

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE (DD-MM-YYYY) 05-26-04		2. REPORT TYPE Technical Paper		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Taming Hazardous Reactive Materials for Single Crystal X-ray Diffraction Studies: Dealing with Handling and Disorder Nightmares				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Ashwani Vij				5d. PROJECT NUMBER DARP	
				5e. TASK NUMBER A205	
				5f. WORK UNIT NUMBER DARPA205	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB, CA 93524-7048				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB, CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-VG-2004-181	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES Condensed Phase Workshop Poland, 1-10 July 2004					
14. ABSTRACT					
20040715 194					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Linda Talon
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code)
Unclassified	Unclassified	Unclassified	A	7	(661) 275-5283

Taming Hazardous Reactive Materials for Single Crystal X-ray Diffraction Studies: Dealing with Handling and Disorder Nightmares



July 9, 2004
University of Bialystok
Bialowicza, Poland

Ashwani Vij
Research Scientist
Air Force Research Laboratory
California, USA

Approved for Public Release. Distribution Unlimited

AFRL/USC/UC Coworkers and Collaborators

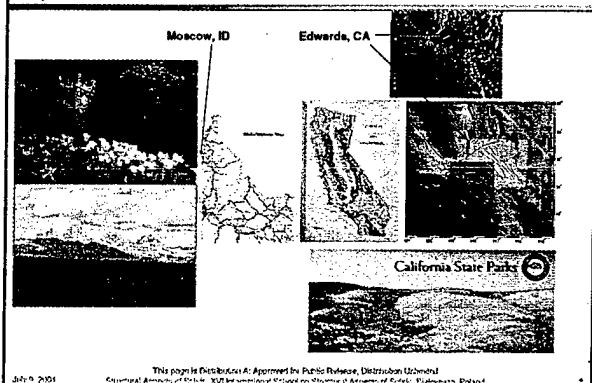
Air Force Research Laboratory, Edwards
Dr. Bill Wilson, Ms. Vandana Vij
Dr. Jerry A. Boatz (computations)

University of Southern California
Dr. Karl Christe, Dr. Ralf Haiges

University of California, Riverside
Dr. Fook Tham

This page is Distributed As Approved for Public Release. Distribution Unlimited
Approved for Release of Science. XVI International Symposium on Macromolecular Chemistry, Bialowicza, Poland

The challenging transition !



This page is Distributed As Approved for Public Release. Distribution Unlimited
Approved for Release of Science. XVI International Symposium on Macromolecular Chemistry, Bialowicza, Poland

The exciting world of high nitrogen chemistry



This page is Distributed As Approved for Public Release. Distribution Unlimited
Approved for Release of Science. XVI International Symposium on Macromolecular Chemistry, Bialowicza, Poland

Why Carbon forms polymers and Nitrogen does not?

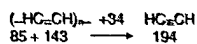
- All the energy must come from endothermicity, and sensitivity typically increases with endothermicity
- Basis for high energy content is the large differences in bond energies

Carbon bond enthalpies

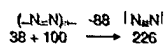
C-C	85 kcal/mol
C=C	143 kcal/mol
C≡C	194 kcal/mol

Nitrogen bond enthalpies

N-N	38 kcal/mol
N=N	100 kcal/mol
N≡N	226 kcal/mol



stable polymers,
unstable monomers



unstable polymers,
stable monomer

This is the reason why N-N polymers don't exist

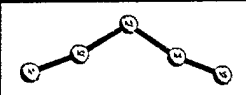
This page is Distributed As Approved for Public Release. Distribution Unlimited
Approved for Release of Science. XVI International Symposium on Macromolecular Chemistry, Bialowicza, Poland

N-F Compounds

- N-F Compounds

This page is Distributed As Approved for Public Release. Distribution Unlimited
Approved for Release of Science. XVI International Symposium on Macromolecular Chemistry, Bialowicza, Poland

What is So Unusual About the N_5^+ Cation?

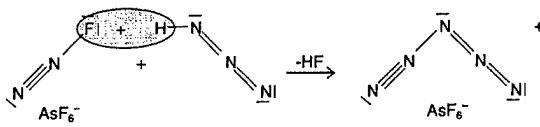


The N_5^+ cation is unusual because it is a linear, five-membered nitrogen cation. It is the first example of a linear, five-membered nitrogen cation. It is also the first example of a linear, five-membered nitrogen cation.

References: *Nitrogen N-Heterocyclic Compounds*, *Journal of Organometallic Chemistry*, 1972, 25, 1-10.


This paper is Distributed As Approved for Public Release, Distribution Unlimited
 Research Agency of Science, XVI International School on Spectroscopy of Solids, Warszawa, Poland
 July 9, 2004

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 endothermic
 - Suitable solvent must be used as a heat sink and for stabilization
- Ideal candidate system:
 

This paper is Distributed As Approved for Public Release, Distribution Unlimited
 Research Agency of Science, XVI International School on Spectroscopy of Solids, Warszawa, Poland
 July 9, 2004

Fluorodiazonium Salts: Crucial Intermediates in Polynitrogen Chemistry



Synthesis of N_2F^+ Salts

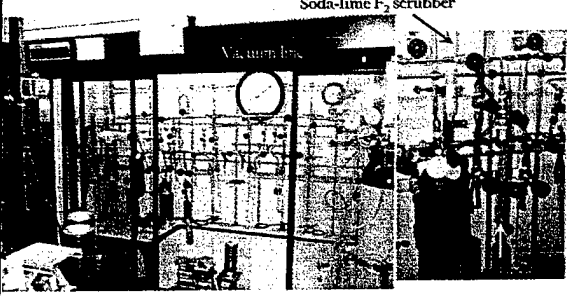
$$N_2F^+AsF_6^- + NaF \xrightarrow{-HF} cis-N_2F_2$$

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

$$N_2F^+AsF_6^- + HN_3 \xrightarrow[-98 \text{ to } -78^\circ C]{} N_5^+AsF_6^-$$

This paper is Distributed As Approved for Public Release, Distribution Unlimited
 Research Agency of Science, XVI International School on Spectroscopy of Solids, Warszawa, Poland
 July 9, 2004

Right Tools for the Right Job



Soda-lime F_2 scrubber

Stainless steel, Teflon-FEP vacuum line fitted with Hoke® valves and a Heise gauge

This paper is Distributed As Approved for Public Release, Distribution Unlimited
 Research Agency of Science, XVI International School on Spectroscopy of Solids, Warszawa, Poland
 July 9, 2004

Reactions of $trans-N_2F_2$ with SbF_5 ?

$$trans-N_2F_2 + SbF_5 \xrightarrow{-65^\circ C} \begin{cases} N_2F^+SbF_6^- \\ NF_4^+Sb_3F_{16}^- \end{cases}$$


$$4 trans-N_2F_2 \xrightarrow[-65^\circ C/4days]{[SbF_5]} [2NF_3 + F_2 + 3N_2]$$

Mechanism


$$SbF_5 \xrightarrow{-65^\circ C/4days} NF_4^+Sb_3F_{16}^-$$

This paper is Distributed As Approved for Public Release, Distribution Unlimited
 Research Agency of Science, XVI International School on Spectroscopy of Solids, Warszawa, Poland
 July 9, 2004

Using "inert" organic solvents



Before recrystallization



After recrystallization

Using "inert" anhydrous solvents such as methylene chloride (CH_2Cl_2) or acetonitrile (CH_3CN) may not be a good idea for N_2F^+ or N_5^+ compounds

This paper is Distributed As Approved for Public Release, Distribution Unlimited
 Research Agency of Science, XVI International School on Spectroscopy of Solids, Warszawa, Poland
 July 9, 2004

Recrystallization

- *HF is used as a solvent in most of the cases. It can be removed from the reaction product at low temperature: useful for thermally unstable compounds.*
- *SO₂ can also be used, if there are no compatibility issues. Sometimes complexation can be observed, i.e. Cs azide*
- *Mixtures of SO₂ and SO₂ClF can be used to alter solubility, i.e. N₅⁺ is very soluble in SO₂ but not much soluble in SO₂ClF. SO₂ b.p. = -10°C; SO₂ClF (b.p. = -12°C). SO₂ evaporates first resulting in reduced solubility*

This page is Distribution A: Approved for Public Release, Distribution Unlimited
Support of Research at Sandia National Laboratories is provided by the Strategic Arms Reductions Office, Department of Defense

Mounting using LT apparatus

- *Specially designed dewar vessel where crystals are loaded into a glass lip under a closed nitrogen gas flow. The mounting is then accomplished using PFPE oil and Cryoloops.*
- *Useful for thermally unstable material, and compounds which are liquids at room temperature.*

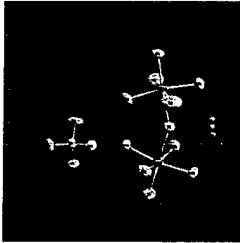
This page is Distribution A: Approved for Public Release, Distribution Unlimited
Support of Research at Sandia National Laboratories is provided by the Strategic Arms Reductions Office, Department of Defense

Hungry for cryoloops?

Contact from the oxidizer can chew up the cryoloop. In this case, the crystal can be embalmed in Kel-F grease to protect the Cryoloop. The crystal needs to be transported on the pre-centered goniometer head using a magnetic mount.

This page is Distribution A: Approved for Public Release, Distribution Unlimited
Support of Research at Sandia National Laboratories is provided by the Strategic Arms Reductions Office, Department of Defense

Ball and Stick Representation of $NF_4^+Sb_2F_{11}^-$



The Structure of $NF_4^+Sb_2F_{11}^-$

- ✓ The crystals grown from HF
- ✓ Monoclinic space group $P2_1/c$.
- ✓ Cell constants: $a = 17.968(2) \text{ \AA}$, $b = 17.939(2) \text{ \AA}$, $c = 14.0693 \text{ \AA}$; $\beta = 90.143^\circ$
- ✓ $Z = 16$
- ✓ $R = 0.0497$

Average N-F distance = $1.281(2) \text{ \AA}$

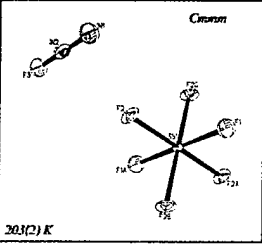
4 km pairs of $NF_4^+Sb_2F_{11}^-$ found in the asymmetric unit

The N-F bond distance has been estimated to be 1.31 and 1.32 Å from its general valence force field and ab initio calculations.*

* Christie, K. O. Spectrochim. Acta, Part A 1986, 42A, 939 and references therein.

This page is Distribution A: Approved for Public Release, Distribution Unlimited
Support of Research at Sandia National Laboratories is provided by the Strategic Arms Reductions Office, Department of Defense

Molecular Structure of $N_2F^+SbF_6^-$



Unit cell dimensions (Å)

Orthorhombic

$a = 6.8824(9)$, $b = 7.5398(9)$, $c = 5.5695(7)$

Volume (Å³) = 288.67(6), $Z = 2$

$\theta_{min}(\max) = 25.33^\circ$

$R1^* = 0.0389$

$wR2^* = 0.0687$

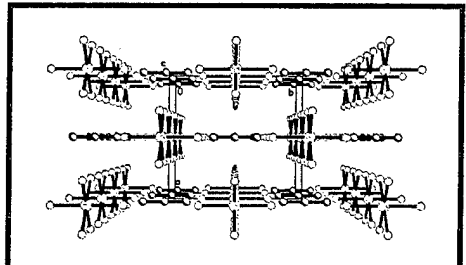
$S = 1.109$

* All Data

The N₂F⁺ and SbF₆⁻ ions are located in separate planes

This page is Distribution A: Approved for Public Release, Distribution Unlimited
Support of Research at Sandia National Laboratories is provided by the Strategic Arms Reductions Office, Department of Defense

Crystal Packing Diagram of $N_2F^+SbF_6^-$ (c-axis)



The N₂F⁺ and SbF₆⁻ ions are located in separate planes

This page is Distribution A: Approved for Public Release, Distribution Unlimited
Support of Research at Sandia National Laboratories is provided by the Strategic Arms Reductions Office, Department of Defense

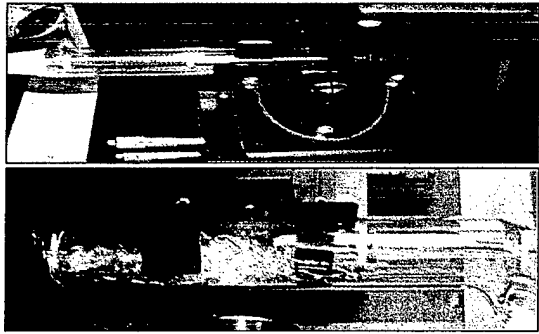
Actual Synthesis of $N_5^+AsF_6^-$

- 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% $H_2N_5^+AsF_6^-$
- > 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 $\Delta H_f (298^\circ C) = 351 \text{ kcal/mol}$

This page is Distribution A: Approved for Public Release, Distribution Unlimited
Source of Release of Title: "On Nitrogen Fluoride Complexes Formed on Reaction of Nitrogen Fluoride with Nitrogen"
July 9, 2004

How hazardous can N_5^+ salts get?



This page is Distribution A: Approved for Public Release, Distribution Unlimited
Source of Release of Title: "On Nitrogen Fluoride Complexes Formed on Reaction of Nitrogen Fluoride with Nitrogen"
July 9, 2004

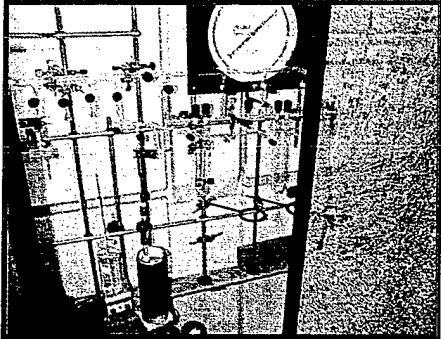
The Taming of $N_5^+SbF_6^-$

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

$$N_2F^+SbF_6^- + HN_3 \xrightarrow[-78^\circ C \text{ to RT}]{HF} N_5^+SbF_6^- + HF$$
- Properties of $N_5^+SbF_6^-$:
 - > White solid
 - > Stable to 70°C
 - > Obtained in high purity
 - > Does not explode at 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

This page is Distribution A: Approved for Public Release, Distribution Unlimited
Source of Release of Title: "On Nitrogen Fluoride Complexes Formed on Reaction of Nitrogen Fluoride with Nitrogen"
July 9, 2004

The need for caution dealing with high nitrogen compounds



This page is Distribution A: Approved for Public Release, Distribution Unlimited
Source of Release of Title: "On Nitrogen Fluoride Complexes Formed on Reaction of Nitrogen Fluoride with Nitrogen"
July 9, 2004

Following a strict dress code!



This page is Distribution A: Approved for Public Release, Distribution Unlimited
Source of Release of Title: "On Nitrogen Fluoride Complexes Formed on Reaction of Nitrogen Fluoride with Nitrogen"
July 9, 2004

Structure of the N_5^+ Cation

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

- ✓ The crystals grown from a mixture of SO_2 and SO_2ClF
- ✓ Crystal belong to the *Monoclinic* space group *C2/c*.
- ✓ Cell constants: $a = 10.913 \text{ \AA}$, $b = 12.654 \text{ \AA}$, $c = 16.675 \text{ \AA}$; $\beta = 104.72^\circ$
- ✓ $Z = 8$
- ✓ $R = 0.0678$ C&E News, 2000, 78, 41

Inter-ionic Clipping!!

The N_5^+ cation fits into the $Sb_2F_{11}^-$ bend thus locking it, thereby precluding any possibilities of twisting

This page is Distribution A: Approved for Public Release, Distribution Unlimited
Source of Release of Title: "On Nitrogen Fluoride Complexes Formed on Reaction of Nitrogen Fluoride with Nitrogen"
July 9, 2004

Geometry of the N_5^+ Cation

V-Shaped Geometry

Calculated Structure

Experimental Structure

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

V.J. Wilson, V.J. Thorn, Sheehy & Christie, J. Am. Chem. Soc., 2001, 123, 6306-6313

This paper is Distributed A: Approved for Public Release, Distribution Unlimited
Structural Aspects of Solids, XVI International Symposium on Structural Aspects of Solids, Budapest, 1999

Unexpected complexation of SO_2 with the azide ion in CsN_3

Structure shows novel SO_2N_3 as well as SO_2N_2 groups

This paper is Distributed A: Approved for Public Release, Distribution Unlimited
Structural Aspects of Solids, XVI International Symposium on Structural Aspects of Solids, Budapest, 1999

NOF_2^+ cation case

NOF₂⁺ Disorder

This paper is Distributed A: Approved for Public Release, Distribution Unlimited
Structural Aspects of Solids, XVI International Symposium on Structural Aspects of Solids, Budapest, 1999

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.

This paper is Distributed A: Approved for Public Release, Distribution Unlimited
Structural Aspects of Solids, XVI International Symposium on Structural Aspects of Solids, Budapest, 1999

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: $a = 7.513(2) \text{ \AA}$, $b = 8.083(2) \text{ \AA}$, $c = 10.314(2) \text{ \AA}$; $\beta = 107.46(2)^\circ$
- ✓ $Z = 4$
- ✓ $R = 0.0372$
- ✓ Refined oxygen occupancy in NOF_2^+ cation is 55%

This paper is Distributed A: Approved for Public Release, Distribution Unlimited
Structural Aspects of Solids, XVI International Symposium on Structural Aspects of Solids, Budapest, 1999

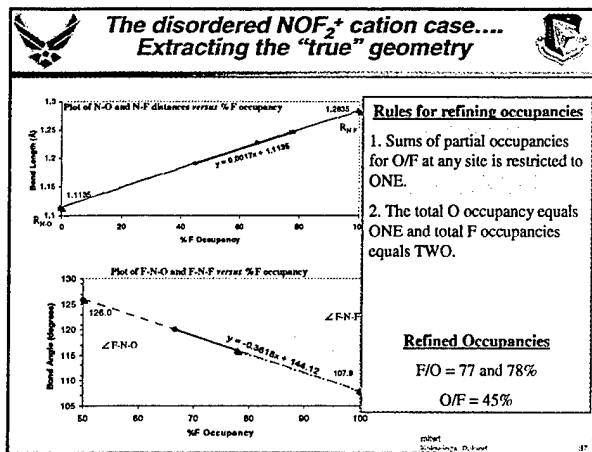
General approach for treating disorder

Plot of O-X and X-F distances versus %F occupancy

Plot of F-X-O and F-X-F angles versus %F occupancy

- 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° . Also angle $F-X-O = (1/2)(360^\circ - \text{angle } F-X-F)$

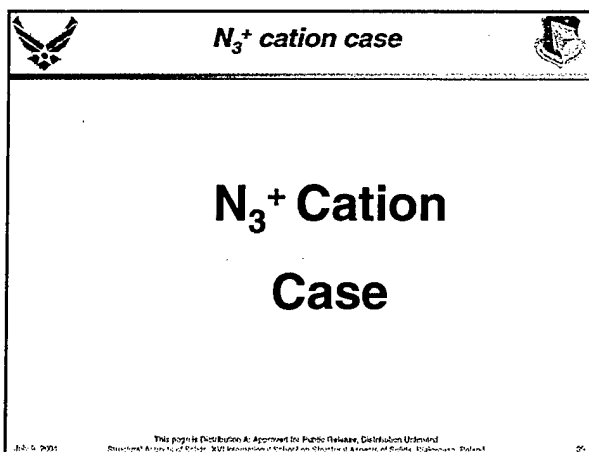
This paper is Distributed A: Approved for Public Release, Distribution Unlimited
Structural Aspects of Solids, XVI International Symposium on Structural Aspects of Solids, Budapest, 1999



Results of Geometric "Extraction"

Calculated	Experimental	
	"Apparent"	"Extraction" Method
B3LYP/CCSD(T)/631+G(2d)*, VTZ		
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 (°)	125.8 125.6	122.0(3), 122.1(3) 126.0
F-N-F (°)	108.4 108.8	115.9(3) 107.9
R (wR2) (%)	---	3.17-7.33 3.03, 6.68

publ. 2002, 30, 1000, 1000



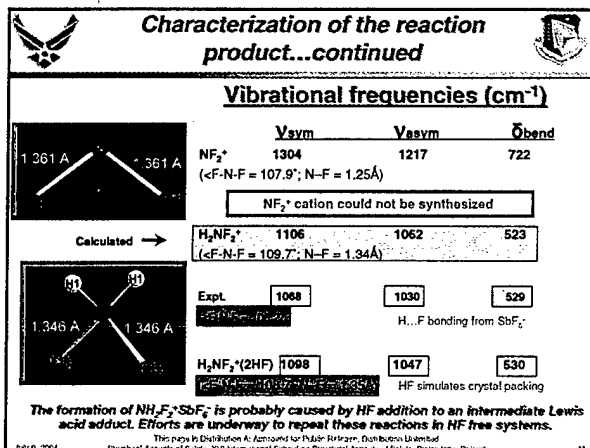
Characterization of reaction product: Theory & experimentation symbiosis

Vibrational frequencies (cm^{-1})

	Vsym	Vasym	δ bend
Cyclic ($\angle \text{N-N-N} = 60.0^\circ$)	1522-1550	1035-1060	
Linear	1170-1426	275-1307	307-426
Bent* ($\angle \text{N-N-N} = 120.8^\circ$)	1020	434(i)	424
Expt. ($\angle \text{X-N-X} = -105^\circ$)	1068	1030	529

Vibrational frequencies have a large range and are not very reliable, which make characterization of N_3^+ cation very difficult.

publ. 2001, 29, 1000, 1000



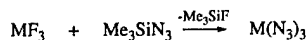
AZIDES

METAL AZIDES

publ. 2001, 29, 1000, 1000

Reactions of Group 15 halides with Trimethylsilylazide

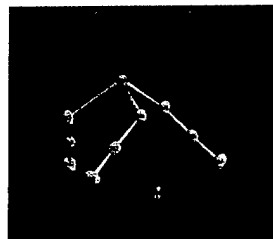
Crystalline binary metal azides were obtained upon reacting the corresponding metal fluorides with TMSN_3 . These compounds were reported as either liquids or tacky solids by Klapoetke et al.



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

This page is Distribution A: Approved for Public Release, Distribution Unlimited
Structural Abstracts of Solid State Chemistry, 2004, 30(1), 45-46, doi:10.1021/bk-2004-0001

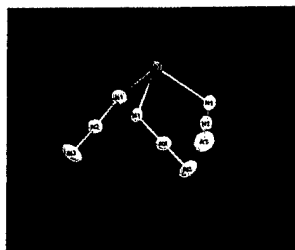
Structure of $\text{As(N}_3)_3$



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

This page is Distribution A: Approved for Public Release, Distribution Unlimited
Structural Abstracts of Solid State Chemistry, 2004, 30(1), 46-47, doi:10.1021/bk-2004-0001

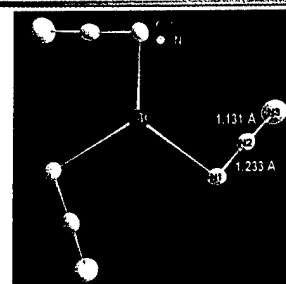
Crystal Structure of $\text{Sb(N}_3)_3$



All azide groups oriented in a propeller-like fashion

This page is Distribution A: Approved for Public Release, Distribution Unlimited
Structural Abstracts of Solid State Chemistry, 2004, 30(1), 46-47, doi:10.1021/bk-2004-0001

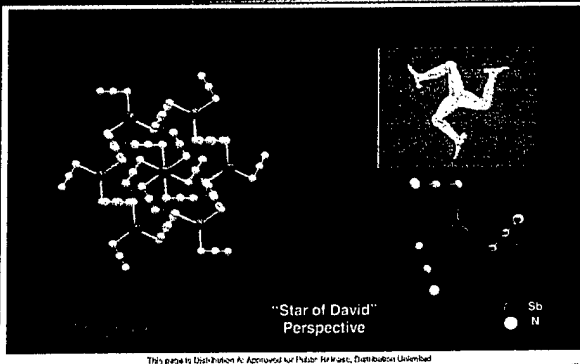
Observing "normal" N-N distances in $\text{Sb(N}_3)_3$



View down the three-fold axis, all azide groups equivalent
Example of perfect C_3 symmetry

This page is Distribution A: Approved for Public Release, Distribution Unlimited
Structural Abstracts of Solid State Chemistry, 2004, 30(1), 46-47, doi:10.1021/bk-2004-0001

The Art in Crystal Structure of $\text{Sb(N}_3)_3$



"Star of David" Perspective

This page is Distribution A: Approved for Public Release, Distribution Unlimited
Structural Abstracts of Solid State Chemistry, 2004, 30(1), 46-47, doi:10.1021/bk-2004-0001

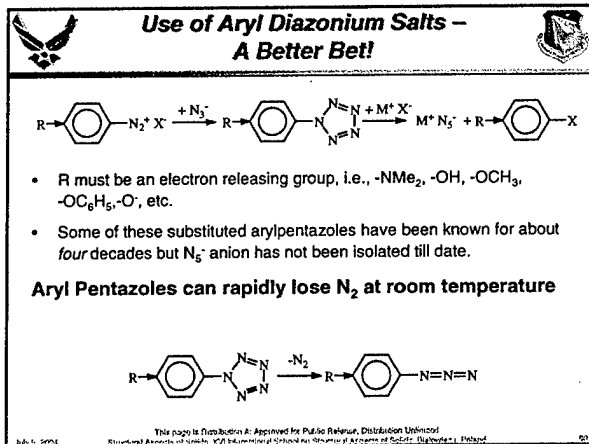
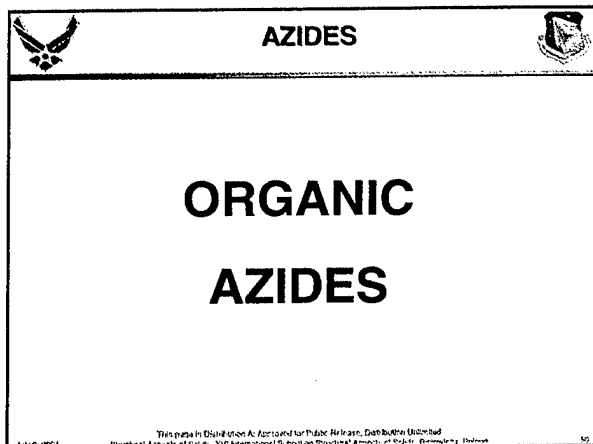
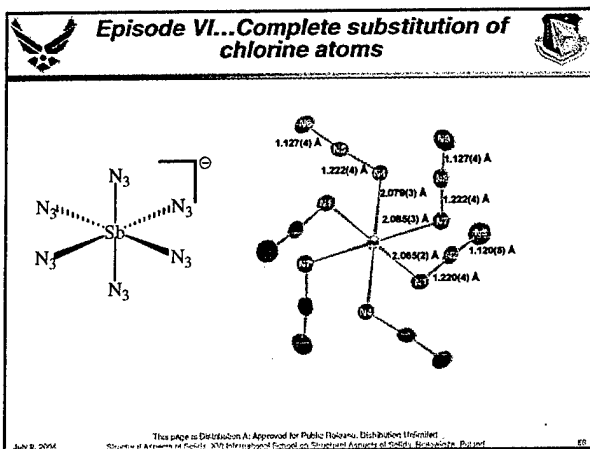
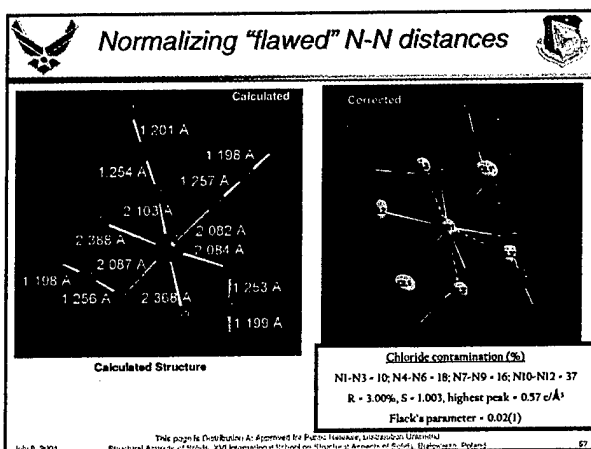
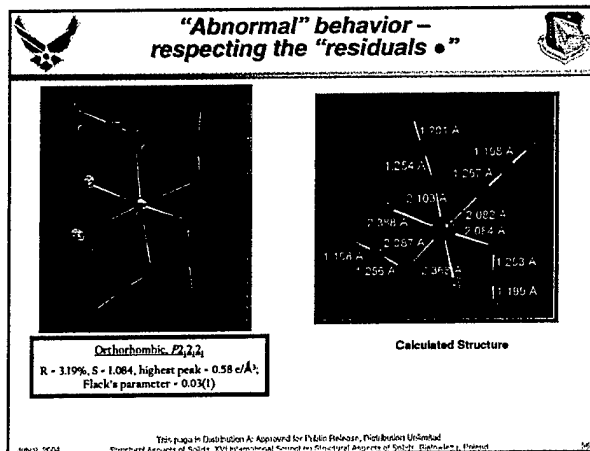
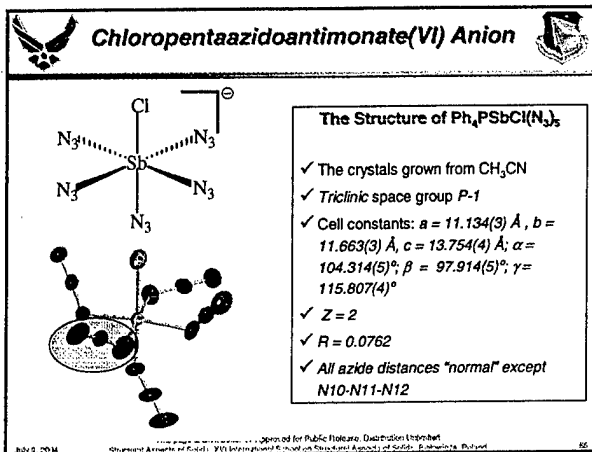
How appealing are these structures?

CHEMISTRY
A EUROPEAN JOURNAL
10/2

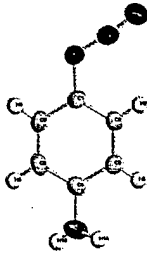
Recognizing: Isle of Aran National Symbol: Three-legged unicorn

Page 10, Christe et al. Chemistry Eur. J., 2004, 10, 506.

This page is Distribution A: Approved for Public Release, Distribution Unlimited
Structural Abstracts of Solid State Chemistry, 2004, 30(1), 46-47, doi:10.1021/bk-2004-0001



Crystal structure of 4-Hydroxyphenylazide



The thermal decomposition of 4-hydroxyphenylpentazole (4-HPP) results in the loss of N₂ gas and the formation of 4-hydroxyphenylazide. The "two" hydrogen atoms present on the *p*-oxygen atom are disordered.

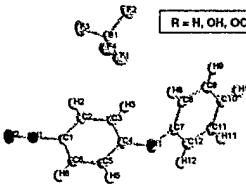
This page is Distributed As Approved for Public Release, Distribution Unlimited
 Copyright & copies of 5 days, 2003 International Chemical Union, International Union of Pure and Applied Chemistry, IUPAC

Synthesis of Aryldiazonium Salts

Aqueous Media

$$R-\text{C}_6\text{H}_4-\text{NH}_2 \xrightarrow[\text{< 0 } ^\circ\text{C}]{\text{NaNO}_2/\text{HCl}} R-\text{C}_6\text{H}_4-\text{N}_2^+\text{Cl}^- \xrightarrow{\text{NaBF}_4} R-\text{C}_6\text{H}_4-\text{N}_2^+\text{BF}_4^-$$

R = H, OH, OCH₃, OC₂H₅, OC₃H₇, N(CH₃)₂



This page is Distributed As Approved for Public Release, Distribution Unlimited
 Copyright & copies of 5 days, 2003 International Chemical Union, International Union of Pure and Applied Chemistry, IUPAC

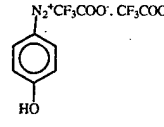
Synthesis of Aryldiazonium Salts...Non-aqueous synthesis

Non-aqueous Media

$$R-\text{C}_6\text{H}_4-\text{NH}_2 \xrightarrow[\text{CF}_3\text{COOH}]{\text{isoamyl nitrite}} R-\text{C}_6\text{H}_4-\text{N}_2^+\text{CF}_3\text{COO}^-$$

CF₃COOH
CH₂Cl₂

> Colas and Goeldner reported that the *p*-phenyldiazonium 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!

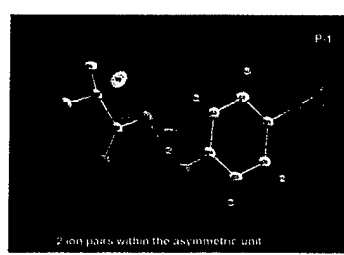
$$R-\text{C}_6\text{H}_4-\text{N}_2^+\text{CF}_3\text{COO}^- \cdot \text{CF}_3\text{COOH}$$


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

This page is Distributed As Approved for Public Release, Distribution Unlimited
 Copyright & copies of 5 days, 2003 International Chemical Union, International Union of Pure and Applied Chemistry, IUPAC

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

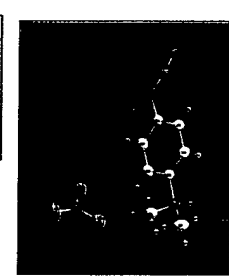
We DO NOT find any trifluoroacetic acid double salt. In fact, such a double salt would kill the pentazole formation



Two lone pairs within the asymmetric unit

This page is Distributed As Approved for Public Release, Distribution Unlimited
 Copyright & copies of 5 days, 2003 International Chemical Union, International Union of Pure and Applied Chemistry, IUPAC

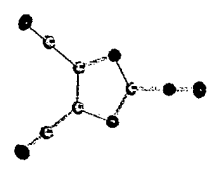
**Pentazole Formation...
Role of the Substituent Electronic Effects**

$$R-\text{C}_6\text{H}_4-\text{NH}_2 \xrightarrow[\text{-0 } ^\circ\text{C, II, NaN}_3]{\text{I as NaNO}_2/\text{HCl}} R-\text{C}_6\text{H}_4-\text{N}_2^+\text{NO}_2^- \xrightarrow{-\text{N}_2} R-\text{C}_6\text{H}_4-\text{N}_3$$


$$3\text{HONO} \rightleftharpoons \text{H}_2\text{O} + \text{NO} + 2\text{NO}$$

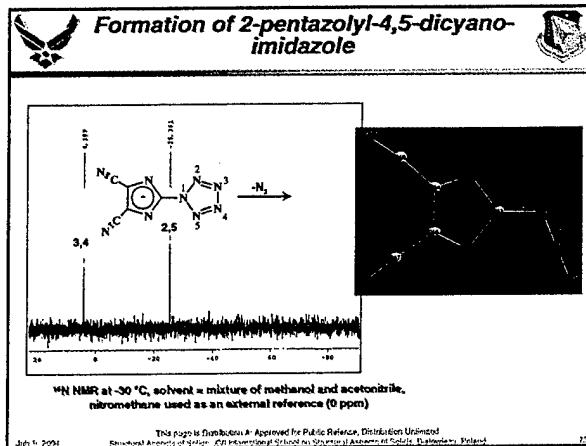
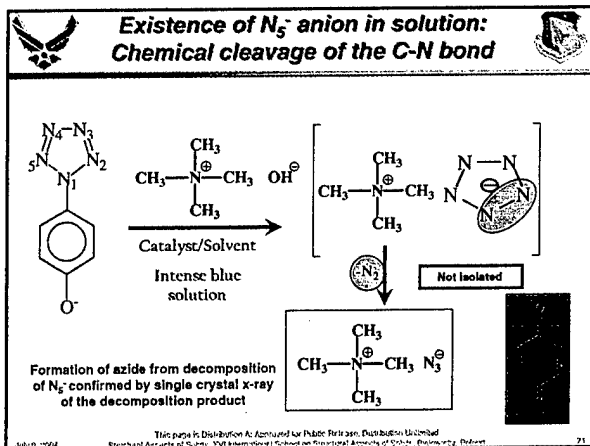
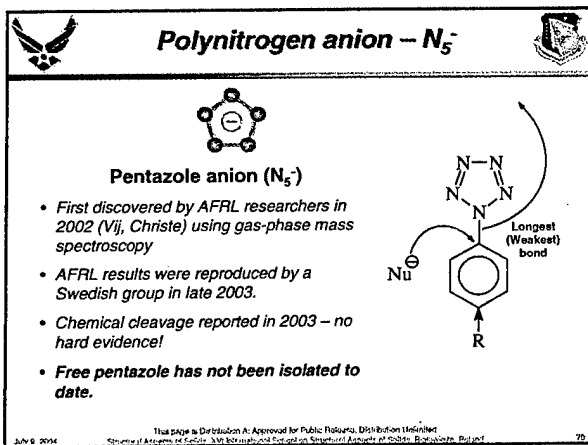
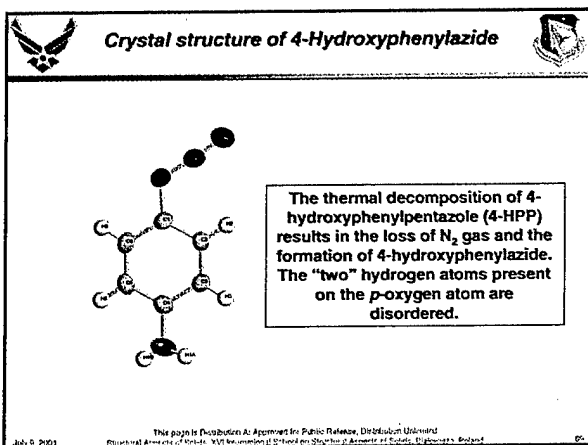
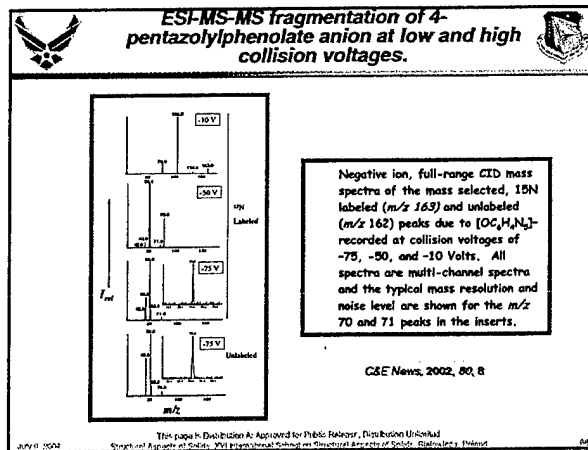
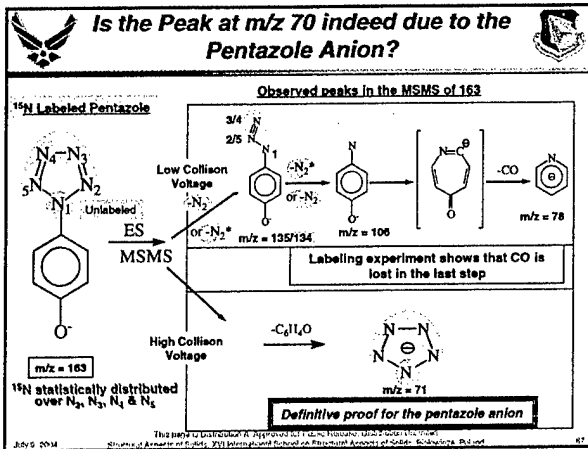
This page is Distributed As Approved for Public Release, Distribution Unlimited
 Copyright & copies of 5 days, 2003 International Chemical Union, International Union of Pure and Applied Chemistry, IUPAC

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



N-N = 1.096 Å
C-N = 1.334, 1.336 Å

This page is Distributed As Approved for Public Release, Distribution Unlimited
 Copyright & copies of 5 days, 2003 International Chemical Union, International Union of Pure and Applied Chemistry, IUPAC



Summary Highlights

- ✓ The first ordered crystal structure of an N_2F^+ salt, thus providing individual $N=N$ and $N-F$ bond lengths. $N_2F^+Sb_2F_{11}^-$ compound contains the shortest known $N=N$ bond, which is shorter than that of N_2 .
- ✓ The low temperature and safe preparation of NF_4^+ polyantimonates without the use of fluorine gas and high temperature/pressure. A non-disordered NF_4^+ anion is structurally characterized.
- ✓ The unique preparation of the $N_2F_4^+$ cation by the disproportionation of N_2F^+ salts. The disorder has not been resolved yet!
- ✓ Solving the bond distance anomaly in the structure of NO_2^+ cation by site occupancy refinement technique.
- ✓ Crystal structure of N_2^+ cation to prove the skeptics wrong on the existence of this exotic species.


This page is Distribution A. Approved for Public Release, Distribution Unlimited
 Statement of Approved for Public Release: 2013-08-01, Approved for Release by NSA on 05-08-2014 pursuant to E.O. 13526

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_6^- , SnF_8^{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-Pentazoly-4,5-imidazole appears to undergo chemical C-N bond cleavage. Results are under investigation!

This page is Distribution A. Approved for Public Release, Distribution Unlimited
 Statement of Approved for Public Release: 2013-08-01, Approved for Release by NSA on 05-08-2014 pursuant to E.O. 13526

Acknowledgments



Dr. Michael Berman (AFOSR)
 Dr. Arthur Morrish (DARPA)
 Dr. Don Woodbury (DARPA)
 Dr. Jerry Roatz (AFRL)

FUNDING

DARPA
 AFOSR
 ERC Inc.

This page is Distribution A. Approved for Public Release, Distribution Unlimited
 Statement of Approved for Public Release: 2013-08-01, Approved for Release by NSA on 05-08-2014 pursuant to E.O. 13526

BACKUP

This page is Distribution A. Approved for Public Release, Distribution Unlimited
 Statement of Approved for Public Release: 2013-08-01, Approved for Release by NSA on 05-08-2014 pursuant to E.O. 13526

Improved Syntheses of N_2F^+ Precursors

Synthesis of N_2F_2

Formation of the First Stage Graphite Intercalate and its Reaction with N_2F_4

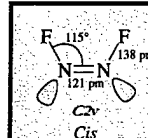
$$C_x + AsF_5 \longrightarrow C_x \cdot AsF_5 \quad (x = 10-12)$$

$$2 C_x \cdot AsF_5 + N_2F_4 \longrightarrow 2 C_x \cdot AsF_6^- + trans-N_2F_2 \quad (x = 10-12)$$

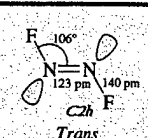
- ✓ Highly oriented pyrolytic graphite (HOPG) is very expensive, hard to grind and takes a long time to form the intercalate.
- ✓ Natural flake graphite (50-60 μ) is inexpensive and intercalates rapidly with AsF_5 .
- ✓ The *First-Stage Intercalate* has an average composition $C_{21.4}AsF_5$

This page is Distribution A. Approved for Public Release, Distribution Unlimited
 Statement of Approved for Public Release: 2013-08-01, Approved for Release by NSA on 05-08-2014 pursuant to E.O. 13526

The *Cis*- and *Trans* Isomers of N_2F_2



Cis



Trans

- ✓ *Cis*- N_2F_2 has a melting point $< -195^\circ C$ and a boiling point of $-105^\circ C$, whereas the *trans*-isomer melts at $-172^\circ C$ and boils at $-111.4^\circ C$. Separation of these isomers by fractional condensation is very difficult.
- ✓ Although the enthalpy of formation of the *cis*-isomer is lower than that of the *trans*-isomer by $3.04 \text{ kcal mol}^{-1}$, the *trans*-isomer is exclusively formed via the intercalate reaction.

This page is Distribution A. Approved for Public Release, Distribution Unlimited
 Statement of Approved for Public Release: 2013-08-01, Approved for Release by NSA on 05-08-2014 pursuant to E.O. 13526

Reactions of *trans*-N₂F₂ with Lewis Acids

- ✓ Only the *cis*-N₂F₂ isomer forms the with Lewis acids at room temperature.
- ✓ The *trans*-isomer forms the N₂F⁺ salts when heated with AsF₅. SbF₅ is reported to be unreactive.*
- ✓ To prepare N₂F⁺SbF₆⁻, *trans-cis* isomerization of N₂F₂ is required.

$$\begin{array}{l} \text{trans-N}_2\text{F}_2 + \text{AsF}_5 \xrightarrow{70^\circ\text{C}} \text{N}_2\text{F}^+\text{AsF}_6^- \\ \text{trans-N}_2\text{F}_2 + \text{SbF}_5 \xrightarrow[X]{70^\circ\text{C}} \text{N}_2\text{F}^+\text{SbF}_6^- \end{array}$$

* Roesky, H. W.; Glemser, O.; Bormann, D. Chem Ber., 1969, 99, 1589.

This page is Distribution A: Approved for Public Release, Distribution Unlimited
Structural Aspects of Solids, 1973 Symposium on Structural Aspects of Solids, Baltimore, Poland
July 9, 2004 73

Polynitrogen for Dummies

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

Thermodynamics
It is an uphill battle !!

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

Kinetics
Low Barrier towards catastrophic downfall

This page is Distribution A: Approved for Public Release, Distribution Unlimited
Structural Aspects of Solids, 1973 Symposium on Structural Aspects of Solids, Baltimore, Poland
July 9, 2004 80

Polynitrogen for Dummies

• Metastability requires a delicate balancing act !!

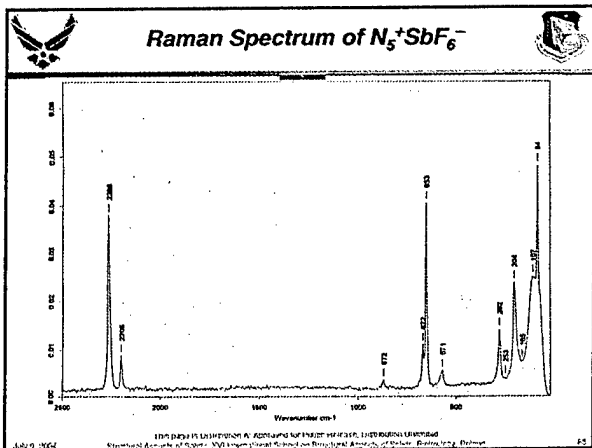
This page is Distribution A: Approved for Public Release, Distribution Unlimited
Structural Aspects of Solids, 1973 Symposium on Structural Aspects of Solids, Baltimore, Poland
July 9, 2004 81

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

This page is Distribution A: Approved for Public Release, Distribution Unlimited
Structural Aspects of Solids, 1973 Symposium on Structural Aspects of Solids, Baltimore, Poland
July 9, 2004 82



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 ¹⁵N labeled pentazoles.
- First experimental detection of pentazolate anion.
- Synthesis of pentazoles with a heterocyclic substituents
- Addition of OH⁻ ions to a solution of pentazole suggest C-N bond cleavage.
- Offers potential pathway for bulk synthesis of N₅⁻ salts

This page is Distribution A: Approved for Public Release, Distribution Unlimited
Structural Aspects of Solids, 1973 Symposium on Structural Aspects of Solids, Baltimore, Poland
July 9, 2004 85