U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND – ARMY RESEARCH LABORATORY

Synthesis, Scale-Up, and Characterization of High Energy Explosive and Propellant Materials

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CCDC-ARL, Energetics Synthesis & Formulation Branch

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OVERVIEW

- **Why do we go after particular heterocyclic compounds?**
  -Power is not the only factor in why we design a molecule
  -IMHO, formulation chemists hold the key for a synthesis chemist's success

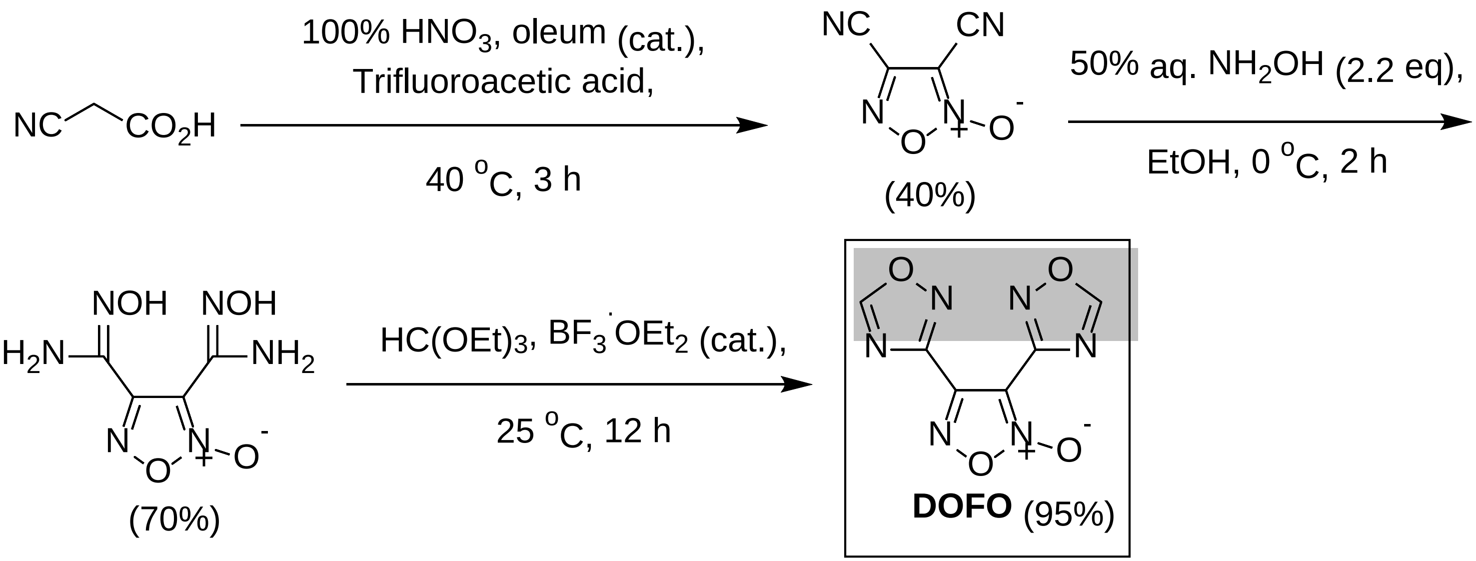
- **Synthesis of isoxazole- and 1,2,4-oxadiazole-based materials**
  -Dual function as potential melt-castable explosives and propellant plasticizers/surfactants

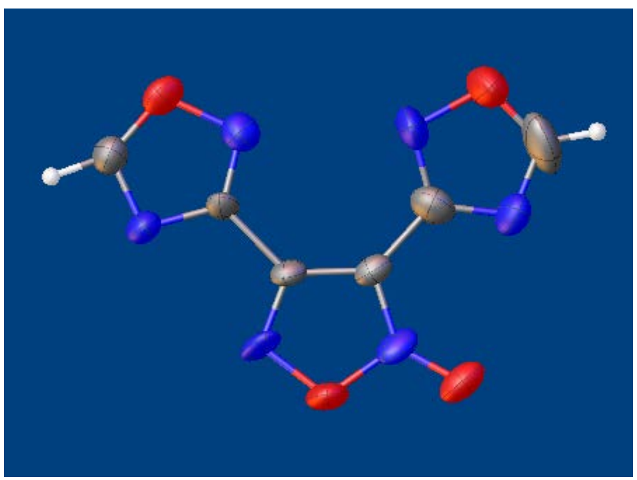
- **Synthesis of stereo- and regiochemical energetic materials**
  -Physical properties differ dramatically

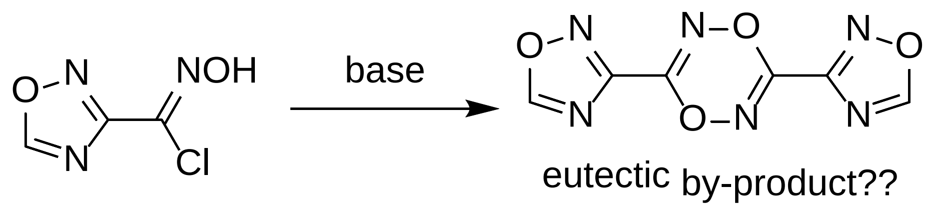
- **Development of new synthetic methods along the way**
  -Target directed, methods driven
  -Compounds must be scalable in our labs in order to be relevant

- **Concluding remarks**

SYNTHESIS OF BIS-OXADIAZOLE-BASED ENERGETICS







1) C. Yan, K. Wang, T. Liu, H. Yang, G. Cheng, Q. Zhang, *Dalton Trans.* **2017,** *46*, 14210–14218.

2) L. L. Fershtat, I. V. Ananyev, N. N. Makhova, *RSC Adv.* **2015,** *5*, 47248–47260.

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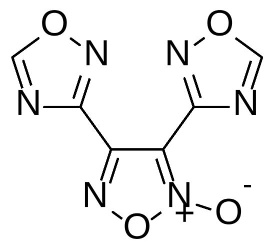


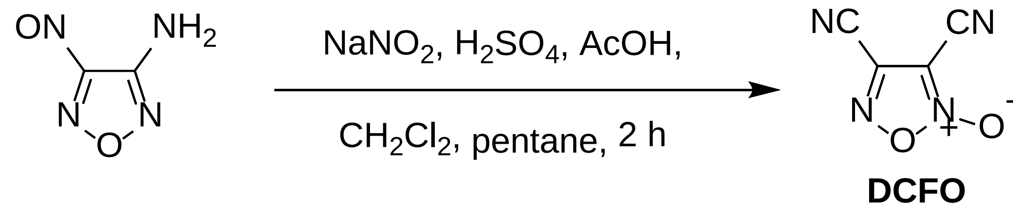
DOFO

Data category	TNT	**DOFO**
Density	1.65 g/cc	1.79 g/cc
T_{melt}	80.4 ^{o}C	114.3 ^{o}C
T_{dec}	295 ^{o}C	227 ^{o}C
$\Delta_f H^o$	-59.3 kJ/mol	+357 kJ/mol
Ωco_2	-74%	-64.9%
Ωco	-24.70%	-21.6%
V_{det}	6950 m/s	7577 m/s
P_{cj}	20.5 GPa	24.1 GPa
I_{sp}	-	220.0 s
Impact	15 J	>34.7 J
Friction	240 N	>360 N
ESD	0.25 J	0.25 J

- Potential melt-castable eutectic ingredient
- Insensitive material
- Detonation pressure 20% higher than TNT

PREVIOUS SYNTHESES OF 3,4-DICYANOFUROXAN (DCFO)

1)



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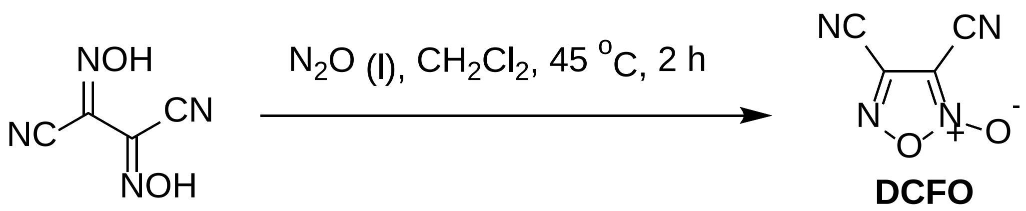

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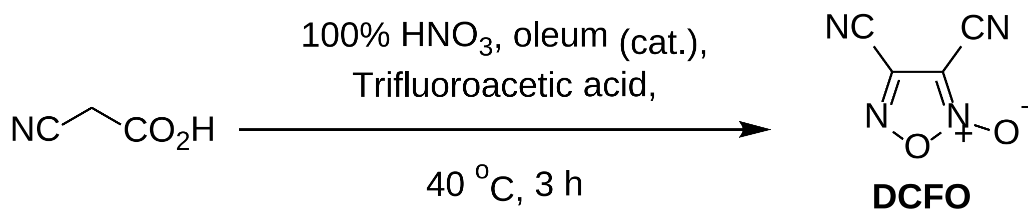
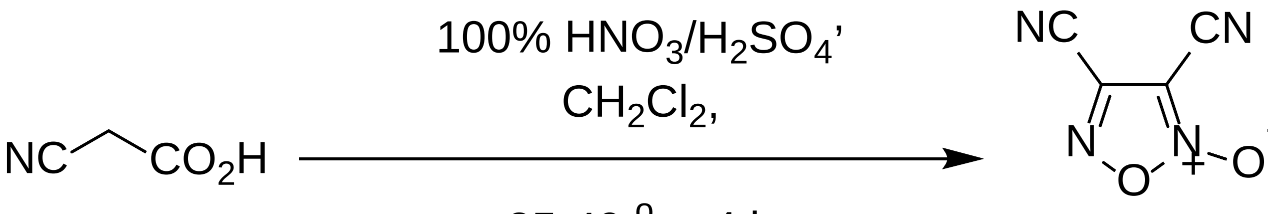


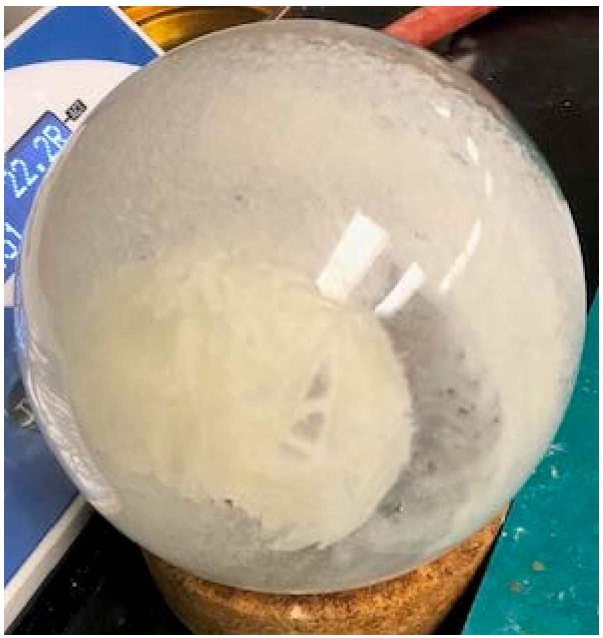
- 1) T. M. Mel'nikova, T. S. Novikova, L. I. Khmel'nitskii, A. B. Sheremeetev, *Mendeleev Commun.,* **2001,** *11,* 30-31.
- 2) C. Grundmann, G. W. Nickel, R. K. Bansal, *Justus Liebigs Ann. Chem.,* **1975,** *1029-1050*
- 3) C. O. Parker, W. D. Emmons, H. A. Relewicz, K. S. McCallum, *Tetrahedron,* **1962,** *72*, 79.

- These synthesis are too lengthy, and/or irreproducible, and suffer from safety concerns

IMPROVED SYNTHESIS OF 3,4-DICYANOFUROXAN (DCFO)

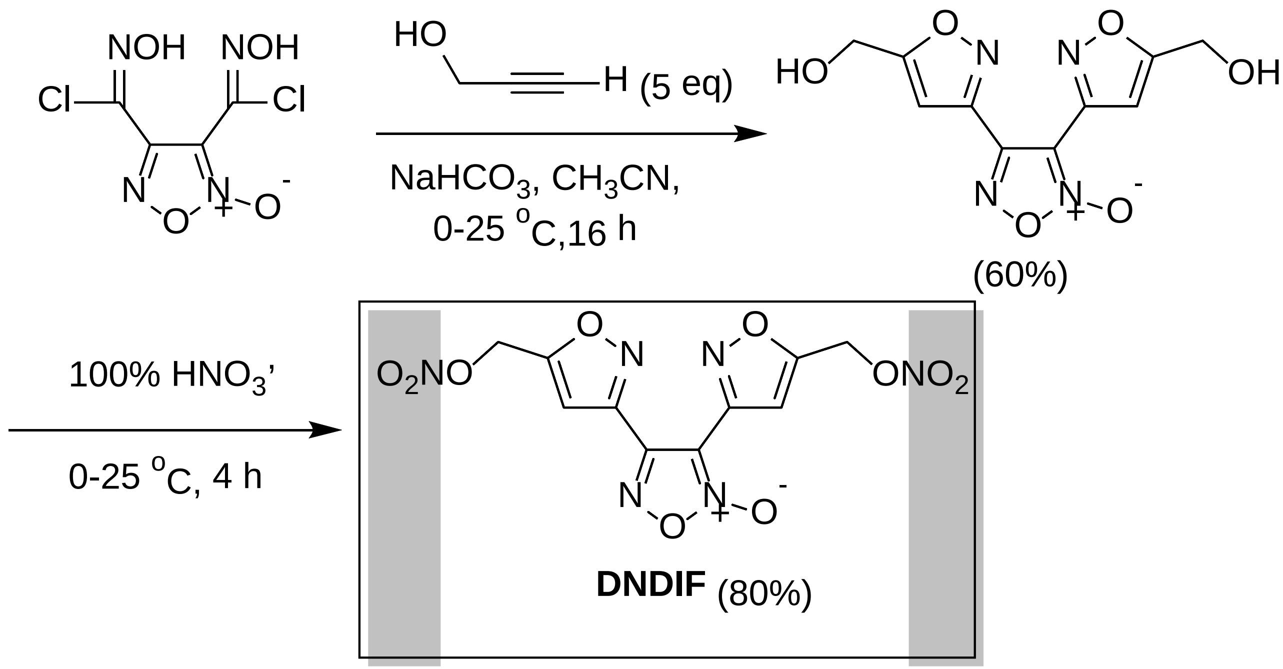


13 (73%)



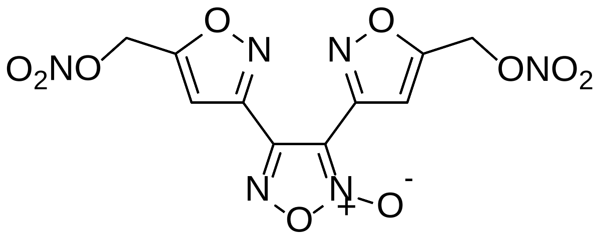
- Synthesized on 100 g scale
- New synthesis is cheaper, “greener” and is safer, due to minimal exothermic profile upon addition of mixed acid

SYNTHESIS OF BIS-ISOXAZOLE-BASED ENERGETICS



- Cycloaddition with 2-butyne-1,4-diol was unsuccessful
- *Bis*-hydroximoyl chloride is not stable to heating

SYNTHESIS OF BIS-ISOXAZOLE-BASED ENERGETICS

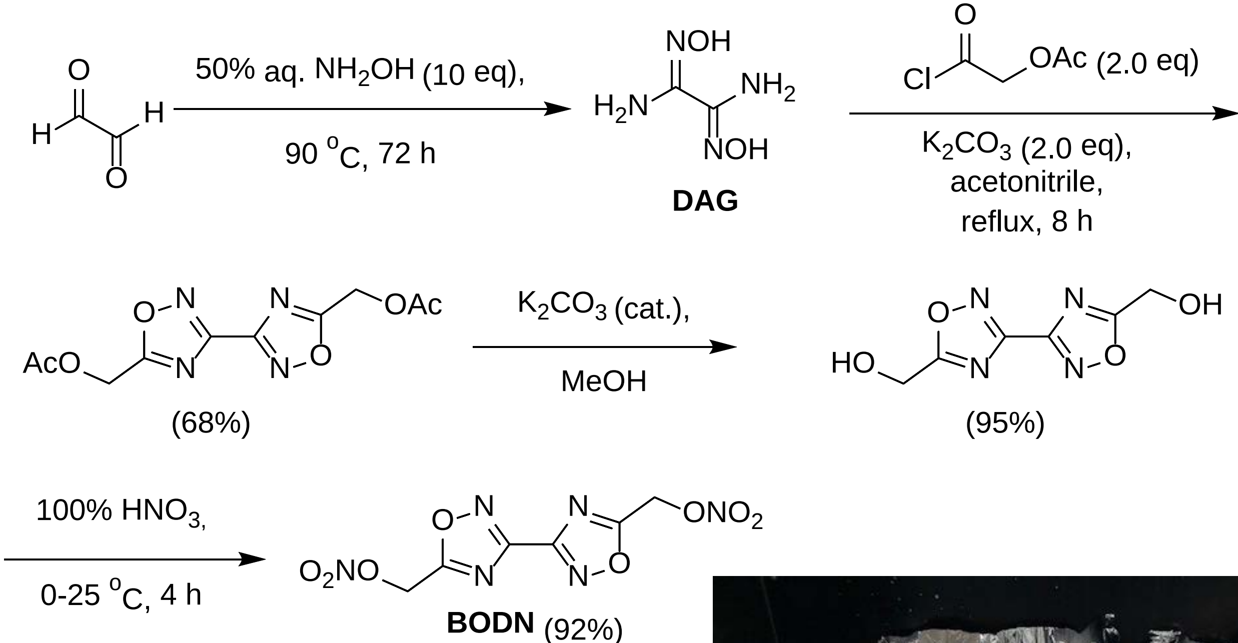


DNDIF

Data category	TNT	**DNDIF**
Density	1.65 g/cc	1.72 g/cc
T_{melt}	80.4 ^{o}C	91 ^{o}C
T_{dec}	295 ^{o}C	194 ^{o}C
$\Delta_f H^o$	-59.3 kJ/mol	+49.5 kJ/mol
Ωco_2	-74%	-56.2%
Ωco	-24.70%	-13%
V_{det}	6950 m/s	7374 m/s
P_{cj}	20.5 GPa	25.1 GPa
I_{sp}	-	224.0 s
Impact	15 J	7.8 J
Friction	240 N	240 N
ESD	0.25 J	0.125 J

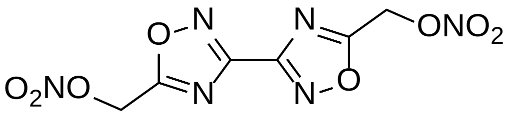
- Potential standalone melt-castable explosive
- Detonation pressure is 25% higher than TNT. Sensitivity is on par with RDX
- Scale-up synthesis admittedly needs work.

SYNTHESIS OF BIS-OXADIAZOLE-BASED ENERGETICS



- DAG and BODN diol synthesized on kilogram scale.
- DAG synthesis is a safer improvement over the previously existing procedure.

SYNTHESIS OF BIS-OXADIAZOLE-BASED ENERGETICS



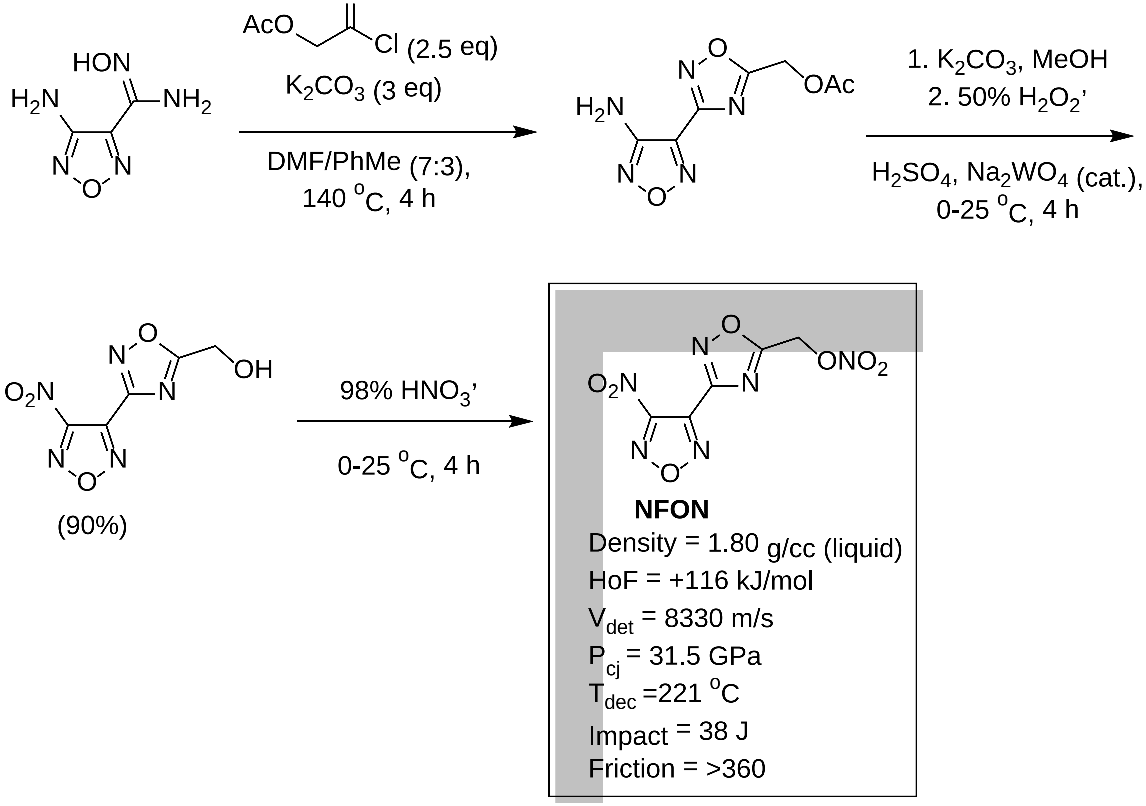
BODN

Data category	TNT	**BODN**
Density	1.65 g/cc	1.832 g/cc
T_{melt}	80.4 ^oC	84.5 ^oC
T_{dec}	295 ^oC	183.4 ^oC
$\Delta_f H^o$	-59.3 kJ/mol	-79.4 kJ/mol
Ωco_2	-74%	-33.3%
Ωco	-24.70%	0%
V_{det}	6950 m/s	8180 m/s
P_{cj}	20.5 GPa	29.4 GPa
I_{sp}	-	236.0 s
Impact	15 J	8.7 J
Friction	240 N	282 N
ESD	0.25 J	0.125 J

- BODN is a potential standalone melt-castable explosive material.
- Detonation pressure is 50% higher than TNT. Sensitivity is in between TNT and RDX
- Successfully melt-poured into rate sticks to get experimental detonation velocity

SYNTHESIS OF HIGH-ENERGY PROPELLANT INGREDIENTS

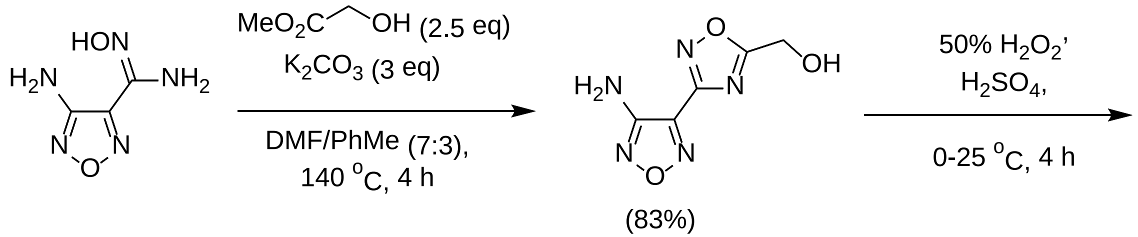
Chinese route

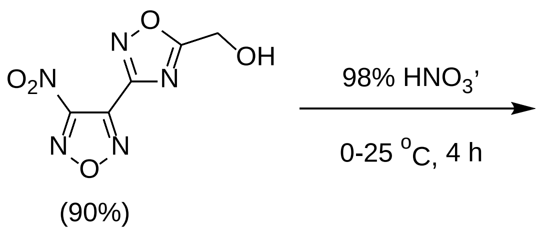


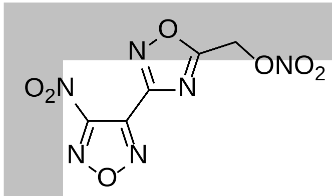
- We know that the synthesis and performance of NFON reported by the Chinese is not accurate.
- We synthesized this compound ca. 4 years ago (unpublished, but coming soon.
- We attempted the same chemistry as the Chinese route, and did not get the products they claim
- Their impact sensitivity numbers are grossly inaccurate
- Frankly, many Chinese procedures are not reproducible
- Our coming paper will be direct in pointing out these inaccuracies.

SYNTHESIS OF HIGH-ENERGY PROPELLANT INGREDIENTS

ARL route







NFON

Density = 1.63 g/cc (liquid)

HoF = +186 kJ/mol

V_{det} = 8100 m/s

P_{cj} = 30.6 GPa

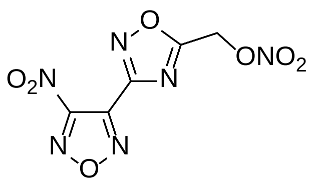
Isp = 249 s

T_{dec} =187 °C

Impact = 2 J

Friction = 240 J

Chinese reported data



NFON

Density = 1.80 g/cc (liquid)

HoF = +116 kJ/mol

V_{det} = 8330 m/s

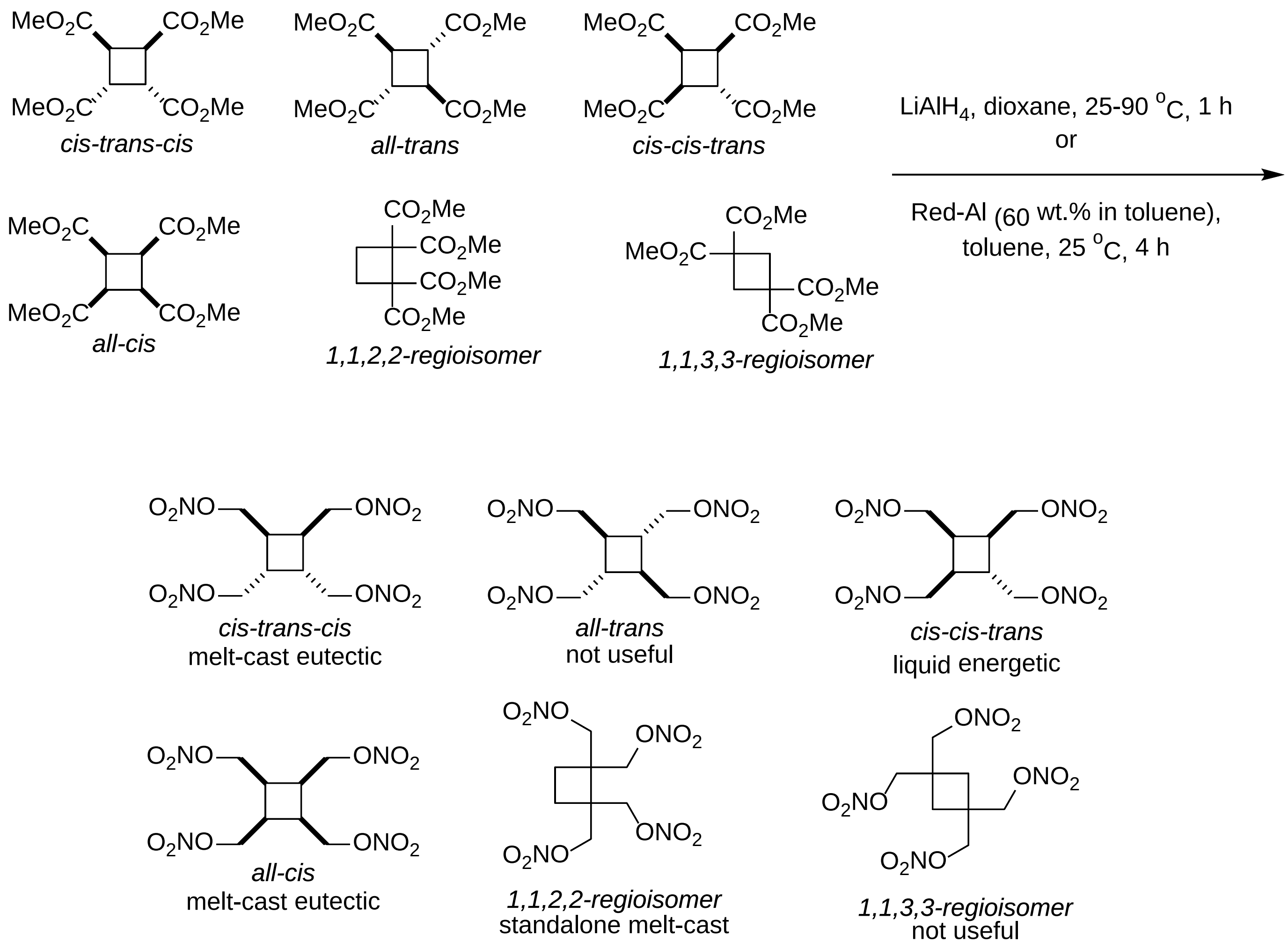
P_{cj} = 31.5 GPa

T_{dec} =221 °C

Impact = 38 J

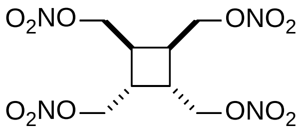
Friction = >360

STEREO- AND REGIOCHEMISTRIES MATTER WHEN DESIGNING ENERGETICS



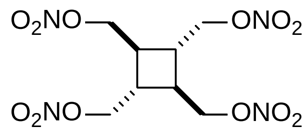
- Collaboration between CCDC ARL and Scripps (Prof. Phil Baran)
- Red-Al is just as good, but is non-pyrophoric and is fully soluble in organic solvents
- Depending on the stereo- and regiochemistry, one can obtain wide tunability.
- Liquids, standalone melt-castable materials, melt-castable eutectic ingredients, and some useless compounds.

STEREO- AND REGIOCHEMISTRIES MATTER WHEN DESIGNING ENERGETICS



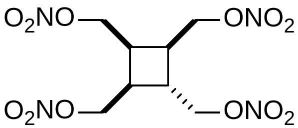
cis-trans-cis

Density = 1.64 g/cc
HoF = -510 kJ/mol
T_{melt} = 106 ^oC
T_{dec} = 199 ^oC
V_{det} = 7438 m/s
P_{cj} = 24.5 GPa
I_{sp} = 241 s
Impact = 6.2 J
Friction = 240 N
ESD = 0.125 J



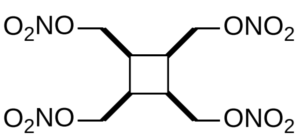
all-trans

Density = 1.61 g/cc
HoF = -536 kJ/mol
T_{melt} = 48 ^oC
T_{dec} = 200 ^oC
V_{det} = 7544 m/s
P_{cj} = 22.9 GPa
I_{sp} = 239 s
Impact = 6.2 J
Friction = 240 N
ESD = 0.125 J



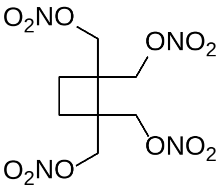
cis-cis-trans

Density = 1.54 g/cc
HoF = -512 kJ/mol
T_{freeze} = <-40 ^oC
T_{dec} = 187 ^oC
V_{det} = 7577 m/s
P_{cj} = 24.5 GPa
I_{sp} = 240 s
Impact = 9.0 J
Friction = >360 N
ESD = 0.125 J



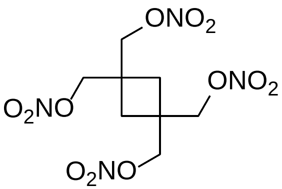
all-cis

Density = 1.66 g/cc
HoF = -481 kJ/mol
T_{melt} = 101 ^oC
T_{dec} = 194 ^oC
V_{det} = 7504 m/s
P_{cj} = 24.5 GPa
I_{sp} = 243 s
Impact = 6.2 J
Friction = 240 N
ESD = 0.125 J



1,1,2,2-regioisomer

Density = 1.68 g/cc
HoF = -466 kJ/mol
T_{melt} = 86 ^oC
T_{dec} = 193 ^oC
V_{det} = 7604 m/s
P_{cj} = 24.6 GPa
I_{sp} = 243 s
Impact = 4.7 J
Friction = >360 N
ESD = >0.25 J



1,1,3,3-regioisomer

Density = 1.65 g/cc
HoF = -509 kJ/mol
T_{melt} = 147 ^oC
T_{dec} = 196 ^oC
V_{det} = 7472 m/s
P_{cj} = 24.4 GPa
I_{sp} = 241 s
Impact = 6.2 J
Friction = >360 N
ESD = >0.25 J

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