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A Novel Energetic Dinitrobenzofuroxan: Trinitrobenzene Co-crystal

by
Lawrence Baldwin, Thomas Groshens, Kenneth Young,
Andrew Nelson, Nicholas Zurn, and Lee Cambrea
Chemistry Division
Research and Engineering Group

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NAVAL AIR WARFARE CENTER WEAPONS DIVISION
CHINA LAKE, CA 93555-6100

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FOREWORD

This report documents efforts by personnel at the Naval Air Warfare Center Weapons Division (NAWCWD) China Lake to develop insensitive munitions via energetic co-crystallization. This final report, completed in fiscal year 2017 (FY17), was funded by the Office of Naval Research (ONR) In-House Laboratory Independent Research (ILIR) program.

Approved by	Under authority of
A. VAN NEVEL, Head	W. S. DILLON
Research and Engineering Group	RDML, U.S. Navy
19 November 2018	*Commander*

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14. ABSTRACT

(U) A 1,3,5-Trinitrobenzene (TNB):4,6-Dinitrobenzofuroxan (DNBF) energetic co-crystal has been prepared by three methods: its sensitivity to friction, shock, and impact are reported. Also, its thermal properties have been determined. The co-crystal forms in a 1:1 ratio through primarily hydrogen-bonding and π–stacking interactions. Its single crystal X-ray structure contains alternating bilayers of TNB and DNBF, with TNB having non-centrosymmetric V-shaped troughs.

15. SUBJECT TERMS
1,3,5-Trinitrobenzene, 4,6-Dinitrobenzofuroxan, Co-crystallization, Differential Scanning Calorimetry, DNBF, DSC, TNB

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INTRODUCTION

Explosives development is generally accomplished via the synthesis of new nitro-group containing targets based upon calculated predictions of properties or intuitiveness. Only explosive materials with specific properties are useful for military applications, with the main considerations being explosive power and cost, and the major constraint being safety. Therefore, although numerous compounds have been synthesized, the vast majority are not fit for incorporation into weapons systems.

Crystal engineering uses knowledge of structure-property relationships between inter- or intra-molecular constituents to allow for the design of novel crystalline, self-assembled systems. The presence of strong associative interactions, caused by ionic or polar substituents on a molecule for example, allow for the prediction of if, and how, the crystal may self-assemble. Crystallization of two or more materials—co-crystallization—can generate a new material that has different melting point, solubility, and thermal and chemical characteristics compared to its individual components (Reference 1).

Specific to energetics, co-crystallization can potentially provide vast improvements in desired properties such as oxygen balance, sensitivity, and processibility (solubility and stability to binder formulations). In 2011, Matzger reported the growth of a co-crystal containing trinitrotoluene (TNT) and hexanitrohexaazaisowurtzitane (CL-20) (Reference 2). It crystallizes primarily via hydrogen bonding between the nitro-group oxygens of TNT and aliphatic protons of the CL-20, as well as via interactions between the nitro-groups of CL-20 with the electron-deficient aromatic ring of TNT. The co-crystal was found to have a density (1.84 grams per cubic centimeter [g/cm^3]) located between that of its individual components (ε-CL-20, 1.95 to 2.08 g/cm^3 and TNT, 1.71 g/cm^3), and an impact sensitivity (h 50%=99 centimeters [cm]) that is half as sensitive as ε-CL-20 (h 50%=47 cm).

In 2012, Matzger (Reference 3) successfully grew a co-crystal of CL-20 and cyclotetramethylene tetranitramine (HMX) that showed a favorable density of 2.01 g/cm^3 (related to explosive power) that is near that of CL-20 but decreased impact sensitivity compared to neat CL-20 (Reference 3). He surmised that the decrease in impact sensitivity was a result of increased hydrogen bonding within the co-crystal as opposed to simple dilution by the less sensitive HMX. His research results have become a major impetus for the current growing interest in the co-crystallization of energetics.

In order to increase the current knowledge base regarding energetic co-crystals, this report presents the preparation and characterization of a novel, one-to-one, energetic co-crystal-1,3,5-Trinitrobenzene (TNB):4,6-Dinitrobenzofuroxan (DNBF) (Figure 1). TNB and DNBF are similar in that they are both electron acceptors and each contain benzene rings. DNBF can be considered a derivative of TNB in that, when compared to TNB, DNBF has an additional nitrogen atom that acts as a bridge between a benzene ring carbon and an oxygen atom from an adjacent nitro-group (Figure 1). TNB and DNBF have detonation velocities of 7,280 and 7,700 meters per second (m/s), respectively (Reference 4). They also have comparable impact sensitivities and measured densities. DNBF is considered a sensitive secondary explosive with impact and electrostatic sensitivities comparable to that of cyclotrimetheylenetrinitramine (RDX) and tetryl (Reference 5). Herein, we report the preparation and characterization of a 1:1 TNB:DNBF co-crystal.

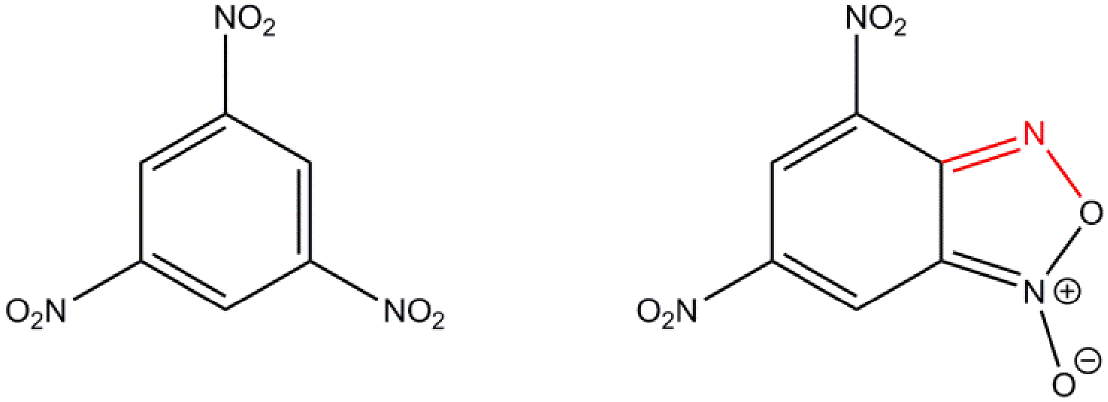

FIGURE 1. Molecular Structures of TNB (Left) and DNBF (Right).

The DNBF-TNB co-crystals can be prepared by three methods. They can be grown from evaporation acetonitrile solution, grown from a melt, or produced via resonance acoustic® mixing (RAM), all from an initial 1:1 ratio of TNB to DNBF. Powder X-ray diffraction patterns for the co-crystals are displayed in Figure 2 (a through c). All peaks are located in identical positions in all three cases. The identical location of the peaks indicates the presence of the same material. Preferred orientation accounts for the observed differences in peak intensities (Figure 2a versus 2b and 2c). The crystals produced via RAM and the melt have powder peaks with similar intensities, thus, similar directional growth. However, the crystals produced from RAM are very fine and generate broader powder peaks upon analysis, whereas those prepared from the melt have sharp, well-defined peaks that are indicative of long-range order.

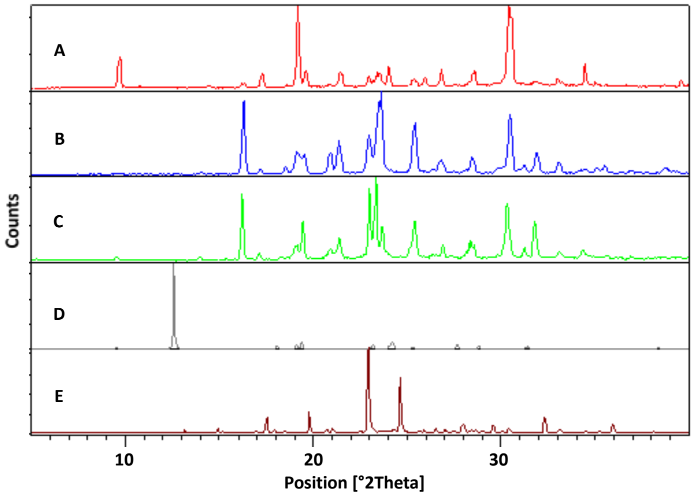

FIGURE 2. X-ray Diffraction Powder Patterns of TNB-DNBF Prepared by (a) Co-crystallization from Acetonitrile (Top), (b) RAM, and (c) Melt. Patterns (d) and (e) are neat DNBF and TNB, respectively.

Differential Scanning Calorimetry (DSC) data for the co-crystal is presented in Figure 3. The co-crystal melts at 143.3°Celsius (C), whereas the melting points of TNB and DNBF are 121.5°C and 168 to 172°C, respectively. The autoignition temperature of the co-crystal (268.2°C) is the same as that of DNBF alone.

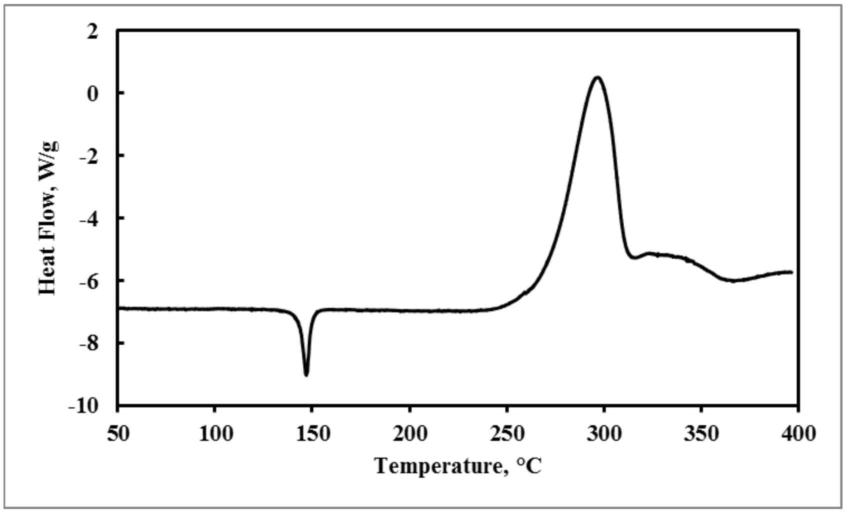

FIGURE 3. DSC of TNB-DNBF Co-crystal.

Preliminary safety data for the co-crystal are shown in Table 1. The co-crystal is considerably less prone to ignition by impact compared to DNBF alone, and it appears to have friction sensitivity that is below our instrument’s capabilities.

TABLE 1. Explosive Properties.

Property	TNB:DNBF	DNBF	TNB	PETN
Electrostatic sensitivity	No fires 0.25 J	No fires 0.25 J	No fires 0.25 J	No fires 0.25 J
Friction (50% Pt)	No fires 1,000 pounds (lbs)	No fires 1,000 lbs	No fires 1,000 lbs	244 lbs
Impact Sensitivity $h_{50\%}$	39 cm	20 cm	49 cm	10 cm

PETN = pentaerythritol tetranitrate.

Although the orthorhombic TNB-DNBF co-crystal's density value would be expected to fall between the individual component's density values, it is instead the same as DNBF alone (1.76 g/cm^3). TNB itself has a density value of 1.69 g/cm^3.* The co-crystal is composed of alternating bilayers of each component (Figures 4 and 5). The DNBF molecules display a staggered zig-zag motif relative to the AB plane (Figure 4), whereas TNB is arranged in staggered V-shaped troughs relative to the BC plane (Figure 5), with alternating layers pointing in the same direction.

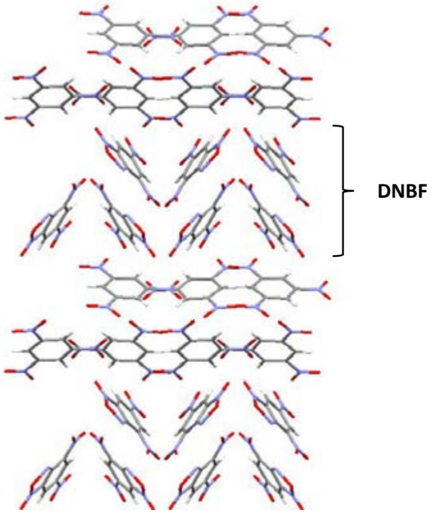

FIGURE 4. Crystal Packing of DNBF-TNB. The AB plane is horizontal to the page.

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*A single crystal of approximate dimensions 0.064 millimeter (mm) x 0.210 mm x 0.222 mm was purged cooled with a nitrogen stream at 100 K throughout data collection. Data were collected on a Bruker Smart Apex single crystal X-ray diffractometer using Mo-Kα radiation (λ = 0.71073Ǻ) and processed using Bruker Saint software. Data were refined using SHELXL-2013. Experimental summary: chemical formula-C12H5N7O12, formula weight 439.23, unit cell dimensions a = 9.3609(5) Ǻ, b = 18.4354(9) Ǻ, c = 9.5968(5) Ǻ, temperature 100K, crystal system orthorhombic, space group Pca21, number of formula units in cell 4, linear absorption coefficient 0.162 mm-1, number of measured reflections = 18280, independent reflections = 3079, observed reflections 2769 (89.93%) greater than 2σ(F^2), final R_{int} = 3.51%, R1 = 4.67%, and wR2 = 13.14%.

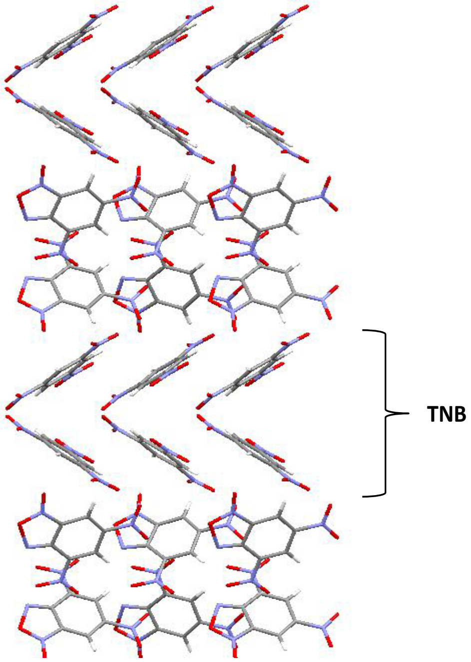

FIGURE 5. Crystal Packing of DNBF-TNB After 90-Degree Rotation.
The BC plane is horizontal to the page.

Atomic assignments for the DNBF-TNB co-crystal are given in Figure 6. Intermolecular hydrogen bonding is observed between H4 and O9 of TNB (2.349 Ǻ), O2 of DNBF and H5 of TNB (2.426 Ǻ), H1 of DNBF and O12 of TNB (2.438 Ǻ), and slightly between H2 on DNBF and O6 from a nitro-group on DNBF (2.501 Ǻ) (Figure 7).

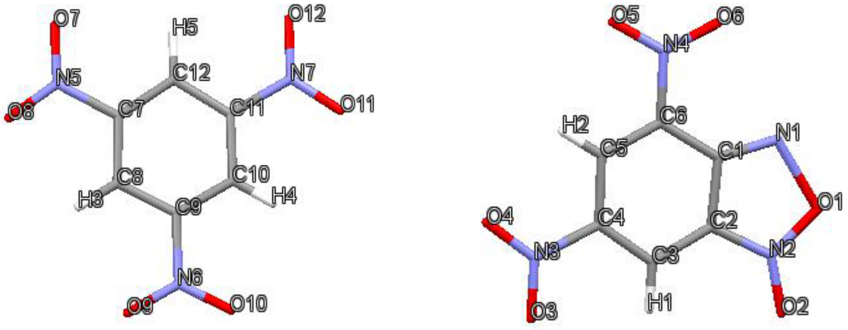

FIGURE 6. Atomic Assignments for Co-crystal Components.

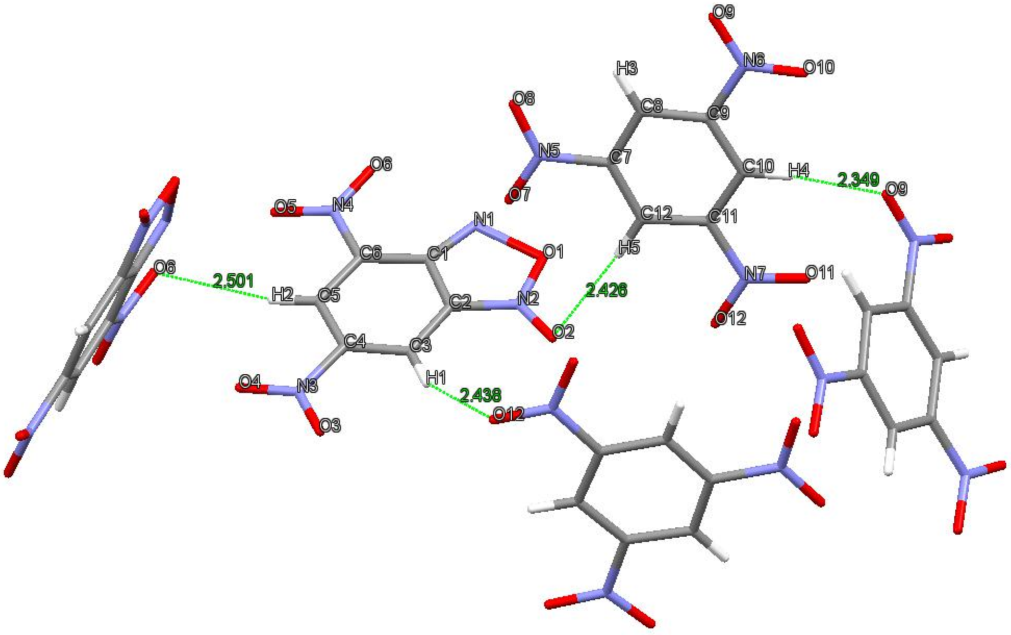

FIGURE 7. H-Bonding in Co-crystal.

Select bond lengths and angles for DNBF of the co-crystal and neat DNBF are shown in Table 2. The intramolecular non-bonding distance between N1 and O6 of DNBF in the co-crystal (2.71 Å) is slightly larger than DNBF itself (2.63 Å) (Reference 6). The most significant differences compared to neat DNBF are observed for the C1-N1-O1-N2 furan atoms (lengths and angles) and the angle made by C6-N4-O6. Dissimilarities of the furan ring could be a result of the O1 oxygen having short non-bonded contacts to O5 on the nitro-group of the nearest DNBF molecule (2.938 Å vs. 3.04 Å) and to a lesser extent an O1 short non-bonded contact to a nitro-group oxygen (O7) on TNB (3.006 Å) (Figure 8). The widening of angle C6-N4-O6 is likely caused by hydrogen bonding between O6 to H2 (Figure 8).

TABLE 2. Select Bond Angles and Interatomic Distances for DNBF of DNBF:TNB Co-crystal and Neat DNBF From Crystallographic Data.

Crystal	DNBF:TNB	DNBF[a]
N1-O1-N2	102.2	107
C1-N1-O1	105.8	108
C2-C1-N1	110.5	110
C1-C2-N2	111.2	107
C2-N2-O1	110.3	109
C6-C1-N1	132.9	135
C3-C2-N2	124.4	125
C6-N4-O6	118.2	114
C1-N1	1.255	1.37(2)
N1-O1	1.694	1.42(2)
N2-O1	1.321	1.41(2)
C2-N2	1.399	1.40(2)
N2-O2	1.195	1.22(2)
C1-C2	1.407	1.40(2)
N1-O6 (non-bonded)	2.717	2.63(2)
C1-C6	1.405	1.36
C5-C6	1.367	1.40

[a] Reference 6.

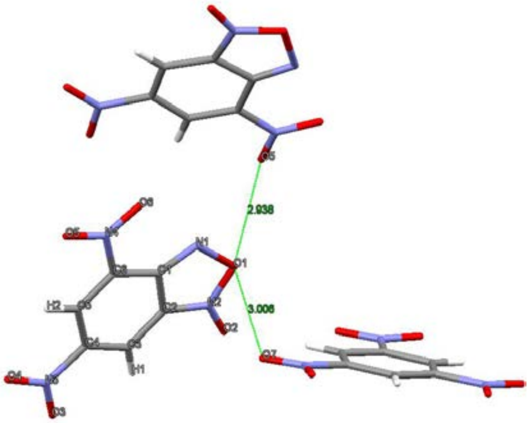

FIGURE 8. Furan Oxygen Close Contacts in Co-crystal.

Neat crystalline TNB was first reported to exist primarily in a centrosymmetric form where V-shaped troughs were observed in alternating layers but pointing in opposite directions (Reference 7). More recently, a non-centrosymmetric polymorph of TNB was found to exist where the V-shaped troughs pointed in the same direction (Reference 8). The growth of the crystal was promoted by addition of trisindane. The author reported that this polymorph was only observed once and could not be grown again after numerous attempts using various solvents. This non-centrosymmetric motif can be repeatedly observed in the DNBF:TNB system.

CONCLUSION

In conclusion, a novel energetic cocrystal—DNBF:TNB—has been discovered. The co-crystal has been prepared from solvent evaporation, RAM, and melt. The TNB is present as V-shaped troughs pointed in the same direction and DNBF moieties assembled in a zig-zag formation, roughly 90 degrees from the troughs. The co-crystal's impact sensitivity is much better than DNBF alone, but the density is the same as DNBF, which may imply that detonation velocity has not been altered; therefore, co-crystallization of these species may have led to a more stable energetic with no loss in power.

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NOMENCLATURE

C	Celsius
CL-20	hexanitrohexaazaisowurtzitane
cm	centimeters
DNBF	4,6-Dinitrobenzofuroxan
DSC	Differential Scanning Calorimetry
g/cm^3	grams per cubic centimeter
HMX	cyclotetramethylene tetranitramine
ILIR	In-house Laboratory Independent Research
lbs	pounds
m/s	meters per second
mm	millimeters
ONR	Office of Naval Research
ORTEP	Oak Ridge Thermal Ellipsoid Plot Program
PETN	pentaerythritol tetranitrate.
RAM	Resonant Acoustic® Mixing
RDX	cyclotrimetheylenetrinitramine
TNB	1,3,5-Trinitrobenzene
TNT	trinitrotoluene

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