# ENERGETIC INGREDIENTS RESEARCH FOR FREEDM PROGRAM

## 2015 Insensitive Munitions & Energetic Material Technology Symposium

## ROME, ITALY

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## ABSTRACT

ARDEC's FREEDM program (Future Requirements of Enhanced Energetics for Decisive Munitions) encompasses a wide array of requirements and technologies for explosives and propellants. BAE Holston (BAE Systems at Holston Army Ammunition Plant) has been tasked with developing energetic ingredients for this program, specifically to support the explosives portion of the effort. Crystalline ingredients, to potentially replace RDX in future munitions, are a major focus of this project. The efforts to date by BAE Systems include research on HK-55, TNABN, BNT salts, DNP, and Ditrolone. These ingredients are being evaluated for ease of producibility and sensitivity characteristics, primarily impact and friction sensitivity in the early phases of the program. The compounds being studied could also find use in propellant applications as well and will be considered.

Another focus of the program is to develop novel formulations to generate IM compliant Octol and PBXN-9 replacements. Novel formulation candidates have been developed using the various input ingredients described above and evaluated for processability, sensitivity and explosive performance. Explosive performance has been characterized by LSGT, detonation velocity and plate dent testing.

This paper describes lab-scale synthesis and formulation of the listed ingredients including justifications and rationale for evaluating these materials, technical challenges encountered with the synthesis efforts, and preliminary testing results.

## 1. INTRODUCTION

The overall goal of the FREEDM (Future Requirements of Enhanced Energetics for Decisive Munitions) program is to provide insensitive, green energetic materials, enabling the capability to increase the lethality, range, precision, and utility of munitions while providing focused and variable effects through tailored energy release. General products being considered as part of this program include: Higher energy density multi-purpose IM explosives for anti-armor and blast-frag warhead applications; extended range propulsion system prototypes; novel processing and precision coating techniques for highly efficient progressive charges; energetic technologies for focused & tailored energy release on target; and novel materials to enable and compliment next generation IM initiation and ignition systems

BAE SYSTEMS Ordnance Systems has been manufacturing RDX and HMX explosives and their derivatives at Holston Army Ammunition Plant (HSAAP) for over 70 years. Recently, new types of insensitive explosive ingredients such as DNAN, NTO, TATB, and NQ were added to the product portfolio. Although RDX and HMX are established, powerful explosive ingredients, there is an ever-growing need for IM explosives. Several methods are in development for achieving IM response (particle modification, new binders, packaging, etc.); however, a dramatic improvement in IM can be achieved if the main component of a formulation (RDX, HMX) can be replaced with a new less-sensitive (but with equivalent performance) explosive molecule. Most new IM energetic molecules developed in recent times lack the power of RDX and, especially, HMX. This program aims to address this inadequacy through novel molecules and/or novel synthesis routes as part of the FREEDM program.

## 2. Energetic Ingredient Synthesis Overview

A goal of this program is to synthesize a new, low cost energetic material that is less sensitive than traditional explosives (RDX, HMX) while maintaining performance. Candidate compounds will be evaluated as many other molecules that are determined to fit the criteria (inexpensive, scalable, and insensitive). The central idea is to find cheap materials and use them to build energetic materials as opposed to most approaches involving extensive theory, modeling, and calculations to design a molecule and then painstakingly synthesizing the target compound. The downselected materials will be synthesized in the lab on a small scale in order to provide enough material for initial characterization. Materials found to be acceptable will be scaled up to larger lab scale in order to determine the ease of manufacture and the projected cost of manufacture. The synthesis approach will be developed with the intent of utilizing the existing production scale infrastructure at Holston AAP for scale-up, minimizing the capital cost for implementing the new process, and hence the product cost for the new material. The large lab scale process will provide sufficient material to allow additional characterization and optimization of the synthesis process.

The FREEDM program looked at a total of 10 energetic ingredients at BAE Systems. The ingredients were downselected because of their calculated performance, reported insensitivity, and potential for scale-up. Four of those compounds will be highlighted in this paper as shown in Figure 1 with some basic pros and cons described in Table 1.

**Figure 1**

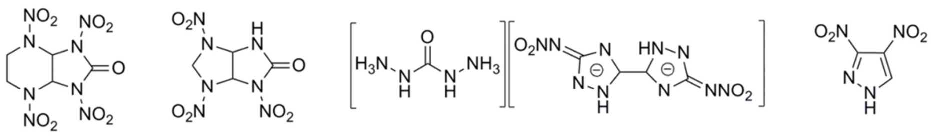



**Table 1**

| Compound | Pros | Cons |
|---|---|---|
| **TNABN** | High density, good performance | Conflicting sensitivity information |
| **HK-55** | High density, good performance | Conflicting sensitivity information |
| **CBNT** | Good density, good performance | Material not mature |
| **DNP** | Melt-pour candidate with Comp-B performance | Availability of starting material |

### 2.1 Synthesis of TNABN

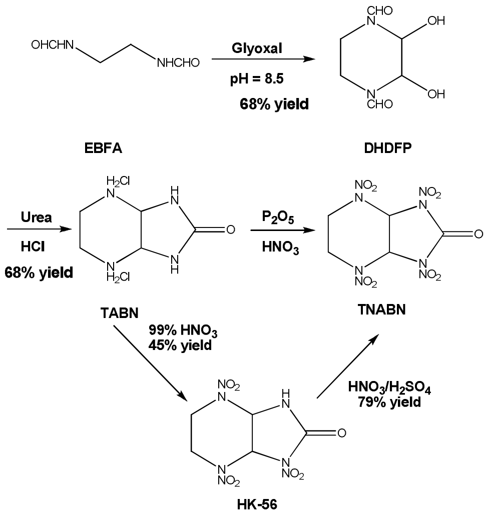
TNABN is a relatively new high-explosive with calculated performance between RDX and HMX. However, there is conflicting information about impact sensitivity data in the literature. As shown in Table 2, there is a report that the impact sensitive of TNABN is ~115 cm, however other reports have the impact sensitivity closer to RDX or worse.

**Table 2**

| Property | RDX | HMX | TNABN |
|---|---|---|---|
| Density ($g/cm^3$) | 1.82 | 1.91 | 1.97 |
| $\Delta H_f$ (kJ/mol) | 92.6 | 104.8 | 70.31 |
| Det. Pressure (GPa) | 35.2 | 39.6 | - |
| Det. Vel (m/s) | 8850 | 9320 | 9015 |
| Impact $H_{50}$ (cm) | 26 | | >80 |

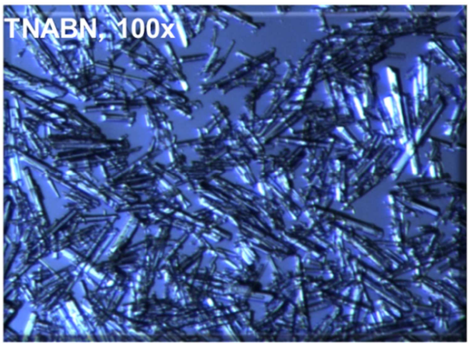
TNABN is synthesized in either a 3- or 4-step reaction from ethylene bisformamide. TNABN was successfully synthesized from the intermediate TABN directly using a $P_2O_5/HNO_3$ mixture or through the HK-56 intermediate as shown in Figure 2. Both routes produce TNABN in high yield and purity.

**Figure 2**




Multiple recrystallizations of TNABN were attempted, although all batches yielded crystalline needles as shown in Figure 3. It was found that TNABN has impact sensitivity much lower than RDX (closer to PETN). The needle-like form of TNABN crystals may contribute to the sensitivity.

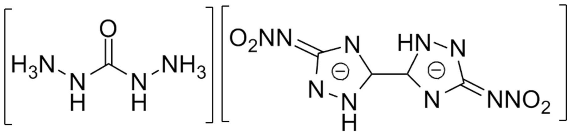
**Figure 3**



## 2.2. Synthesis of CBNT

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 in 2010. Of the energetic salts reported, CBNT (Figure 4) was downselected as an initial target based upon performance, density and sensitivity.

**Figure 4**



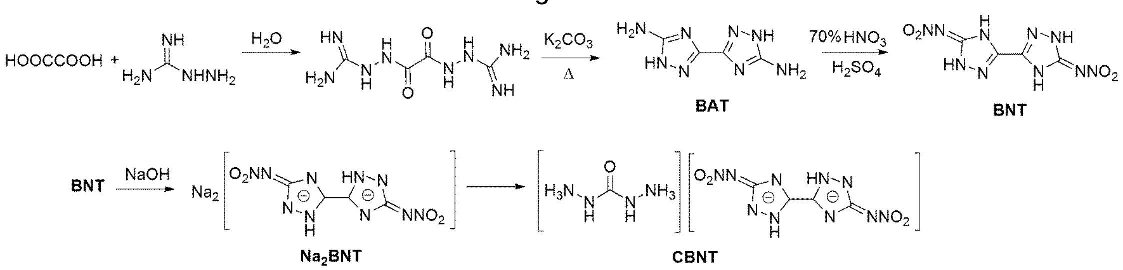
The reported performance and sensitivity of CBNT are shown in Table 3 based upon a measured density of 1.96 g/mL. Based upon CHEETAH calculations, CBNT is expected to have a detonation velocity greater than HMX, but a detonation pressure between RDX and HMX.

**Table 3**

| Property | RDX | HMX | CBNT |
|---|---|---|---|
| Density ($g/cm^3$) | 1.82 | 1.91 | 1.95 |
| ΔH (kJ/mol) | 92.6 | 104.8 | 47.2 |
| Det. Pressure (GPa) | 35.2 | 39.6 | 36 |
| Det. Vel (m/s) | 8850 | 9320 | 9399 |
| Impact $H_{50}$ (cm) | 26 | | >80 |

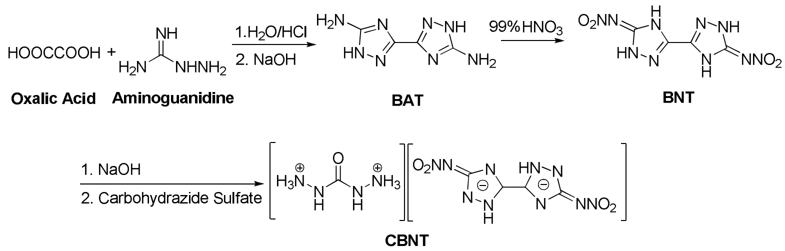
Original synthesis showed promise, but there were some issues: (a) Attempts to synthesize BAT by this process failed; (b) Undesirable exotherm observed with nitration of BAT in 70% nitric/sulfuric acid; (c) $Na_2$BNT only isolated upon letting the solution sit for a few days; (d) $Na_2$BNT has high solubility in water, giving a low yield. The original synthesis is shown below in Figure 5.

Figure 5




A modified process was developed in order to reduce steps and improve yield. The initial and final steps were modified to use a one-pot process. Strong (99%) nitric acid was used for the nitration in order to increased yield and purity. The CBNT synthesized matches literature IR and DSC and the compound was confirmed HPLC-MS. The optimized process is shown below in Figure 6.

**Figure 6**




CBNT is a very IM energetic salt with HMX performance, inexpensive starting materials, can be produced in a high yielding 3-step synthesis, and has chemistry that can be readily scaled at HSAAP. To date, over 500-g of CBNT has been produced by BAE Systems. The path forward for this compound includes scale-up of the process to the kg-scale and a formulation effort with CAB and other binders. The formulated material will be subjected to critical diameter and the full array of IM and performance testing.

### 2.3 Synthesis of DNP

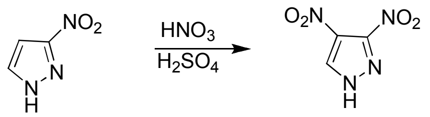
DNP (3,4-dinitropyrazole) is an IM melt-pour base with measured explosive performance greater than Composition B. DNP is synthesized from 3-NP in one-step reaction, which should give an inexpensive product upon further scale-up. The IM and performance data is summarized in Table 4.

**Table 4**

| Property | Comp. B | DNP |
|---|---|---|
| Melting Point (°C) | 80 | 87 |
| Density ($g/cm^3$) | 1.68 | 1.79 |
| Exotherm Onset (°C) | | 276 |
| Impact Sensitivity $h_{50\%}$ (cm) | 75 | 147 |
| VOD (m/s) | 7960 | 8115 |
| Detonation Pressure (GPa) | 29.2 | 29.4 |
| Oxygen Balance (%) | -43.0 | -30.4 |
| ERL Impact (cm) | 59 | 67 |

The lab-scale synthesis of DNP has been developed previously at BAE Systems and ARDEC, with batches as large as 5-lbs produced on the lab-scale. The current program involves the scale-up and IM explosive testing of DNP. The synthesis of DNP is shown below in Figure 7.

**Figure 7**




3-Nitropyrazole (3-NP) 3,4-Dinitropyrazole (DNP)

As measured, DNP is insensitive to impact, friction, and ESD with performance exceeding Comp-B. It is synthesized from inexpensive starting materials (pyrazole) and can be produced in a high yielding, 1-step synthesis with chemistry that can be readily scaled at HSAAP. The synthesis process is currently ready for pilot-plant scale-up. There is also an ongoing formulation effort  currently ongoing, with DNP formulations predicted to have exceptional IM and performance characteristics. As shown in Table 5, a DNP/RDX formulation is calculated in CHEETAH to have performance greater than PBXN-9.

**Table 5**

| | Density (g/cc) | Pressure (GPa) | Det. Velocity (m/s) | Energy of Det. (kJ/cc) |
|---|---|---|---|---|
| DNP:RDX (60:40) | 1.80 | 31.5 | 8,460 | 9.7 |
| PBXN-9 | 1.6 | 30.3 | 8,450 | 9.4 |

## 3. CONCLUDING REMARKS

ARDEC's FREEDM program  encompasses a wide array of requirements and technologies for explosives and propellants.  BAE Systems Holston has developed the chemistry of a number of novel energetic ingredients for this program in order to replace legacy ingredients such as RDX, HMX, and TNT. The efforts to date by BAE Systems include research on HK-55, TNABN, CBNT, and DNP. These ingredients are being evaluated for ease of producibility and sensitivity characteristics, primarily impact and friction sensitivity in the early phases of the program.  The compounds being studied could also find use in propellant applications as well.

## 4. ACKNOWLEDGEMENTS

The author would like to thank and acknowledge Kelly Guntrum, Robyn Wilmoth, Dr. Jeremy Headrick, Denise Painter, Matt Hathaway, Brian Alexander, all of BAE Systems, for their hard work, input and support on this program.   We would also like to thank Anthony Di Stasio, Catherine Maier,  Dr. Paul Anderson and Dr. Alex Paraskos, and all of ARDEC, for funding, guidance and support for this program.