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About this book

This book represents a collection of lectures presented at the NATO Advanced study Institute(ASI) on "Chemistry & Physics of the Molecular Processes in Energetic Materials", held at Hotel Torre Normanna, Altavilla Milicia, Sicily, Italy, September 3 to 15, 1989. The institute was attended by seventy participants including twenty lecturers, drawn from thirteen countries. The purpose of the institute was to review the major ad vances made in recent years in the theoretical and experimental aspects of explosives and propellants. In accordance with the format of the NATO ASI, it

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CHEM 4600 / PHYS 4950 Energetic Materials and Devices (2cr)

Spring 2016

Lecture TR 11:00-11:50 (SC2502).

Instructor: Dr. Clifford W. Padgett	**Phone** : (office) 912-344-2719
Office: SC 2005	**Office Hours**: 9-11 TR,
Email: Clifford.Padgett@armstrong.edu	10-11 F, and by appointment.

Instructor: Dr. Bill Baird	**Phone** : (office) 912-344-2708
Office: SC 2014	**Office Hours**: MW 10-11 am,
Email: William.Baird@armstrong.edu	TR 1–2 pm and by apt.

Recommended Text: The Chemistry Of Explosives, by Jacqueline Akhavan.
Other required materials: Scientific calculator.

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Exams are worth 80% of the class grade. Exams will be problems, definitions and short answer questions. You will be required to show all work, use correct units and use the correct number of significant figures. Bring a calculator to each exam, just in case. You will also be required to justify your answers.

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Ignition, Initiation and Thermal Decomposition (Ch 4).

Thermochemistry of Explosives (Ch 5).

Kinetics of Explosive Reactions (Ch 6).

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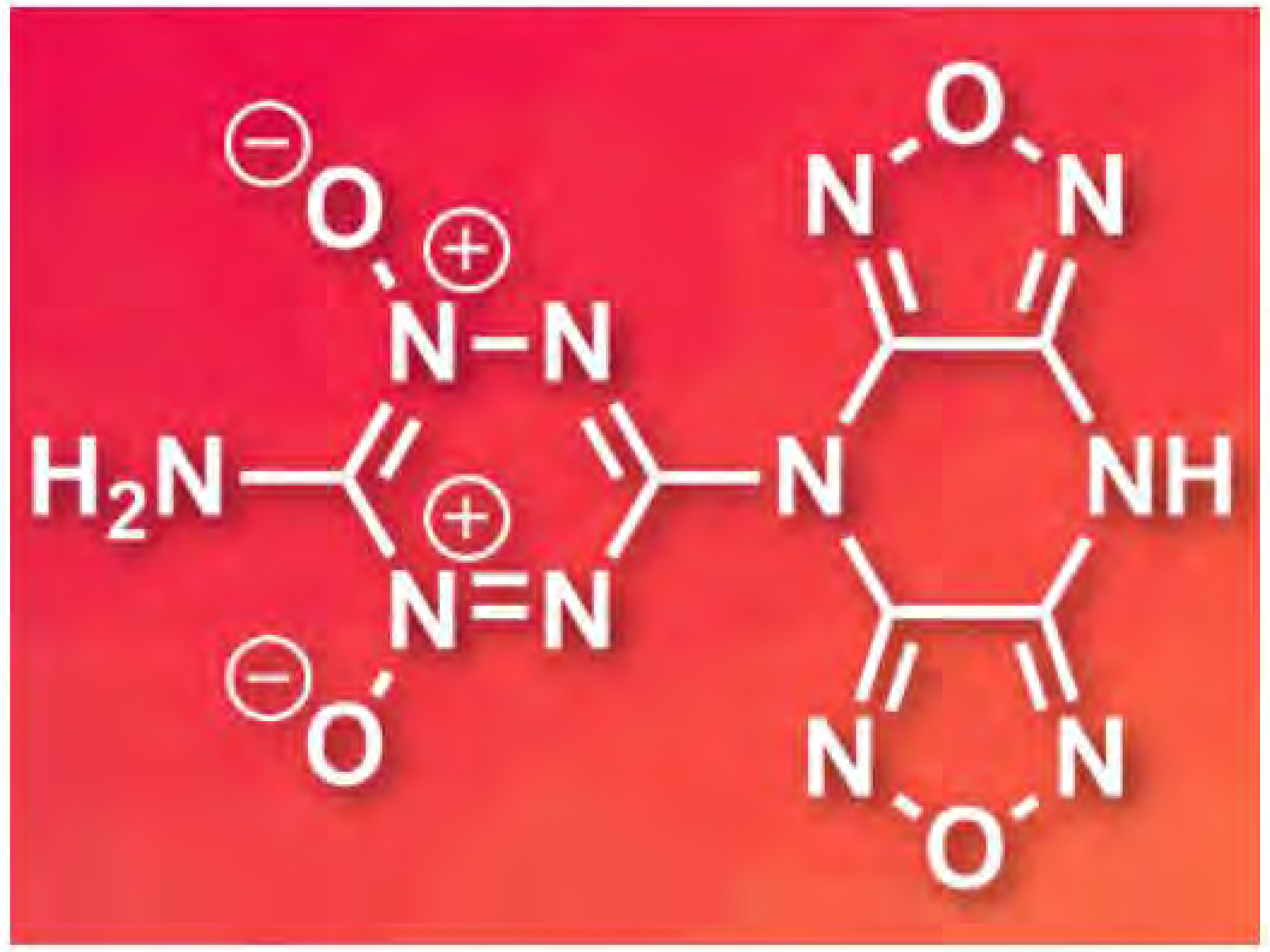

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Polycyclic compounds often stack very efficiently in crystals due to interactions between their π-electron systems. This can be useful for the development of energetic materials (explosives, propellants, etc.), which usually require a high density for good performance.

Christopher J. Snyder, David E. Chavez, Los Alamos National Laboratory, NM, USA, and colleagues have developed polycyclic N-oxides based on 1,2,4,5-tetrazine and 4*H*,8*H*-difurazano[3,4-*b*:3',4'-*e*]pyrazine (DFP), which can be used as energetic materials. The team performed an addition reaction between DFP as a nucleophile and 3-chloro-6-(3',5'-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine as an electrophile in different ratios to give 1:2 or 1:1 adducts. These intermediates were then treated with ammonia and finally oxidized using peroxytrifluoroacetic acid (PTFA) to give the desired products (example pictured based on 1:1 adduct).

The synthesized polycyclic N-oxides were found to be less sensitive to impact and friction than the widely used explosive RDX (cyclotrimethylenetrinitramine). They also have excellent thermal stabilities and detonation performances. According to the researchers, the sensitivity and detonation properties of the materials can be tuned by varying the size of the polycyclic N-oxide system.

- Polycyclic N-Oxides: High Performing, Low Sensitivity Energetic Materials,

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Magazine: New High-Density Energetic Material

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- Polycyclic N-Oxides: High Performing, Low Sensitivity Energetic Materials,
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Energetic Materials (EM)

Future ordnance systems must be adaptable in size to fit a family of delivery systems, contain sufficient energy to defeat the target, have the capability to fly further and faster, while being insensitive munition (IM) compliant and affordable. The Energetic Materials (EM) program explores materials/synthetic chemistry, advanced dynamic diagnostics and theoretical/computational/predictive approaches to provide novel energetic material concepts (explosives, propellants, reactive materials) that maximize molecular and formulation energy densities, synthesis efficiencies and predicted properties to achieve performance goals. These goals include delivering maximum energy in compact volumes, significantly extending weapon range, and improving resistance to unintended catastrophic failure in stressful environments.

EM is the pillar which establishes future advanced warhead and solid rocket motor performance and characteristics, and considered with associated weapon systems can be "game changers" by increasing warfighters' lethality and area of dominance. Advanced warhead development provides catastrophic damage, improving battlefield damage assessment and reducing sorties while equally powerful, but smaller weapons optimize internal carry and facilitate higher weapon load outs. Similarly, improved propellant ingredients and design concepts provide reduced time to target and extended ranges needed in volume limited ordnance systems.

Research Concentration Areas

The broad thrust areas within the EM program include high performance (rocket) propulsion where current needs include improved control over energy release and the ability to use energy more efficiently, and explosives development where the desire is to provide greater lethality in smaller form factors and couple energy output to targets more effectively. These thrusts require fundamental understanding and combined efforts in the current EM program research concentrations areas:

Issue 13, 2019

From the journal:
Journal of Materials Chemistry A

Multipurpose [1,2,4]triazolo[4,3-*b*][1,2,4,5] tetrazine-based energetic materials

Yingle Liu,*[ab] Gang Zhao,[b] Yongxing Tang,[b] Jichuan Zhang,[b] Lu Hu,[b] Gregory H. Imler,[c] Damon A. Parrish[c] and Jean'ne M. Shreeve*[b]

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Abstract

Two series of [1,2,4]triazolo[4,3-*b*][1,2,4,5]tetrazine-based energetic materials were synthesized effectively by using monosubstituted tetrazine or tetrazine-based fused rings as starting materials. Among them,

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Yi Wang, Yuji Liu, Siwei Song, Zhijian Yang, Xiujuan Qi, Kangcai Wang, Yu Liu, Qinghua Zhang & Yong Tian

Nature Communications **9**, Article number: 2444 (2018) | Download Citation

Abstract

Finding new high-energy-density materials with desired properties

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Propellant & Explosives Development and Characterization (PEDCS) Subcommittee

Technical Objectives

1. Conduct technical sessions, workshops, and other appropriate exchanges of technical information relative to development and characterization of propellant and explosive ingredients and formulations.
2. Provide a forum for discussing and resolving issues involving process development in the production of propellants and explosives; guns and other devices with high gas output; solid propellant ingredients and formulations; liquid propellant production and usage; propellant surveillance and aging; and analytical methods for characterization of energetics.
3. Maintain awareness of any problems within the Integrated High-Payoff Rocket Propulsion Technology (IHPRPT) program related to energetic materials, and suggest possible means of resolution.
4. Maintain awareness of activities within The Technical Cooperation Program (TTCP) and communicate the same to other organizations as appropriate.
5. Promote increased engagement in JANNAF by organizations that are producing and/or using energetic materials but expressed only limited interest in our activities.
6. Discern how to take advantage of relatively highly funded areas, such as insensitive munitions (IM) and the IHPRPT program.

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TEACHING HIGH-TEMPERATURE MATERIALS CHEMISTRY AT UNIVERSITY

(IUPAC Technical Report)

Prepared for publication by
GIOVANNI BALDUCCI[1,‡], ANDREA CICCIOLI[1], GIOVANNI DE MARIA[1], FIQIRI HODAJ[2],
AND GERD M. ROSENBLATT[3]

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Theoretical chemical characterization of energetic materials

Betsy M. Rice (a1) and Edward F.C. Byrd (a1)

https://doi.org/10.1557/jmr.2006.0329 Published online: 03 March 2011

Abstract

Our research is focused on developing computational capabilities for the prediction of properties of energetic materials associated with performance and sensitivity. Additionally, we want to identify and characterize the dynamic processes that influence conversion of an energetic material to products upon initiation. We are attempting to achieve these goals through the use of standard atomistic simulation methods. In this paper, various theoretical chemistry methods and applications to energetic materials will be described. Current capabilities in predicting structures, thermodynamic properties, and dynamic behavior of these material

Tailoring the physical properties of energetic materials

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Energetic materials are a class of material that have large amounts of chemical energy stored within their molecular structure. This energy is released upon decomposition, generally in the form of rapidly expanding, hot gases. They are therefore used for a wide range of applications such as; mining, military, and space exploration, and there is therefore a strong desire to improve the overall performance and safety of such materials. On account of reduced sensitivity to initiation by shock and impact, 2,4-dinitroanisole (DNAN) is a potential replacement for 2,4,6-trinitrotoluene (TNT) in melt-cast formulations for military applications. However, up to 15 % irreversible growth of DNAN has been previously observed upon thermal cycling and is a key reason why DNAN has not yet been universally accepted as a replacement for TNT. DNAN exhibits a complex system of polymorphism. One particular transition from DNAN-II to DNAN-III, which occurs at 266 K, has been observed in these studies to cause 8 - 10 % growth of DNAN-II pellets when temperature cycled for 30 cycles between 256 K and 276 K. What was even more concerning was the appearance of cracking of DNAN pellets after being temperature cycled. Doping the crystal structure of DNAN-II with related molecules, such as 2,4-dinitrotoluene or 2,4-dinitroaniline, was investigated in order to probe how steric and electronic factors affect the transition. The addition of varying amounts of 2,4-dinitroaniline suppressed this transition to varying extents and

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Energetic Materials

EMPHASIS IN ENERGETIC MATERIALS

PROGRAM OVERVIEW

Why Should You Apply

The Colorado School of Mines has recently approved the addition of a special emphasis sequence in Energetic Materials (Explosives) to the Materials Science graduate program. This special emphasis in Energetic Materials (Explosives) will be offered to students pursuing Ph.D. and M.S. degrees in Materials Science. This new and interdisciplinary area of emphasis will endeavor to recruit professional students from U.S.

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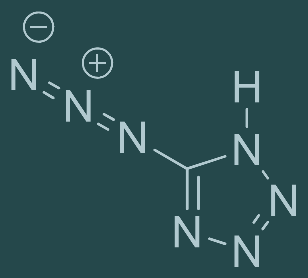

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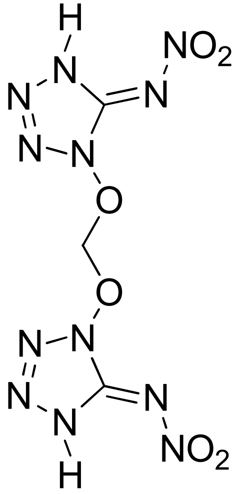
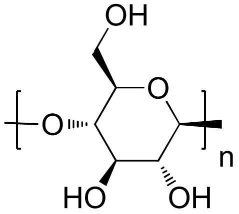


Energetic Materials In Daily Life

A Delta rocket launches NASA's Mars Phoenix Lander mission from Cape Kennedy in 2007. Image courtesy NASA.

Materials Explode for the Same Reason they Burn



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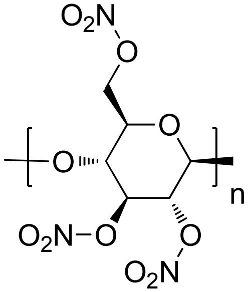
Standard Combustion



Nitrocellulose (Gun Cotton)

$$\xrightarrow[\Delta]{O_2} C_{(s)} + CO_2 + H_2O + N_2 + NO_2 \quad \text{etc.}$$

Deflagration

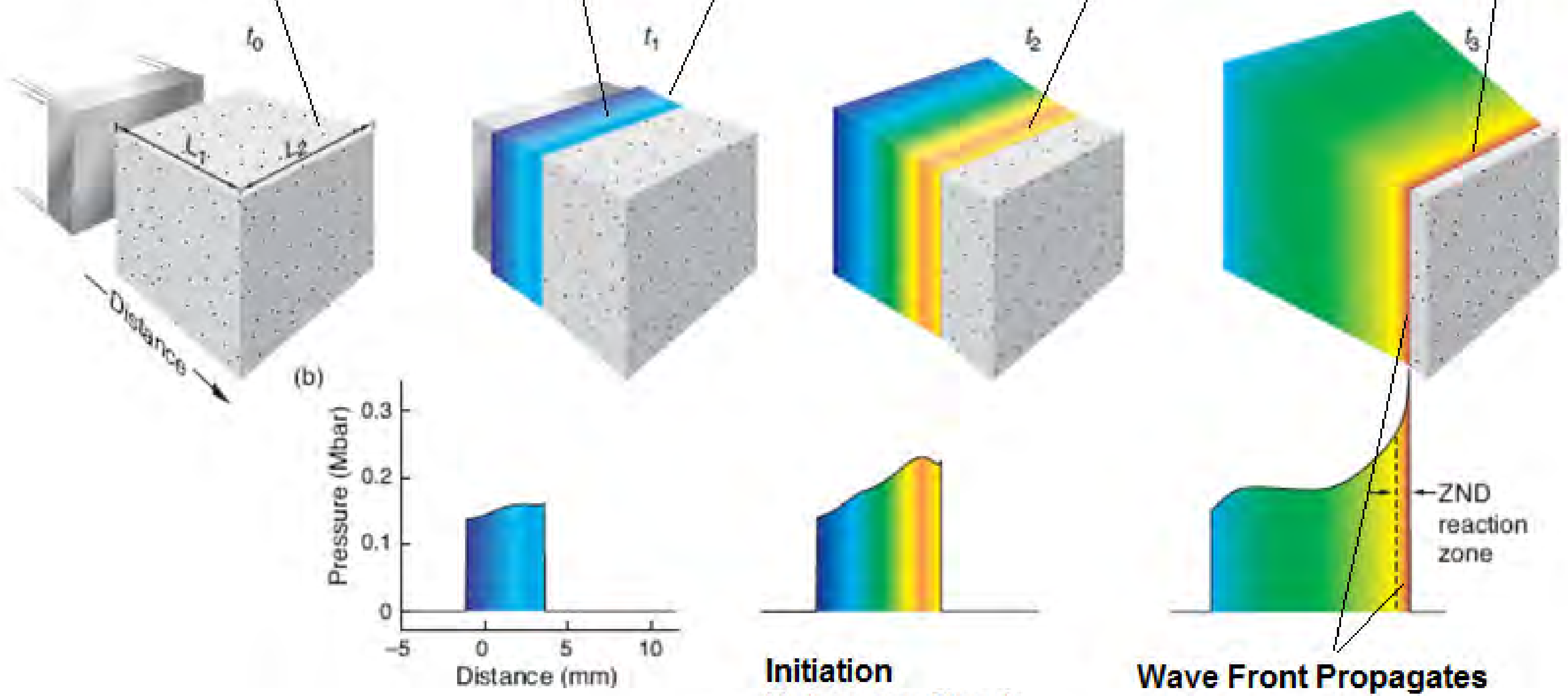
High Pressure Shock Wave

$$\searrow C_{(s)} + CO_2 + H_2O + N_2 + NO_2 \quad \text{etc.}$$

Detonation

- Rate of burning is dependant on consistency (paper vs. wood)
- Different Rates of combustion determine mode of energetic release
- Energy given off from combustion or formation of N_2

Detonation: The Zeldovich, von Neuman, Doring Model



Explosive

Shock Wave Propagates

High Local Pressure

Initiation - Degradation and Combustion Induced by Pressure

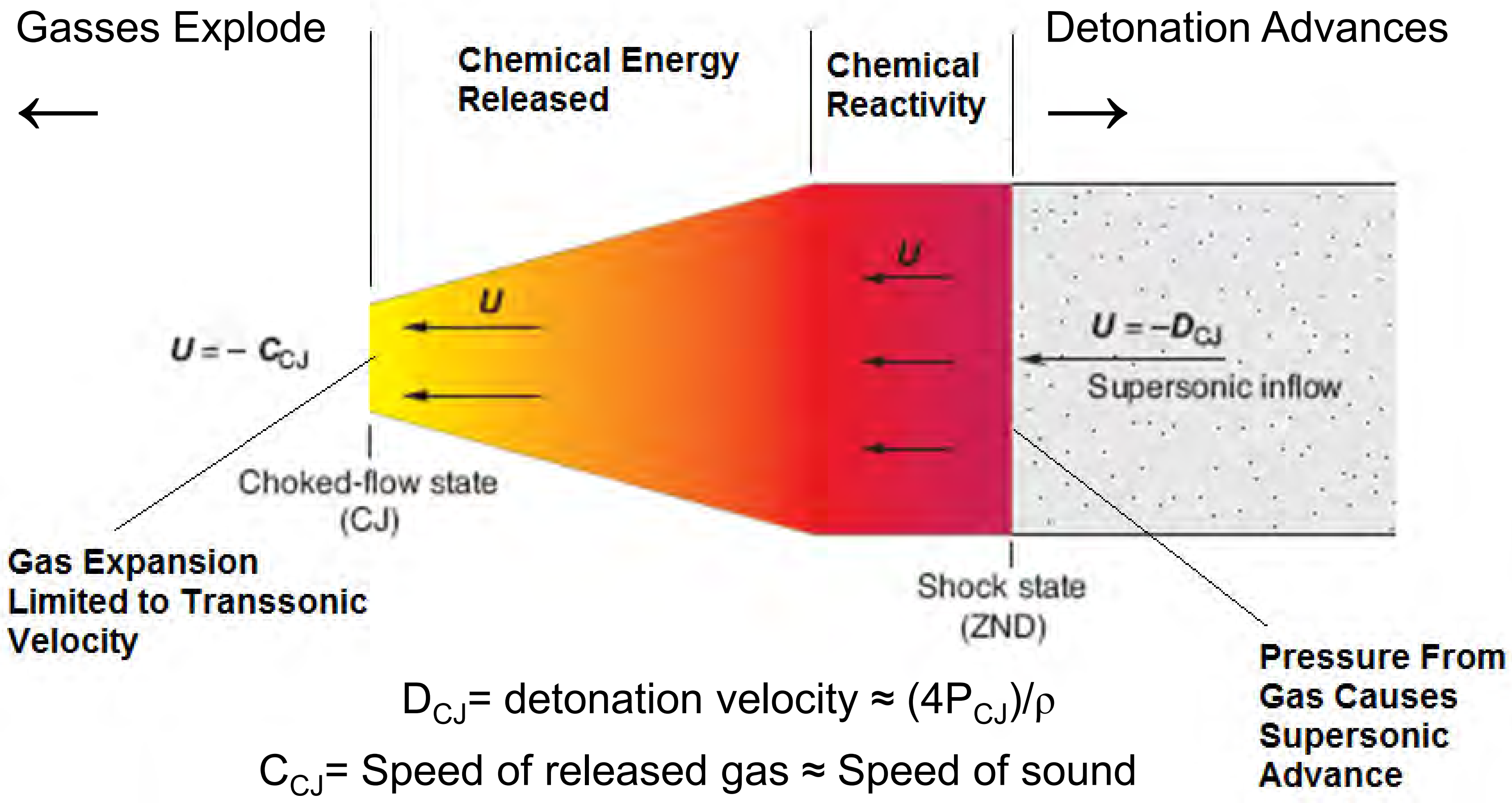
ZND State - Self Sustaining Detonation Fuelled by Combustive Reactions

Initiation Enhances Shock Pressure

Wave Front Propagates at Chapman Jouguet Velocity

Bdzil, J. B.; Aslam, T. D.; Henninger, R.; Quirk, J. J. *Los Alamos Science* **2003,** *28*, 96.

Another Look at The ZND State



D_{CJ}= detonation velocity ≈ $(4P_{CJ})/\rho$

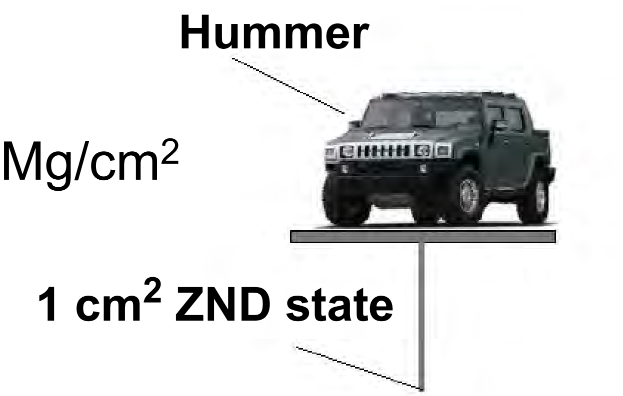
C_{CJ}= Speed of released gas ≈ Speed of sound

Bdzil, J. B.; Aslam, T. D.; Henninger, R.; Quirk, J. J. *Los Alamos Science* **2003,** *28*, 96.

Tremendous Pressure is Produced During Detonation

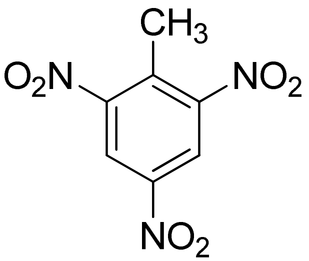
- Reported in GPa; 1.00 GPa = 72.5 Tons/in^2 = 10.2 Mg/cm^2

10.2 Mg /cm^2 ≈ 3.4 Hummer H2/cm^2

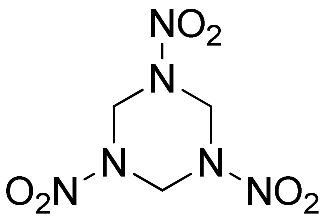


Hummer

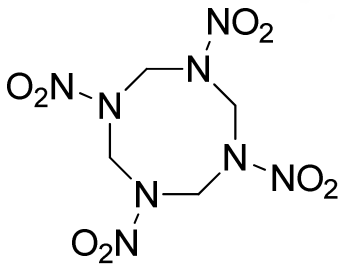
1 cm^2 ZND state



TNT



RDX



HMX

20.3 Gpa = 207 Mg/cm^2
≈ 69.0 Hummer H2/cm^2

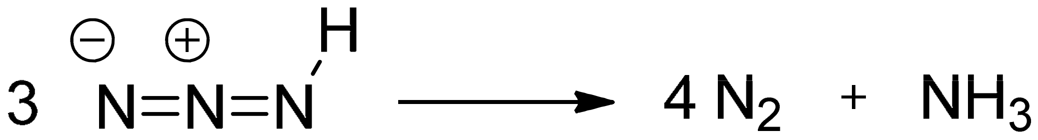
34.1 GPa = 348 Mg/cm^2
≈ 116 Hummer H2/cm^2

39.6 Gpa = 404 Mg/cm^2
≈ 135 Hummer H2/cm^2

Agrawal, J. *High Energy Materials: Propellants, Explosives and Pyrotechnics.*; Wiley-VCH: Weinheim, 2010.

How Much Energy is Actually Being Released?

- Energy results from formation of combustion products and N_2 from materials with high ΔH_f



$$3\ \overset{\ominus}{N}{=}\overset{\oplus}{N}{=}N\text{-}H \longrightarrow 4\,N_2 + NH_3$$

ΔH_f= 72.0 kcal/mol ΔH_f = 0 kcal/mol ΔH_f = -11.02 kcal/mol

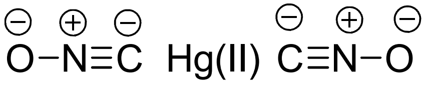
= 75.6 kcal/mol = 1.75 kcal/g

Snickers Bar: 280 kcal/bar (58.7g) = 4.7 kcal/g

Rodgers, D.; McLafferty, F. *J. Chem. Phys.* **1995,** *103*, 8302.

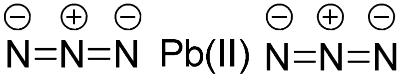
High Explosives are Categorized by Sensitivity

- Primary Explosives – Detonate easily by application of heat, mechanical shock, spark



$\overset{\ominus}{O}-\overset{\oplus}{N}\equiv\overset{\ominus}{C}\ \mathrm{Hg(II)}\ \overset{\ominus}{C}\equiv\overset{\oplus}{N}-\overset{\ominus}{O}$

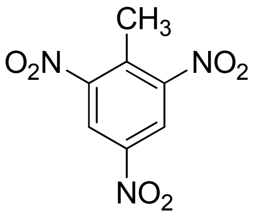
Mercury Fulminate



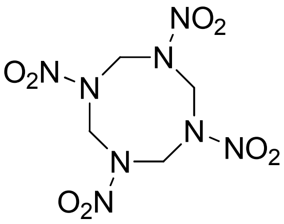
$\overset{\ominus}{N}=\overset{\oplus}{N}=\overset{\ominus}{N}\ \mathrm{Pb(II)}\ \overset{\ominus}{N}=\overset{\oplus}{N}=\overset{\ominus}{N}$

Lead Azide

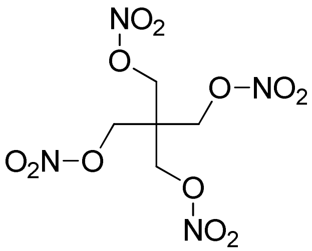
- Secondary Explosives – Detonate by shockwave from primary explosive



TNT



HMX



PETN

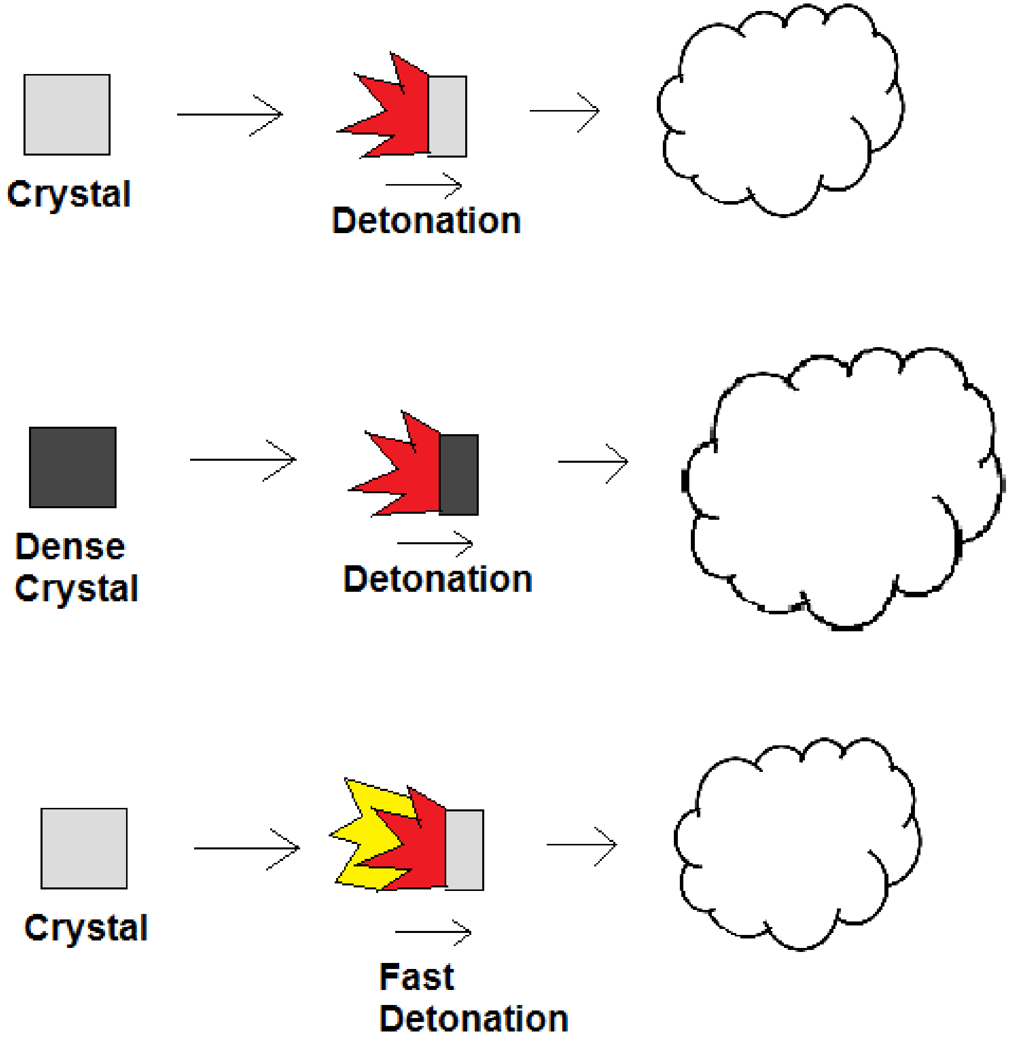
Agrawal, J. *High Energy Materials: Propellants, Explosives and Pyrotechnics*.; Wiley-VCH: Weinheim, 2010.

A Good Secondary Explosive Has Good Detonation Performance

- Detonation performance is mostly judged by detonation pressure and detonation velocity
- $P_d \approx \frac{1}{4} v_d \rho$, P_d is detonation pressure v_d is detonation velocity
- Work is done by an explosion through a sharp increase in pressure

Agrawal, J. *High Energy Materials: Propellants, Explosives and Pyrotechnics*.; Wiley-VCH: Weinheim, 2010.

How are Detonation Pressure, Detonation Velocity and Density Related?



Total Gas proportional to mass of crystal = density x volume

More Gas

= More Gas/Time

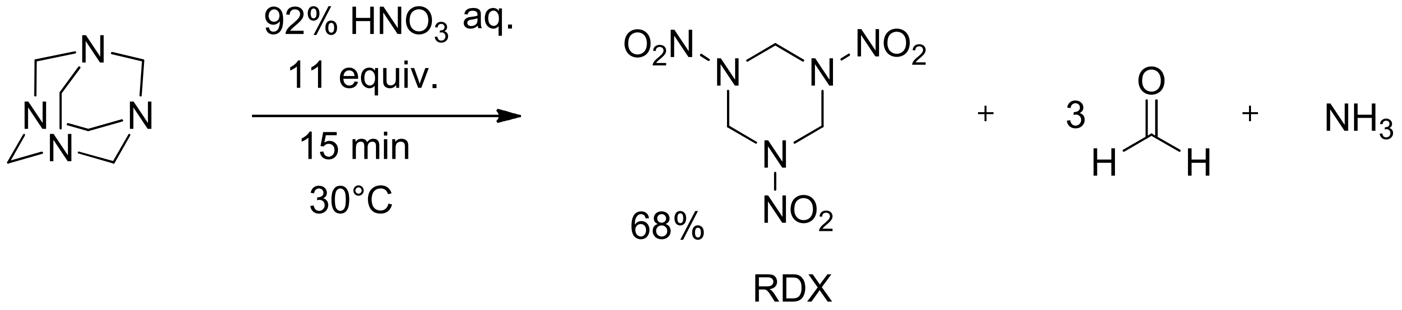
= More Pressure During Detonation

Same Amount of Gas as Case 1, but faster release

= More Gas/Time

= More Pressure During Detonation

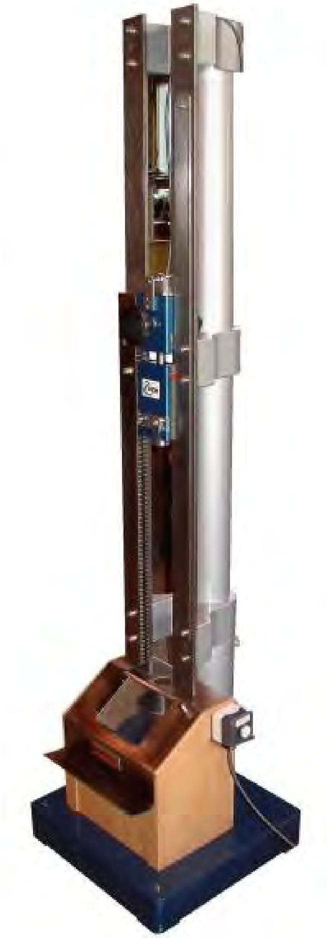
Good Secondary Explosives are Easily Accessible From Stable Materials



- Procedure is tricky – extensive optimization was necessary
- Reasonable yield possible from single step in single pot
- Purified by recrystallization from acetone

Hale, G.C. *J. Am. Chem. Soc.* **1925,** *47*, 2754**.**
Agrawal, J. *High Energy Materials: Propellants, Explosives and Pyrotechnics*.; Wiley-VCH: Weinheim, 2010.

A Good Secondary Explosive Is Relatively Stable



Fallhammer Apparatus

- Hammer dropped on powdered sample
- Drop height with 50% probability of causing explosion is considered fail point
- Usually reported in J delivered at fail height
- RDX is NATO and DoD mandated standard explosive for most applications (7.5J)
- RDX often stabilized in applications

Department of Defense Test Method Standards Safety and Performance Tests for the Qualification of Explosives, MIL-STD-1751A, Dec. 11, **2001.**
Klapotke, T. M.; Stierstorfer, J. *Helvetica Chimica Acta* **2007**, *90*, 2132

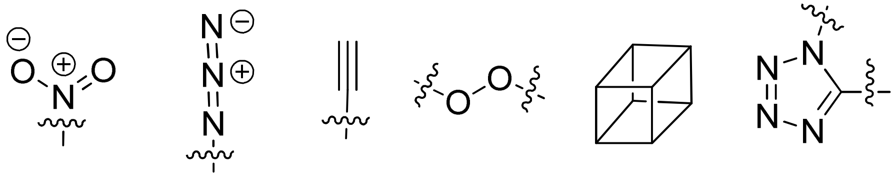
A Well Defined Melting Point is Desirable for Melt Casting

- To produce solid state charges, explosives are added to molten TNT (mp = 82°C T_d = 300°C) and cooled
- In order to replace TNT, an explosive would need a similar window of thermal stability
- Very few explosives have the potential compete with TNT as melt casting binders

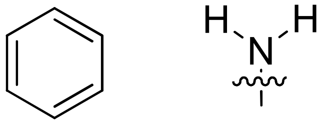
Agrawal, J. *High Energy Materials: Propellants, Explosives and Pyrotechnics*.; Wiley-VCH: Weinheim, 2010.

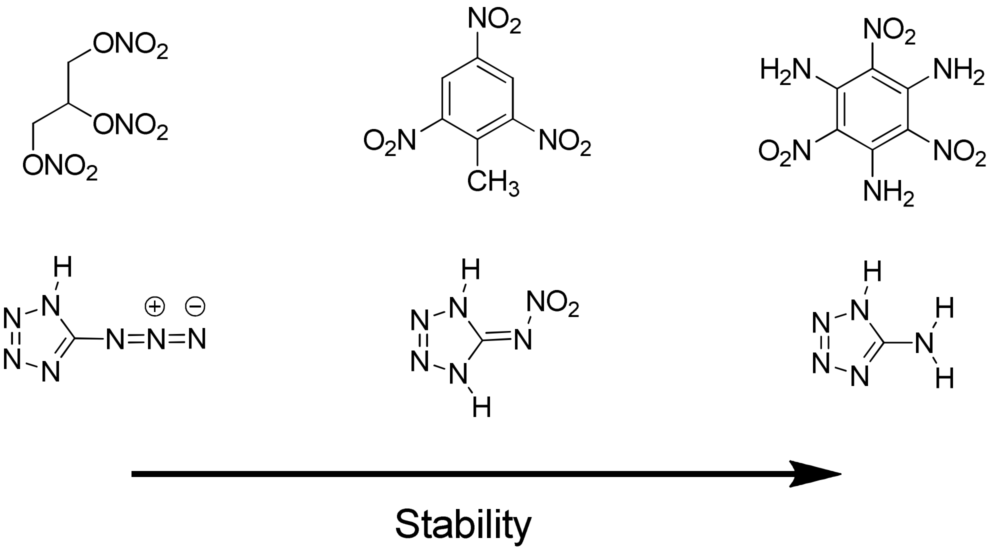
The Stability of Explosives is Related to The Chemistry of The Energetic Groups

Energetic Groups



Stabilizing Groups





- Its easy to design material that will explode
- Its hard to make good explosives
- Structure functional relationships are approximate

Agrawal, J. *High Energy Materials: Propellants, Explosives and Pyrotechnics*.; Wiley-VCH: Weinheim, 2010

How Would You Work With a Relatively Unstable Compound?

Prof. Klapotke in Protective Equipment

Kemsley, J. *Chem. Eng. News* **2008,** *86,* 22-23.

- Typical Personal Protective Equipment Includes:

- Helmet
- Face Sheild
- Leather Coat
- Kevlar Gloves
- Kevlar Suit
- Blast Sheild

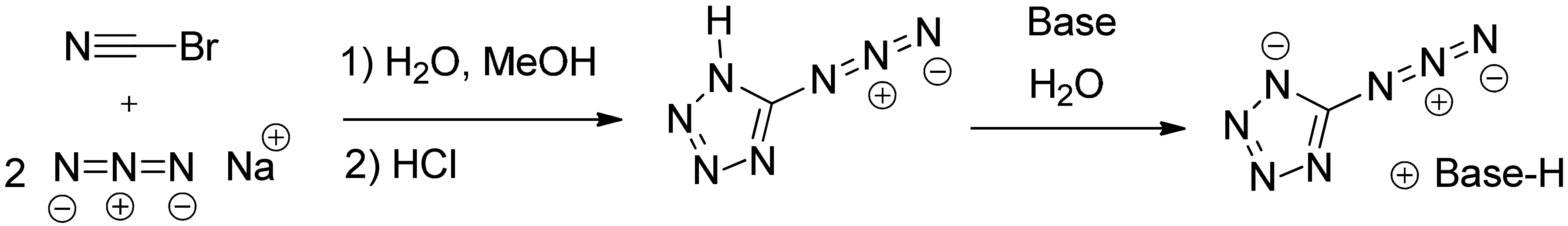
- Typical Scale:

250 mg

- Both Klapotke and Shreeve groups have approval process for new reactions

- Students who neglect safety are let go

Isn’t All This Caution Excessive?



Base:

$LiOH$

NH_2NH_2

KOH

$Ca(OH)_2$

NH_3

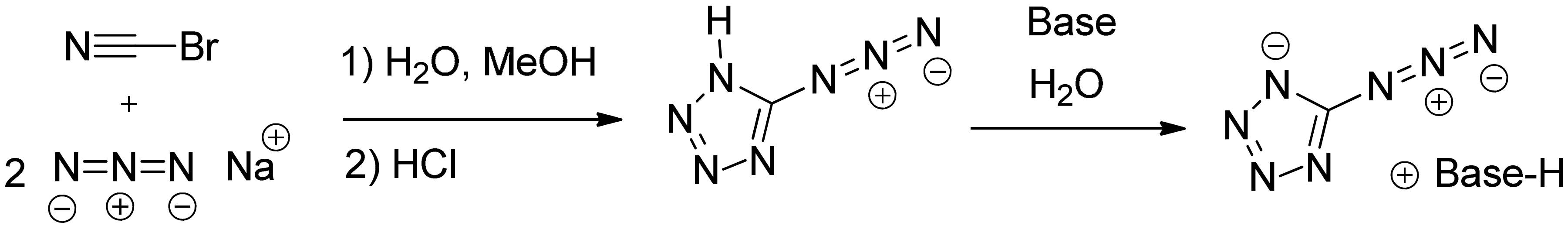
$NaOH$

Cs_2CO_2

- “The aqueous solution was left for crystallization on a watch glass and ‘fortunately’ three single crystals could be isolated from the border of the solution. A few hours later the whole preparation exploded spontaneously”

Klapotke, T. M.; Steirstorfer, J. *J. Am Chem. Soc.* **2009,** *131*,1122-1134.

Isn’t All This Caution Excessive?



Base:

$LiOH$

NH_2NH_2

KOH

$Ca(OH)_2$

NH_3

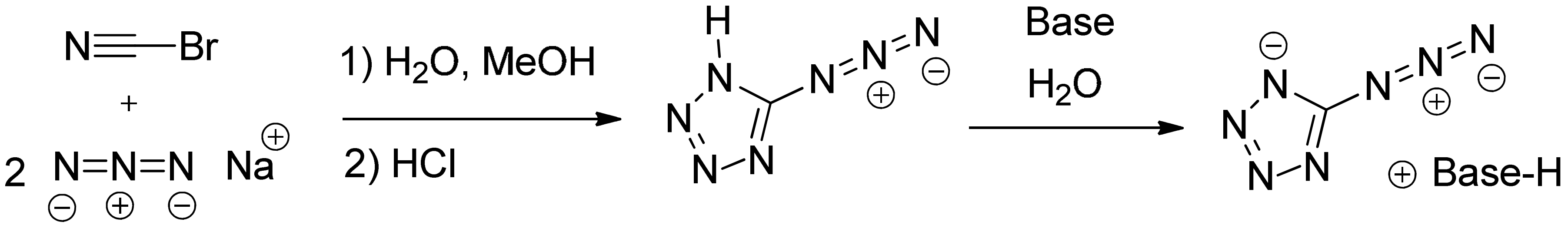
$NaOH$

Cs_2CO_2

- “The synthesis of the Rubidium 5 – azidotetrazolate had been tried a few times. However, we never could observe the solid material, and the reaction mixture (left undisturbed in an explosive case and in the dark) detonated spontaneously for each preparation.”

Klapotke, T. M.; Steirstorfer, J. *J. Am Chem. Soc.* **2009,** *131*,1122-1134.

Isn’t All This Caution Excessive?



Base:

$LiOH$

NH_2NH_2

KOH

$Ca(OH)_2$

NH_3

$NaOH$

Cs_2CO_2

- Authors land JACS publication for materials “probably only of academic interest”
- In fairness some salts may be stable enough to be primary explosives

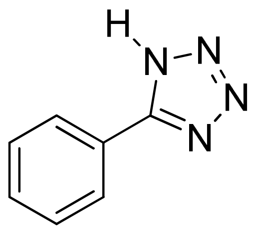
Klapotke, T. M.; Steirstorfer, J. *J. Am Chem. Soc.* **2009,** *131*,1122-1134.

What do Tetrazoles Have to Offer?

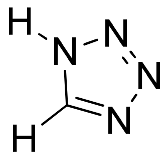
- Clean - tetrazole is 80% nitrogen by mass
- Powerful - tetrazole derivatives will be shown to compete with RDX and HMX for performance
- Tunable - tetrazole has a similar pK_a to acetic acid, making energetic salts easy to synthesize
- Are tetrazoles a recent development?

The History of the Tetrazole

- Bladin, University of Upsala,

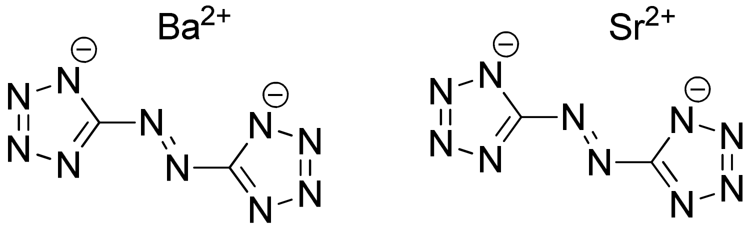


1885



1892

- Salts of 5, 5-diazotetrazolate investigated by Thiele

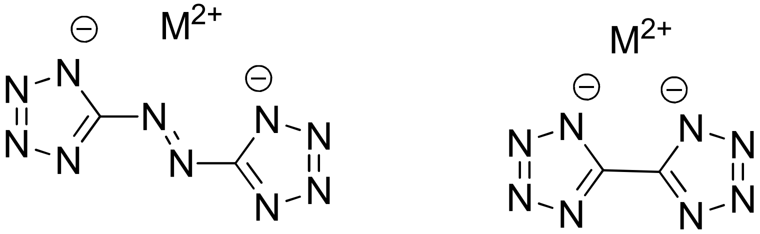


1898

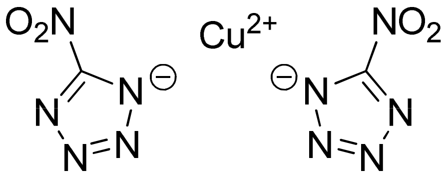
Benson, F. *Chem. Rev.* **1947**, *41*, 1-61.

The History of the Tetrazole

- Rathsburg patents several tetrazoles as primary explosives in place of mercury fulminate in England



1921 - Patented as Explosives



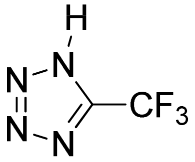
1931 - Patented in Germany

- Summary of tetrazole chemistry published in Meyer and Jacobson's *Lehrbuch der Organischen Chemie* in 1923

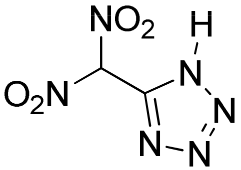
Benson, F. *Chem. Rev.* **1947**, *41*, 1-61.

The History of the Tetrazole

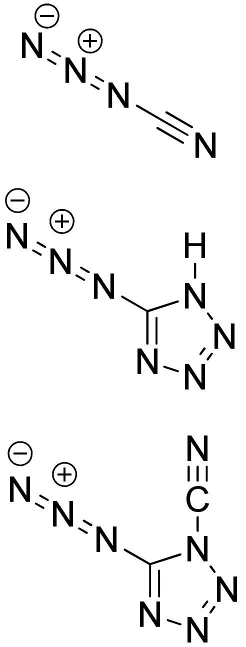
- Sporadic publication of tetrazole containing energetic materials between 1950 and 1999



Norris, 1962
Naval Ordinance Test Station
China Lake, California



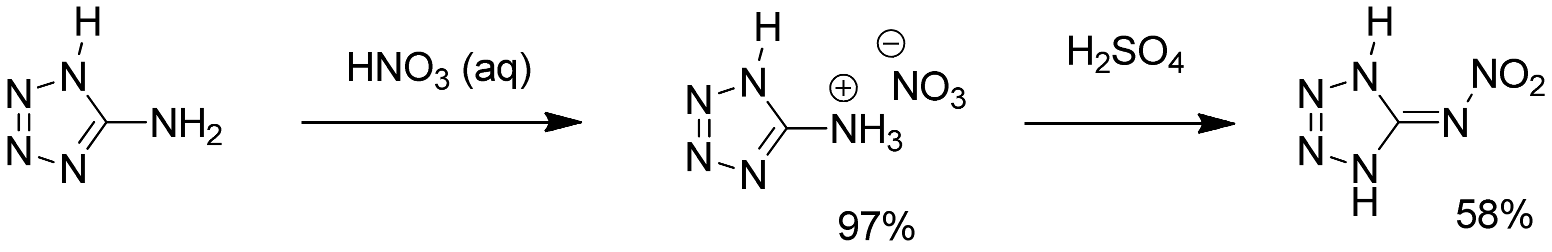
Einberg, 1963
Pittman-Dunn Institute
United States Army Munitions Command



Marsh, 1972
E I du Pont de Nemours and Company

Norris, W. P. *J. Org. Chem.* **1962,** *27,* 3248.
Einberg, F. *J. Org. Chem.* **1963,** *29,* 2021.
Marsh, F. D. *J. Org. Chem.* **1972,** *37*, 2966.

Herbst and Garrison, 1953, Michigan State College

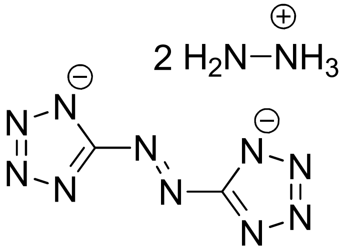


- Observed decomposition at 135°C on heating block "with reddish flash"
- Capillary melting point attempt showed decomposition with gas evolution at 160 – 170°C
- Lowered temperature of drying procedure from 100°C to 70° C after unexpected explosion
- Estimated 2 water molecules per tetrazole using wet techniques

Herbst, R. M; Garrison, J. A. *J. Org. Chem.* **1953,** *18*, 941.

The History of the Tetrazole

- Klapotke Group publishes its first paper on tetrazole material



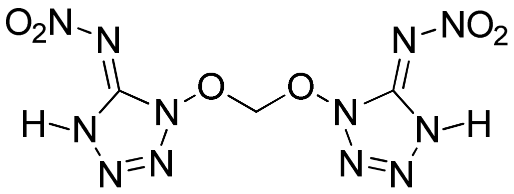
Hammerl et Al., 2001
University of Munich

- 2006 - Shreeve Group publishes a review on energetic materials section on tetrazoles features Theile, Klapotke and Shreeve.

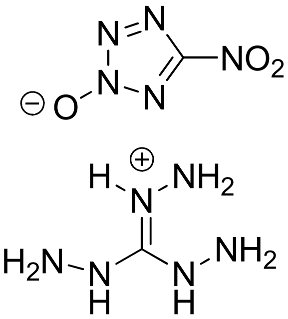
Hammerl, A.; Klapotke, T. M.; Noth, H.; Warchhold, M.; Holl, G. *Inorg. Chem.* **2001**, *40*, 3570.
Singh, R. P.; Verma, R. D.; Meshri, D. T.; Shreeve, J. M. et al. *Angew. Chem. Int. Ed.* **2006**, *45*, 3584.

The History of the Tetrazole

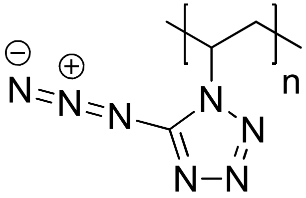
- 2009 – 2010 – More than 20 energetic materials papers feature Tetrazole moiety.



Joo Y.; Shreeve, J. M.
2010 University of Idaho



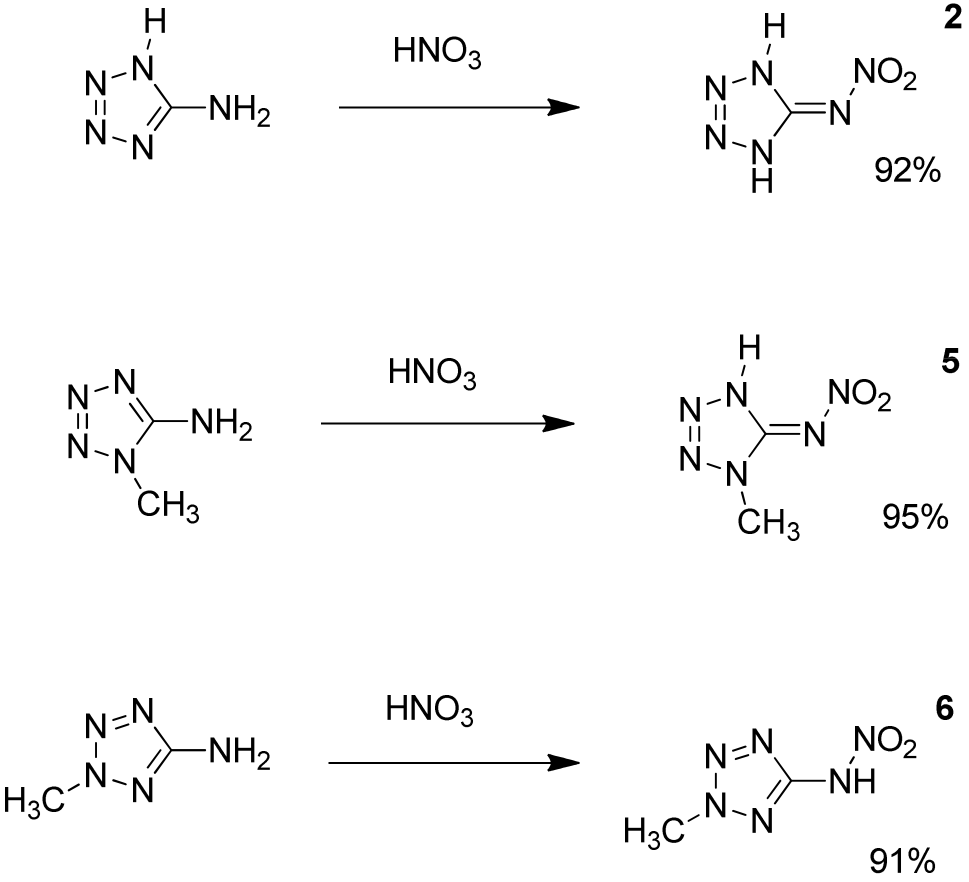
Gobel, M.; Klapotke T. M. et Al.
2010



Klapotke, T.M.; Sproll, S.M.
2010

Gobel, M.; Karaghiosoff, K.; Klapotke, T.; Piercy, D.; Steirstorfer, J. *J. Am. Chem. Soc.* **2010,** *132,*17216.
Joo, Y.; Shreeve, J. M. *Angew. Chem. Int. Ed.* **2010,** *49*, 7320.
Klapotke, T. M.; Sproll, S. M. *Eur. J. Org. Chem.* **2010,** 1169.

Synthesis of Nitroiminotetrazoles by Klapotke Group

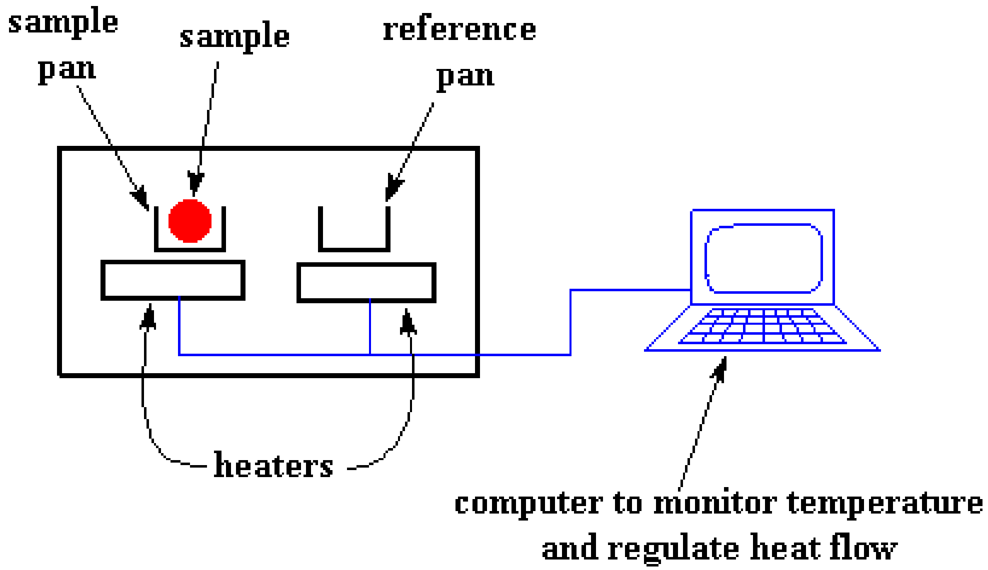


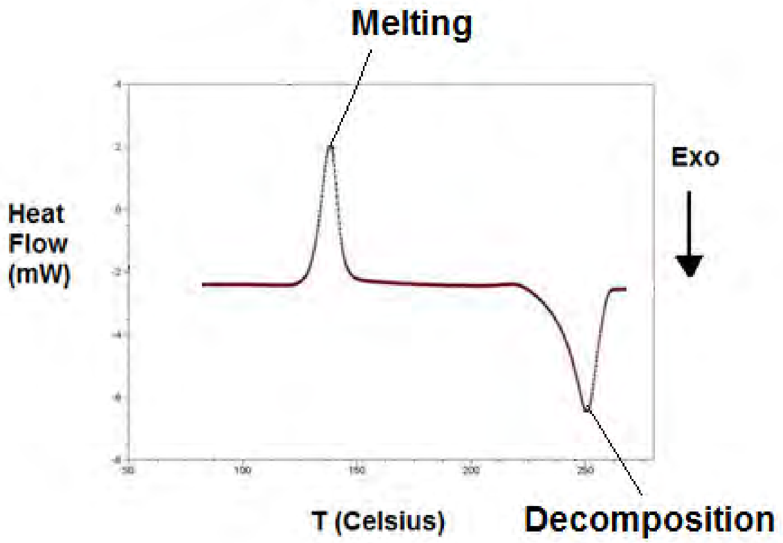
- Synthesis was improved by directly nitrating with concentrated HNO_3

Klapotke, T. M.; Stierstorfer, J. *Helvetica Chimica Acta* **2007**, *90*, 2132.

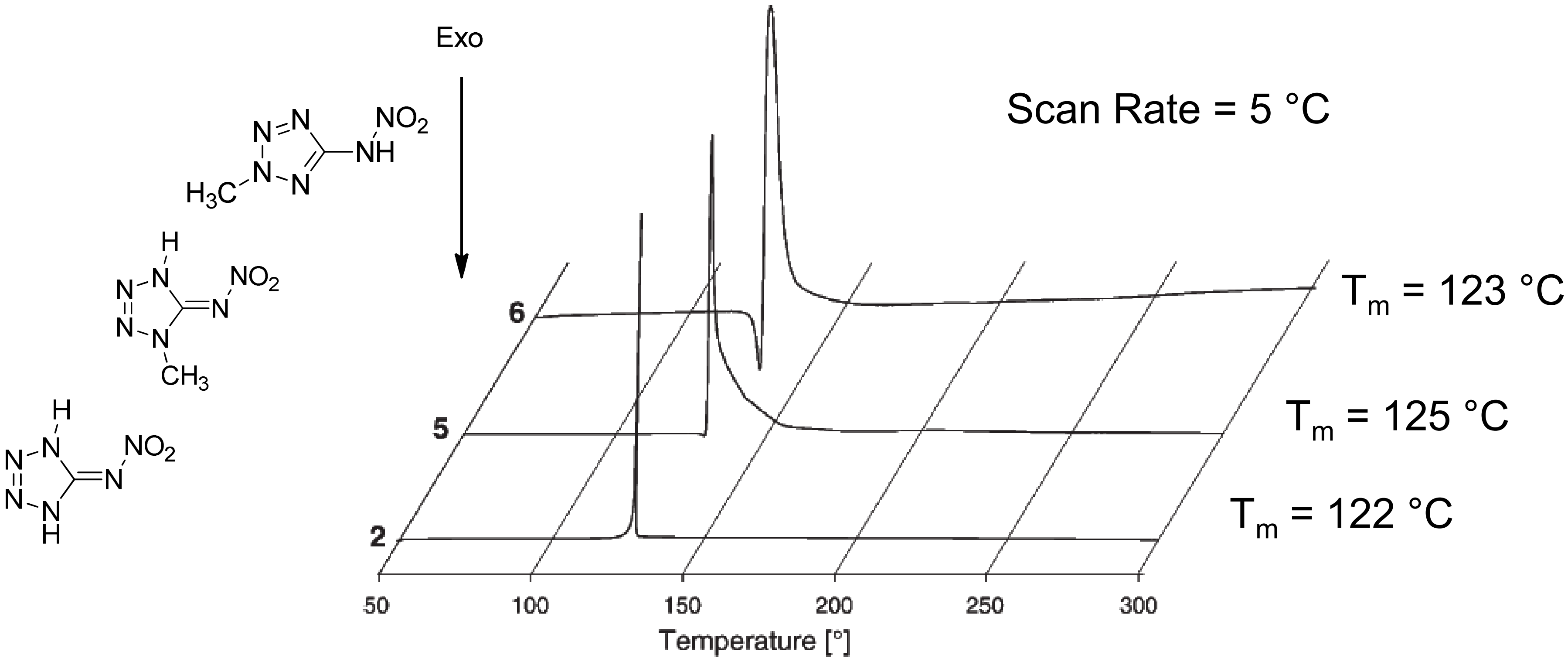
Differential Scanning Calorimetry

- Calorimetric technique used to identify reorganization events in bulk material such as melting and decomposition





Thermal Stability of Nitroiminotetrazoles



Scan Rate = 5 °C

T_m = 123 °C

T_m = 125 °C

T_m = 122 °C

- DSC shows that decomposition occurs with melting

Klapotke, T. M.; Stierstorfer, J. *Helvetica Chimica Acta* **2007**, *90*, 2132.

Characterization of Gasses Released from Bomb Calorimetry of Nitroiminotetrazoles

- Small samples were placed in bomb calorimeter
- After thermal decomposition bomb was vented into an FTIR
- Product profiles were qualitatively characterized
- Oxygen balance is important factor in products of decomposition

Oxygen Balance (OB or Ω)

For a compound of empirical formula $C_aH_bN_cO_d$

$$\Omega\% = \frac{d-2a-b/2}{M} \times 1600$$

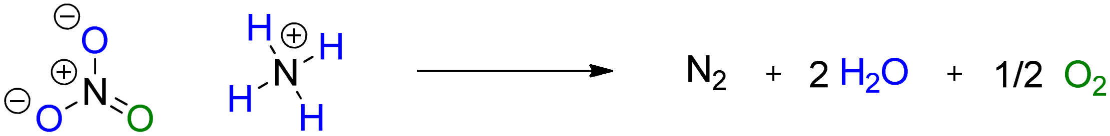
For a metal containing compound of empirical formula $C_aH_bN_cO_dM_n$

$$\Omega\% = \frac{d-2a-b/2-n}{M} \times 1600$$

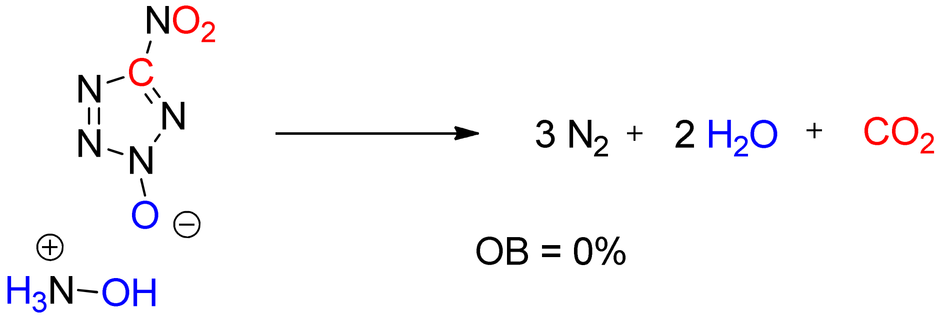
Determines mass% oxygen needed to fully combust a compound

Agrawal, J. *High Energy Materials: Propellants, Explosives and Pyrotechnics.*; Wiley-VCH: Weinheim, 2010.

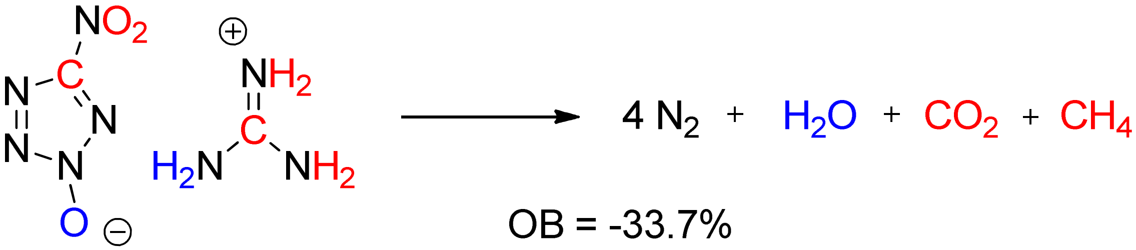
Examples of Positive, Negative and 0% Oxygen Balance


$\rightarrow N_2 + 2\,H_2O + 1/2\,O_2$

OB = 20.0%


$\rightarrow 3\,N_2 + 2\,H_2O + CO_2$

OB = 0%


$\rightarrow 4\,N_2 + H_2O + CO_2 + CH_4$

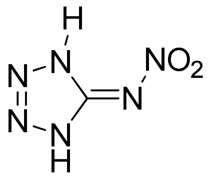
OB = -33.7%

- If a compound has an OB of 0% it can fully combust without external oxygen
- A negative percentage indicates that external oxygen is necessary
- A low oxygen balance leads to a faster release of energy, less toxic products

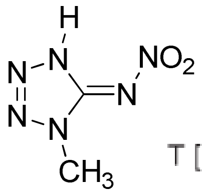
Gobel, M.; Karaghiosoff, K.; Klapotke, T.; Piercy, D.; Steirstorfer, J. *J. Am. Chem. Soc.* **2010,** *132,*17216.

Gasses Detectible From the Combustion of Nitroiminotetrazoles

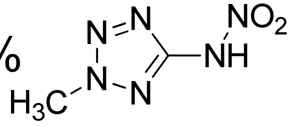
OB= -12.30%

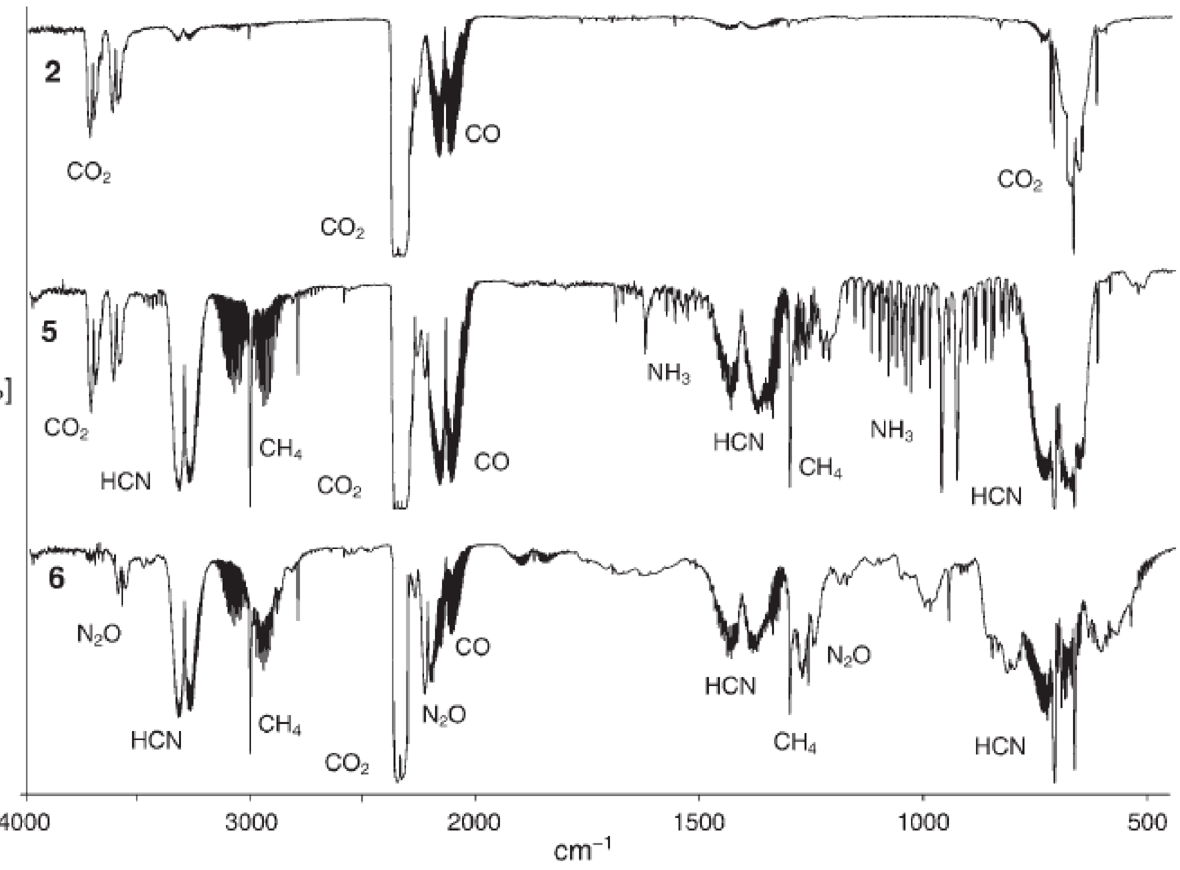


OB= -44.41 %



OB= -44.41%

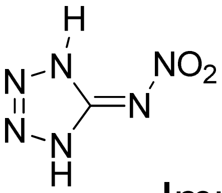




Klapotke, T. M.; Stierstorfer, J. *Helvetica Chimica Acta* **2007**, *90*, 2132.

Oxygen Balance is Negatively Correlated to Stability

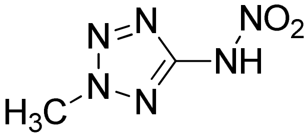
- Oxygen balances tend to be negatively correlated with sensitivity to mechanical and other stimulus



2

OB= -12.30%

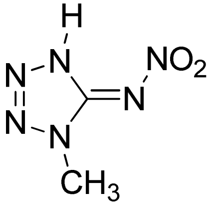
Impact sensitivity: 1.5 J



6

OB= -44.41 %

Impact sensitivity: 3.0 J



5

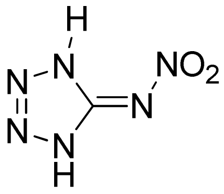
OB= -44.41 %

Impact sensitivity: 12.5 J

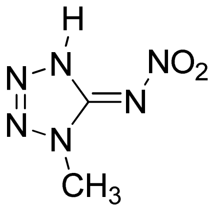
Klapotke, T. M.; Stierstorfer, J. *Helvetica Chimica Acta* **2007**, *90*, 2132.

Nitroiminotetrazoles are comparable to RDX in Performance and Stability

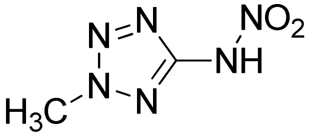
	Impact Sensitivity (J)	**ρ (g/cm^3)**	**ΔH_f (kCal/mol)**	**P_d (Gpa)**	**V_d (m/s)**
2	1.5	1.87	63.1	36.3	9173
5	12.5	1.76	62.1	29.5	8433
6	3.0	1.67	90.8	28.9	8434
RDX	7.5	1.80	16.7	34.1	8906



2



5



6

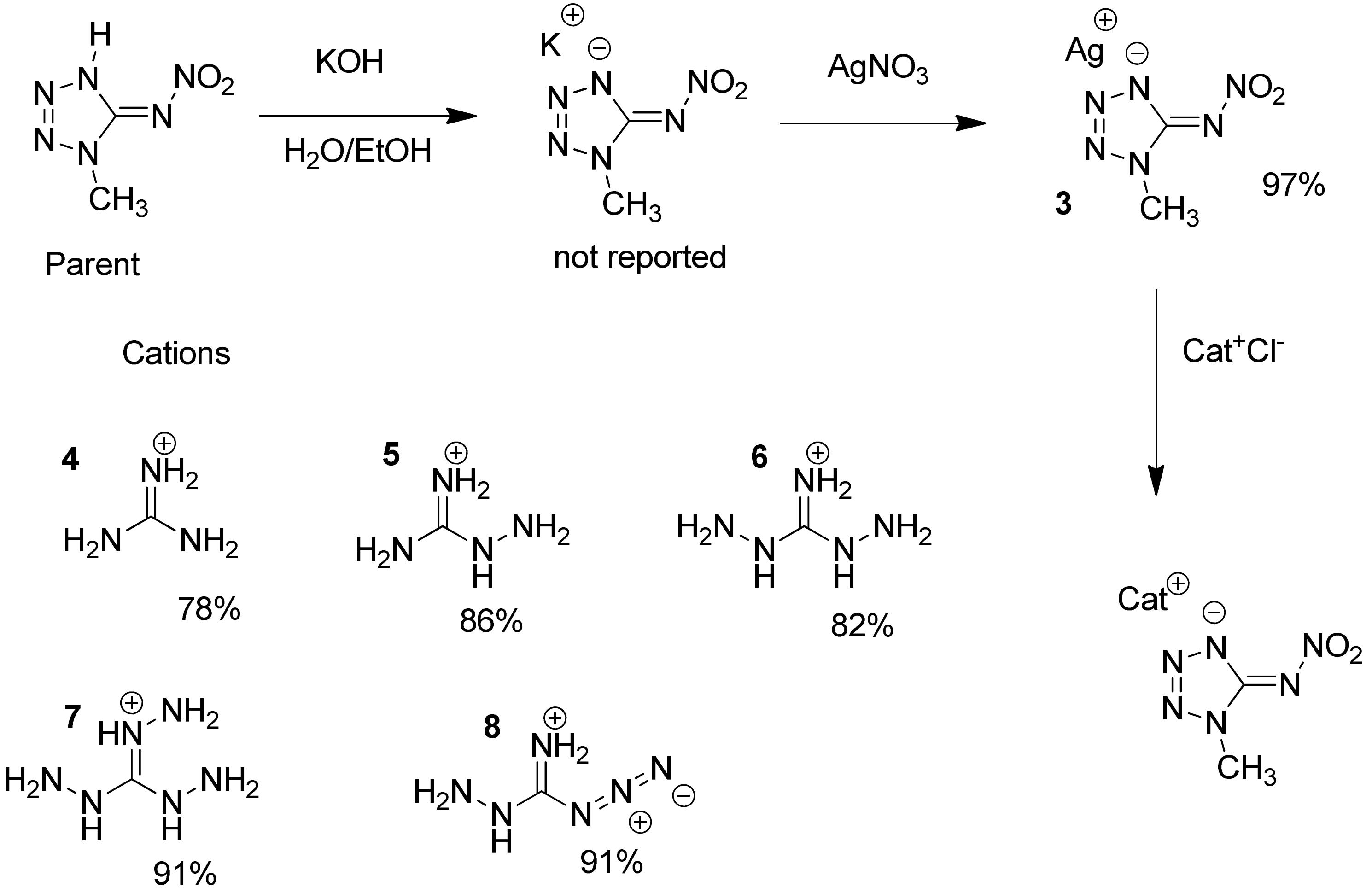
RDX

Klapotke, T. M.; Stierstorfer, J. *Helvetica Chimica Acta* **2007**, *90*, 2132.

The Production of Energetic Salts as an Optimization Strategy

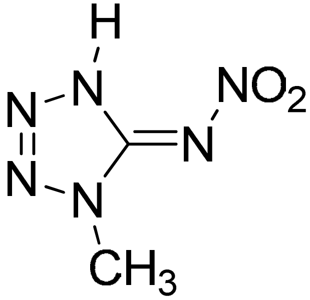
- Salts of guanidine, hydrazine and amine bases can easily be produced, allowing many materials to be produced from one parent.
- Ionic attractions said to improve density, stability
- Extensively utilized in recent literature not just with tetrazole, but with tetrazine, triazole and other heterocycles

Energetic Salts are Produced in an Optimization Attempt



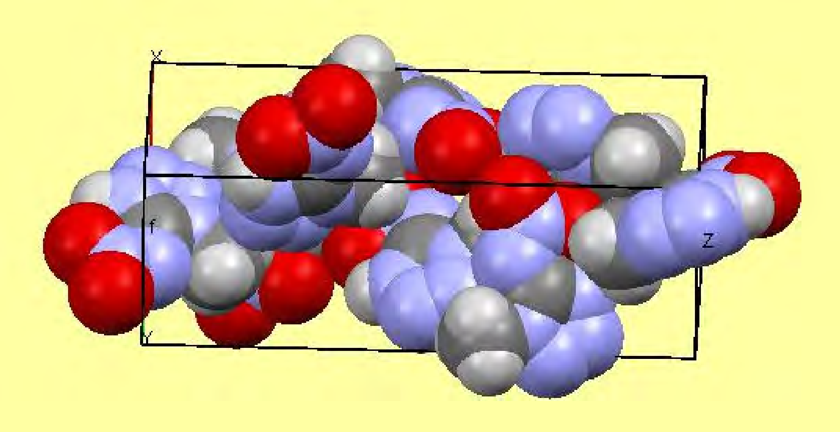
Klapotke, T. M.; Stierstorfer, J.; Wallek, A. U. *Chem. Mater.* **2008,** *13*, 4519.

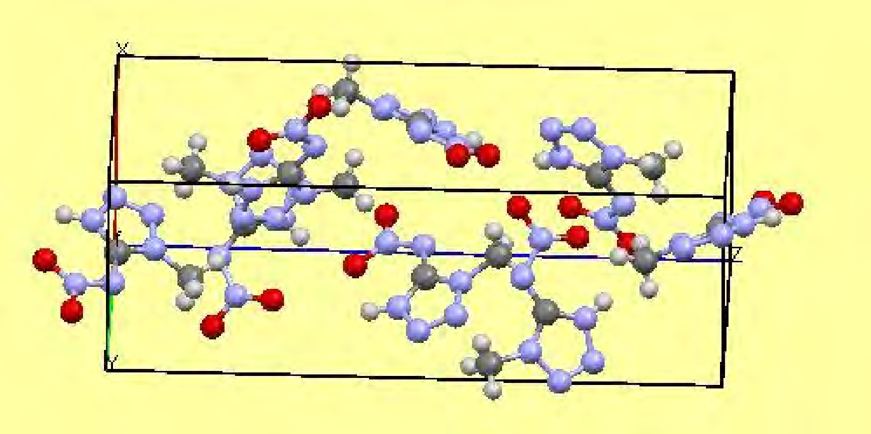
Density and Crystal Structure: Packing in 1-methylnitroiminotetrazole



Density = 1.76 g/cm^3

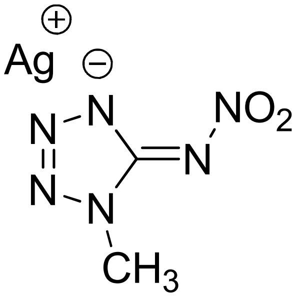
- Relatively high density despite low packing symmetry
- No noticeable gaps in lattice
- High density is important for performance





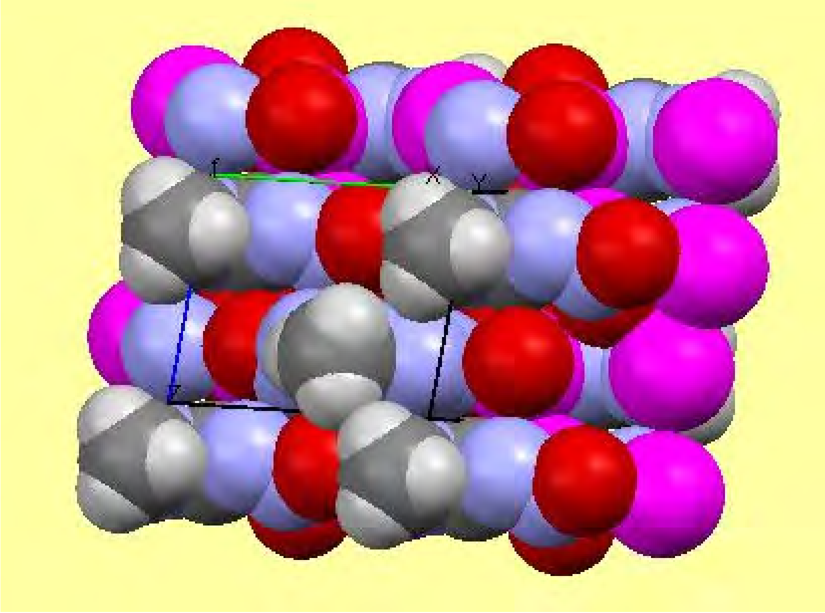
Klapotke, T. M.; Stierstorfer, J. *Helvetica Chimica Acta* **2007**, *90*, 2132.

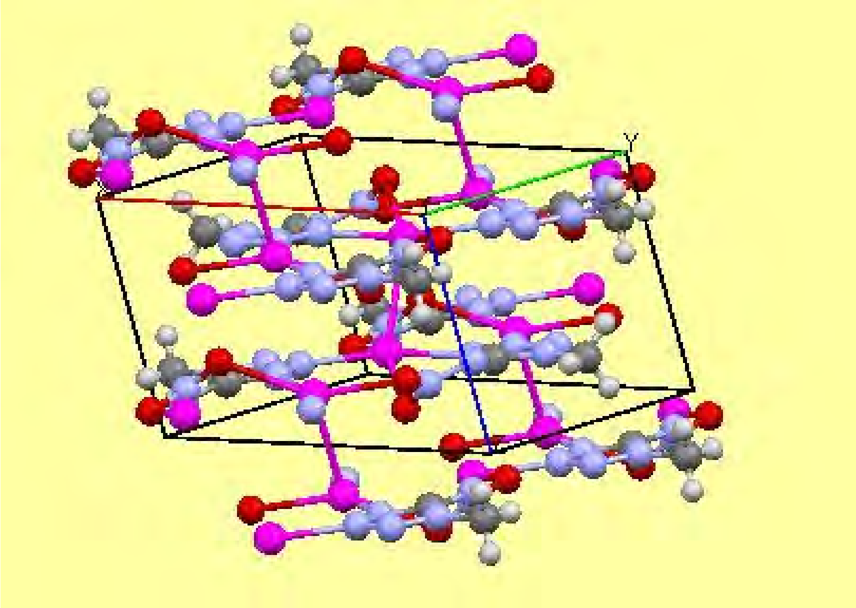
Density and Crystal Structure: Packing in Silver Salt



Density = 2.95 g/cm^3

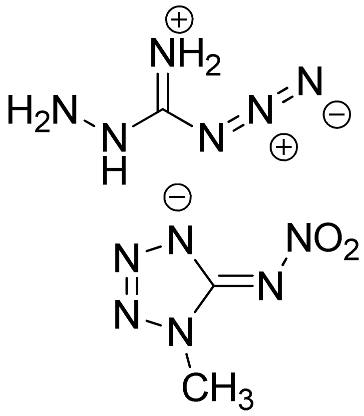
- Highly symmetrical packing mode leads to high density
- Silver salt also has very high impact stability (>50J)
- Density adjusted for to remove silver 2.6 - 2.7 g/cm^3





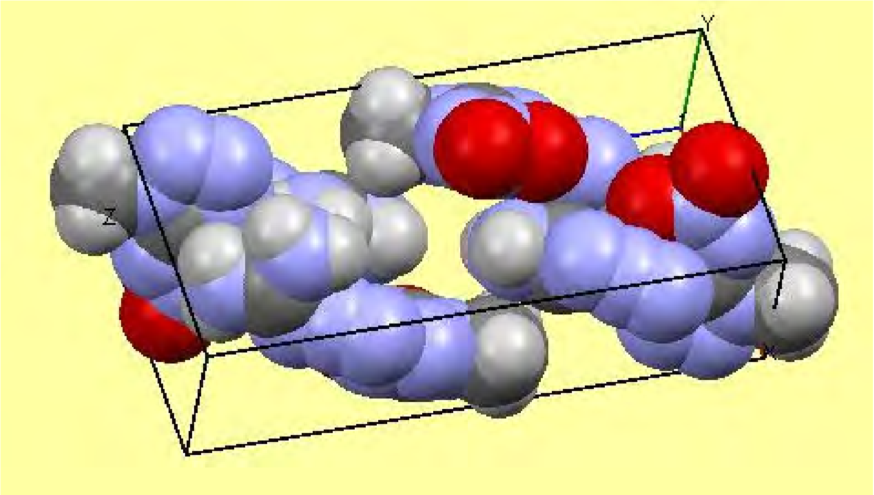
Klapotke, T. M.; Stierstorfer, J.; Wallek, A. U. *Chem. Mater.* **2008,** *13*, 4519.

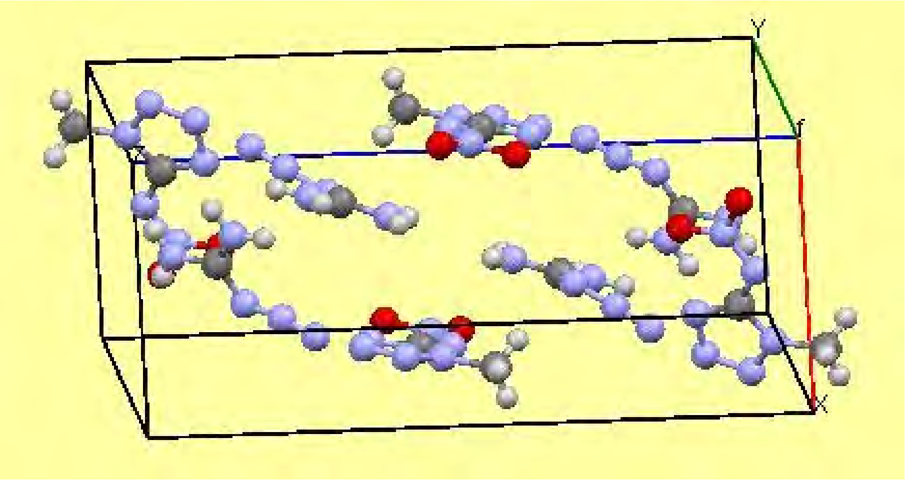
Density and Crystal Structure: Packing With Azidoformidinium Counter Ion



Density = 1.61 g/cm^3

- Ionic interactions and actually lead to poor packing due to low symmetry of molecules
- Gaps in the lattice

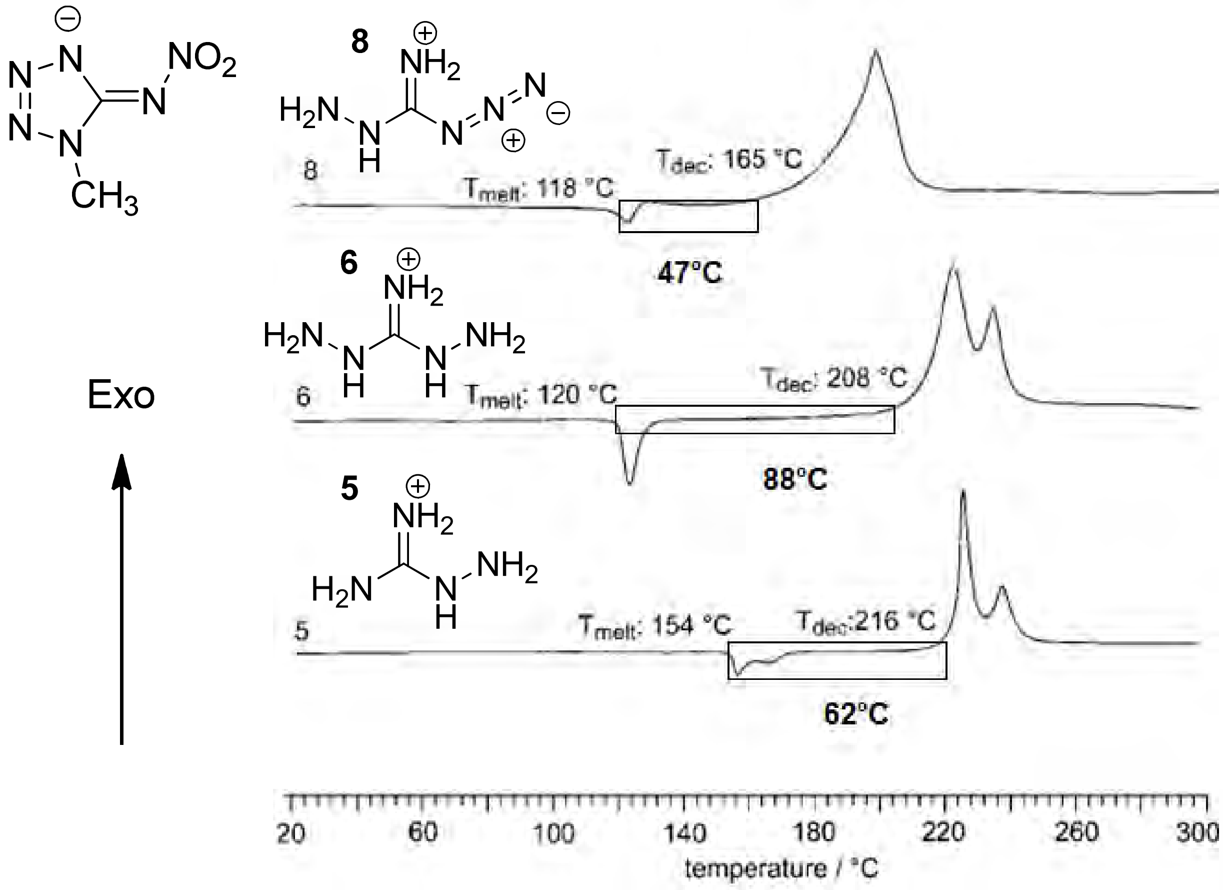




Klapotke, T. M.; Stierstorfer, J.; Wallek, A. U. *Chem. Mater.* **2008,** *13*, 4519.

Nitroiminotetrazolate Salts Have a Stable Liquid Phase

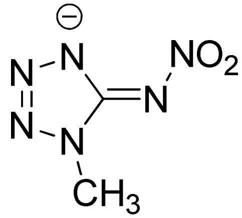
- Enhancement in thermal stability was noted
- Molten material was stable within a significant window
- Desirable for potential melt-casting applications



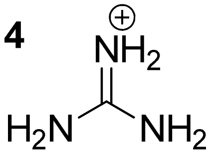
Klapotke, T. M.; Stierstorfer, J.; Wallek, A. U. *Chem. Mater.* **2008,** *13*, 4519.

Guanidinium Salts Trade Power for Stability

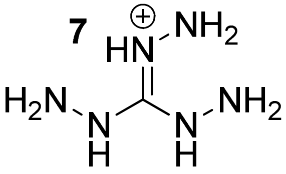
	Impact Senstivity (J)	**ρ (g/cm^3)**	**ΔH_f (kcal/mol)**	**P_d (Gpa)**	**V_d (m/s)**
4	40	1.55	37.1	20.6	7747
7	6	1.57	136.0	27.3	8770
Parent	12.5	1.76	62.1	29.5	8433
RDX	7.5	1.80	16.7	34.1	8906

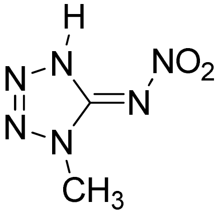


4

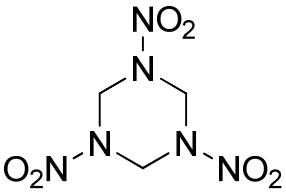


7





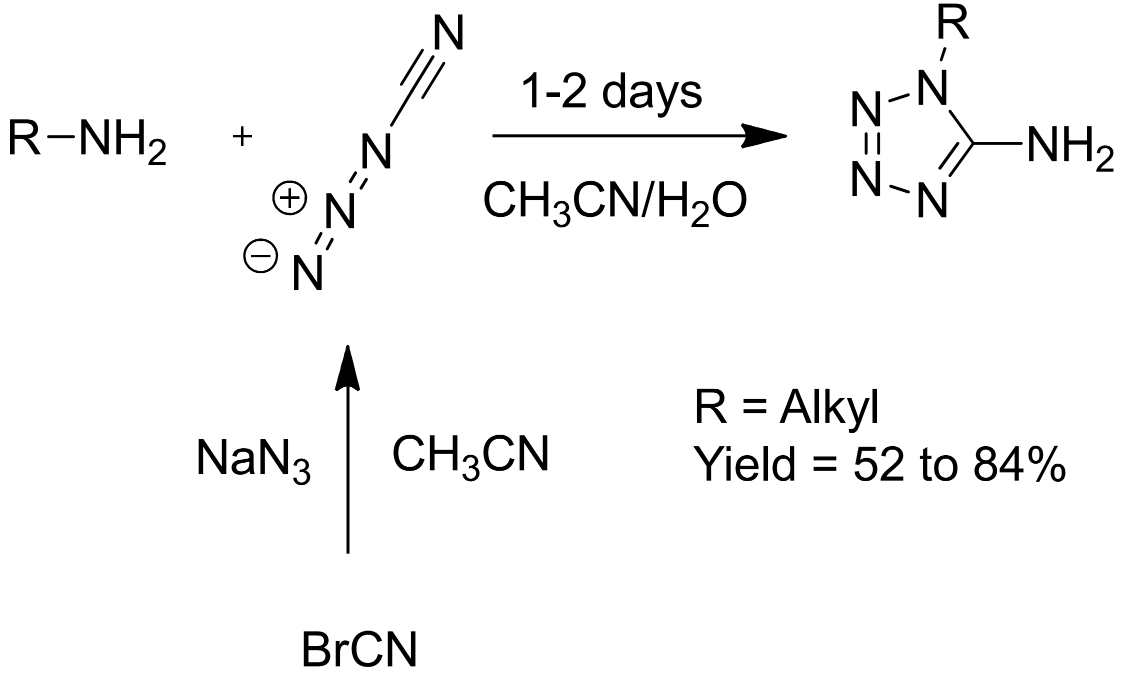
Parent



RDX

Klapotke, T. M.; Stierstorfer, J. *Helvetica Chimica Acta* **2007**, *90*, 2132.
Klapotke, T. M.; Stierstorfer, J.; Wallek, A. U. *Chem. Mater.* **2008,** *13*, 4519.

A Recently Developed Synthetic Method Provides Access to Bis-nitroiminotetrazoles



R = Alkyl
Yield = 52 to 84%

- Provides selective access to 1 – functionalized 5 – aminotetrazoles
- NCN_3 is generated in dry CH_3CN
- Transferred to solution of amine in wet CH_3CN

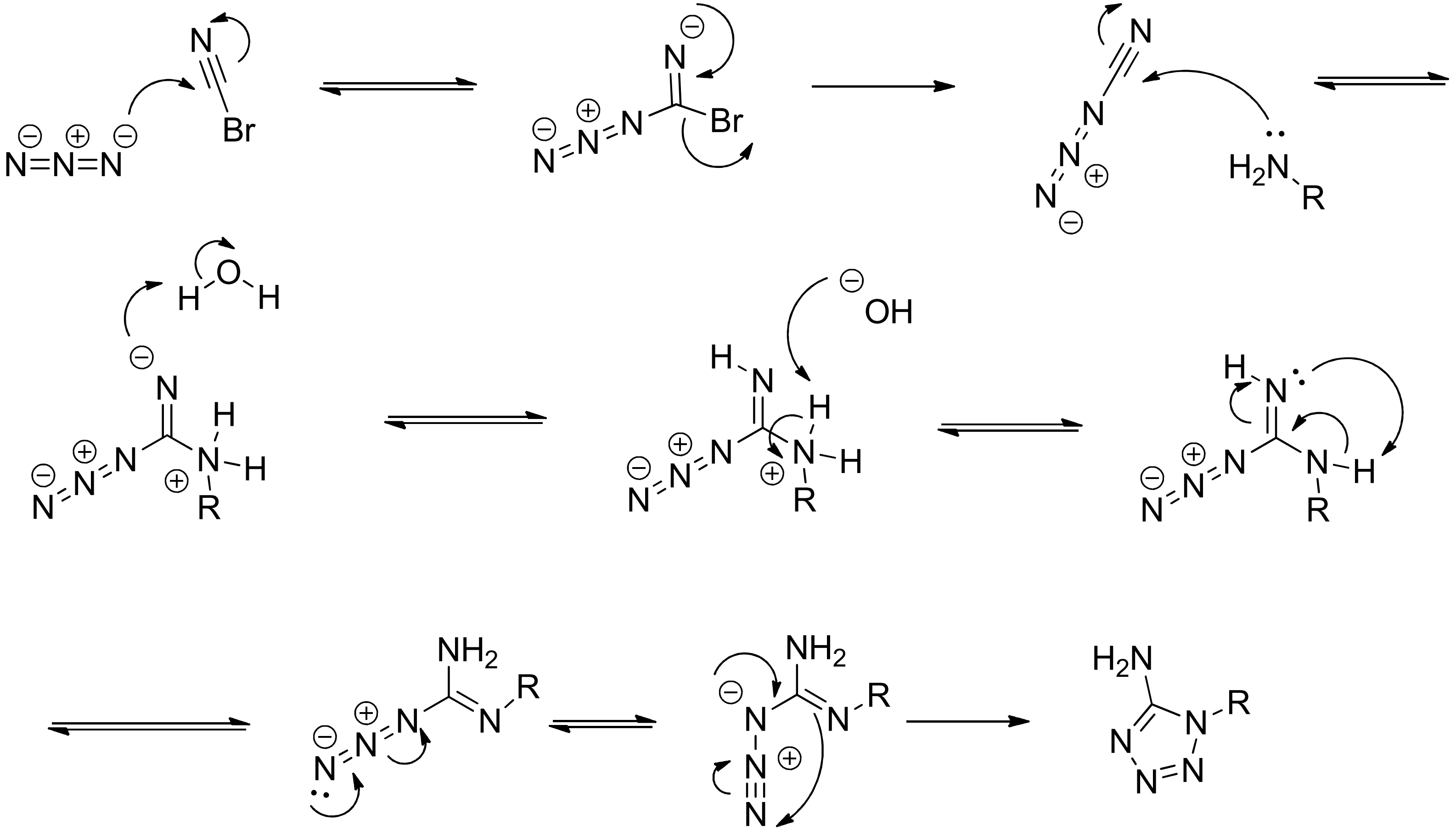
Joo, Y.; Shreeve, J. M. *Org. Lett.* **2008**, *10*, 4665.

How to Handle Cyanogen Azide

- Avoid storing in cold – may oil out and explode- use every drop you make
- Don't isolate it – it may explode
- Don't generate it in a new solvent – may oil out and explode
- When filtering NaBr from solution, do not allow filter cake to dry completely. Place filter cake in aqueous solution.
- Do not breath vapor – highly toxic

Marsh, F. D. *J. Org. Chem.* **1972,** *19,* 2996.
Joo, Y.; Shreeve. J. M. *Org. Lett.* **2008**, *10*, 4665.

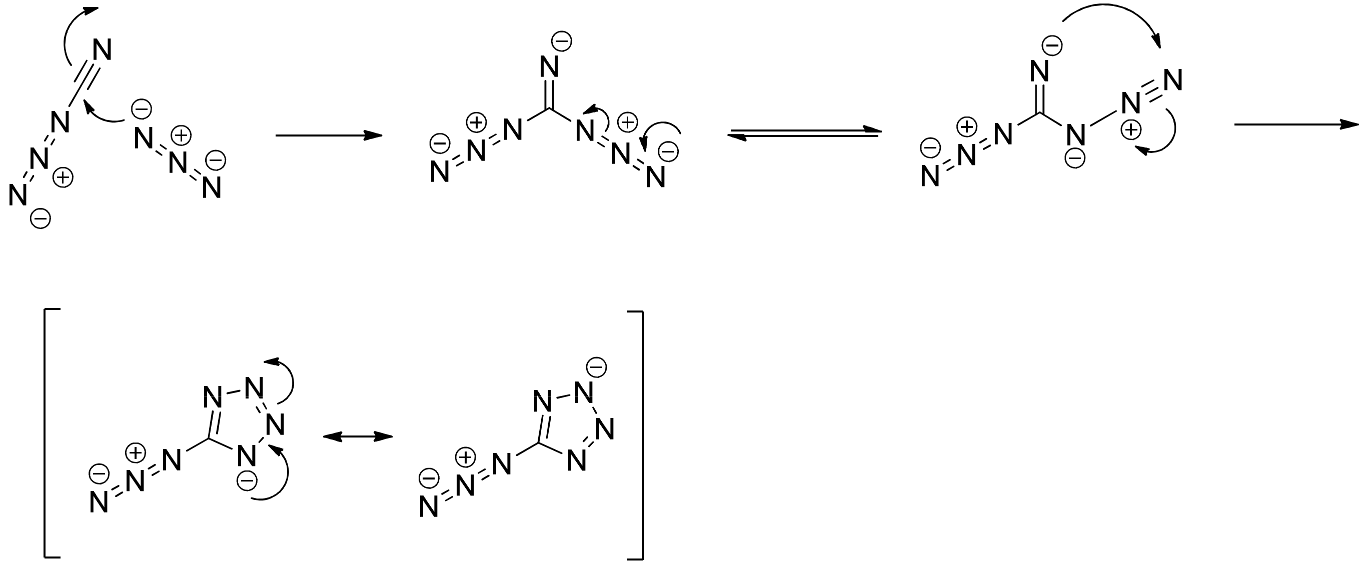
A Proposed Mechanism for the Reaction



Joo, Y.; Shreeve. J. M. *Org. Lett.* **2008**, *10*, 4665**.**

Himo, F.; Demko, Z. P.; Noodleman, L.; Sharpless, K. B. *J. Am. Chem. Soc.* **2003,** *125*, 9983.

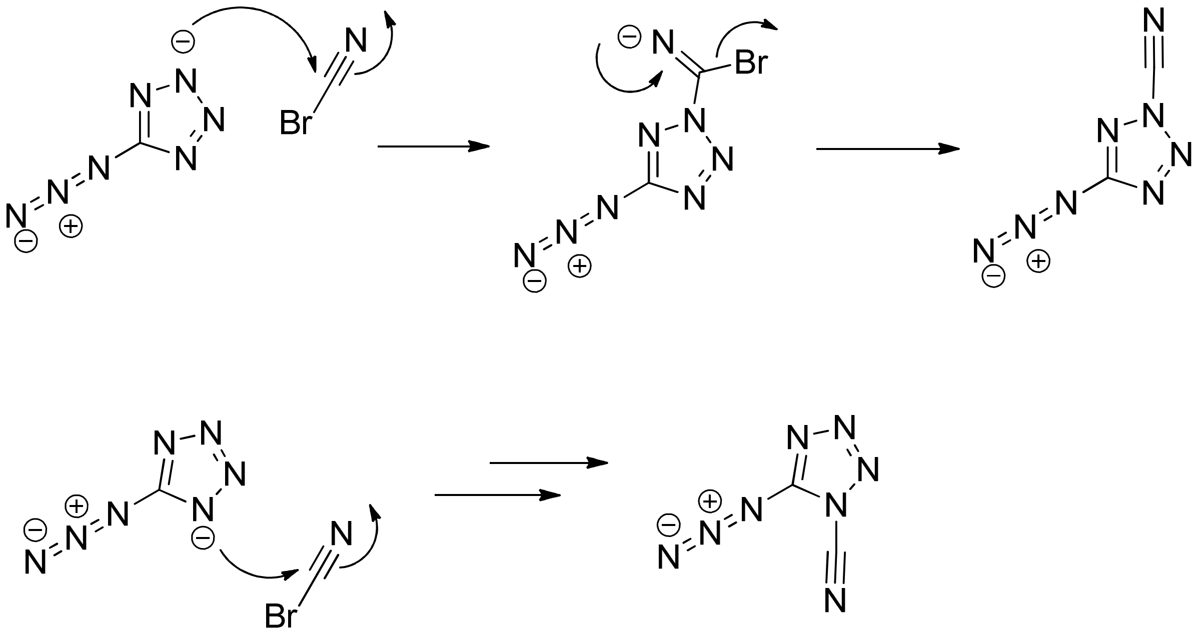
Cyanogen Azide Can Form Tetrazole Azides in Aqueous Conditions



- Sodium 5-azidotetrazolate is formed through condensation with sodium azide
- Klapotke utilized this reaction to produce tetrazole azide salts described earlier
- Shreeve and coworkers report sodium 5-azidotetrazolate as a side product of their method

Marsh, F. D. *J. Org. Chem.* **1972,** *37*, 2966.
Klapotke, T. M.; Steirstorfer, J. *J. Am Chem. Soc.* **2009,** *131*,1122.

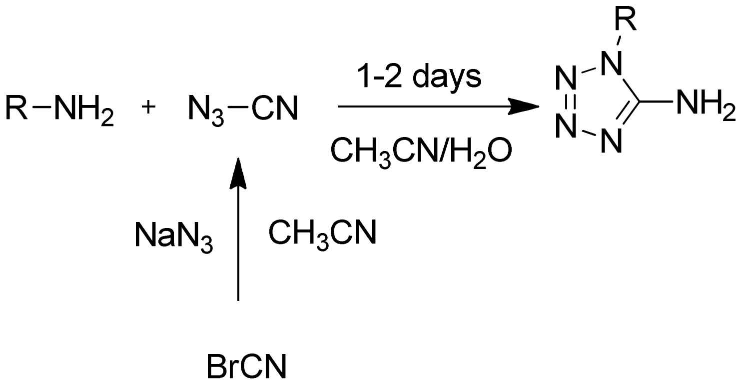
Tetrazole Azides can be Alkylated by Unreacted Cyanogen Bromide

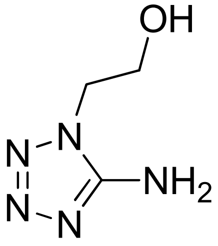


- These alkylation products are avoided by employing two equivalents of NaN_3 per equivalent CNBr
- Approach causes formation of sodium 5-azidotetrazolate in isolable amounts

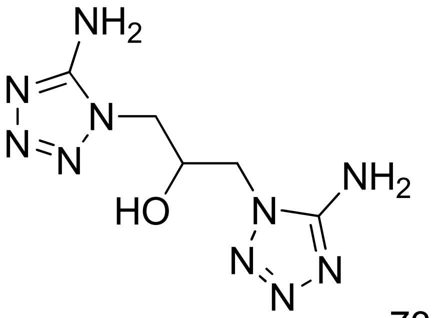
Marsh, F. D. *J. Org. Chem.* **1972,** *37*, 2966.

Various Substrates Were Reported





53%



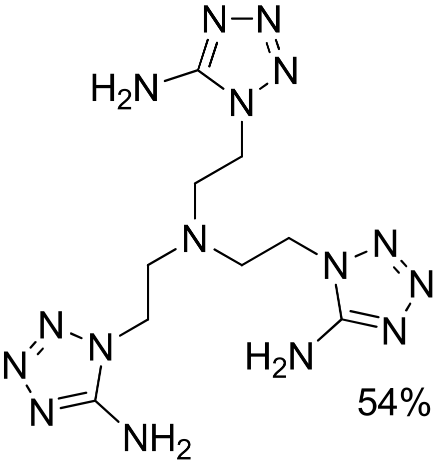
73%

2 equiv CN_4 for monoamines

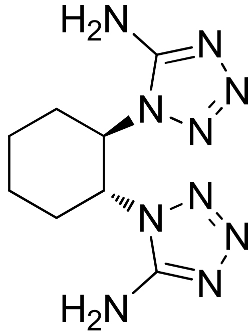
5 equiv for diamines

7 equiv for triamines

Di and triamines typically got lower yields.



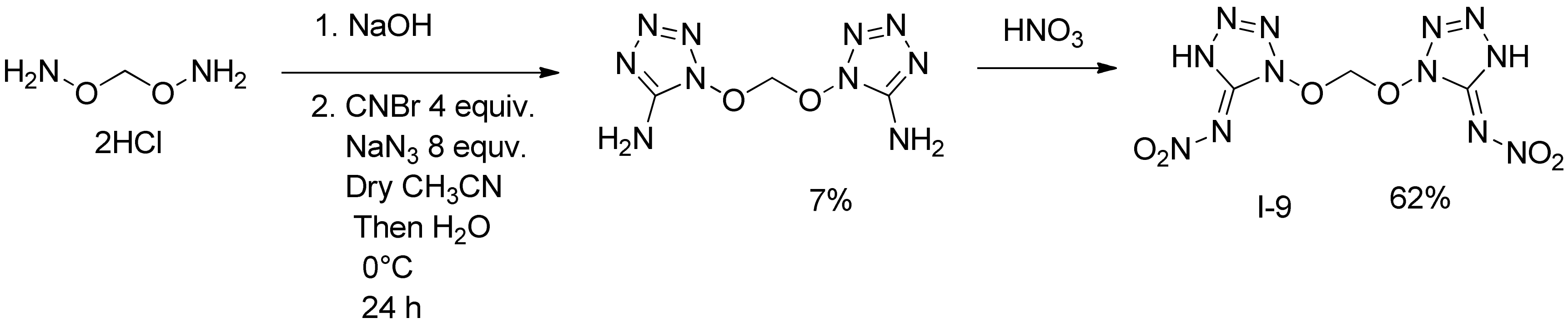
54%

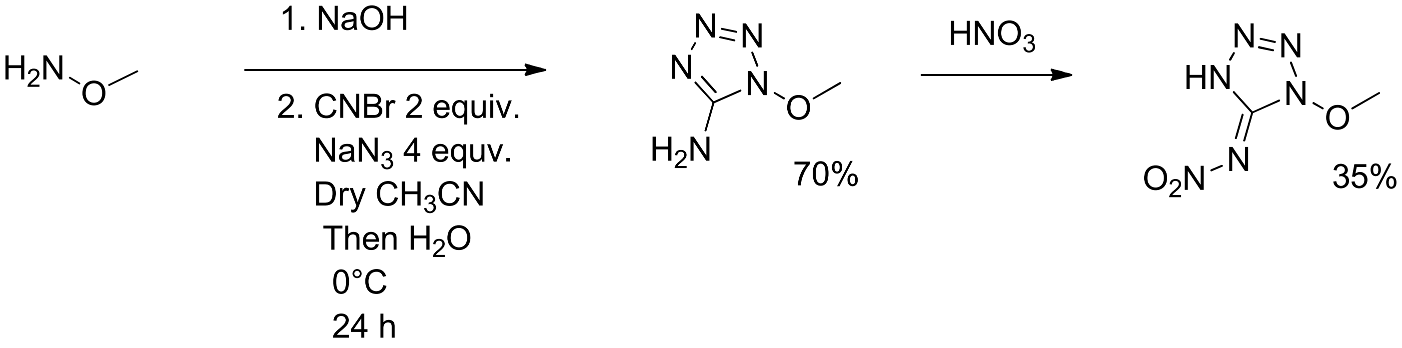


79%

Joo, Y.; Shreeve. J. M. *Org. Lett.* **2008**, *10*, 4665.

Synthesis of Oxynitroiminotetrazoles



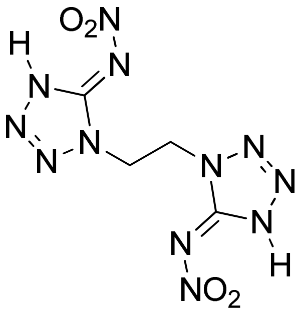


- Ring synthesis was a problem in bis compounds sterics were used to explain this

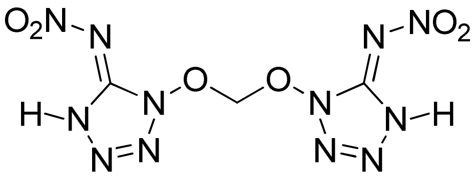
Joo, Y.; Shreeve, J. M. *Angew. Chem. Int. Ed.* **2010,** *49*, 7320.

I-8 and I-9 are as Powerful as HMX

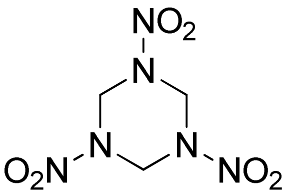
	I_s (J)	**ρ (g/cm^2)**	**T_d (°C)**	**OB%**	**P_d (Gpa)**	**V_d (m/s)**
I-8	10	1.86	194	-39	38.2	9329
I-9	1	1.90	157	-11	46.7	9867
RDX	7.5	1.80	230	-22	34.1	8906
HMX	7.5	1.91	287	-22	39.6	9320



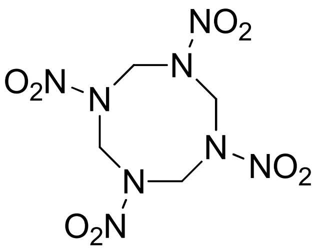
I-8



I-9



RDX

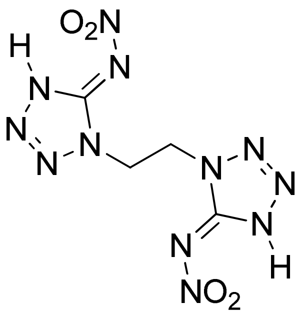


HMX

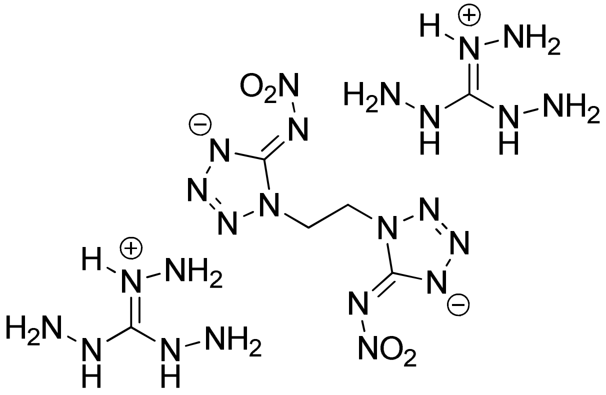
Joo, Y.; Shreeve, J. M. *Angew. Chem. Int. Ed.* **2010,** *49*, 7320.

Energetic Salts Increase the Stability to Heat and Impact

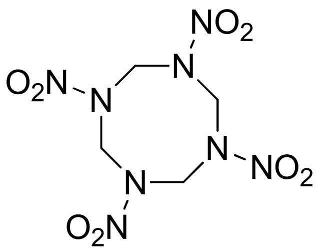
	I_s (J)	ρ (g/cm^2)	T_d (°C)	T_m (°C)	OB%	P_d (GPa)	V_d (m/s)
I-8	10	1.86	194	-	-39	38.2	9329
15	>40	1.604	195	132	-61	28.64	8860
HMX	7.5	1.91	287	-	-22	39.6	9320



I-8



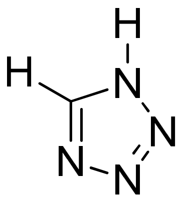
14



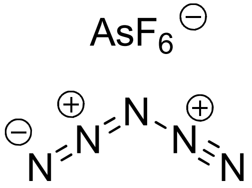
HMX

Joo, Y.; Shreeve, J. M. *J. Am. Chem. Soc.* **2010,** *132*, 15081.

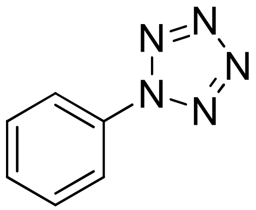
Why High Nitrogen Compounds and not All Nitrogen Compounds?



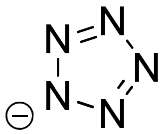
mp = 157 - 158°C



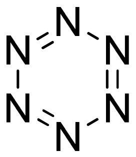
Marginally
Stable at 22°C



Decomposes violently
above - 20°C



Detected in
Tandem MS
Experiment



Existence
Ambiguous

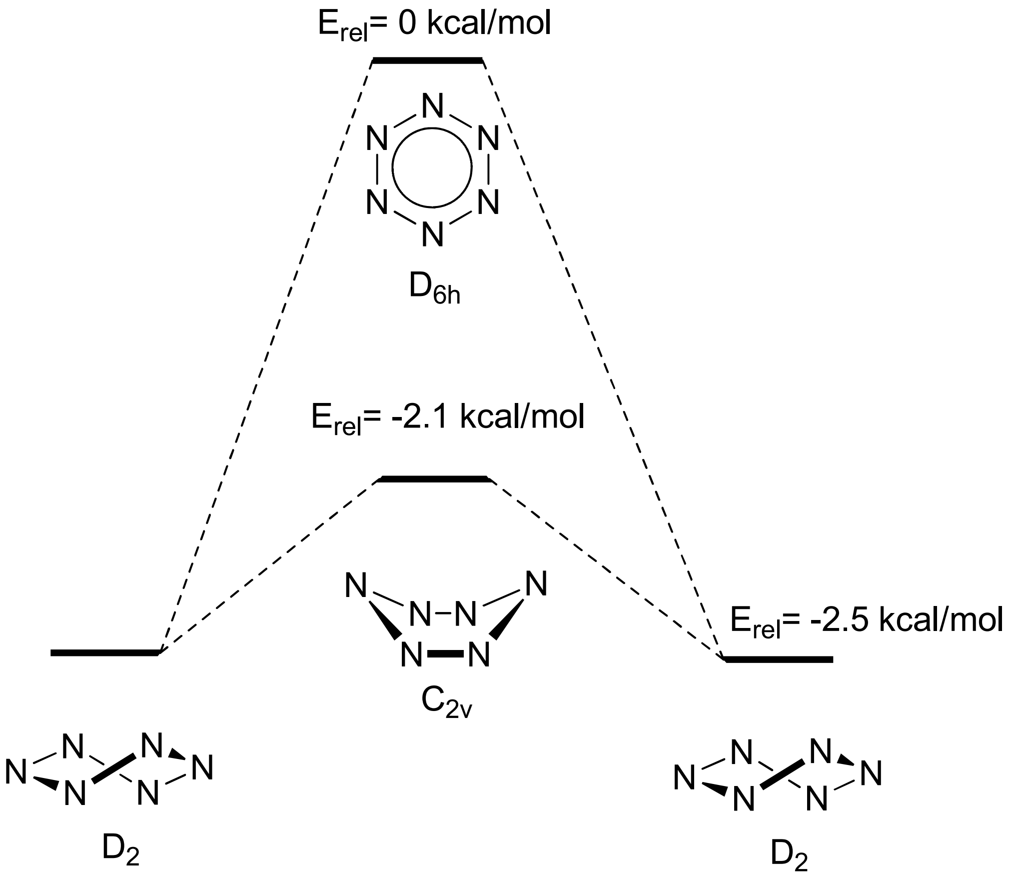
- General lack of stability in nitrogen rich materials can be easily rationalized by invoking thermodynamics

N−N	N=N	N≡N
38.2 kcal/mol	99.9 kcal/mol	228. kcal/mol

- Actual trends in stability are complicated and sometimes surprising
- As a general rule nitrogen compounds are not “stable” but may be persistent in the kinetic sense

Christie, K.O.; Wilson, W. W.; Sheehy, J.A.; Boatz, J.A. *Angew. Chem. Int. Ed.* **1999,** *38*, 2004.
Vij, A.; Pavlovich, J.G.; Wilson, W. W.; Vij, V.; Christie, K.O. *Angew Chem Int. Ed.* **2002,** *41, 3051.*
Carlqvist, P.; Ostmark, H.; Brinck, T. *J. Phys. Chem. A* **2004,** *108, 7463.*

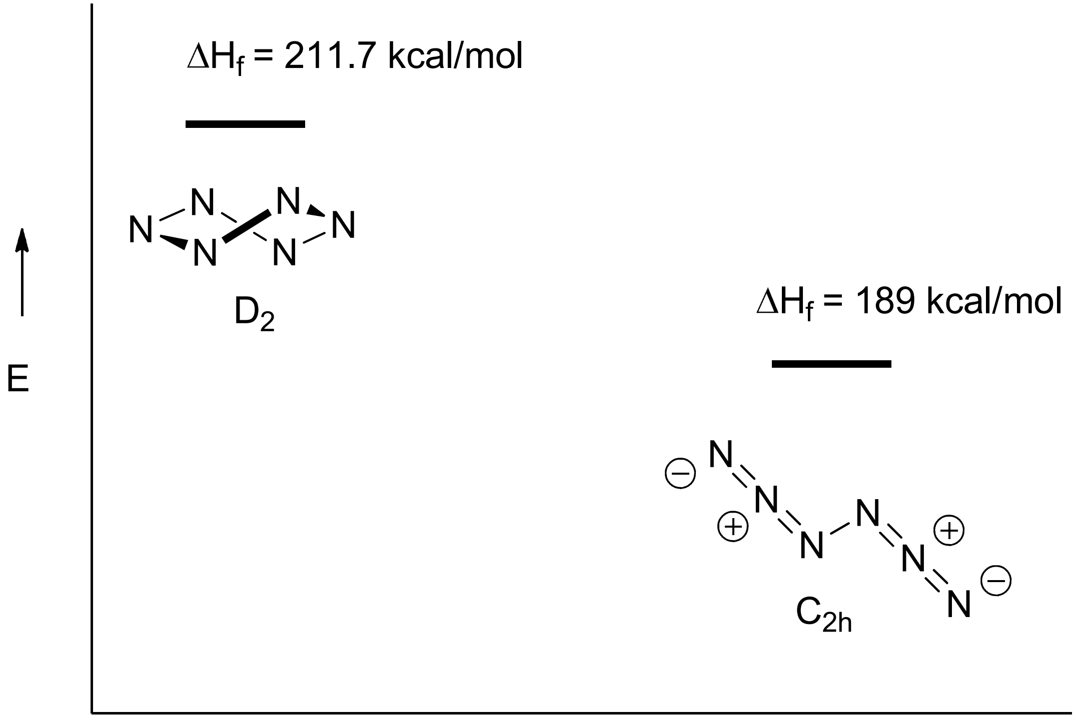
Theoretical Methods Disagree on the Conformational Energies of Cyclo N_6



- Initial calculations done at HF with modest basis sets showed D_{6h} isomer as a minimum
- MP2/6-31G(d) was used to establish the picture shown (energies given at this level)
- CCSD(T) /aug-cc-pVDZ does not show any of the neutral cyclo N_6 species to be bound molecules.
- CCSD(T)/cc-pVTZ argues for picture shown
- Better correlation = less stable species

Noyman, M.; Zilberg, S.; Haas, Y. *J. Phys. Chem. A* **2009,** *113,* 7376.
Tobita, M.; Bartlett, R.J. *J. Phys. Chem. A*. **2001,** *105,* 4105.
Glukovtsev, M.; von Rague Schleyer, P. *Chem. Phys. Lett.* **1992,** *198*, 547.

On the Failure of Aromaticity to Stabilize Neutral Cyclo N_6

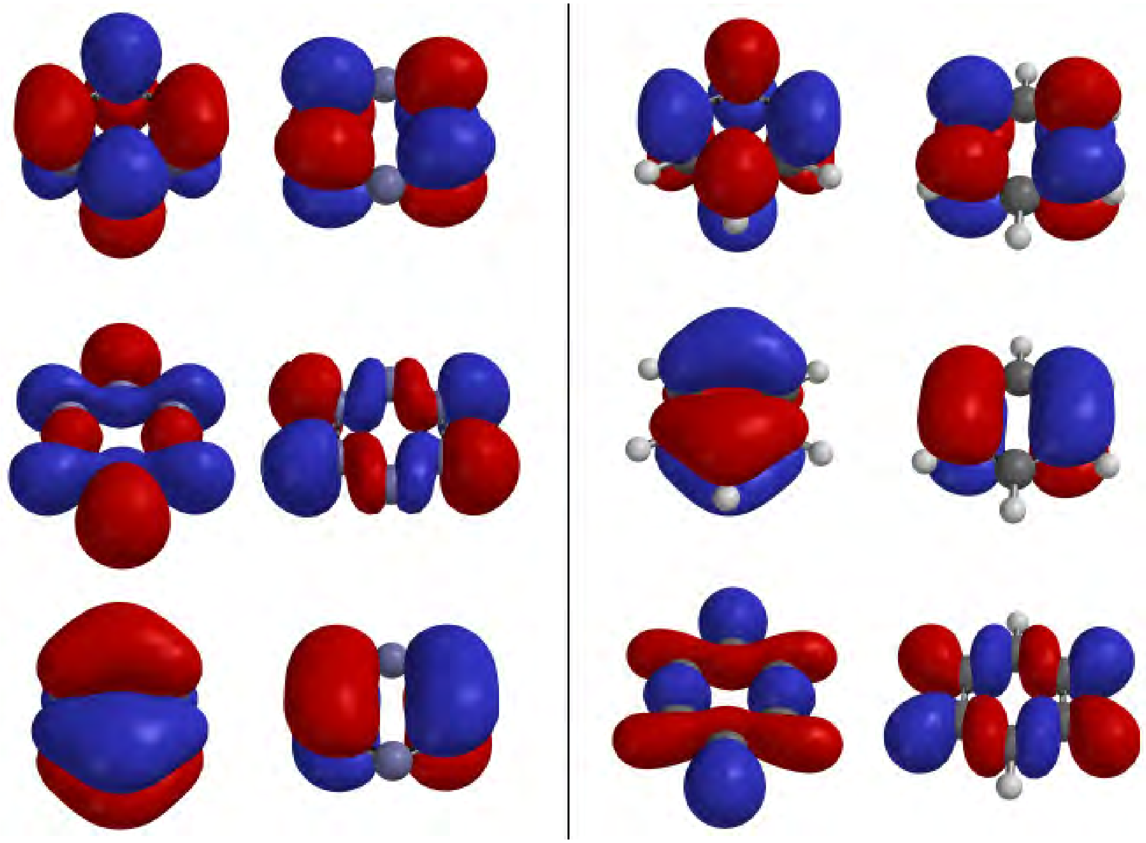


- Benzene gains roughly 44 kcal/mol over cyclohexatriene
- N_6 is more stable as a diazide
- Despite being isoelectronic to benzene, N_6 is not stabilized by aromaticity

- Energies calculated at the CCSD(T)/cc-pVTZ level of theory

Tobita, M.; Bartlett, R.J. *J. Phys. Chem. A*. **2001,** *105,* 4105.

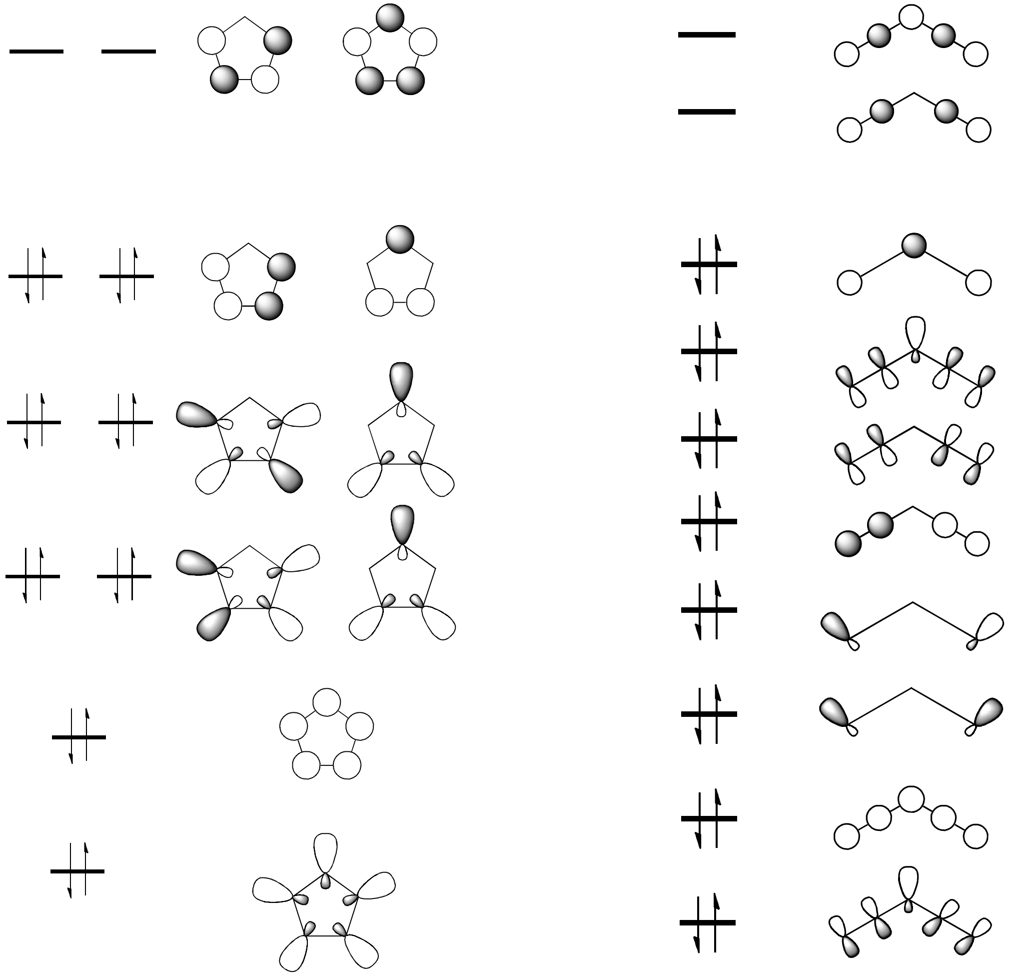
Frontier Molecular Orbitals in Benzene and Cyclo N_6



- Sigma orbitals in N_6 have less bonding character than in benzene and lie at higher energy
- Degenerate sigma HOMO in N_6 leads to second order Jahn – Teller distortion which causes D_2 symmetric minimum
- calculated at the HF/cc-pVDZ level

Noyman, M.; Zilberg, S.; Haas, Y. *J. Phys. Chem. A* **2009,** *113,* 7376.

Orbitals in Relatively More Stable N_5 Structures



- Cyclo N_5^- has 6 π electrons, but one less lone pair than N_6
- N_5^+ has linear arms which act to maximize π electron contribution at the expense of σ
- Neither has σ orbital at HOMO level
- Model: N structures that minimize σ electron contribution to frontier orbitals are more stable

Noyman, M.; Zilberg, S.; Haas, Y. *J. Phys. Chem. A* **2009,** *113,* 7376.

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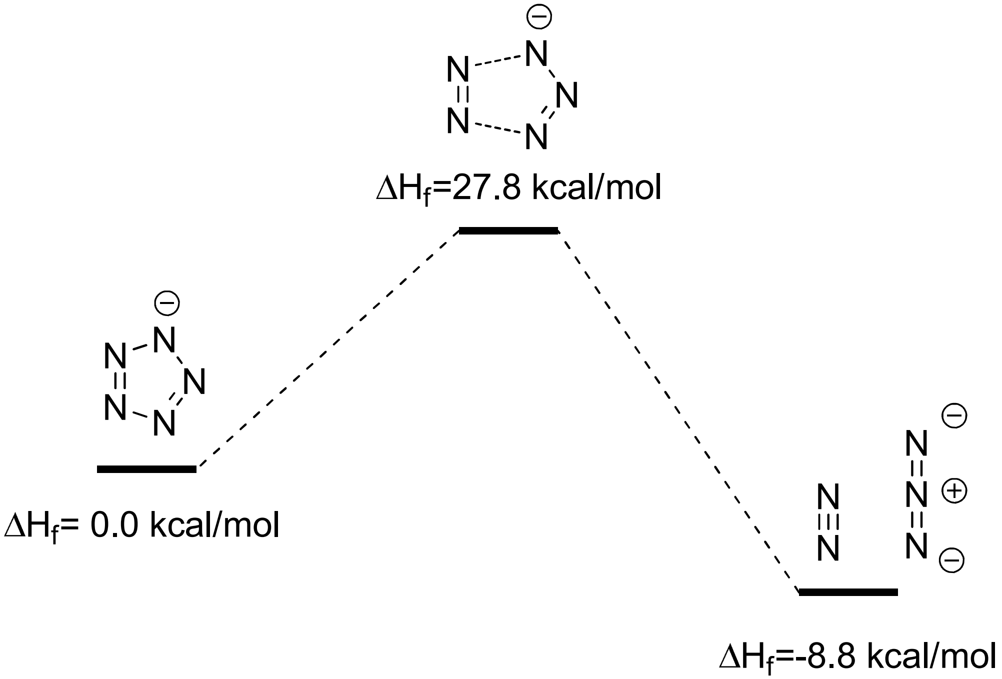
Using Calculated Unimolecular Decomposition Reactions to Assess stability

- Calculated energy barriers for unimolecular reactions provide insight into the favorability of various pathways to simpler products
- Strongly favorable pathways are likely to retain importance even at high P
- May be unrealistic due to the presence of bimolecular pathways with lower barriers

Unimolecular Decomposition of Pentazolate Anion

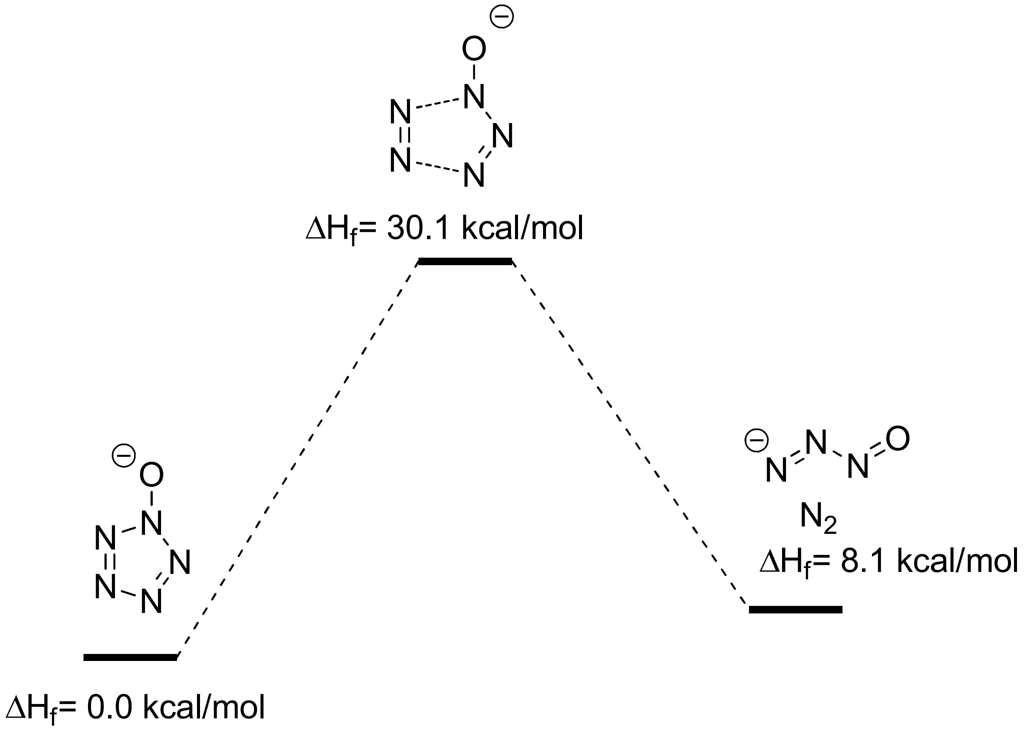


Calculated in the gas phase at CBS – QB3 Level of theory

- Pentazole can undergo Retro [3+2], Process is exothermic
- Reaction is well studied; current results used for consistency and level of theory.

Rahm, M.; Brinck, T. *Chem. Eur. J.* **2010,** *16,* 6590.

Effect of an Added Oxygen: Nitrogen Emission Pathways

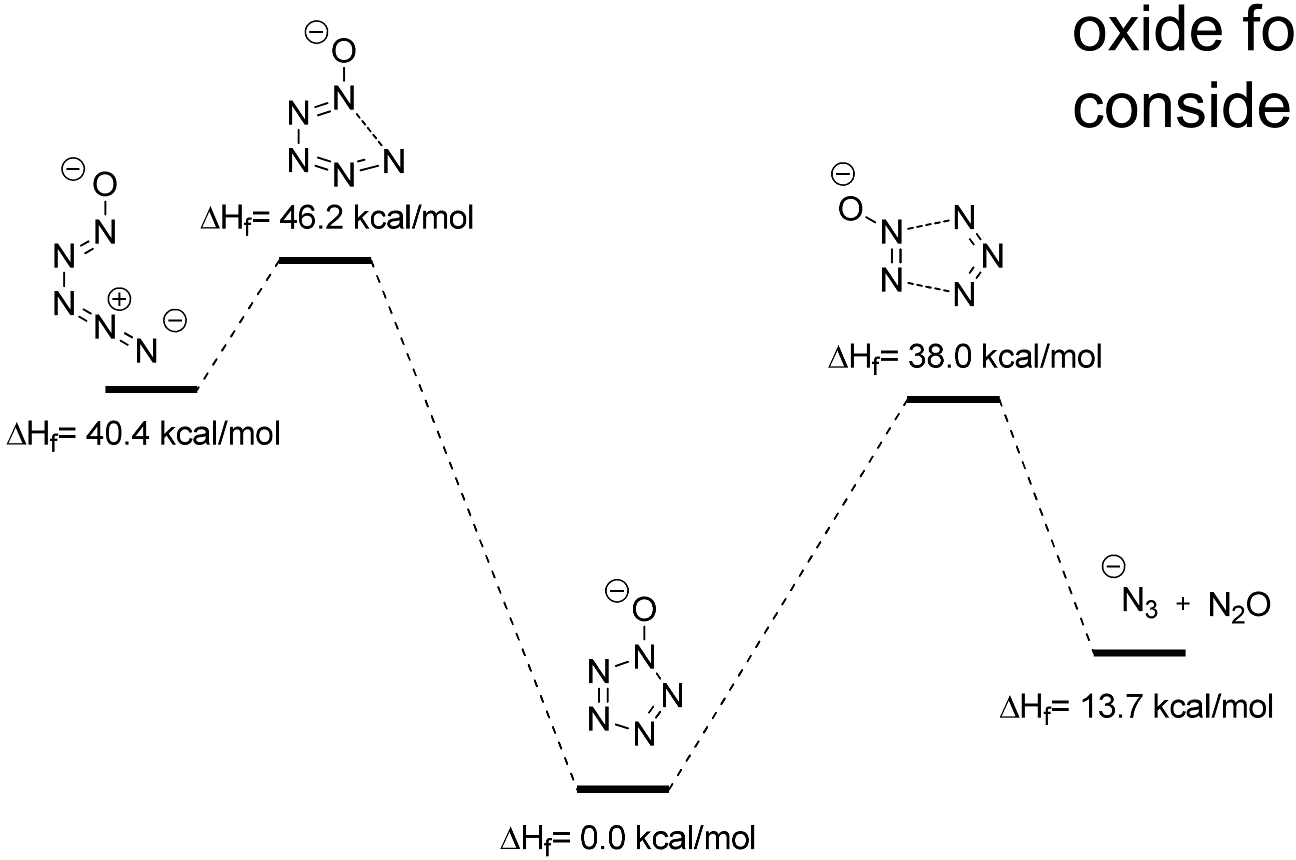


- Relative to N_5^- lowest kinetic barrier to nitrogen emission is 2.3 kcal/mol higher
- Subsequent decomposition of N_3O is exothermic by 3.3 kcal/mol

Rahm, M.; Brinck, T. *Chem. Eur. J.* **2010,** *16,* 6590.

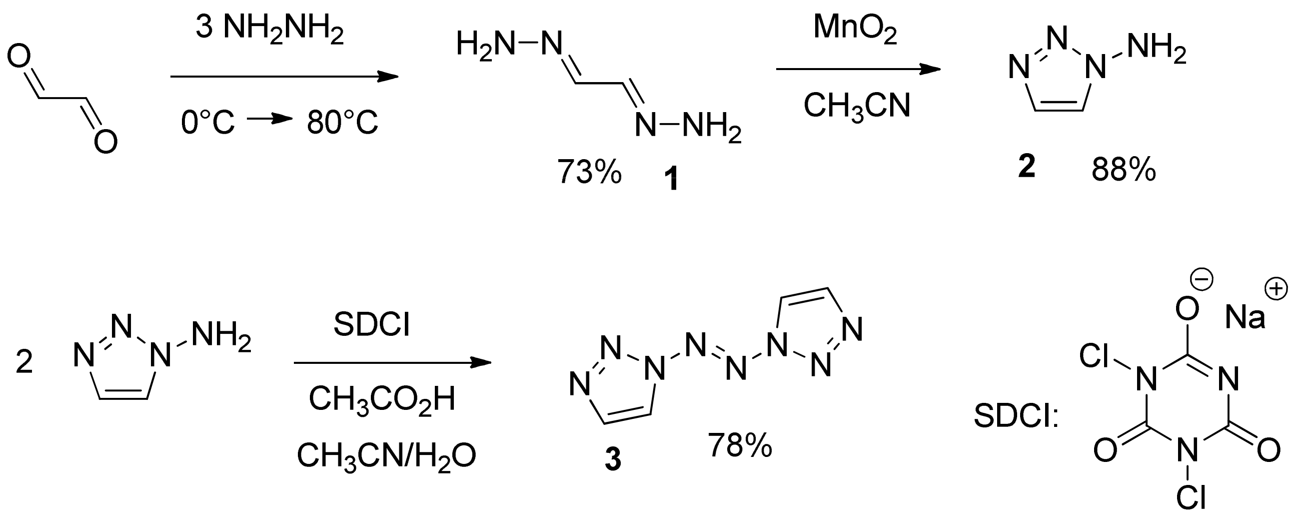
Other Pathways to Decomposition in N_5O^-

- Ring breaking and Nitrous oxide formation are lesser considerations for stability.



Rahm, M.; Brinck, T. *Chem. Eur. J.* **2010,** *16,* 6590.

Long Nitrogen Arrays Can be Stabilized With Carbon Containing Aromatic Systems



- $C_4H_4N_8$ Reported in Good Yield From 3 Step Procedure
- 3 melts and decomposes at 193°C
- Extensive characterization not done

Li, Y. Qi, C.; Li, S.; Zhang, H.J.; Sun, C.; Yu, Y.; Pang, S. *J. Am. Chem. Soc.* **2010,** *132,* 12172.
Kaplan, G.; Drake, G.; Tollison, K.; Hall, L.; Hawkins, T. *J. Heterocyclic Chem.* **2005,** *42,* 19.
Galluci, R. *J. Chem. Eng. Data* **1982,** *27,* 217.

Conclusions

- A variety of stabilities and detonation properties can be produced using nitrogen rich materials.
- Tetrazole have already outperformed mainstream commercial explosives
- Energetic salts are a mixed bag and can improve or decrease the performance of a compound
- Recent insights in the stability of all nitrogen ions may lead to powerful new materials

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- Family

- Friends

Questions?