Energetic Ingredients Synthesis

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Analytical Requirements-Crystalline Ingredients

- Primary focus of BAE's effort is crystalline energetic ingredients.

- DSC Melting Point and Exotherm Onset Temperature
- ^{1}H
- ^{13}C NMR
- FT-IR
- Small-scale safety Properties vs. RDX Class 5
  - Impact
  - Friction
  - ESD
  - Size distribution of particles (laser diffraction)

- Thermogravimetric Analysis (TGA) (at 5 °/min w/ weight loss)
- Vacuum Thermal Stability (VTS) – ml gas/gram at 100 degrees C for 48 hours
- Approximate Purity (Gas or Liquid Chromatography)
- Density (Gas Pycnometry or Immersion)
- Heat of Formation (theoretical or preferably from heat of combustion)
- DSC compatibility, VTS compatibility and SEM/optical microscopy

Properties	***Method***	***Minimum***	***Maximum***
Density (g/cm^3)	Gas Pycnometry or Immersion	1.7	-
Exotherm Onset	Differential Scanning Calorimetry (DSC)	150°C	-
Thermal Stability	Vacuum Thermal Stability (VTS) (48h@100°C)	-	2cc/gm
Purity	Chromatography (GC or HPLC)	95%	-
Detonation C-J Pressure	Calculated by Cheetah 6.0	30GPa	-
Detonation Velocity	Calculated by Cheetah 6.0	8.0km/s	-

Properties of RDX/HMX Replacement Candidates

Property	RDX	Ditrolone	HK-55	K-56(TNABN)	HCO	$(NH_4)_2BNT$	CBNT
Density (g/cm^3)	1.82	1.91	1.91	1.97	1.96	1.83	1.95
ΔH (kJ/mol)	80.6	79.5		70.31	-	105.8*	47.2*
Det Velocity (m/s)	8850	8870	8631	9015	8839	9407	9399
H_{50} (cm)	26 (2.5 kg)	-	61 (32 for HMX)	115 (2 kg)	-	-	38 (10 kg)

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Properties of RDX Replacement Candidates

Compound	Pros	Cons
TNABN	High density, good performance	Conflicting sensitivity information
HCO	Similar to TNAZ, High density	Unconfirmed synthetic route
Ditrolone	Similar to NTO, reduced water solubility	Stability and performance unknown
BNT salts	Good density, good performance	Material not “mature”
HK-55	High density, good performance	Conflicting sensitivity information

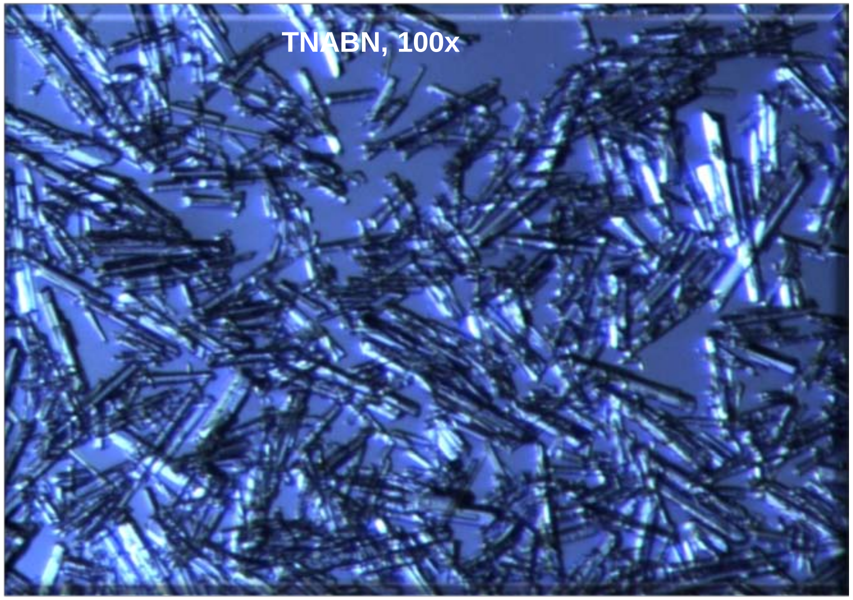
TNABN-Synthesis

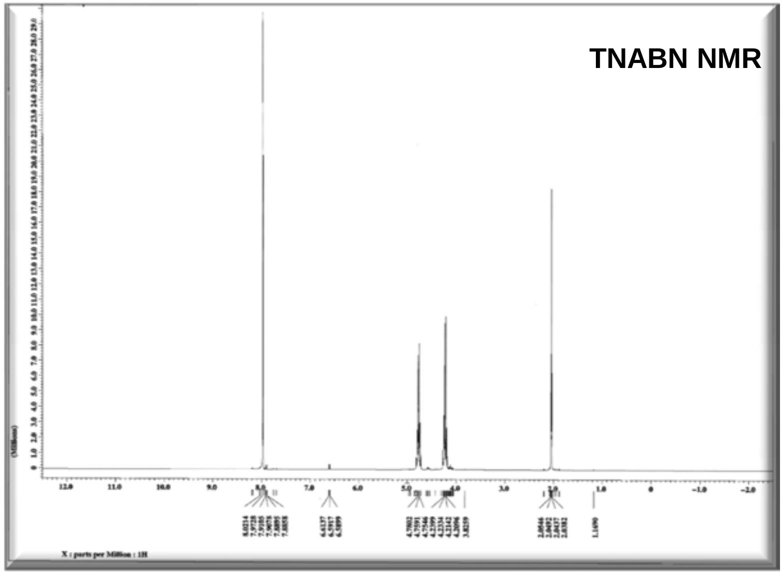
- Syntheses of both DHDFP and TABN proceed smoothly
  - TABN reaction completed at 5 g, 25 g scale and on RC1
  - TABN analyzed via DSC, IC, IR, NMR
- TNABN synthesized from P_2O_5/HNO_3
  - Product pure via NMR
- TNABN also synthesized via HK-56
  - Product ~98% pure via NMR
- Multiple crystallizations completed
  - All yielded highly crystalline needles

TNABN-Analytical

- TNABN has impact sensitivity much lower than RDX (closer to PETN)
- Needle-like form of TNABN crystals may contribute to sensitivity

Material	Holston Impact (50%, cm)	BAM Friction (50%, N)
TNABN	20	132.4
Class 5 RDX	51.25	134.2





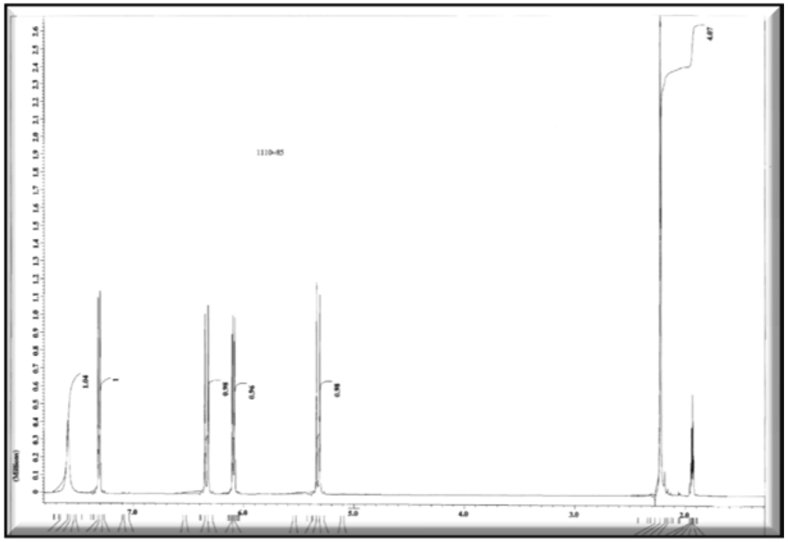
TNABN dropped from program due to poor sensitivity

HK-55-Synthesis

- DHDFI reaction slow with low yield
  - Yield lower than that given in the literature
  - No optimization attempted
- HIID reaction facile but low yielding
  - Yield in line with that given in the literature
  - No optimization attempted
- Nitration of HIID completed using HNO_3/Ac_2O as described in literature by Pagoria
  - Scale up concerns associated with use of this method

HK-55-Synthesis

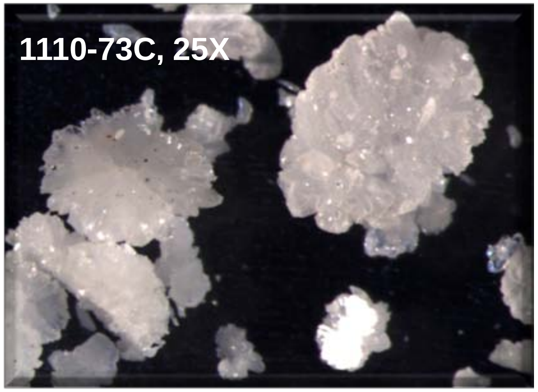
- Second literature process by Boyer, et. al describes nitrosation of HIID followed by nitration with HNO_3
- Nitrosation reaction and nitration both proceed easily as is described in the literature

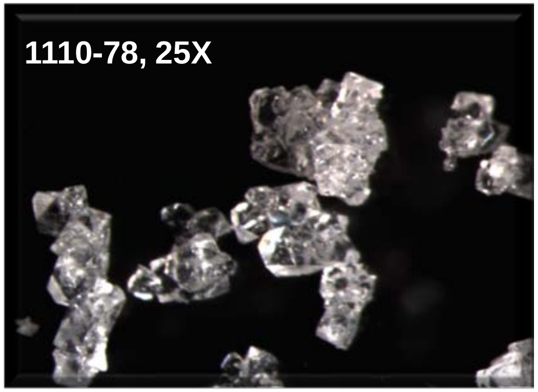


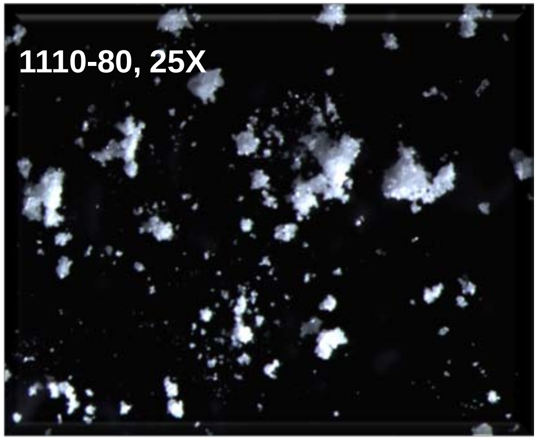
HK-55 NMR

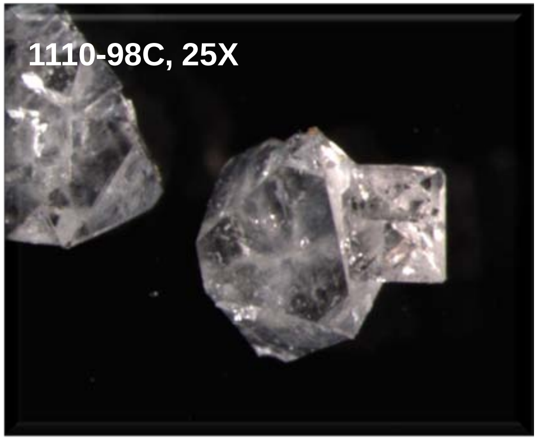
HK-55-Analytical

Sample #	% Purity	Holston Impact (cm)
1110-73C	~99.5	~25
1110-78	99.2	~20-25
1110-86	99. 7	~20
1110-81	98.9	~20-25
1110-86#2	99.4	~20
1110-91C	95.8	~20-25
1110-94C	~98-99	~20-25
1110-101	~98-99	~15-20







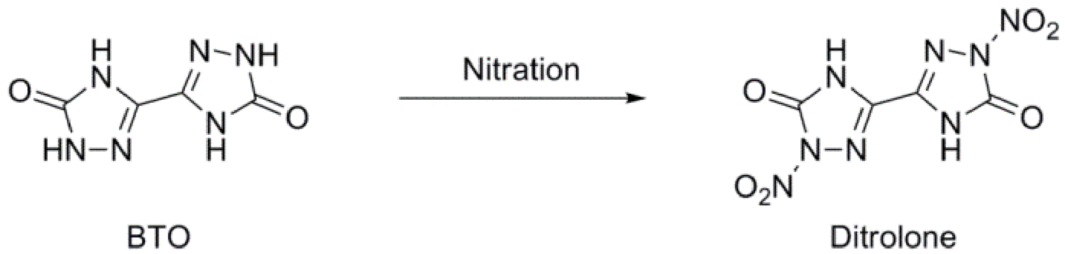


- Crystallizations completed using various conditions
  - Purity not an issue
- Purities determined by NMR and/or HPLC
- Impact testing performed on eight samples
  - Most have PETN-like sensitivity

HK-55 dropped from program due to poor sensitivity

Ditrolone-Background

- Ditrolone has NTO-like structure with improved performance and potentially reduced water solubility
- Ditrolone has not been previously synthesized
- Proposed reaction scheme is similar to the chemistry of NTO:



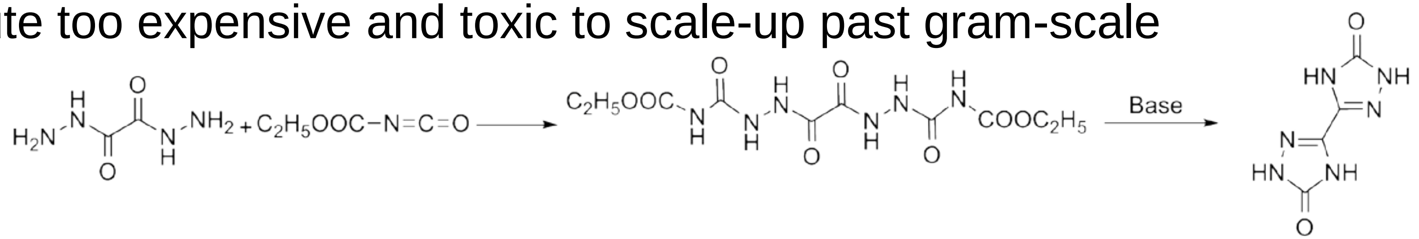
Property	RDX	Ditrolone
Density (g/cm^3)	1.82	1.91[c]
ΔH (kJ/mol)	92.6	79.5[c]
Det Press (GPa)	33.2[c]	34.2[c]
Det Vel (m/s)	8.84[c]	8.87[c]
Impact (J)	7.4	-

C = Calculated

BTO Synthesis

BTO Synthesis #1

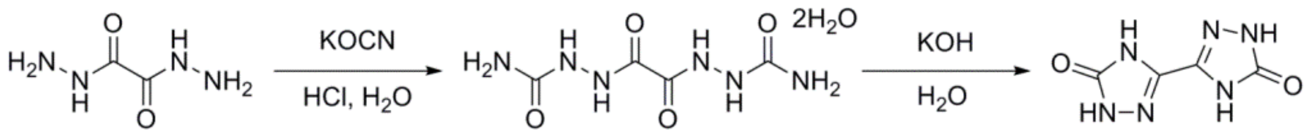
- BTO has been synthesized previously using alternate chemistry (*Acta Poloniae Pharmaceutica* 2001, **58**, 307-311)
- Route too expensive and toxic to scale-up past gram-scale



Oxalyldihydrazide **Ethyl Isocyanantoformate** **BTO**

BTO Synthesis #2

- Another literature method explored (*Justus Liebigs Annalen der Chemie* 1952, **577**, 237-243) which uses potassium cyanate vs ethylisocyantoformate.
- Have synthesized PBTO at 50 gram scale and BTO at 15 gram scale

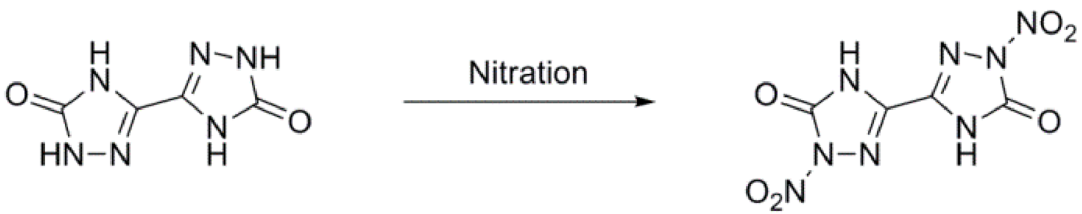


PBTO BTO

Path Forward

Future Work

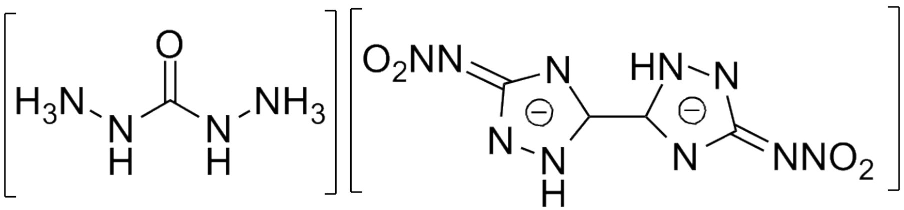
- Currently working on conditions to synthesize Ditrolone on small scale
    - Various nitrating conditions are being explored
- Early reactions will focus on isolating Ditrolone to determine safety, chemical properties, and some small scale performance data



BTO — Ditrolone

Ditrolone still in early development

CBNT-Background



CBNT

Carbonic dihydrazidinium bis[3-(5-nitroimino-1,2,4-triazolate)]

- The amine salts of BNT (bis[3-(5-nitroimino-1,2,4-triazolate)]) are insensitive high-explosives with RDX/HMX performance

- Compounds first reported by Jean'ne Shreeve group at the U. of Idaho (2010)[4]

- CBNT downselected as initial target based upon performance, density and sensitivity

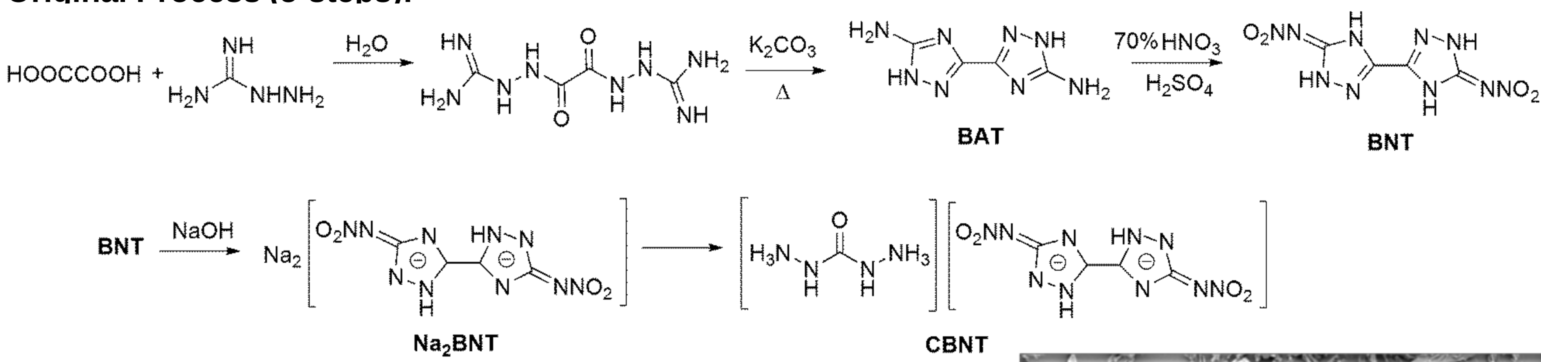
Property	RDX	HMX	CBNT
Density (g/cm^3)	1.82	1.91	1.95
ΔH (kJ/mol)	92.6	104.8	47.2
Det Press (GPa)	35.2	39.6	36
Det Vel (m/s)	8850	9320	9399

Refs:

4. Wang, R.;Xu, H.; Guo, Y.; Sa, R.; Shreeve, J. M. *J. Am. Chem. Soc.* **2010**, *132*, 11904.

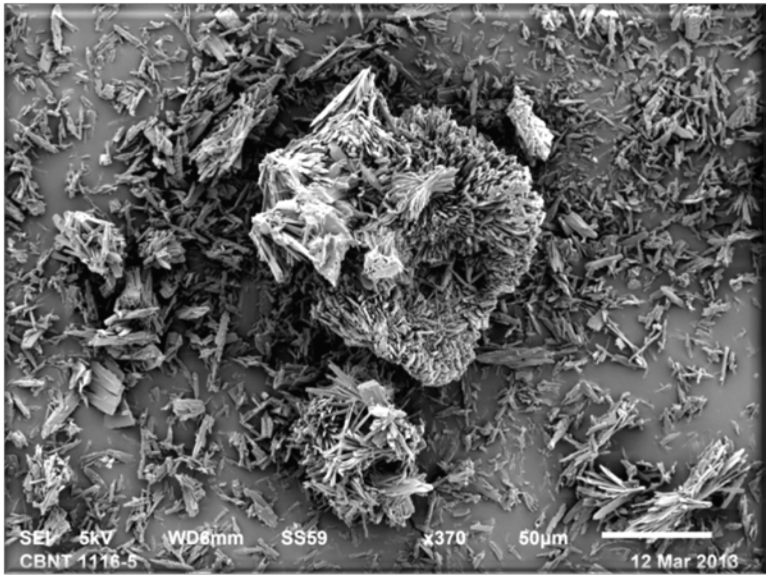
CBNT Synthesis

Original Process (5-steps):



▪Original synthesis showed promise, but there are some issues:

- ▪ Attempts to synthesize BAT by this process failed
- ▪ Moderate exotherm with nitration of BAT in 70% nitric/sulfuric acid
- ▪ Na_2BNT only isolated upon letting the solution sit for a few days
- ▪ Na_2BNT has high solubility in water, giving a low yield



SEM of CBNT Crystals 370x

CBNT

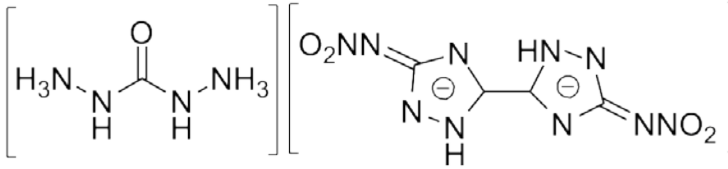
BAE Modified Process (3-steps):

88% **96%**

Current Reproducible Yields: **98%**

- Modified process to reduce steps and improve yield
- Initial and final steps use a one-pot process
- 99% nitric acid for nitration (Increased Yield and Purity)
- Na_2BNT is no longer isolated
- CBNT matches literature IR and DSC (T_d= 220 ^{o}C)
- Confirmed compound by HPLC-MS

CBNT



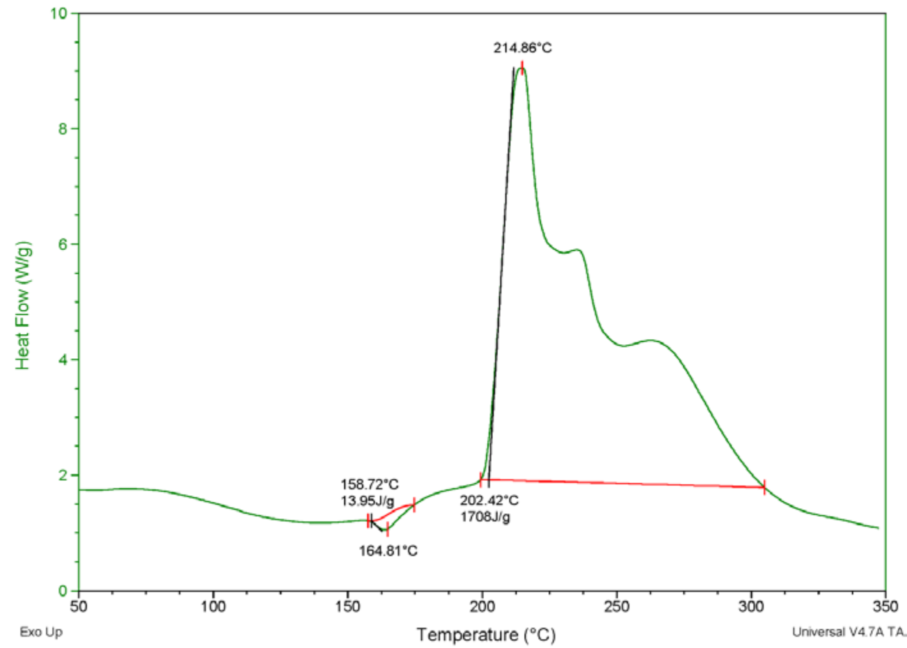
CBNT Advantages

- CBNT has low water solubility
- CBNT has HMX performance but is significantly less sensitive
- Inexpensive starting materials
- High yielding, 3-step synthesis

Chemistry could be readily scaled at HSAAP

Path Forward

- Scale-up of process to 1-kg scale
- Compatibility testing
- Formulation effort with CAB and other binders
- Critical diameter and performance testing
- Particle size and shape modification



Property	RDX	HMX	CBNT
Density (g/cm^3)	1.82	1.91	1.95
Impact (cm)	44	31	>85
Friction (N)	160	186	216

>100 g of CBNT have been produced by BAE Systems

Conclusions

- **TNABN** was synthesized using two different processes
  - Product has needle crystal morphology
  - Impact sensitivity comparable to that of PETN
- **HK-55** also synthesized using two different processes
  - Product has impact sensitivity similar to PETN
  - Various crystallization processes attempted in order to reduce sensitivity
    - Particle size and purity changes did not affect sensitivity
  - Tested impact sensitivity for both materials did not match literature values
- **Ditrolone** is still in early phases of development and evaluation
- **CBNT** is showing great promise as a new energetic ingredient with:
  - Good insensitivity
  - Good performance
  - Simple synthesis route

50-, 100-, and 200-gal reactors in new R&D pilot facility at HSAAP!

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