Insensitive Munitions & Energetic Materials Technology Symposium
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Emerging Trends in Energetic Materials

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Beauty in Science

The scientist studies science not because it is useful but because he derives pleasure from it, and he derives pleasure from it because it is beautiful.

H. Poincaré

Disclaimer

- Not all interesting trends or molecules will be discussed.
- I apologize if I left out your favorite compound.

Main Themes in Energetics

- High-nitrogen materials
  - Air bags
  - Gun propellants
- Insensitive high explosives
  - Target: Haz C/D 1.6 – all energetic materials must be EIDS (Haz C/D 1.5)
- Green energetics
  - Lead-free propellants and pyrotechnics
  - Replacement for environmentally suspect ingredients, especially AP
- Nanotechnology
  - Nonideal explosives
  - Pyrotechnics
- Modeling & simulation
  - Guide the synthesis of new materials
  - Predict behavior of materials early in life cycle
- New Forms of Old Ingredients
- Enhanced Blast Explosives
- Reduced life cycle cost

Note that there is little emphasis on enhanced energy per se.

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Emerging Trends

- Melt-cast alternatives to TNT
  - Success already with DNAN
  - Ionic liquids being evaluated
- Coatings on particles
  - To reduce sensitivity
  - To increase intimacy of admixture (reactive materials)
  - To reduce parasitic weight (nano-Al, other metals)
- Turning inert into energetic
  - Structural energetics
- Ultra-high energy compounds
  - All-nitrogen species

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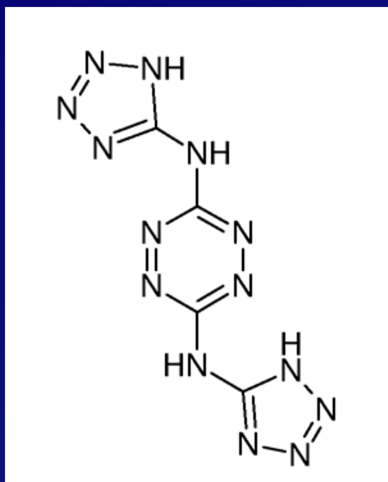
Performance

- For a selected application, a new ingredient must provide comparable or better performance than current ingredients
  - Performance depends on the application.
    - Greater energy content
    - Higher (more positive/less negative) ΔH_f
    - Higher density
    - Higher oxygen balance
  - Corollary: If there is no performance benefit, there must be some other reason to adopt the new material
    - Lower sensitivity
    - Lower cost
    - Better processability
    - Greater reliability
    - Thermal stability

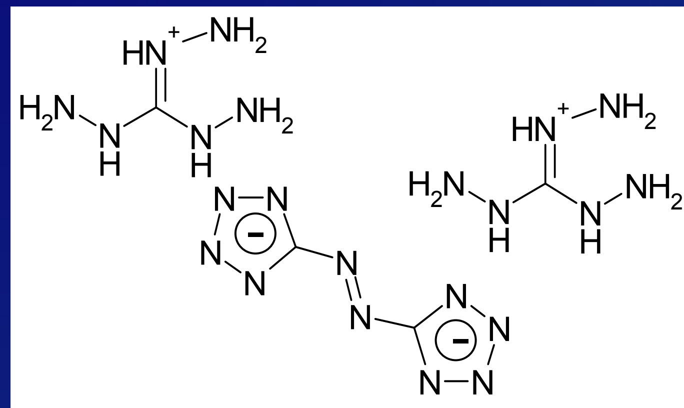
High Performance Ingredients

- Heterocycles
  - Not super-high nitrogen (no oxygen)
  - High density
  - High heat of formation combined with good oxygen balance
- All-N species
  - Calculated to be very energetic
  - Calculated to have high density
  - Obtained only in miniscule quantities to date

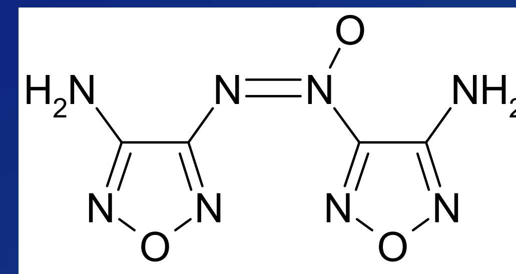
High-nitrogen Structures



BTATz



TAGzT



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Why High-nitrogen?

- Really high heats of formation

Compound	Formula	ΔH_f (kJ/kg)	ρ (g/cm^3)
RDX	$C_3H_6N_6O_6$	+318	1.80
DAAF	$C_4H_4N_8O_3$	+2255	1.7
BTATz	$C_4H_4N_{14}$	+3560	1.76
TAGzT	$C_4H_{14}N_{22}$	+2908	1.60

- But what is the consequence of this?
  - If N replaces C, density is generally higher (less H)
  - Products have lots of N_2 ($\Delta H_f = 0$)
  - Fewer products with large, negative ΔH_f
- Not ideal for applications, but can be very useful in propellants

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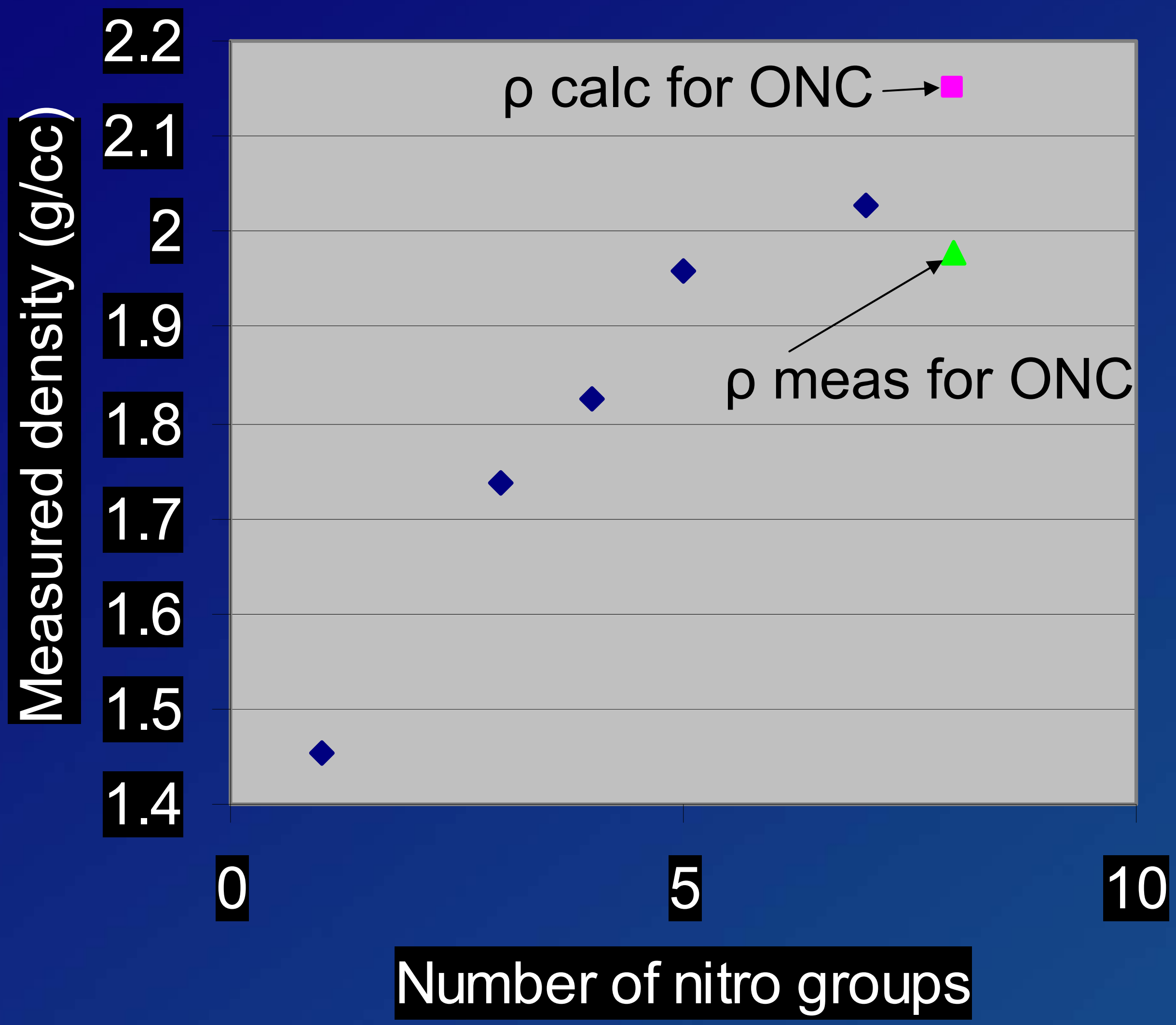
Octanitrocubane

- Proposed as a target molecule in the 1980s
- Advertised as "potential explosive of great power."*
- Compound has a high oxygen balance: 0.0 → balanced to CO_2
- Predicted density was high: 2.1 to 2.2, based on "latest and most sophisticated calculation" and extrapolation of densities of lower nitrocubanes*
- Calculated ΔH_f for ONC in solid state very high: +309 cal/g (compared to +206 for CL-20)
- Expected to be less shock sensitive than major competitors (C-nitro vs. N-nitro in nitramines)

ONC still a subject of study: Several papers in past two years

* P. E. Eaton *et al.*, *Propellants, Explosives and Pyrotechnics*, **27**, 1 – 6 (2002)

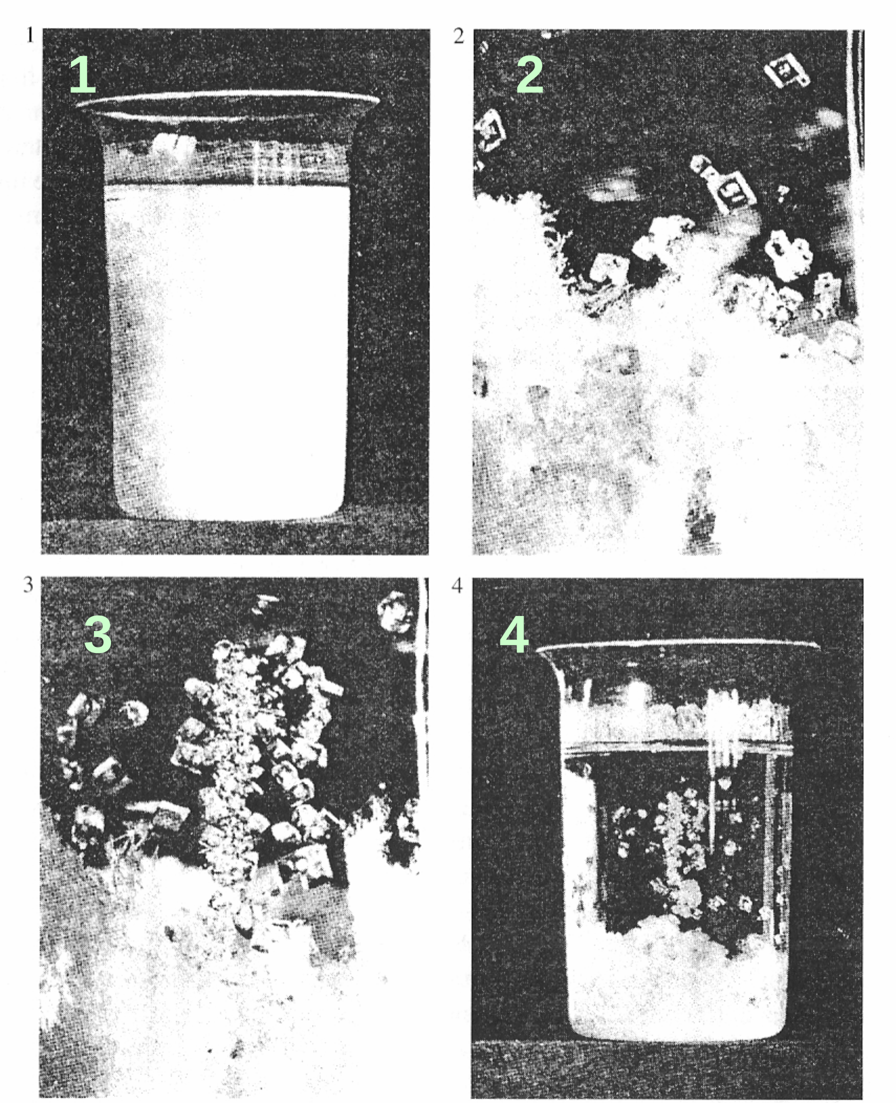
Density Trends in Nitrocubanes



Octanitrocubane in practice

- The crystal form of ONC isolated had a density substantially lower than predicted.
  - Estimated: 2.1 – 2.2 g/cm^3
  - Measured: 1.979 g/cm^3
  - Existence of other polymorphic forms is possible
    - Ostwald Rule of Successive Reactions “on leaving any state and passing into a more stable one, that which is selected is not the most stable one under the existing conditions, but the nearest” (i.e., that which can be reached with the minimum loss of free energy).
    - CL-20 first isolated in lower density form

Spontaneous transformation



"Example of Ostwald's Rule of Successive Reactions.

2,4-dibromoacetanilide initially crystallizes from alcoholic solutions as small needle-shaped crystals, forming the voluminous mass in (1). Successive photos (2,3,4) of the same crystallization vessel, taken at two-day intervals show the transformation to the more stable chunky rhombic crystals."

J. Bernstein, *Polymorphism in Molecular Crystals*, Oxford Science Publications, 2002.

AP Replacement

- One of the most critical needs for the future
  - Anticipated tightening of regulation of perchlorate
  - Lack of another material with equivalent properties
- Burning characteristics of AP broadly exploited in propulsion community
- Potential replacements all have issues associated with their use
  - Hygroscopicity
  - Sensitivity
  - Performance

Oxidizers: ADN, AP, AN

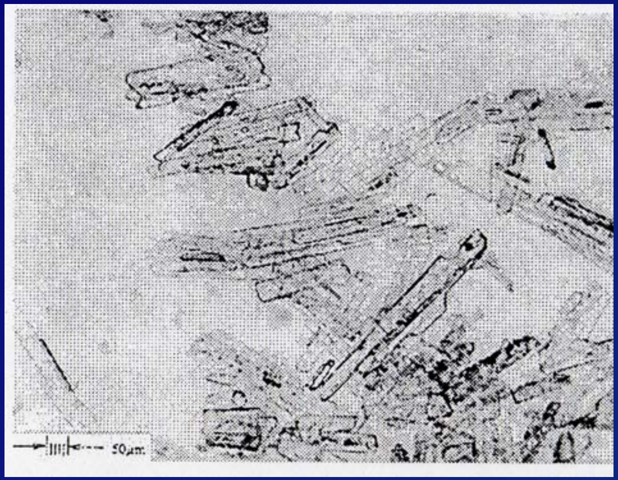
Property	ADN	AP	HNF	AN
Formula	$NH_4N(NO_2)_2$	NH_4ClO_4	$CH_5N_5O_6$	NH_4NO_3
Density (g/cm^3)	1.812	1.954	1.86	1.725[a]
ΔH_f (kJ/mol) (kJ/kg)	-150 -1210	-259.6 -2210	-71 -388	-365.1 -4561
Oxygen balance (%)	+25.8	+33.8	+13.1	+20.0

[a] AN-IV: polymorphic form that is stable at 25ºC

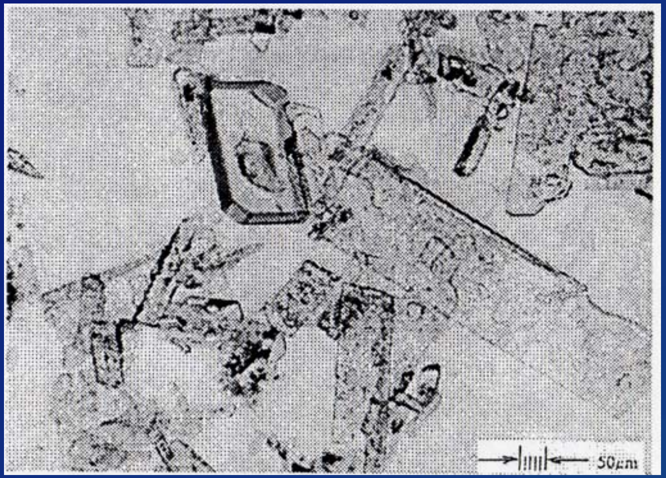
Challenges of ADN

- Particle Morphology
  - Generally forms needles when crystallized from solution
  - Habit can be modified by choice of solvent
  - Low melting point makes prilling feasible

ADN Morphology



ADN recrystallized from methanol



ADN recrystallized from trifluoroethanol, 70°C

ADN's preferred habit is acicular, but it can be modified by choice of solvents

Nanoparticulates

Overcoming diffusion

- Diffusion limited reactions can be accelerated by reducing particles size of species
  - Nanoparticulate metals, especially Al
  - Nanoparticulate oxidizers
- Thermitic mixtures (metal/metal oxide) react faster when the particles are nanosize
- When there is a passivating coating present, it can represent a large fraction of the total particle
- Various approaches to passivating the surface are being pursued

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Energy from oxidation of Al

30 micron aluminum particle	30 nm aluminum particle

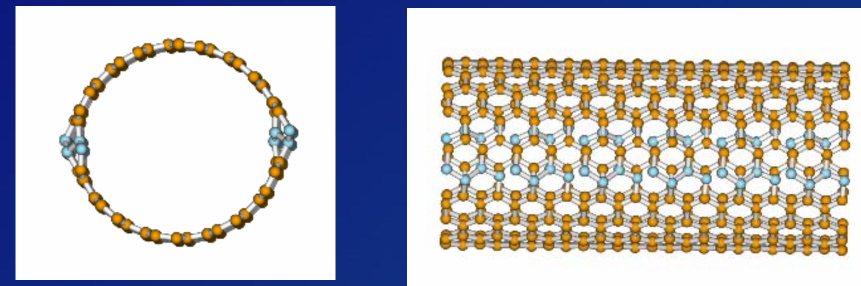
Surface area = 0.1m^2/g	Surface area = 74 m^2/g

Bomb Calorimetry Results, various size Aluminum

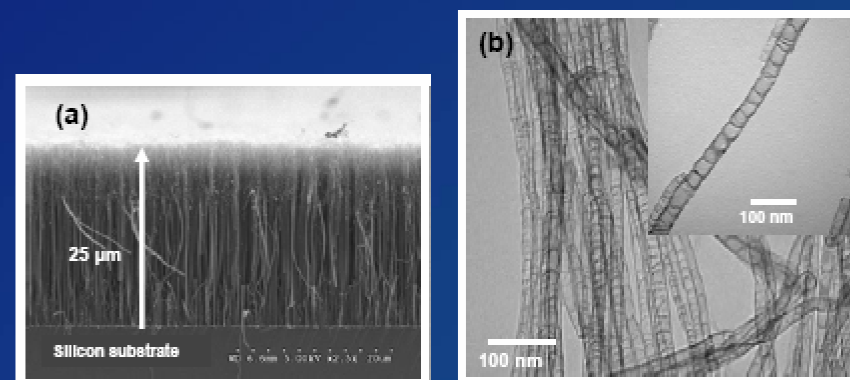
Material	Cal/g (measured)	Cal/g (calculated Max)	%TME
Indian Head aluminum(30nm)	4412	7424	59.43
Technanogy aluminum(110nm)	6355	7424	85.60
exploded aluminum(200nm)	6072	7424	81.79
H-5 aluminum(5microns)	7118	7424	95.88
Cerac aluminum(30microns)	7133	7424	96.08

Carbon Nanotubes + All-N

- Introduction of species into carbon nanotubes (CNTs) to stabilize trapped species has been studied calculationally.
  - Predicts that N_8 and N_4 trapped in CNTs should be stable.
- Nitrogen-doped carbon nanotubes have been produced, but exact nature of doping is not sure.



N4 polynitrogen doped carbon nanotube (10,10)



N-doped carbon nanotubes. (a) SEM image of aligned N-doped nanotubes; (b) TEM images of N-doped nanotubes

H. Abou-Rachid et al, "Novel Nanoscale High Energetic Materials: Nanostructured Polymeric Nitrogen and Polynitrogen," 7th International Symposium on Special Topics in Chemical Propulsion, 17 – 21 Sep 02, Kyoto, Japan.

New Forms of Old Ingredients

- Since mid-1990s attention focused lower sensitivity forms of common ingredients
  - I-RDX® and other forms of Reduced Sensitivity RDX
  - “I-HMX”
  - “I-CL20”
- Known materials with improved crystal properties
  - Lower residual porosity
  - Fewer imperfections (narrower peaks in NQR spectrum)
- Manifestation of reduced sensitivity: lower shock sensitivity
- No significant change in response to thermal threats

Non-chemistry Concepts

- Improvements of several orders of magnitude over conventional high explosives generally involve the nucleus
- Low Energy Nuclear Reactions
  - Outgrowth of Cold Fusion work
  - Phenomenology still not clear
- Nuclear Isomers
  - Based on the energy available due to nucleus being in an excited (non-ground state) spin state
  - Issues
    - Control and triggering of energy release
    - Availability of material
    - Coupling of energy (gamma rays) to target

Modeling and Simulation

- Continuous increases in computational power have enabled the introduction of improved models in codes.
  - Physically realistic description of important phenomena
  - Faster speed → more extensive study of design tradeoffs
- Computations will always be an adjunct to, not a replacement for, experiments and tests.

Summary

- Focus of attention is currently not on substantially higher peformance.
  - Green energetics
  - IM performance
  - Life cycle issues
- Improvements in performance will come mainly from better use of available energy.
- Development of reliable modeling and simulation tools will be critical to improved design for better energy management.

Thank you for your att