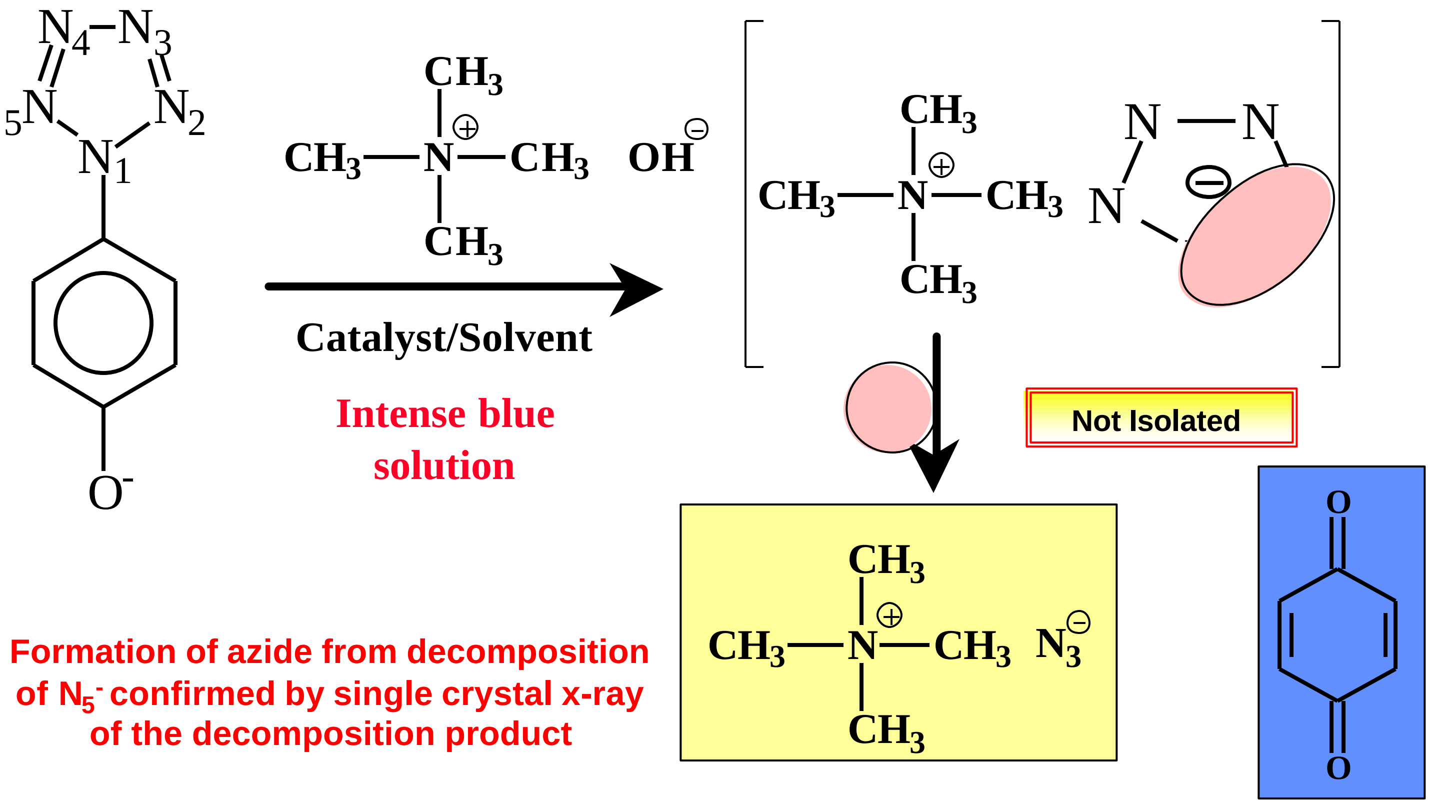
Definitive proof for the pentazole anion

MSMS of the Parent Ion Peak



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

Existence of N_5^- anion in solution: Chemical cleavage of the C-N bond ?

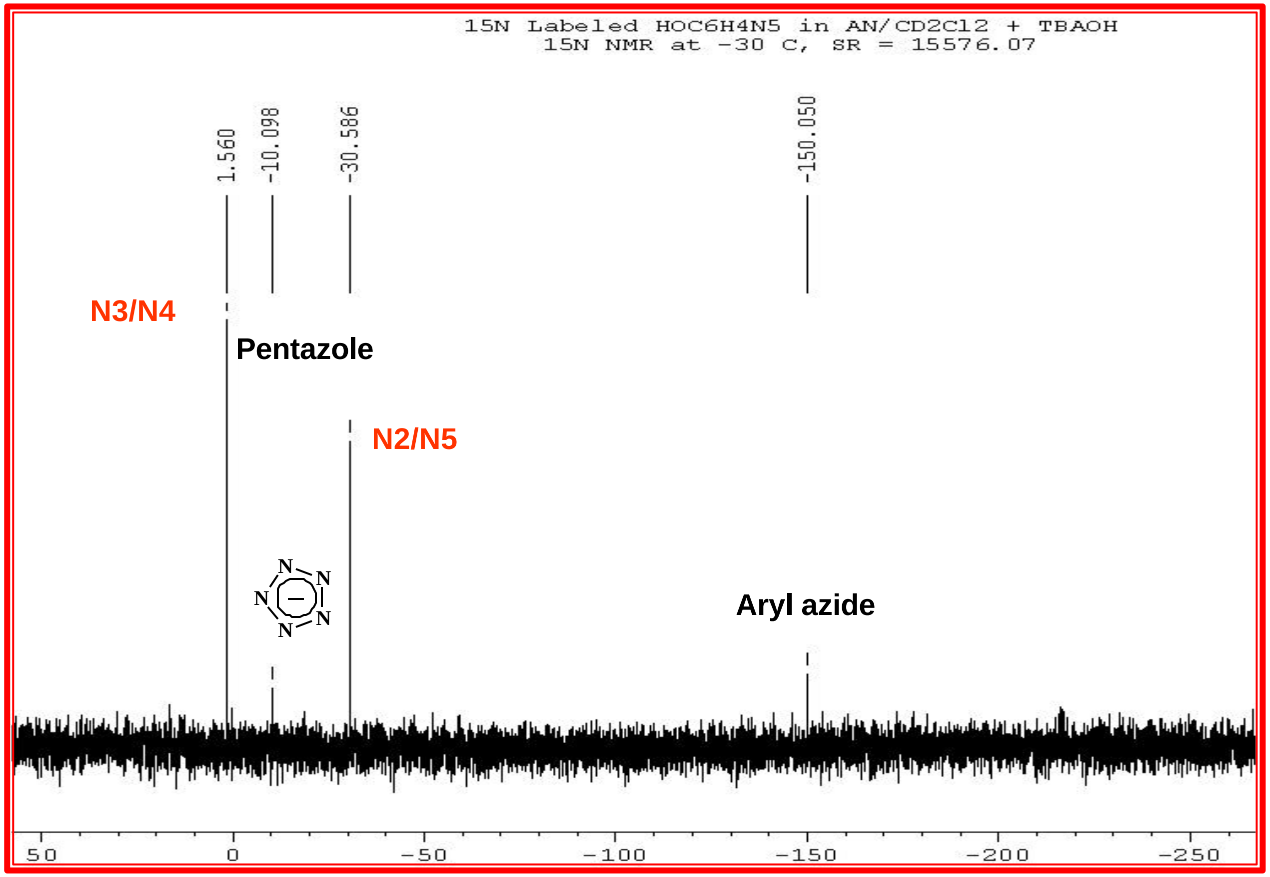


Intense blue solution

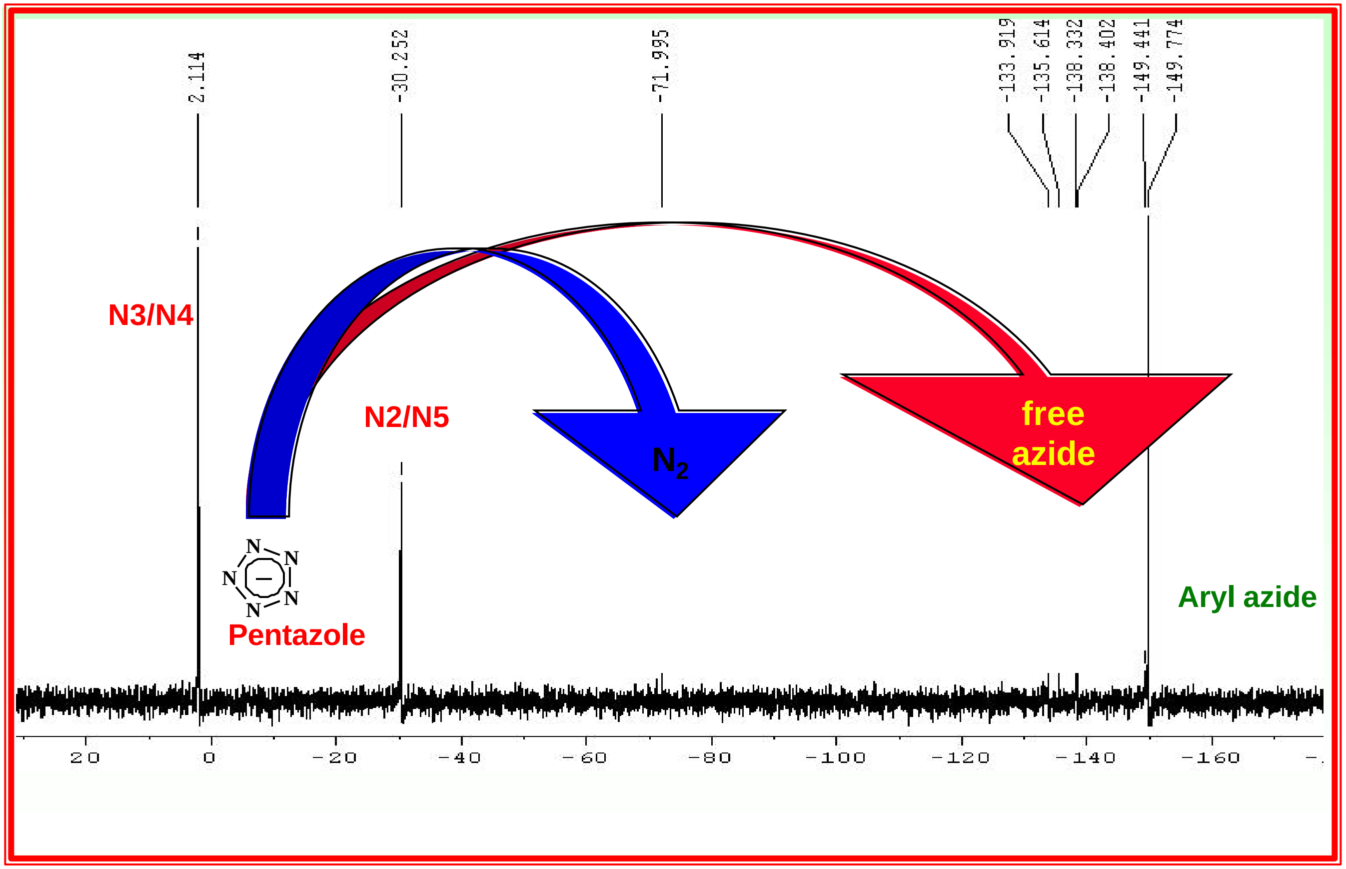
Not Isolated

Formation of azide from decomposition of N_5^- confirmed by single crystal x-ray of the decomposition product

Aryl-pentazole bond cleavage: Existence of N_5^- anion in solution ?

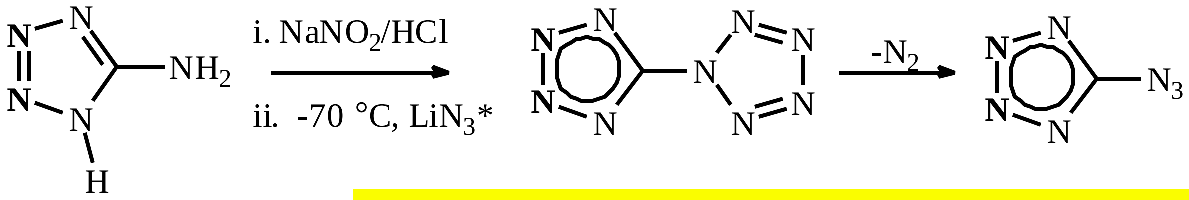


Subsequent decomposition of the pentazole anion



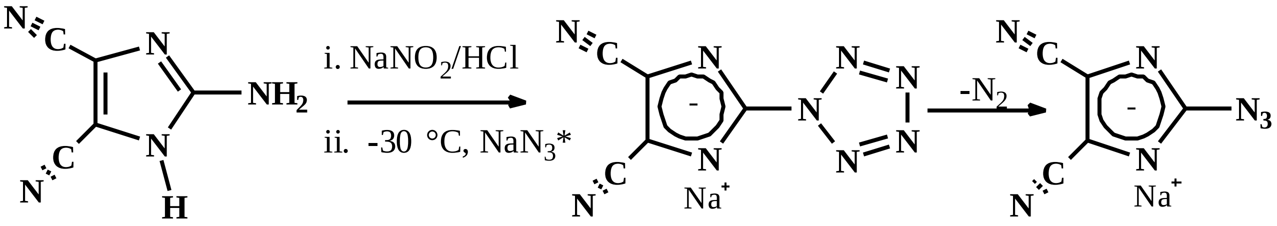
Confirming existence of pentazole anion: Using heterocyclic substituents

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

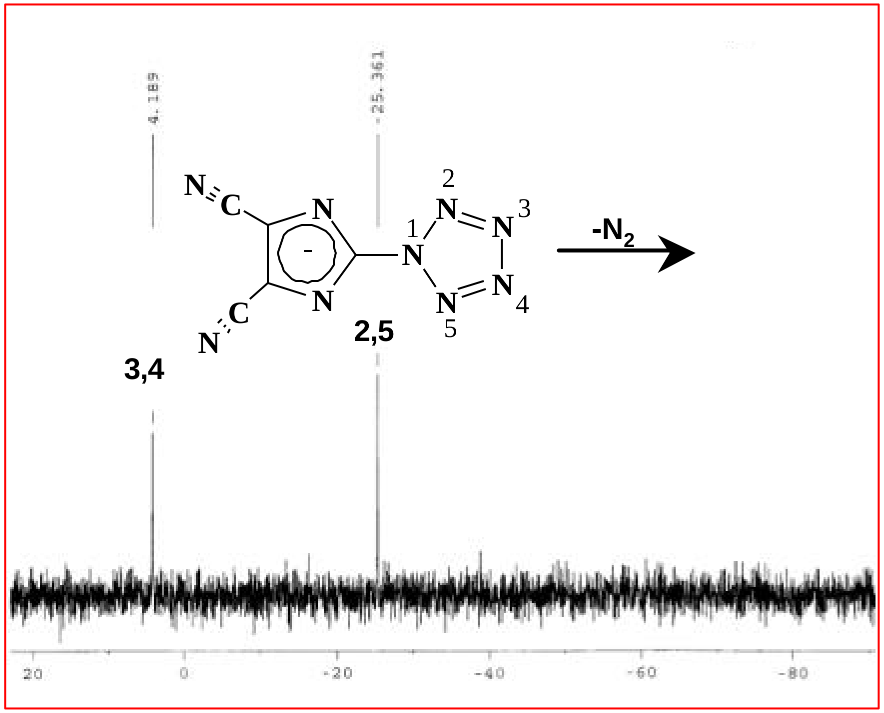


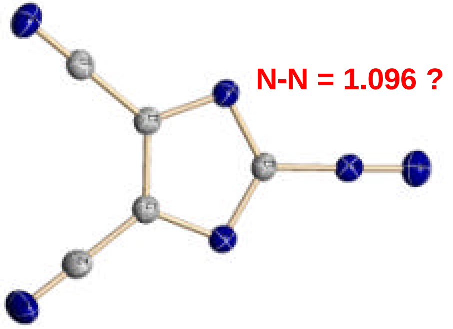
A. Hammerl and T. M. Klapoetke, *Inorg. Chem.* **2002**, *41*, 906-912

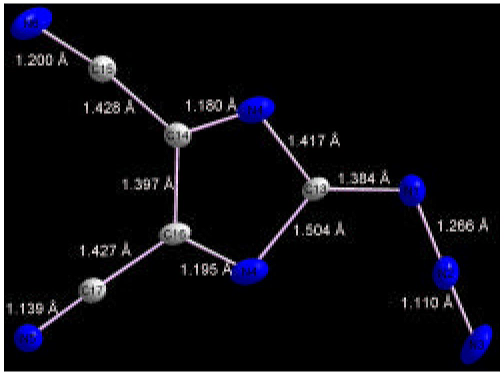
- In comparison, the pentazole ring derived from 2-amino-4,5-dicyanoimidazole shows higher thermal stability (-30 °C)



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

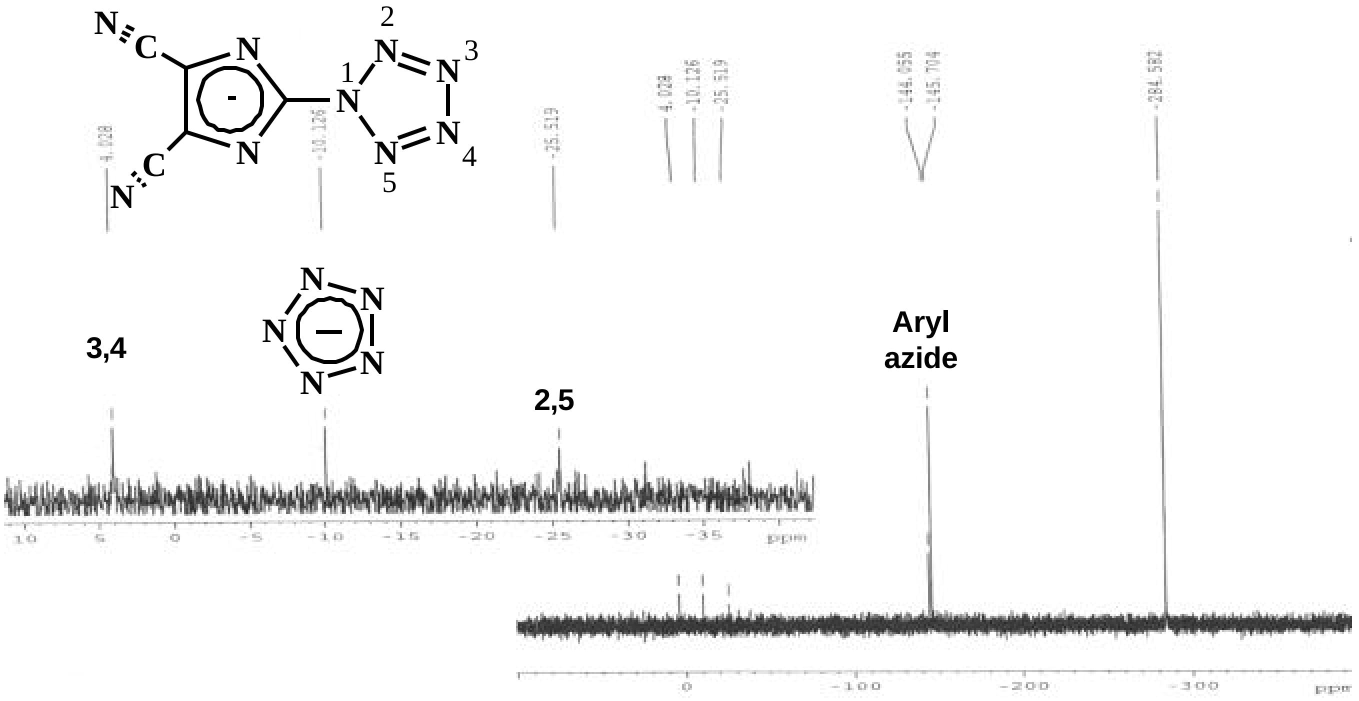






^{15}N NMR recorded in a mixture of methanol and acetonitrile at -30 °C, nitromethane used as an external reference (0 ppm)

Observing pentazolate anion in solution



- ➢ ^{15}N NMR shows a peak at ~ -10 ppm (-30 °C) upon addition of base, 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.

Search for a Bulk Synthesis of N_5^-

- We and others (Butler et al) may have observed N_5^- by ^{15}N NMR at low-temperature in CH_3OH solutions during the cleavage of pentazolylphenolate, but so far N_5^- salts have not been isolated as solids.

- We are still working under AFOSR sponsorship on this problem.

- Although we have observed NMR results similar to previous literature reports, **the validity of these results have not yet been established and require further investigations.**

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 (Ostmark *et al.* have also studied the same problem).
- Synthesis of pentazoles with a heterocylic substituents
- Addition of OH^- ions to a solution of pentazole seem to suggest C-N bond cleavage, which requires further studies
- Offers potential pathway for bulk synthesis of N_5^- salts

Publications, Presentations, Patents, Awards, etc.

- 35 publications in refereed major scientific journals
- Numerous highlights in daily and weekly news media
- 52 Invited presentations and lectures
- Patent on N_5^+
- 2000 Prix Moissan (Christe),

  2003 ACS award in Inorganic Chemistry (Christe),

  2003 Air Force Basic Research Award (Honorable Mention) (Vij)

  2004 Arthur Adamson Award (Haiges)
- One MS degree [AFRL & University of Idaho; Vandana (Tini) Vij]

Advances in the State-of-the-Art

- Have demonstrated that polynitrogen species, other than N_3^-, can be synthesized in bulk, have good thermal stability and can be insensitive
- Have shown that compounds with touching polynitrogen ions can be prepared
- Have greatly increased the number of known polyazides (potential for primary explosives)
- Have discovered NH_3Cl^+ salts which could serve as NH_2Cl gas generators for killing spores

Conclusions and Recommendations

- Highly successful program. Syntheses of N_5^+, N_5^-, N_3NOF^+, polyazides, $N_5^+P(N_3)_6^-$, $N_5^+B(N_3)_4^-$, etc.
- Demonstrates that Polynitrogen and Polyazide Chemistry are viable fields of research and definitely worth pursuing.
- This chemistry is technically very challenging, but offers high potential pay-off in terms of performance and properties (green, low signature, low corrosion applications, etc.).
- Additional maturation is required. Given longer-term funding at the research level and a patient and understanding sponsor, this program can make significant contributions to the state-of-the-art in energetic materials.
- Additional maturation will help to define the extreme limits achievable with chemical HEDM.

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Dr. Art Morrish (DARPA)

Dr. Michael Berman (AFOSR)

Ms. Gail Heim & her staff (SPC)

BACKUP

BACKUP Material

Major Accomplishments during FY 03-04

- *The first N_5^+ salts with energetic counter ions, $N_5^+B(N_3)_4^-$ and $N_5^+P(N_3)_6^-$, were prepared*
- *These salts are extremely energetic. $N_5^+B(N_3)_4^-$ contains 96 weight % of energetic nitrogen*
- *A total of 13 N_5^+ salts have now been prepared and characterized in our laboratories*
- *Demonstrated the existence of pentazole anion in solution.*
- *Isolated and characterized the $H_2NF_2^+$ cation using x-ray crystallography: important data point in structures of fluoroammonium cations, i.e. NF_4^+, HNF_3^+, N_2F^+ etc.*

Presentations during FY03-04

- *National ACS Meeting, New Orleans (Four presentations)*
- *Invited Lecture, UC San Diego*
- *National ACS Meeting, New York (Two presentations)*
- *Molecular Dynamics Conference, San Diego*
- *Energetic Materials Technology Exchange, Aberdeen*
- *Invited Opening Lecture, Canadian Symposium on Inorganic Chemistry, Hamilton, Ontario*
- *Aldrich Lecture, Northwestern University*
- *Samuel McElvain Lecture, University of Wisconsin, Madison*
- *National ACS Meeting, Anaheim (Three presentations)*
- *ACS Local Section - Southern Nevada Section*
- *Cal State University, Fullerton (Invited)*

Publications during the Past Year (Eleven)

- ***“The $(SO_2)_2N_3^-$ Anion,” <u>Inorg. Chem.</u>, <u>42</u>, 419 (2003), K. Christe, M. Gerken, R. Haiges, S. Schneider, T. Schroer, I.Tsyba, and R. Bau.***
- ***“Polynitrogen Chemistry: Preparation and Characterization of $(N_5)_2SnF_6$, N_5SnF_5, and $N_5B(CF_3)_4$,” <u>Chemistry – A European Journal</u>, <u>9</u>, 2840 (2003), W. W. Wilson, A. Vij, V. Vij, E. Bernhardt, and K. O. Christe.***
- ***“Synthesis and Characterization of the trans-$IO_2F_5^{2-}$ Anion,” <u>Inorg. Chem.</u>, <u>42</u>, 5282 (2003), J. A. Boatz, K. O. Christe, D. A. Dixon, B. A. Fir, M. Gerken, R. Z. Gnann, H. P. A. Mercier, and G. J. Schrobilgen.***
- ***“On the Existence of FN_5, a Theoretical and Experimental Study,” <u>J. Phys</u>. <u>Chem. A</u>, <u>107</u>, 6638 (2003), H. M. Netzloff, M. S. Gordon, K. O. Christe, W. W. Wilson, A. Vij, V. Vij, and J. A. Boatz.***
- ***“Quantitative Measure for the Nakedness of Fluoride Ion Sources,” <u>J. Am. Chem. Soc</u>., <u>125</u>, 9457 (2003), K. O. Christe and H. D. B. Jenkins.***
- ***“Enthalpies of Formation of Gas Phase N_3, N_3^-, N_5^+, and N_5^- from Ab Initio Molecular Orbital Theory, Stability Predictions for $N_5^+N_3^-$ and $N_5^+N_5^-$, and Experimental Evidence for the Instability of $N_5^+N_3^-$,” <u>J. Am. Chem. Soc</u>., <u>126</u>, 834 (2004), D. A. Dixon, D. Feller, K. O. Christe, W. W. Wilson, A. Vij, V. Vij, H. D. B. Jenkins, R. M. Olson, and M. S. Gordon.***

Publications during the Past Year

- ***“Polyazide Chemistry: Preparation and Characterization of $Te(N_3)_4$ and $[P(C_6H_5)_4]_2[Te(N_3)_6]$ and Evidence for $[N(CH_3)_4][Te(N_3)_5]$,” Angew. Chem. Int. Ed., 42, 5847 (2003), R. Haiges, J. A. Boatz, A. Vij, M. Gerken, S. Schneider, T. Schroer, and K. O. Christe. (Highlighted in C & E News)***
- ***“First Structural Characterization of Binary As(III) and Sb(III) Azides,” Chemistry – A European Journal, 10, 508 (2004), R. Haiges, A. Vij, J. A. Boatz, S. Schneider, T. Schroer, M. Gerken, and K. O. Christe. (Cover Page)***
- ***“X-ray Crystal Structures of $[XF_6][Sb_2F_{11}]$ (X = Cl, Br, I); ^{35,37}Cl, ^{79,81}Br and ^{127}I NMR Studies and Electron Structure Calculations of the XF_6^+ Cations,” Inorg. Chem., in press, J. F. Lehmann, G. J. Schrobilgen, K. O. Christe, A. Kornath, and R. Suontamo.***
- ***“Preparation and Characterization of the First Binary Group 4 Azides, $Ti(N_3)_4$, $[P(C_6H_5)_4][Ti(N_3)_5]$ and $[P(C_6H_5)_4]_2[Ti(N_3)_6]$ and on Linear Ti-N-NN Coordination,” Angew. Chem. Int. Ed., in press, R. Haiges, J. A. Boatz, S. Schneider, T. Schroer, M. Yousufuddin, and K. O. Christe. (VIP Paper)***
- ***“New High Energy Density Materials. Synthesis and Characterization of $N_5^+P(N_3)_6^-$, $N_5^+B(N_3)_4^-$, $N_5^+HF_2^-\cdot nHF$, $N_5^+BF_4^-$, $N_5^+PF_6^-$, and $N_5^+SO_3F^-$,” Angew. Chem. Int. Ed., in press, R. Haiges, S. Schneider, T. Schroer, and K. O. Christe.***

State-of-the-art assessment: Chronology of the pentazole anion development

- **ESIMS of *para*-hydroxyphenylpentazole (Gas phase detection of pentazolate anion, peak at m/z 70 confirmed by ^{15}N labeling experiment.)**

Vij, Pavlovich, Wilson, Vij, Christe, Angew. Chem. Intl. Ed. Engl. **2002,** *41*, 3051
Submitted: April 30, 2002; accepted July 3, 2002

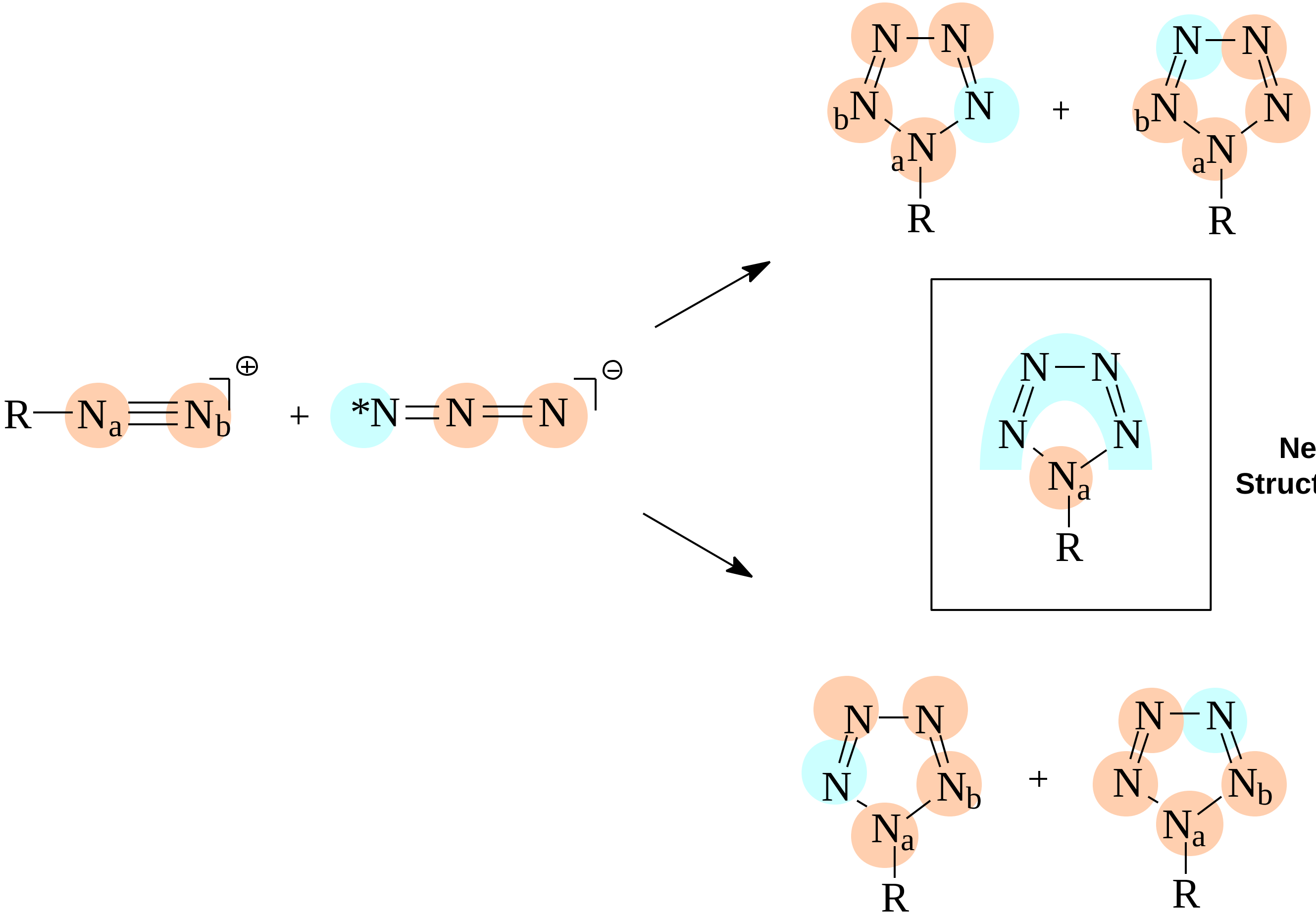
- **^{15}N NMR studies showing a peak at -10.2 ppm (-40 °C) due to the Pentazole anion resulting from cleavage of *para*-methoxyphenylpentazole which slowly decomposes to form N_2 and azide ion. Upon standing for several days, all peaks disappear!**

Butler, Stephens & Burke, Chem. Commun. **2003,** 1016
Submitted: February 6, 2003; accepted February 27, 2003

- **Laser Desorption Ionization (LDI) time-of-flight (TOF) mass spectrometry of solid *para*-*N*,*N*-dimethylaminophenylpentazole shows peaks at m/z: 70 (N_5^-) and -42 (N_3^-). Peak at 70 confirmed by ^{15}N labeling experiment.**

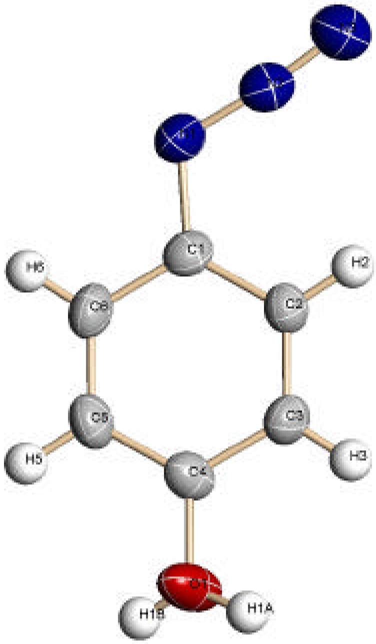
Ostmark, Wallin, Brinck, Carlqvist, Claridge, Hedlund & Yudina,
Chem. Phys Lett., **2003**, *379*, 539
Submitted: Jun. 27, 2003; accepted August 27, 2003

^{15}N Labeling of the Pentazole Ring



Net Structure

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.