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Preparation and Performance of BTF-DNAN Cocrystal Explosive

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Abstract: A novel cocrystal explosive composed of benzotrifuroxan (BTF) and 2,4-dinitroanisole (DNAN) in a 2∶1 molar ratio was prepared by an evaporation solvent method, its structure was characterized by the single crystal X-ray diffraction (SXRD) and the impact sensitivity was studied as well. Results show that the cocrystal explosive belongs to monoclinic system with $P21/c$ space group. The cocrystal displays an H_{50} of above 112 cm, indicating lower sensitivity compared to pure BTF.

Key words: cocrystal explosive; benzotrifuroxan(BTF); 2,4-dinitroanisole(DNAN); safety

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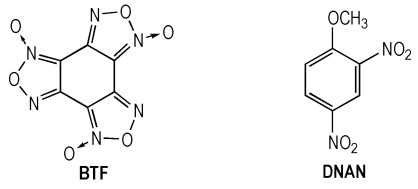
1 Introduction

Energetic materials (Ems) are widely used in military and civilian applications such as the weapons, aerospace explorations and fireworks. However, the inherent safety-power contradiction of existing explosives remains a long-standing problem in the EM field, which limits their practical use.

For a long time, the modifications of existing explosives have often focused mainly on recrystallizing with solution and coating with polymer in order to obtain EMs with lower sensitivity[1-4]. However, these traditional methods can't markedly reduce the sensitivities of existing explosives with only modifying morphology or diluting power due to unchanging the inherent structures of explosive molecules. Recently, the co-crystallization has received a great deal of attention as a potential method of modifying the properties of existing EMs. The physicochemical properties, safety and detonation properties of HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), 2,4,6,8,10,12-hexanitrohexaazaisowurtz-Itane (CL-20) and BTF were changed by co-crystallization[5-10]. In our previous work, CL-20/TNT (2,4,6-trinitrotoluene) and CL-20/DNB (1,3-dinitrobenzene) cocrystals were obtained with good comprehensive properties[11-12]. Results indicate that co-crystallization offers a new opportunity to modify the performances of EMs, since it can endow co-crystals with unique structures and novel properties relative to their pure components. In order to fatherly seek for other co-crystal explosives, the benzotrifuroxan (BTF)/2,4-dinitroanisole (DNAN) cocrystal was studied in this work.

2 Preparation and Characterization of Cocrystals

BTF in Scheme 1 is an important hydrogen-free explosive, belonging to furazan class with high nitrogen content. It possesses high density and excellent detonation performance with high detonation velocity and detonation pressure. But it is sensitive to impact and friction. Besides, it has a difficulty in charge due to its poor flowability and low bulk density. These mainly drawbacks have limited its further application in insensitive ammunitions. On the contrary, DNAN in Scheme 1 has low density, low melting point and poor detonation performance. But it features low sensitivity to impact or friction and low production cost. It is widely used in melt-cast explosives as melt cast binders. Therefore, co-crystallization BTF with DNAN may hopefully tune their safety-power properties and put insights into cocrystal explosive design. In this work, we present a novel energetic-energetic cocrystal composed of BTF and DNAN in a 2∶1 molar ratio. The structure, safety and detonation performance of the cocrystal were studied as well.



Scheme 1 Molecular structures of BTF and DNAN

The BTF-DNAN cocrystal was prepared by cocrystallization from saturated organic solutions through slow evaporation solvents such as ethanol, methanol. The cocrystal obtained from ethanol in good flowability presents prisms with integrated crystal surfaces (see in Fig.1). And it can be easily distinguished from pure BTF and DNAN by their different morphologies. Additionally, according to the experiment, we found the cocrystals grown from ethanol solution with high quality.

Powder X-ray diffraction (PXRD) patterns of the BTF-DNAN cocrystal and pure components are presented in Fig.2. It can be observed that the PXRD pattern of the cocrystal is evidently different from those of pure BTF and DNAN, indicating a new crystalline phases. Moreover, the melting point of the cocrystal is 132 ℃ (confirmed by a Buchi-545 melting point analyzer), which is substantially higher than that of pure DNAN (95 ℃, measured by a Buchi-545 Melting Point analyzer), but obviously lower than that of pure BTF (197 ℃,

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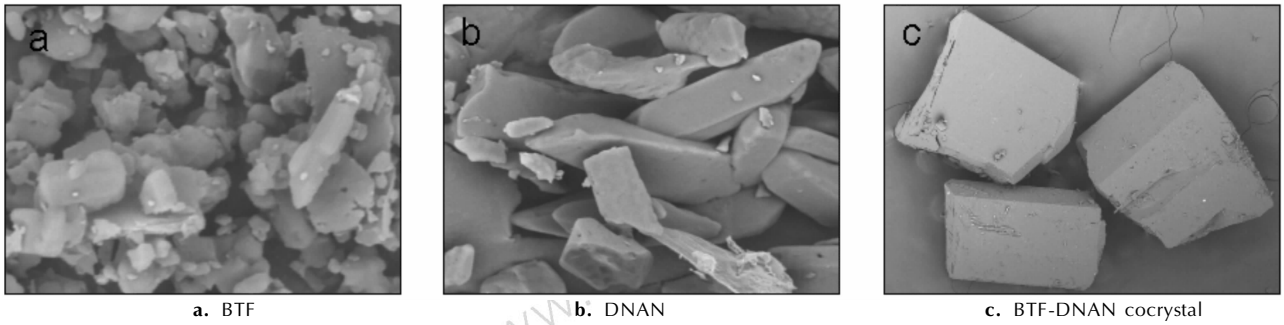
measured by a Buchi-545 Melting Point analyzer), suggesting that drastically altered melting points can be achieved by co-crystallization.

The single crystal X-ray diffraction (SXRD) analysis of the BTF-DNAN cocrystal confirms that it belongs to monoclinic system with $P21/c$ space group, and as shown in Fig. 3, its asymmetric unit consists of two BTF molecules and one DNAN molecule.



a. BTF **b.** DNAN **c.** BTF-DNAN cocrystal

Fig. 1 SEM images for BTF, DNAN and BTF-DNAN cocrystal

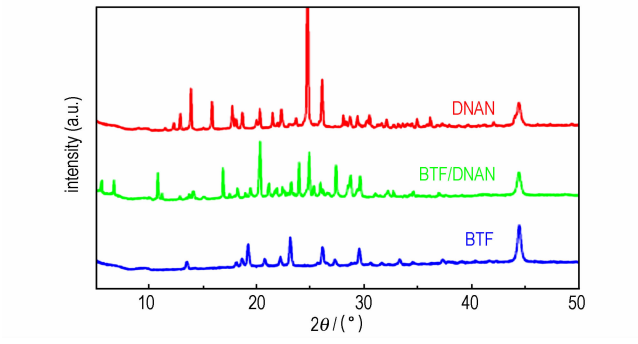


Fig. 2 PXRD patterns for BTF, DNAN and BTF-DNAN cocrystal

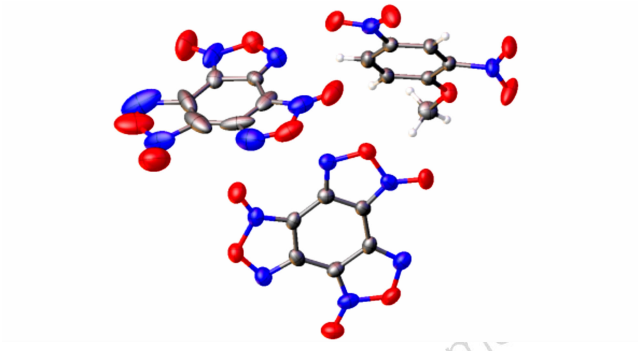


Fig. 3 Molecular structure of BTF/DNAN cocrystal

Crystal structure analysis shows that BTF and DNAN molecules are mainly stacked by lots of CH···N hydrogen bonds between the H(C) atom of the DNAN molecule and a nitrogen atom of the BTF molecule. Distances in the observed range are within the region for hydrogen bonds of this type. Besides, π interaction lies between an electron-rich nitro group of the DNAN molecule and the big electron-poor ring of the BTF molecule. As a result, these intermolecular interactions promote BTF-DNAN cocrystal formation.

The impact sensitivity of each test sample was expressed by the drop height of 50% explosion probability (H_{50}) according to GJB-772A–1997 standard method 601.2. An H_{50} of 34 cm, was measured for pure BTF while the BTF-DNAN cocrystal presents an H_{50} of above 112 cm, which is more than three times of the pure BTF, indicating that cocrystal displays enhanced safety to impact compared with pure BTF. Moreover, the sensitivity of pure BTF was substantially reduced by co-crystallizing with insensitive DNAN, potentially promoting the applications for BTF in insensitive munitions. Through co-crystallization, therefore, it is possible to tune performances of existing EMs and achieve higher density explosives with enhanced properties.

3 Conclusions

We have prepared and characterized a novel furazan-aromatic cocrystal explosive composed BTF and DNAN in a 2∶1 molar ratio. This cocrystal was formed by unique C—H···N hydrogen bonds, and π interactions, foreseeing that some of new cocrystal explosives stacked by the similar intermolecular interactions may be discovered in future. The alterations in structure ultimately produce unique properties in the cocrystal, with respect to the pure components. In particular, BTF-DNAN cocrystal features lower sensitivity to impact relative to pure BTF. Our investigations on the energetic-energetic cocrystal of the BTF-DNAN provide a promising way to tune properties of the existing explosives.

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BTF-DNAN 共晶炸药制备与性能

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摘 要: 采用溶剂挥发方式制备出苯并三氧化呋咱(BTF)和2,4-二硝基苯甲醚(DNAN)以2∶1(摩尔比)结合形成的新型共晶炸药。BTF-DNAN共晶的结构通过单晶衍射表征,同时研究了共晶撞击感度。结果表明,BTF-DNAN共晶属于单斜晶系,*P*21/*c*空间群。共晶的撞击感度特性落高 H_{50} 大于112 cm,较单组分BTF,显著降低了撞击感度。

关键词: 共晶炸药; 苯并三氧化呋咱(BTF); 2,4-二硝基苯甲醚(DNAN); 安全性
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《硼的点火和燃烧》新书简介

《硼的点火和燃烧》由浙江大学能源清洁利用国家重点实验室周俊虎教授、刘建忠教授等含能材料研究专家共同撰写,该书由中国科学院科学出版基金资助,科学出版社出版。

硼的点火和燃烧等相关研究是固体推进技术的关键科学问题。本书结合浙江大学长期在金属燃料(铝、镁、硼、锌)燃烧,煤粉燃烧,催化燃烧,燃烧过程数值计算,燃烧诊断等方面开展的大量研究工作,对硼的点火和燃烧进行了深入的研究。既论述了原理性的基础科学研究,又讨论了实际应用中的工艺和工程问题。

全书共分九章,系统地介绍了硼颗粒及含硼燃料的物理化学特性、点火燃烧特性及其促进方法,点火和燃烧理论模型、微尺度下点火燃烧特性。涉及多种实验技术、测试技术、数值计算技术和化学建模方法,涵盖了含硼燃料在固体火箭冲压发动机推进系统和固体微型推进器两种不同技术背景下的应用。

本书内容丰富,实用性强。可供从事硼颗粒、含硼燃料及固体推进技术研究相关工作的工程技术人员、科研人员阅读使用,也可作为高等院校相关专业师生的教学、参考用书。

(浙江大学能源清洁利用国家重点实验室 刘建忠 供稿)
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