Synthesis Development of Novel Energetic Ingredients
NDIA IM/EM 2018

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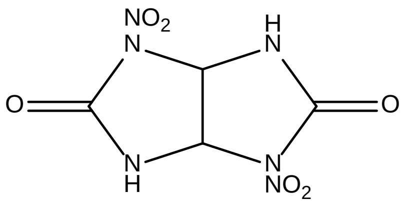
BAE SYSTEMS INSPIRED WORK	**BAE Systems** Matt Hathaway, Dr. Jeremy Headrick, Robyn Wilmoth, Kelly Smith, Chris Long, Dr. Tess Kirchner -Analytical testing

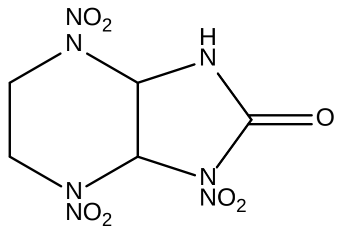
Overview

- Defense scientists constantly scour the literature for new explosive ingredients to fulfill their needs
- Individual needs can vary widely based on system requirements
- Possible material requirements can include:
  - Sensitivity
  - Energetic performance
  - Thermal stability (greater than 300 °C)
  - Crystal morphology
- Today's presentation will highlight BAE Systems' orphan explosive ingredients
  - Synthesis from the gram scale up to pilot scale
  - Did not meet requirements for original intended purpose
  - Could be desirable for future applications

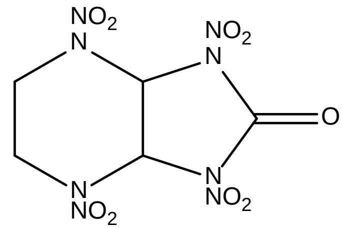
Orphan Ingredients



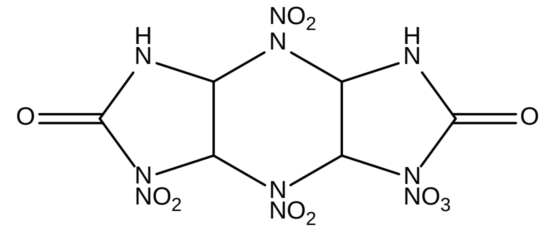
DNGU



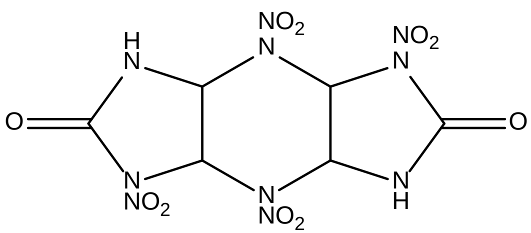
HK-56



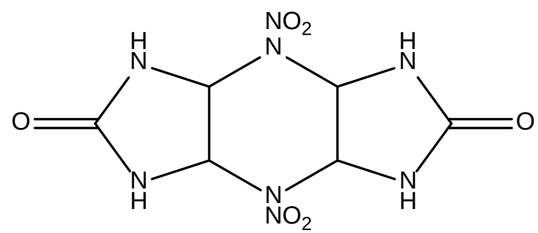
TNABN



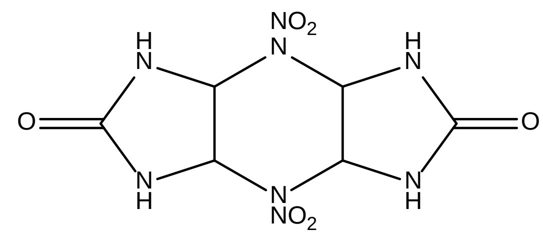
c-TNTC



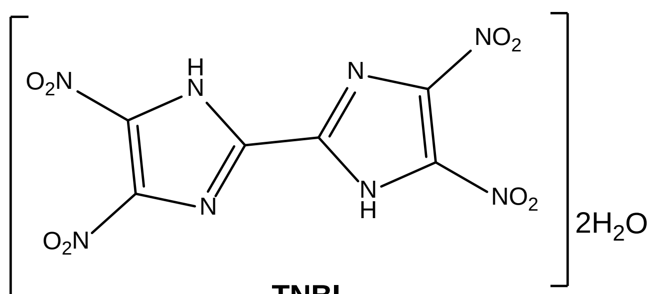
s-TNTC



DNTC



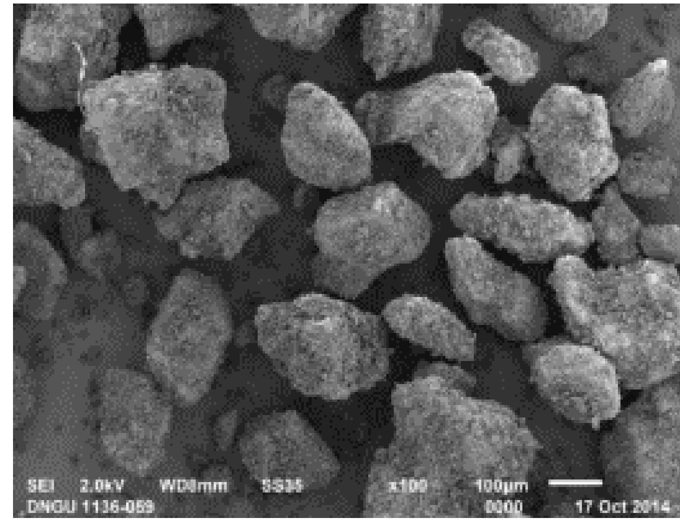
TriNTC

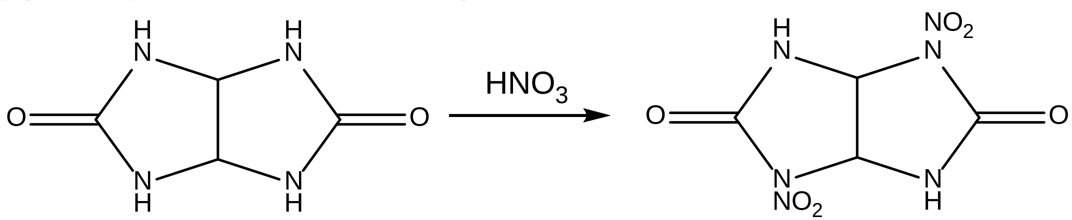


TNBI

DNGU Synthesis and Optimization

- DNGU produced through nitration of glycoluril
  - Glycoluril is commercially available & inexpensive
- DNGU cost estimated to be between RDX and HMX
- DNGU has been synthesized on the pilot scale
- Synthesis process has been optimized:
  - Original DNGU was ~15-20 microns
  - Optimized DNGU much larger (~200-300 microns)
  - Yields typically 90-95% with purities >99%





Glycoluril **DNGU**

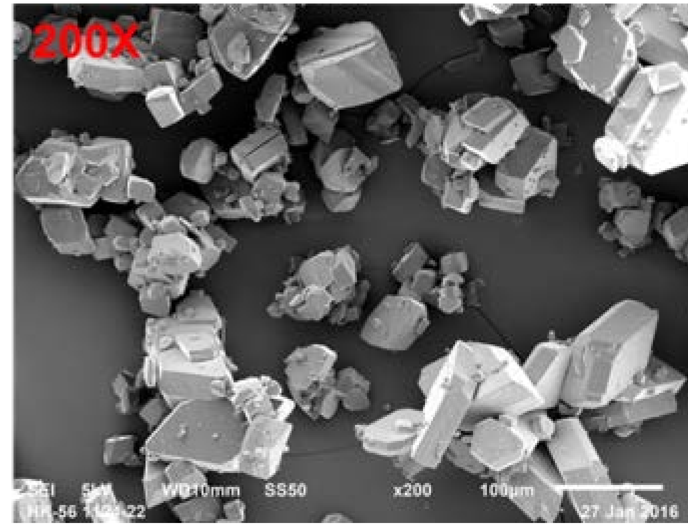
DNGU Properties

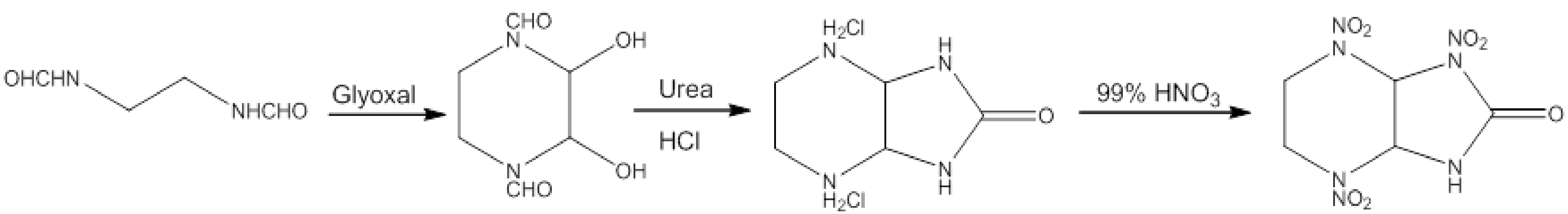
Property	Value
Impact (Naval, cm)	58.64 (18.84)
BAM Friction (N)	>360 (164.0)
ESD (J)	0.0366
DSC Exotherm (°C, 5 °C/min)	241.54
Density (g/cc)	1.94
Heat of Formation (kJ/mol)	-359.4
Oxygen Balance	-27.6
VOD (calcd, km/s)	8.67
CJ Pressure (calcd, GPa)	33.3

- Exceptionally insensitive to impact & friction
- Very high density (similar to HMX)
- Higher DSC exotherm than RDX
- Predicted performance parameters similar to RDX

HK-56 Synthesis

- Simple reactions to produce DHDFP and TABN
  - Commercially available starting materials
  - Yields ~65-70%
- Facile nitration to produce HK-56
- Initial HK-56 particle size quite small (5-10 microns)
  - Plate-like particle shape
- Process improvements yielded larger, more cubic crystals suitable for formulation efforts





EBFA DHDFP TABN HK-56

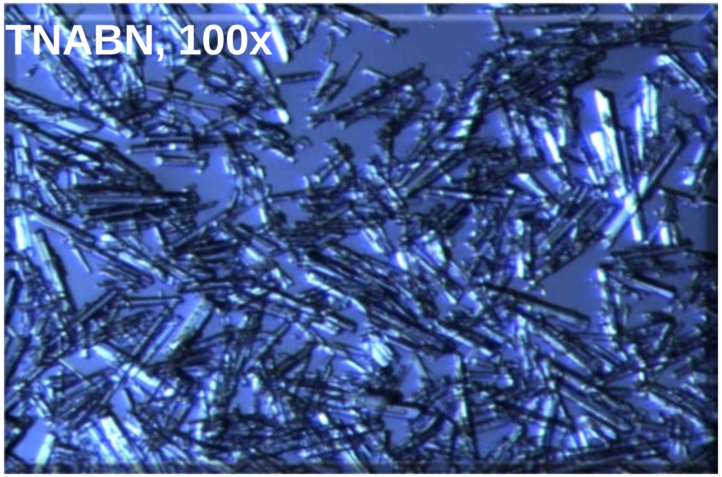
HK-56 Properties

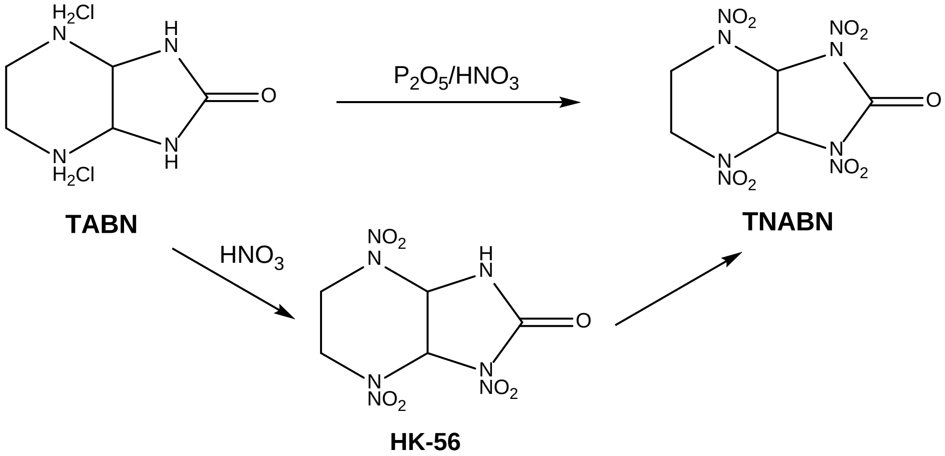
Property	Value
Impact (Naval, cm)	79.35 (56.67)
BAM Friction (N)	>360
ESD (J)	0.0829
DSC Exotherm (°C, 10 °C/min)	203.84
Density (g/cc)	1.86
Heat of Formation (kJ/mol)	-129.9
Oxygen Balance	-37.5
VOD (calcd, km/s)	8.38
CJ Pressure (calcd, GPa)	31.2

- HK-56 is very insensitive to impact, friction and ESD
- Density very similar to RDX
- DSC exotherm similar to RDX
- Predicted performance slightly below that of RDX

TNABN Synthesis & Optimization

- TNABN synthesized from either TABN or HK-56
  - HK-56 nitration yields ~98% pure product
  - HK-56 route is readily scalable
- Multiple crystallizations completed using numerous solvents
  - All yielded highly crystalline needles





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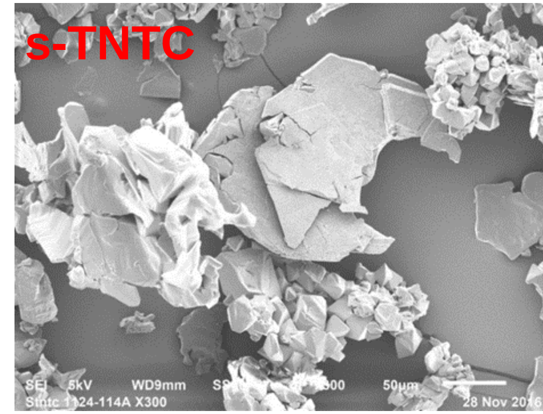
TNABN Properties

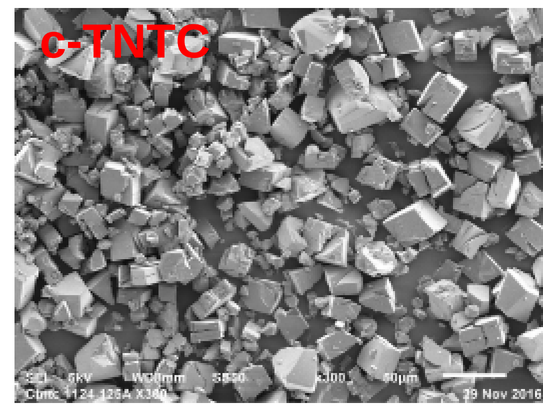
Property	Value
Holston Impact (50%, cm)	20 (51.3)
BAM Friction (N)	132.4 (134.2)
ESD (J)	0.4000 (0.0366)
DSC Exotherm (°C, 10 °C/min)	248.58
Density (g/cc)	1.97
Heat of Formation (kJ/mol)	70.31
Oxygen Balance	-19.9
VOD (calcd, km/s)	9015
CJ Pressure (calcd, GPa)	38.12

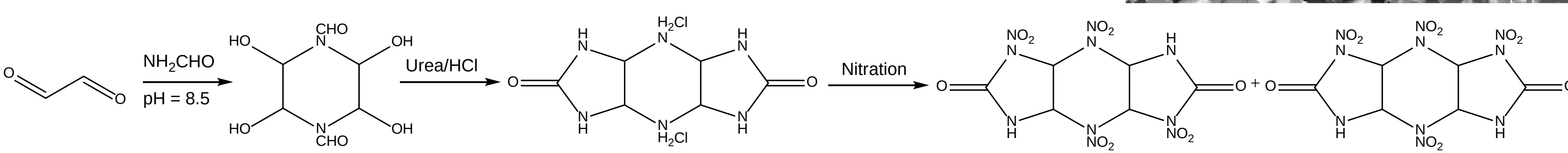
- TNABN very similar to HMX with the following comparable properties:
  - sensitivity
  - DSC exotherm
  - density
  - predicted performance

TNTCs Synthesis

- Precursor THDFP has been produced on the kilogram scale (Gottlieb et al)
- ODPD synthesis process uses inexpensive ingredients
  - Optimization of process needed
- Reaction to product TNTC is uncomplicated using scalable materials
  - Highly pure products can be acquired
  - Optimization of process needed
  - Literature indicates s-TNTC may be a more stable product than c-TNTC
- Overall synthesis route has potential for scalability







THDFP ODPD s-TNTC c-TNTC

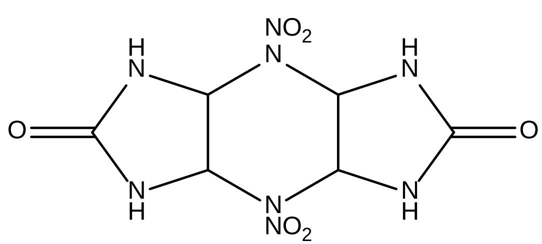
TNTCs Properties

Property	s-TNTC	c-TNTC
Holston Impact (50%, cm)	<12 (33.1)	<12 (33.1)
BAM Friction (N)	301.2 (224.6)	334.0 (224.6)
ESD (J, TIL)	0.0425 (0.0888)	0.0366 (0.0241)
DSC Exotherm (°C, 10 °C/min)	247.73	250.18
Density (g/cc)	1.97	1.96
Heat of Formation (kJ/mol)	-137.7	-163.35
Oxygen Balance	-21.2	-21.2
Predicted VOD (calcd, km/s)	9.02	8.98
CJ Pressure (calcd, GPa)	36.9	37.1

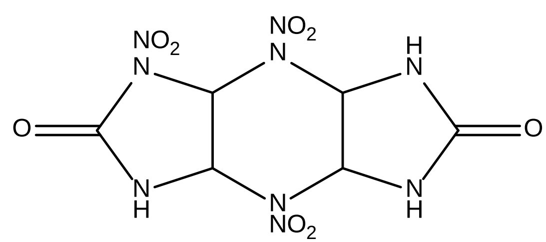
- TNTCs are very sensitive to impact!
- TNTCs are very like HMX in terms of:
  - Density
  - DSC Exotherm
  - Predicted performance

TNTC Intermediates: DNTC & TriNTC

- Two TNTC intermediates were isolated & characterized during TNTCs synthesis activities
- DNTC was previously characterized by Boyer et al.
- DNTC has high DSC exotherm: 311 °C
- TriNTC does not appear in the literature
  - Discovery of TriNTC was surprising & exciting
- TNTC intermediates could be used in the future to selectively produce the TNTCs
- TriNTC predicted performance similar to RDX



DNTC



TriNTC

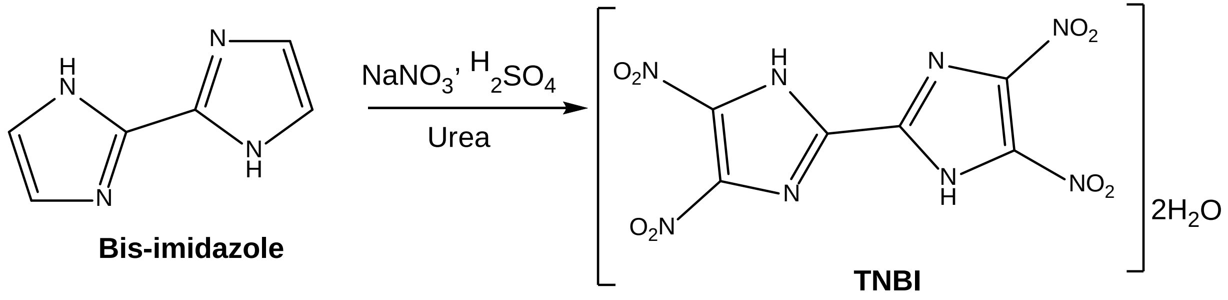
DNTC & TriNTC Properties

Property	DNTC	TriNTC
Holston Impact (50%, cm)	31.9 (41.8)	24.17 (41.8)
BAM Friction (N)	>360 (260.4)	>360 (260.4)
ESD (J, TIL)	0.1375 (0.0241)	0.0738 (0.0241)
DSC Exotherm (°C, 10 °C/min)	311.01	244.3
Density (g/cc)	ND	1.95
Heat of Formation (kJ/mol)	ND	ND
Oxygen Balance	-55.5	-36.0
Predicted VOD (km/s)	7.43	8.13
CJ Pressure (GPa)	ND	ND

- DNTC & TriNTC both fairly sensitive to impact
- TriNTC possesses HMX-like density
- DNTC has a high DSC exotherm; could be useful in applications requiring high thermal stability?

Synthesis of TNBI

- Synthesis of TNBI completed using known synthesis methods
  - Reaction is un-complicated and uses inexpensive ingredients
  - No optimization was completed
- Reaction yield approximately 50-60%
  - In agreement with literature values
- Purification process developed to provide TNBI in 99% organic purity
  - Purification also reduces sulfates content of product



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TNBI Properties

Property	Value
Holston Impact (50%, cm)	60.9 (56.7)
BAM Friction (N)	311.5 (251.1)
ESD (J)	0.1375 (0.1375)
DSC Exotherm (°C, 10 °C/min)	288.9
Density (g/cc)	1.80
Heat of Formation (kJ/mol)	-417.07
Oxygen Balance	-22.8
VOD (calcd, km/s)	8182
CJ Pressure (GPa)	27.86

- TNBI appears to be insensitive to impact and friction
- Density is similar to RDX
- DSC exotherm is higher than RDX
- Performance properties slightly lower than that of RDX

Summary

- Eight orphan explosive compounds were presented
  - All were synthesized through potentially scalable and inexpensive synthesis routes
- DNGU, TNBI and HK-56 have potential applications for insensitive munitions purposes
- TNTCs, TriNTC and TNABN may be suitable for applications requiring higher sensitivity
- DNTC possesses a DSC exotherm above 300 °C
  - Suitable for high temperature applications