Lawrence Livermore National Laboratory

Energetic compound synthesis

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EMC
ENERGETIC MATERIALS CENTER

We have identified five main areas important to the future needs

- Insensitive energetic compounds with >80% the power of HMX.
- High-power explosives with >HMX power and lower sensitivity
- High-nitrogen compounds with >70% nitrogen
- Melt-castable explosives with power >RDX
- Replacement of AP

Targets: ρ= 1.85 g/cc, DSC peak exotherm > 200 ^{o}C, sensitivity will vary depending on application

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Desired Properties are application driver

- **Generally searching for EM's with high density and good oxygen balance**
- **Any compound with density > 1.85 g/cc is fairly rare. A density >1.90 is even rarer. What is the highest density that can be attained by C,H,N,O compounds? Some feel 2.15 g/cc the limit.**
- **Thermal stability > 200 ^{o}C very important**
- **Vacuum stability also an important**
- **Compatibility and solubility important in some applications**

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Outliers are difficult to predict

- Generally, oxygen balance and explosive power of energetic compounds have an inverse relationship to insensitivity
  - Need to find "outliers"
  - Outliers are difficult to predict

- New structural architectures are needed to fulfill the performance and sensitivity requirements. The synthesis of new architectures are generally longer-term, high-risk, high-payoff projects.

- Outliers are needed to fulfill the future sensitivity and performance requirements. The current materials (RDX, HMX, NTO, NQ) are limited by their own sensitivity and performance characteristics. Formulation of sensitive materials (e.g., RDX) to make them insensitive generally requires a reduction in performance.

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Small-scale safety tests are the most important data for initial screening

- Drop hammer, spark sensitivity, friction sensitivity, thermal stability, DSC
- Heat of formation and detonation calorimetry should be important
- Detonation velocity and finally the equation of state measurement are necessary
- Ensuring the purity of the compound is important before performing larger tests very important. Impure compounds can lead to erroneous results.
- First synthesis developed is rarely the procedure used in scale-up.

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Synthetic chemists are still the best "predictors" for new target compounds

Modeling and simulation cannot always replace experience, intuition, technique and the scientific method. No current predictive models can predict and generate new target compounds as effectively as an experienced chemist

- **An energetic compound synthetic chemist can generate new target compounds of interest far better than any model now in place. A synthetic chemist, based solely on literature precedence, ingenuity and experience, can estimate density, stability and performance fairly accurately. Synthetic chemists are their own best "modelers".**
- **Just as models are improved by providing more data, the same applies to synthetic chemists. The longer they are in the field and the more experience they gain the better they are at prediction (and synthesis) of target compounds.**
- **Personally, I look to models (e.g. Cheetah, ARL)) to calculate performance after proposing a compound, estimate density and possibly heat of formation. I rely on experience, literature precedence, looking for areas not studied before (things that cannot be quantified), and I believe this is still the best method to generate target compounds.**

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Scientific method still must ultimately guide our future work

- Experience and the access to previous work, and using scientific method is still the best method to generate new target molecules
- Literature precedent still the best guide to predicting density and performance.
- Investment in personnel through mentoring, providing experience in the laboratory, and allowing them to stay in the laboratory for at least 7 years is important.
- Providing incentive to stay in the laboratory probably the best approach to ensure future EM scientists will have the experience and expertise to generate new target molecules and to understand past work.
- Long-term funding is probably just as important. Year to year funding does not allow a scientist to truly address any problem. 3-5 year funding to address any issue is needed.

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Program Managers must be taught how EM synthetic chemistry is different

- The many aspects and applications that an EM chemists must address demands that the chemist must stay in the field for some time (5-7 years) before he/she understands the area.
- This is different from technology based or Pharma-based chemists who can change fields regularly and are in fact encouraged to do so
- Funding must be appropriated that allows mentoring of new chemists to allow the transfer of experience, knowledge and technique. This may essentially require twice the funding.
- This expertise is necessary.

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Enhanced safety and performance will cost more. Period!

- Program managers will have to pay increased costs for enhanced performance and sensitivity.

- Labor costs drive most of the cost of the synthesis of materials at < 100,000 lbs. Therefore, cost of materials is a small percentage of the total cost. There is now way around this if new materials are really needed.

- Funding for the transition of the scale-up to the 5-50 kg needed to qualify an explosive has been difficult to obtain in the past. This capability is necessary to qualify a new EM.

- Do not throw away potential compounds because the synthesis is "too costly" or because of environmental or toxilogical concerns of the synthesis. These issues that can be addressed during improvements to the scale-up.

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Scale-up is time-intensive

- **Safety protocol demands a scale-up process of least four steps to synthesize >50 grams in one flask.**

  <1g

  10 grams

  50 grams

  >50 grams

  with small-scale safety tests performed at each juncture.
- **R&D work is constantly performed to improve the synthesis, yield, ease of synthesis, purity, cost of synthesis, particle size and morphology, and elimination of toxic reagents. Work continues on promising compounds in the form of scale-up and improvements to make them more attractive to our customers.**
- **A goal should be to develop the synthesis of an EM so that they may be transitioned to a scale-up facility.**

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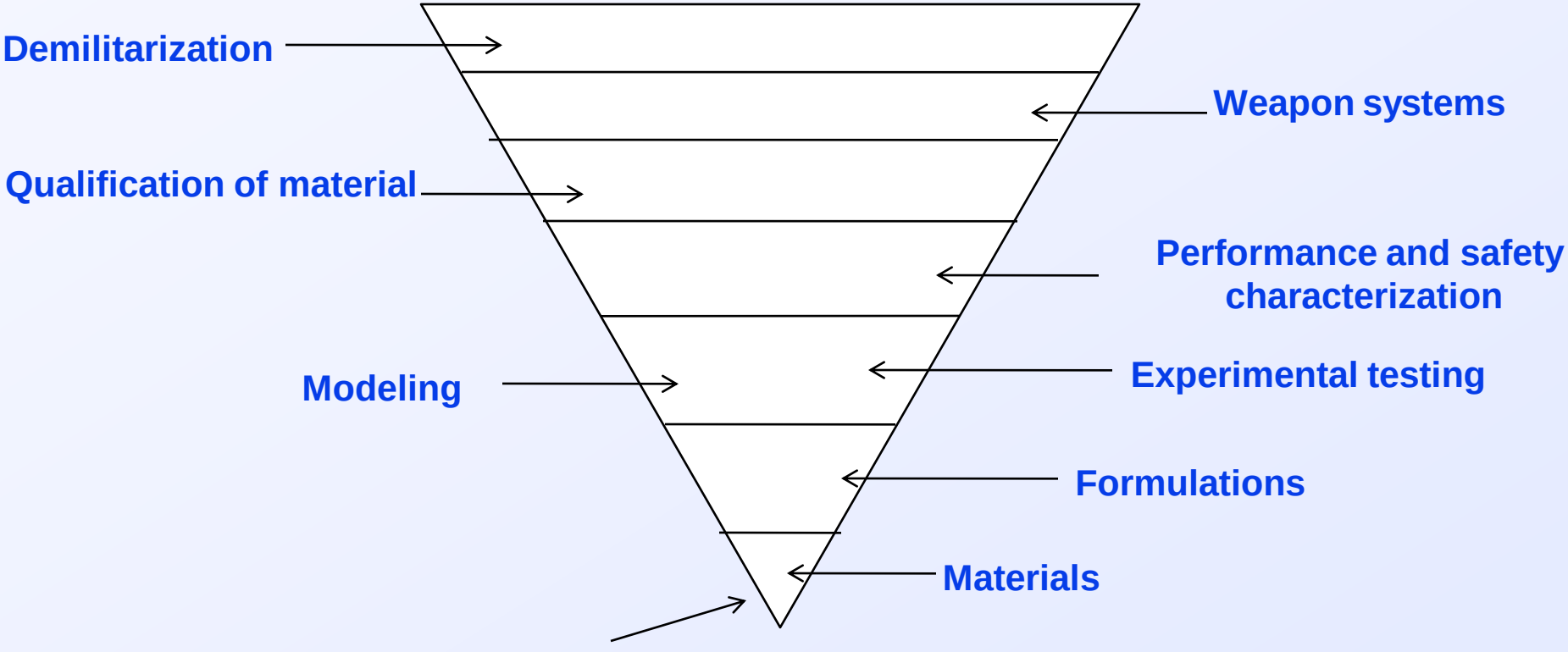
Materials sit at the bottom of an inverse triangle and support most all energetic materials research



This area should not consist only of RDX, TATB, HMX, PETN, TNT, NQ, NTO and AP
Then we are boxed in by their inherent sensitivity, power and thermal stability issues.

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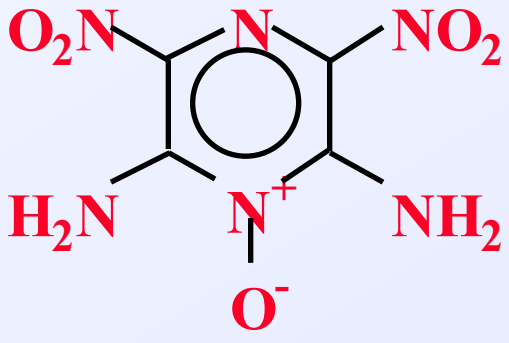
Thermal stability and density of LLM-105 is superior

- **Mol. Formula:** $C_4H_4N_6O_5$
- **Mol. wt.:** 216.04 g/mole
- **Balance:**
  - 3 N_2
  - 2 H_2O
  - 3 CO
  - 1 C



- **Density:** 1.918 g/cc (measured)
- **Dh_{50}:** 98-145 cm (30-32 cm RDX & HMX)
- **Spark Sensitivity:** Insensitive
- **Friction:** Off-scale (BAM)
- **Heat of formation:** -3.1 kcal/mole (measured)
- **DSC exotherm:** 360˚C (10˚C/min)
- **Limited solubility in common organic solvents**

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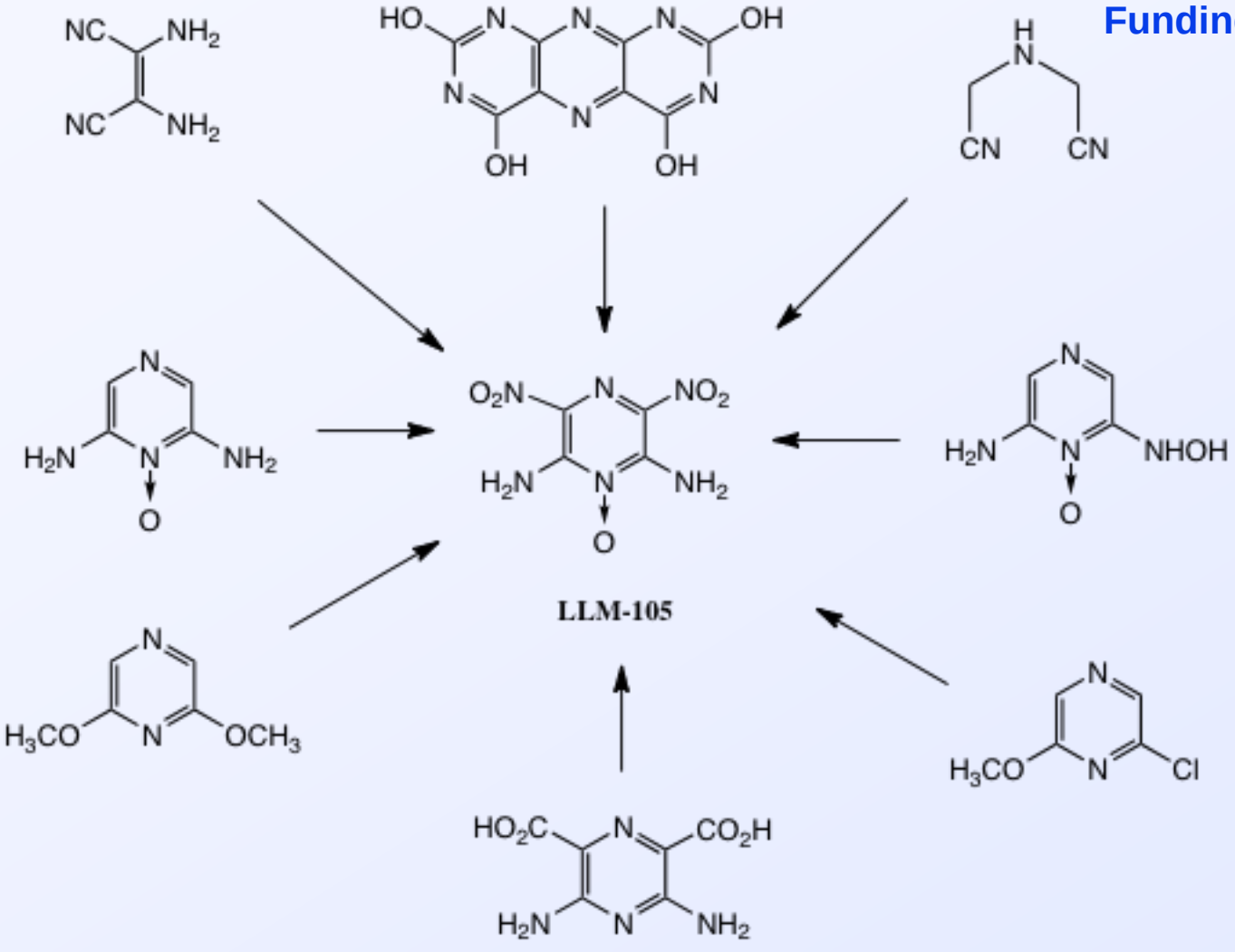
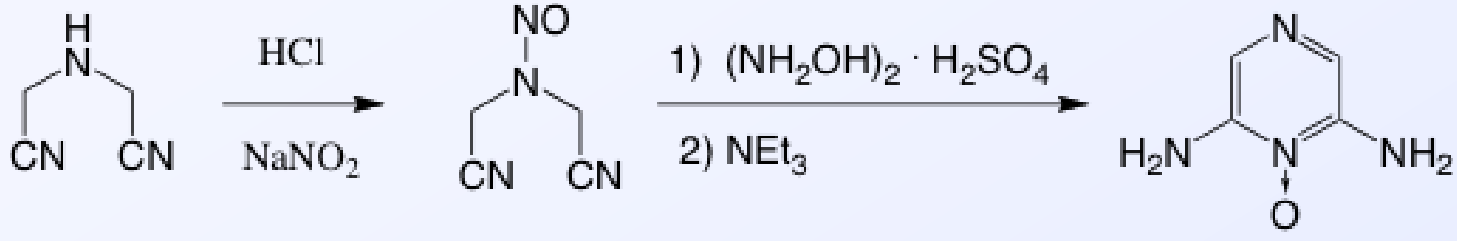
Many approaches to LLM-105 have been investigated since 1995.

Funding low and sporatic



New synthesis of 2,6-diaminopyrazine-1-oxide (DAPO) should greatly decrease the cost of LLM-105

Inexpensive starting materials and reagents



5 kg scale

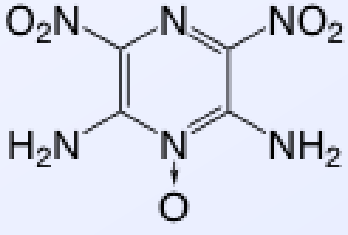
90%

70%

5-20 °C

HNO_3/ H_2SO_4

2 kg scale



65%

Barot and Elvidge, *JCS Perkin Trans 1*, **1973**, 606-12
S.K. Vohra et. al., *JOC*, **1979**, *44*, 1128-1131
Golding and Bellamy, *Cent. Eur. J. Energ. Mater*., **2007**, *4*, 33-57
Perosa et. al. *Tetrahedron Lett*., **1999**, 7573.

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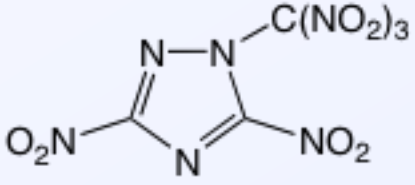
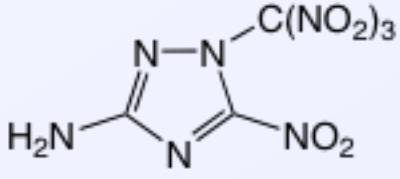
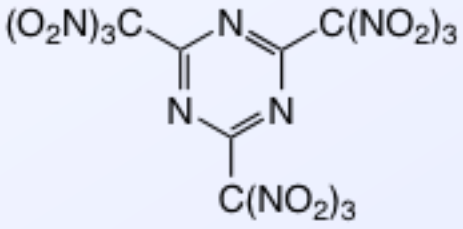
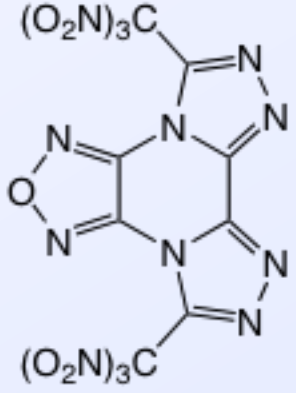
Trinitromethyl derivatives of heterocycles were investigated in the past

TNM derivatives are oxidizers that may have applications as replacements for AP.









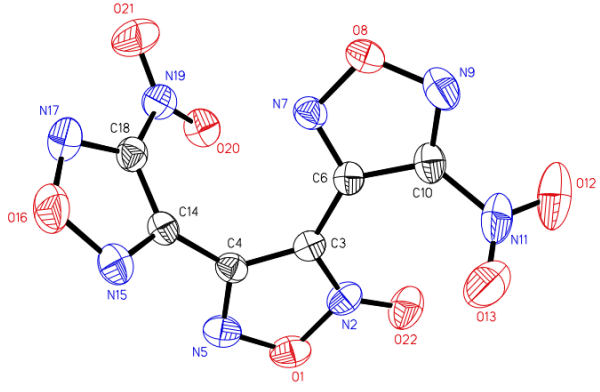
Biggest drawback seems to be thermal stability of these compounds. Dinitromethyl derivatives have less oxygen but their salts may be more thermally stable.

(1) Shasta, A. V.; Godovikova, T. I.; Korsunski, B. L. *Russ. Chem. Rev.* **2003**, *72*, 279-87.

(2) Shastin, A. V.; Godovikova, T. I.; Golova, S. P.; Kuz'min, V. S.; Khmel'nitskii, L. I.; Korsunski, B. L. *Mendeleev Commun.* **1994**, 17-18.

(3) Novikov, S. S.; Khmel'nitskii, L. I.; Novikova, T. S.; Lebedev, O. V.; Epishina, L. V. *Khim. Geterotsikl. Soedin* **1970**, *6*, 619-23,

Physical properties and crystal structure of DNTF were measured



- **Mol. Formula:** $C_6N_8O_8$
- **Mol. wt.:** 312 g/mole
- **Density:** 1.937 g/cc* (1.910 g/cc)
- **Dh_{50}:** 31-54 cm (32 cm for HMX)
- **Spark Sensitivity:** Insensitive
- **Friction:** 2/4 @ 14.4 kg, 0/10 @ 12.8 kg (HMX= 14.4 kg)(BAM)

D. Parrish

- **Heat of formation:** +657 KJ/mole*
- **DSC exotherm:** 279˚C (peak) (10˚C/min) m.p. 110 ºC
- **CRT:** 0.58 cc/g @ 120 ºC

107% the power of HMX

* Z. Feng-qi et. al., *J. Haz. Mat.*, **2004**, *A113*, 67-71

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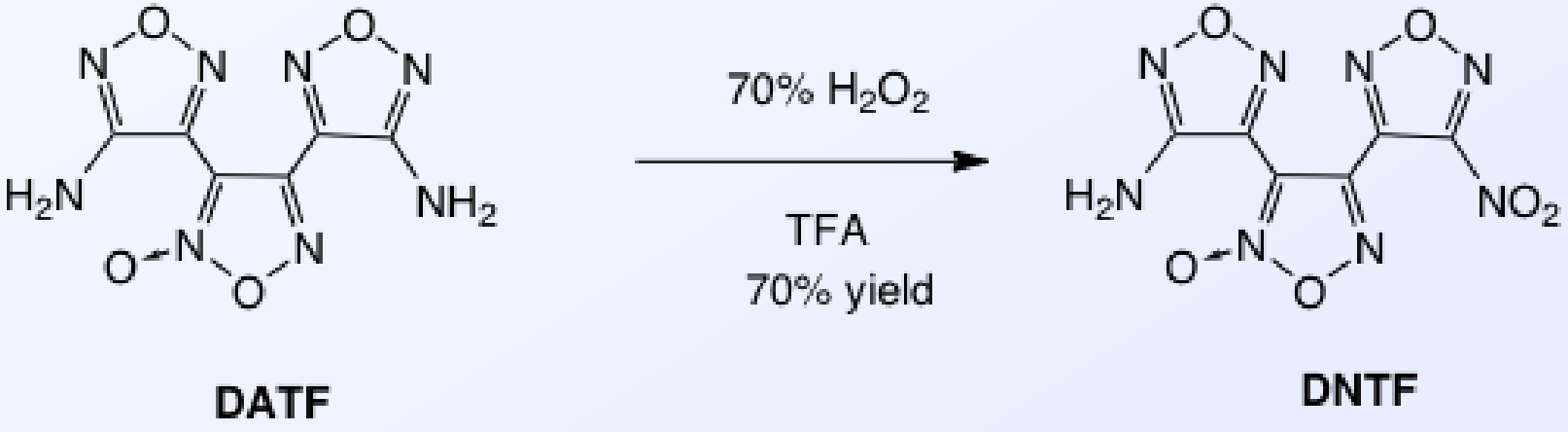
Oxidation of DATF goes smoothly



DATF **DNTF**

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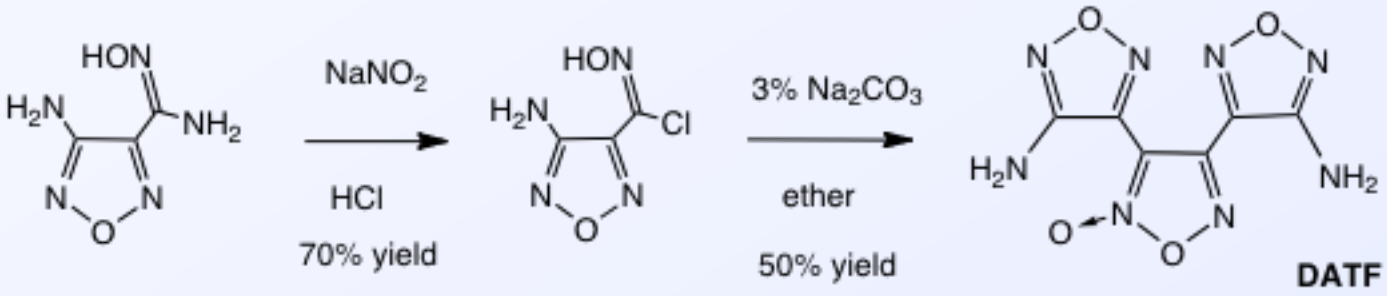
Original synthesis of DATF and DATF-1 needed improvement for scale-up



J. Wang et. al., *PEP*, **2008**, *33*, 347-52
C. Zhang et el., *Cent. Eur. J. Energet. Mater.*, **2005**, *2*, 45-53

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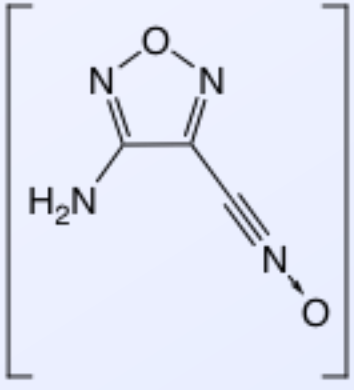
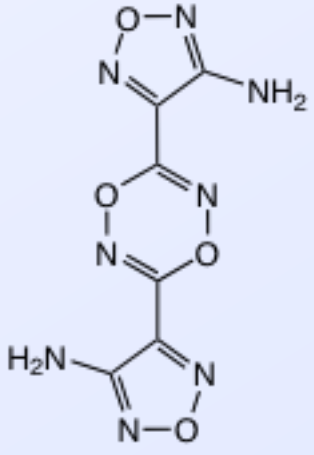
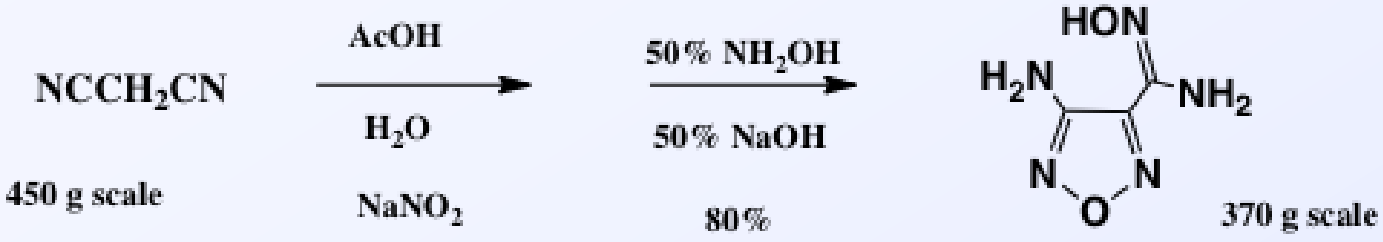


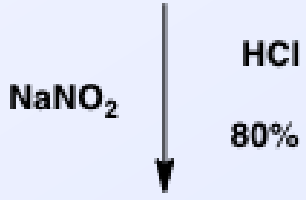


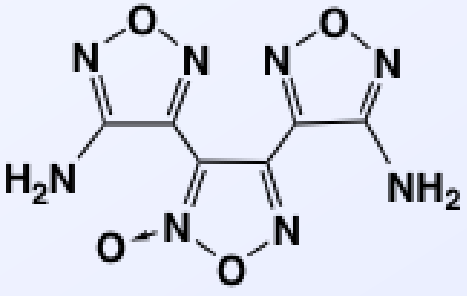
Also contained dioxadiazene

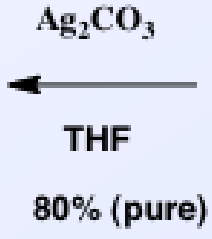
New synthesis of DATF has improved yields and easier work-up procedure

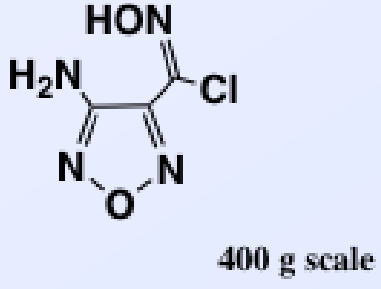


Procedure does not yield any of the side-product, dioxadiazene

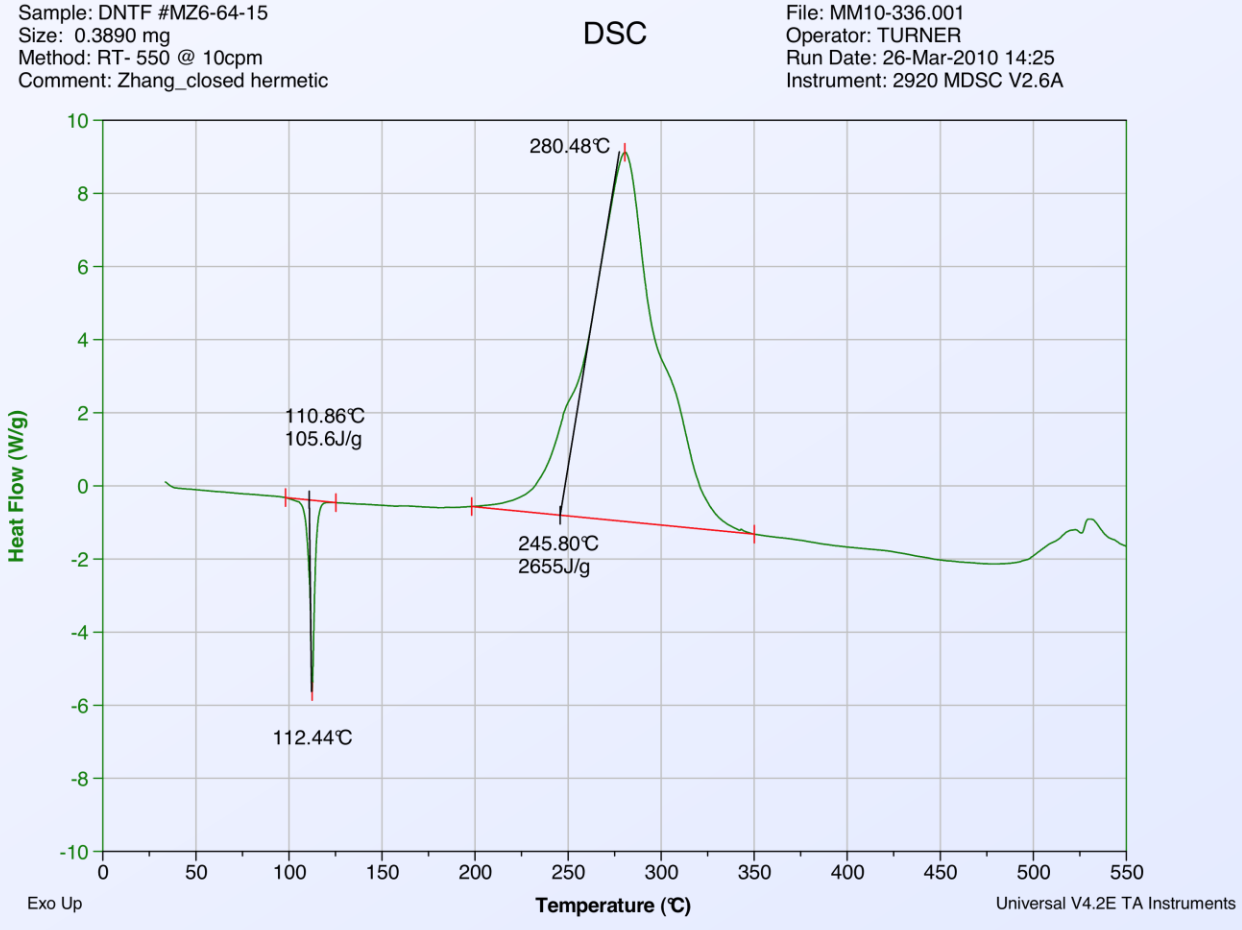








DNTF thermal stability improved with higher purity



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High-nitrogen materials are of interest as burn rate modifiers for gun propellants

- **High-nitrogen compounds comprised of tetrazoles attached to heterocyclic backbone may have applications as pyrotechnic compounds and as burn rate modifiers for gun propellants**
- **Nitrogen content >70%**
- **Heterocycles backbone adds oxygen to the compound to increase the density and oxygen balance.**

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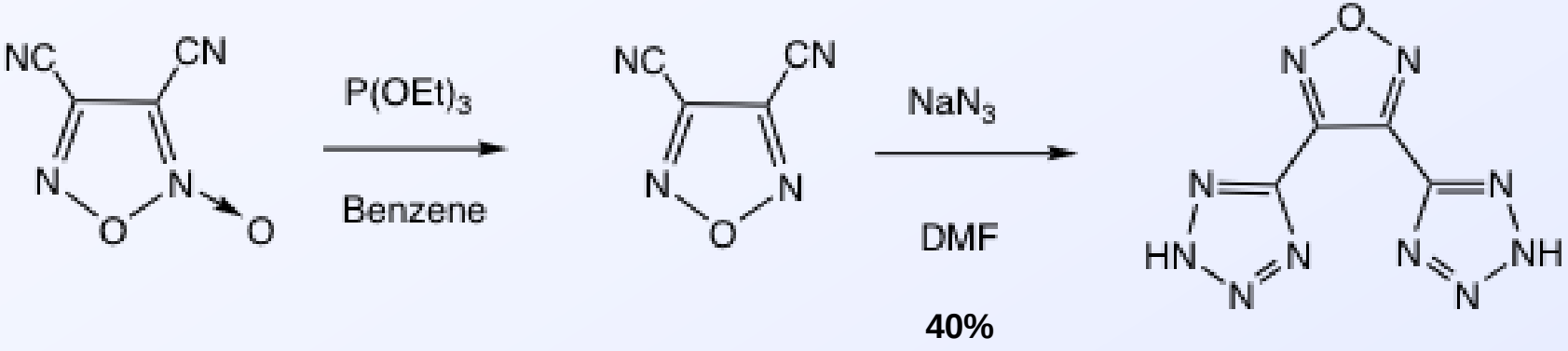
Synthesis of 3,4-bis(tetrazol-5-yl)furazan (LLM-181) was successful

Synthesis not optimized



LLM-181

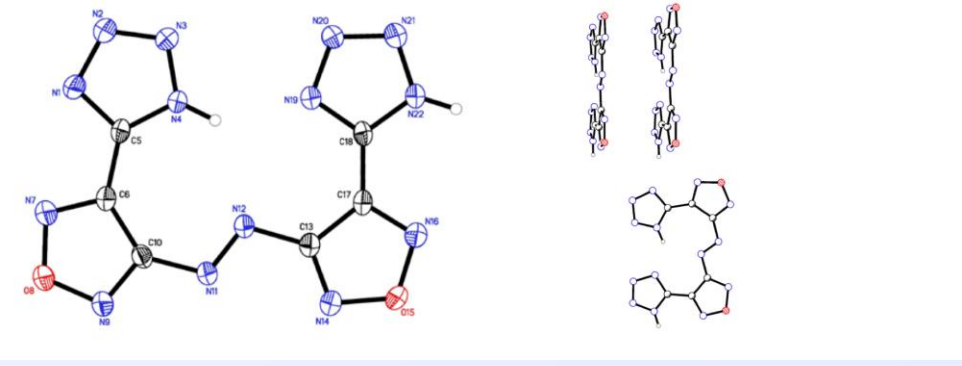
DSC exotherm = 269 °C
Friction: 1/10 @ 36 kg (BAM)
Dh_{50} > 173 cm
CRT: 0.04 g/cc @ 80 °C

$C_4H_2N_{10}O$

Parker et. al., *Tetrahedron Lett.*, **1962**, 79

[(*E*)-1,2-bis(4-(1*H*-tetrazol-5-yl)-1,2,5-oxadiazol-3-yl)diazene] (LLM-182)

- Mol. Formula: $C_6H_2N_{14}O_2$
- Mol wt: 302.05 g/mole
- Density: 1.747 g/cc (Parrish)
- Dh_{50}: 20 cm (32 cm for HMX)
- Spark Sensitivity: 0/10 @ 1.0 J
  (510 ohm resistance)
- Friction: 1/10 @ 19.2 kg (BAM)
- Heat of formation: 267 Kcal/mole
- DSC exotherm: 248˚C (10˚C/min)
- CRT: 0.08cc/ 0.25g @ 120 ºC



TNT in power

Diammonium: 126 kcal/mole, 1.63 g/cc
Dihydrazinium: 156 kcal/mole, 1.62 g/cc
Bis(TAG): 354 Kcal/mole, 1.63 g/cc

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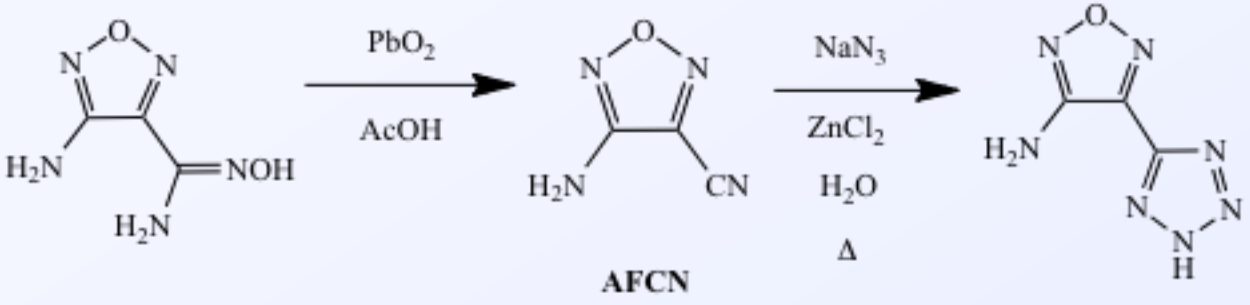
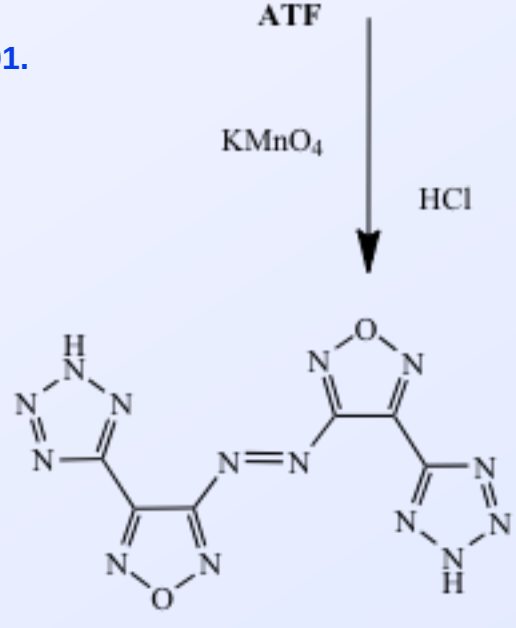
LLM-182 synthesis proceeds smoothly

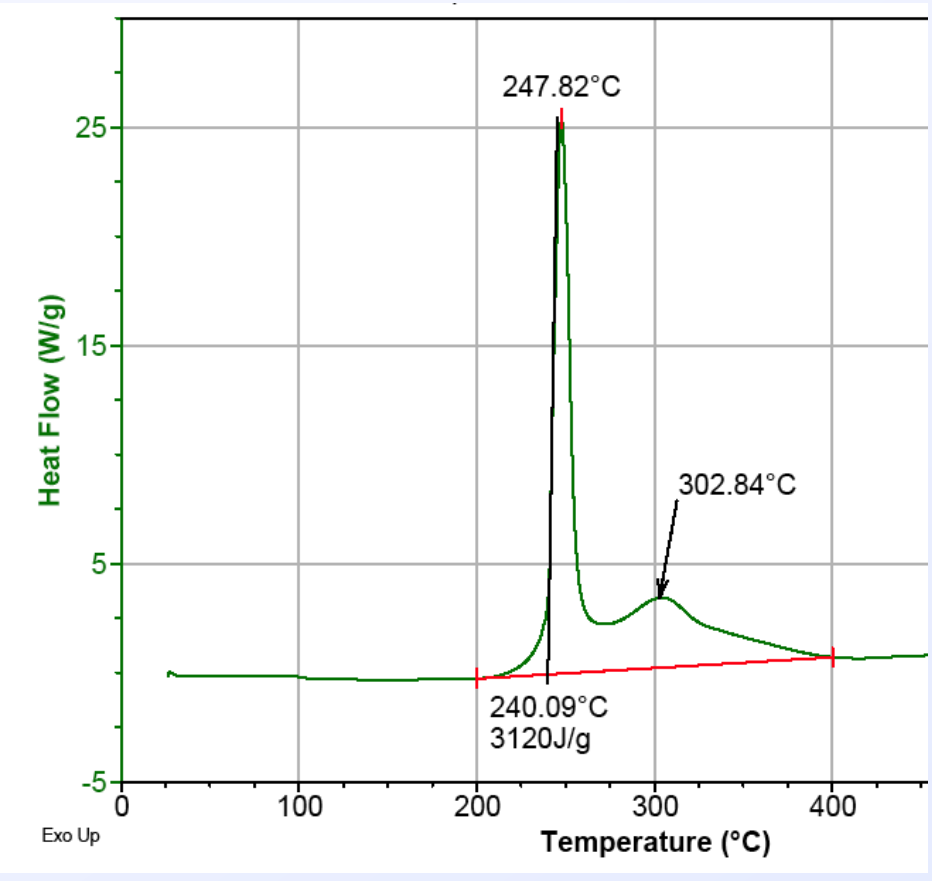


Shreeve, et. al.. *Angew. Chem. Int. Ed.* 2006, *45,* 3584–3601.



LLM-182

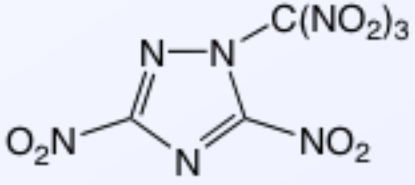
(*E*)-1,2-bis(4-(1*H*-tetrazol-5-yl)-1,2,5-oxadiazol-3-yl)diazene (LLM-182) is thermally stable

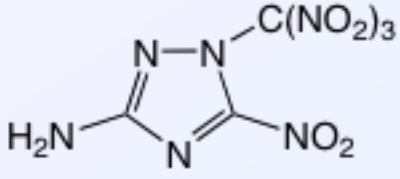


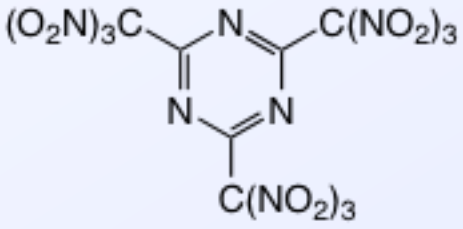
LLM-182 (AzTF)

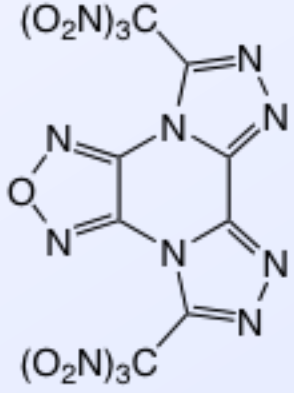
Trinitromethyl derivatives of heterocycles were investigated in the past

TNM derivatives are oxidizers that may have applications as replacements for AP.









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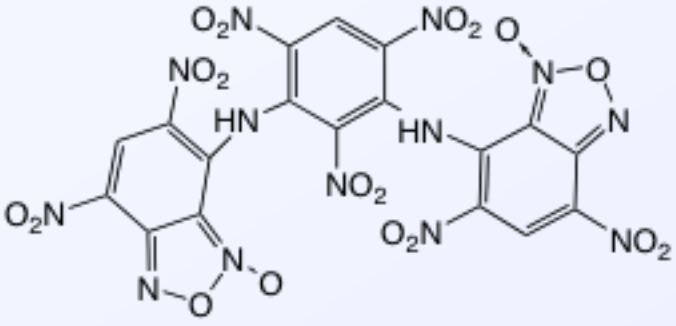
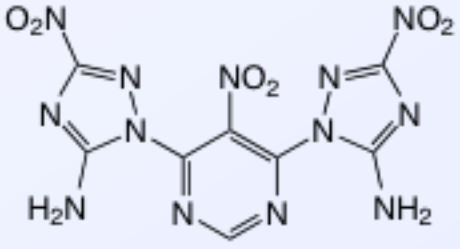
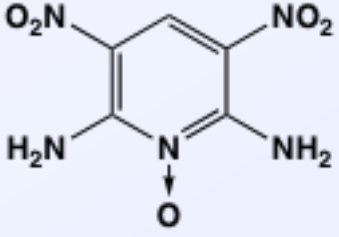
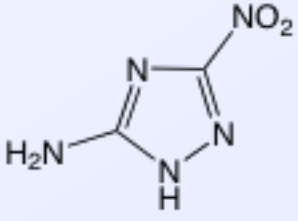
Insensitive compounds of interest





DANTNP





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Thermal stability also important for insensitives