Short Communication

Preparation and Performance of a BTF/DNB Cocrystal Explosive

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Abstract: An energetic cocrystal containing benzotrifuroxan (BTF) and 1,3-dinitrobenzene (DNB) in 1:1 molar ratio was prepared by slow evaporation of solvent. The structure of the cocrystal was determined by single crystal X-ray diffraction (XRD). It belongs to the monoclinic crystal system with space group $P2_1/c$. The performance of the cocrystal was evaluated on the basis of thermolysis, impact sensitivity, and detonation properties. Differential scanning calorimetry (DSC) revealed that the cocrystal has a melting point of 130 °C, which is an increase of 38 °C compared to pure DNB; the decomposition temperature is similar to that of pure BTF. The cocrystal exhibits an impact height with 50 % ignition probability of 88 cm, suggesting a substantial reduction in impact sensitivity compared to pure BTF. Furthermore, the cocrystal is predicted to have a detonation velocity of about 7373 m s^{-1} and a detonation pressure of about 24 GPa, respectively, indicating excellent detonation performance.

Keywords: Cocrystal explosive · BTF · DNB · Preparation · Performance

1 Introduction

In modern battlefield environments, weapon systems must meet a series of stringent performance criteria including low sensitivity, high stability and high detonation velocity, resulting in development of insensitive high explosive (IHE) [1,2]. However, there is a contradiction between the power and safety of energetic materials. Powerful explosives usually have lower safety and vice versa [3]. The combination of high performance and low sensitivity has become a main challenge for the further application and development of explosives.

In the past, various approaches to modify the properties of explosives including crystallizing with solvents and coating with polymers have been adopted (see Refs. [4–9]). Unfortunately, these traditional methods hardly produced remarkable improvements on the performances of existing explosives, since the inherent structures of the molecules remained unchanged. Cocrystallization has emerged as a potential method for tuning the properties of existing explosives. Recent developments revealed that cocrystallization generates solid explosives with different properties compared to their pure educts and is therefore of interest for scientists in the field of energetic materials [10–15].

Recently, a HNIW-BTF energetic cocrystal with improved performance relative to pure BTF has been reported [16]. BTF (Figure 1) is a high energy primary explosive with high nitrogen content and high density, which is used in detonators. However, it is relatively sensitive to impact and friction, which limits its further applications [17,18]. Unlike HNIW, DNB has a low melting point and a low sensitivity, but poor detonation performances (low detonation velocity and detonation pressure) [19]. Stimulated by recent developments of energetic cocrystals, it was concluded that cocrystallizing HNIW with BTF may reduce the sensitivity of BTF and improve the energy of DNB.

In this work, a BTF/DNB cocrystal explosive was prepared by cocrystallization through slow evaporation of the solvent. The structure of the cocrystal was characterized by single crystal X-ray diffraction (XRD). Additionally, the performance of the cocrystal including thermolysis, sensitivity, and detonation properties is presented herein.
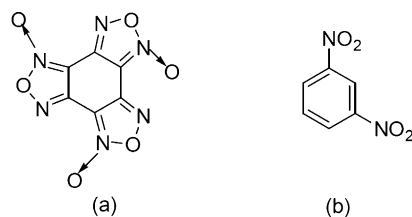

Figure 1. Molecular structures of (a) BTF and (b) DNB.

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2 Experimental Part

2.1 Materials

BTF was synthesized according to the method reported in Ref. [17]. DNB was obtained from Mianyang Rongsheng Chemical Co., Ltd. The other chemicals and reagents used in the present study were purchased from trade without further purification.

2.2 Preparation of BTF/DNB Cocrystal Explosive

A mixture of DNB (168 mg) and BTF (252 mg) (molar ratio 1:1) was added to ethanol (50 mL) and mildly heated until all BTF and DNB had dissolved. The solution was evaporated slowly at room temperature over several days. A light yellow prism-like cocrystal with 300 μm diameter was obtained. This BTF/DNB cocrystals were also produced from alternative solvents, such as methanol or acetone.

2.3 Single-crystal X-ray Diffraction

XRD data were collected with a Bruker D8 Advance diffractometer using Cu-K_α radiation ($\lambda = 1.54056$ Å) at 35 kV and 40 mA. The sample was placed onto a glass circular sample holder and revealed with a glass slide. The sample was scanned within the scan range of $2\theta = 5°$ to $45°$ continuous scan with a step size of $0.015°$ and a scan speed of 0.2 s per step.

2.4 Structural Characterization

A single crystal of BTF/DNB cocrystals was chosen and purged with a cooled nitrogen gas stream at 293 K throughout the data collection. X-ray diffraction data were collected with an Xcalibur Eos CCD detector with graphite-monochromated Mo-K_α radiation ($\lambda = 0.071073$ nm) and processed using Olex2 software. The crystal structure was solved by direct methods and SHELX was used for structure solution and least-squares refinement. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined using the riding model [20–22]. In addition, it is noTable that the BTF molecule has a serious disorder, resulting in two molecular orientations [16].

2.5 Thermal Analysis

Differential scanning calorimetery (DSC) was performed with a TA Q100 instrument. 1–2 mg of BTF/DNB cocrystals were heated from 50 to 350 °C at a heating rate of 10 K min^{-1} in a nitrogen atmosphere (50 mL min^{-1}).

2.6 Impact Sensitivity

Impact sensitivity tests were conducted with a WL-1 type impact sensitivity instrument according to GJB-772A-97 standard method 601.2 [23]. The test conditions are: drop weight 2 kg; sample mass 30 mg. The impact sensitivity of each test sample was expressed by the drop height with a 50% explosion probability (H$_{50}$).

2.7 Detonation Performance Prediction

The detonation velocity and detonation pressure for the cocrystals and pure components were predicted according to the method reported in Ref. [24].

3 Results and Discussion

3.1 XRD Patterns of the BTF/DNB Cocrystal and the Pure Components

The X-ray diffraction patterns of the BTF/DNB cocrystal, BTF, and DNB are shown in Figure 2. There are obvious differences in their XRD curves. New strong peaks in the XRD pattern of the cocrystal indicate that there is only a cocrystal and not a mixture of cocrystal and pure components.

3.2 Structure of the BTF/DNB Cocrystal

The crystal structure of the BTF/DNB cocrystal was identified by XRD. The molecular and 3D structures are shown in Figure 3 and Figure 4, respectively.

The BTF/DNB cocrystal (in a 1:1 molar ratio) crystallizes in the monoclinic system with $P2_1/c$ space group. As shown in Figure 3, the asymmetric unit consists of each one molecule of BTF and DNB. The crystallographic data are as follows: $a = 0.93622$ nm, $b = 1.3005$ nm, $c = 1.4911$ nm, $\alpha = 90°$, $\beta = 96.072°$, $\gamma = 90°$. In the molecular cluster with a radius of 1 nm obtained from the experimental BTF/DNB cocrystal super cell, three types of intermolecular interac-
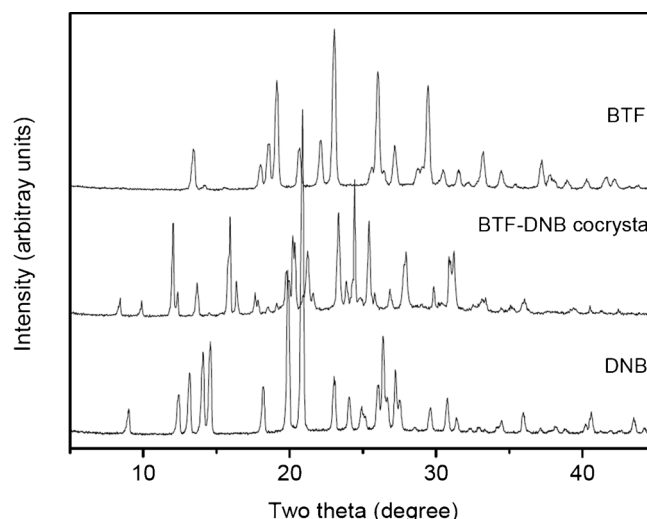

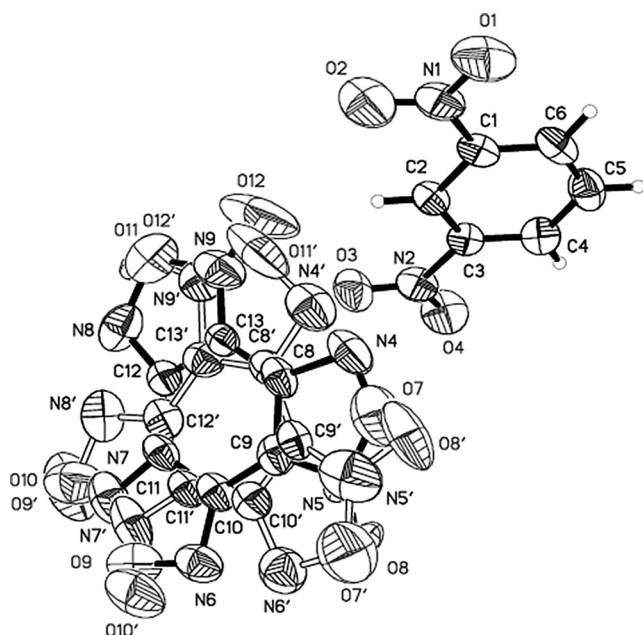**Figure 2.** XRD patterns of the BTF/DNB cocrystal and pure components.

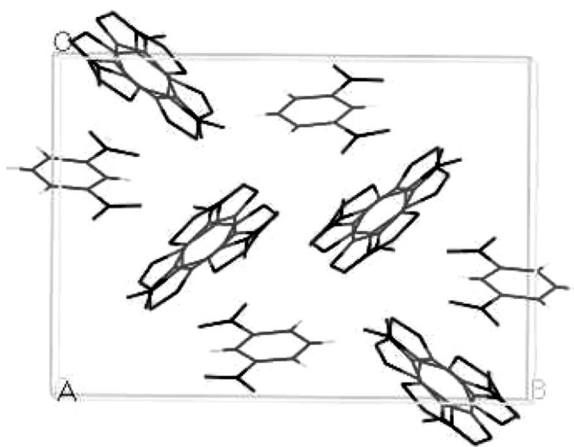**Figure 3.** Molecular structure of the BTF/DNB cocrystal.

Figure 4. 3D packing of the BTF/DNB cocrystal.

tions were found as shown in Figure 5. A weak π interaction between an electron-rich nitro group of the DNB molecule and the big electron-poor ring of the BTF molecule is shown in Figure 5a. As shown in Figure 5b, one C–H···N intermolecular hydrogen bond occurs between a nitrogen

atom of the BTF ring and a hydrogen atom of the DNB molecule. Additionally, hydrogen bonding occurs between the H(C) atom of the DNB molecule and the oxygen atom of the BTF molecule (see Figure 5c).

The BTF/DNB cocrystal has a density of 1.763 g cm^{-3} at 293 K, which is between the densities of BTF (1.901 g cm^{-3}) and DNB (1.571 g cm^{-3}) [25, 26], but obviously higher than that of pure DNB. The density change implies that some properties of the cocrystal might change with respect to the pure components.

3.3 Thermal Analysis

The thermal properties of the BTF/DNB cocrystal were investigated by DSC and the result is shown in Figure 6. A narrow endothermic peak appears at 130 °C, corresponding to the melting point of the cocrystal, which is substantially 68 °C lower than the melting point of BTF ($T_m = 198$ °C) [26] and 38 °C higher than the melting point of DNB ($T_m = 92$ °C) [26]. The results indicate that the melting point can be remarkably changed with respect to pure components through cocrystallization. In addition, a strong exothermic peak occurs at 286 °C, which is attributed to the decomposition of the cocrystal. The decomposition temperature of the cocrystal is close to the decomposition temperature of BTF ($T_{decomp} = 289$ °C) [26] and 152 °C lower than the decomposition temperature of DNB ($T_{decomp} = 438$ °C) [26]. There-
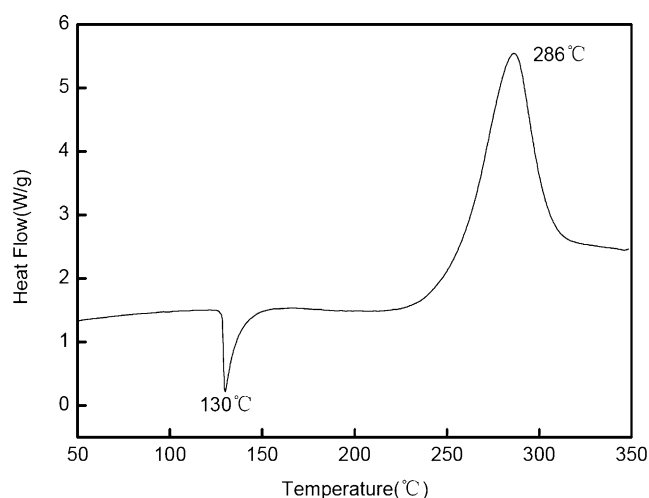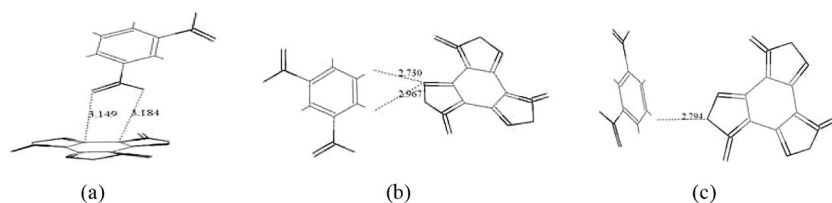

Figure 6. DSC curve of the BTF/DNB cocrystal.

Figure 5. Interactions between BTF and DNB in the cocrystal.

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Table 1. Detonation performance of the BTF/DNB cocrystal and the pure components.

Samples	Density [a] [g m^{-3}]	Detonation performance	
		Detonation velocity [m s^{-1}]	Detonation pressure [GPa]
BTF	1.901	8425 [8582] [b]	34.3 [35.5] [b]
DNB	1.571	5836 [6050] [b]	14.1 [15.6] [b]
Cocrystal	1.735	7373	24.4

a) Crystallographic density at room temperature. b) Experimental values from Ref. [26] are given in square brackets.
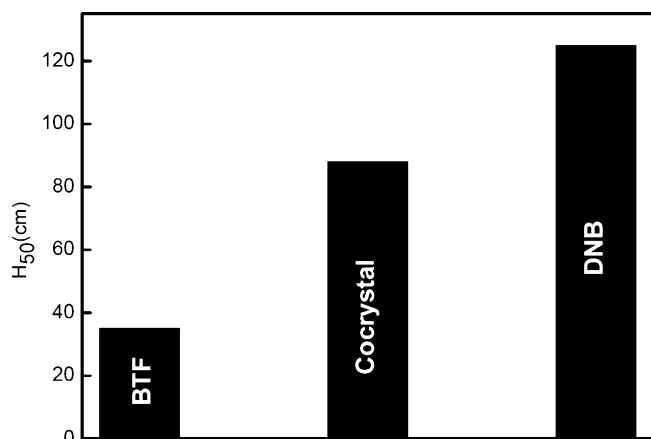
Figure 7. Impact sensitivity data for the BTF/DNB cocrystal and the pure components.

fore, it is concluded that cocrystallization might be able to alter the melting point and the decomposition temperature of explosives. By selecting appropriate constituents, cocrystallization can presumably offer an opportunity to adjust the thermal behavior of energetic materials as needed.

3.4 Impact Sensitivity

The impact sensitivity of the BTF/DNB cocrystal and the pure components, expressed by the drop height of 50% explosion probability (H_{50}), are presented in Figure 7. The cocrystal exhibits a H_{50} of 88 cm, which is more than twice the value of pure BTF ($H_{50} = 35$ cm), suggesting a substantial decrease in the impact sensitivity compared to that of pure BTF. Hydrogen bonds in the cocrystal may play an important role in hindering the formation of hot spots due to an effective dissipation heat through hydrogen bonds, thus causing a reduction of the explosive ignition probability of the cocrystal. Moreover, intermolecular interactions like hydrogen bonds improve the stability of the cocrystal. Furthermore, an explosive with reduced sensitivity can be obtained by cocrystallizing a sensitive explosive with an insensitive explosive.

3.5 Detonation Performance Prediction

To study the detonation performance of the BTF/DNB cocrystal and the pure components, the detonation velocity and the detonation pressure were predicted by the method reported in Ref. [24]. The results are summarized in Table 1.

Cocrystallization can obviously improve the detonation performance. From Table 1 it can be seen that the cocrystal has a detonation velocity of 7373 m s^{-1}, which is 1537 m s^{-1} higher than the detonation velocity of pure DNB. The predicted value is lower than the experimental values of BTF and DNB. However, compared to pure DNB, the detonation velocity and the detonation pressure of the cocrystal are significantly higher, suggesting that the cocrystal may exhibit excellent detonation performance. It can be explained by the fact that the BTF/DNB cocrystal has higher density through cocrystallization in comparison to pure DNB. The results indicate that cocrystallization offers a potential method to tune the properties of existing explosive for achieving explosives with higher density.

4 Conclusions

A 1:1 BTF/DNB cocrystal explosive was prepared by slow evaporation of the solvents. This cocrystal is mainly formed by CH···N and CH···O hydrogen bonds, and π interactions. The cocrystal has a melting point of 130 °C and an exothermic decomposition point of 286 °C. Sensitivity tests indicated that the cocrystal exhibits significantly reduced impact sensitivity with an H_{50} of 88 cm through cocrystallizing with DNB. Further, the cocrystal is predicted to exhibit more excellent detonation performances relative to pure DNB. In summary, cocrystallization is an effective method to achieve explosives with improved performance.

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