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A Novel Cocrystal Explosive NTO/TZTN with Good Comprehensive Properties

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Abstract: In order to decrease the acidity of the high explosive 3-nitro-1,2,4-triazol-5-one (NTO), we cocrystallized NTO with a nitrogen-rich weak base compound 5,6,7,8-tetrahydrotetrazolo[1,5-*b*] [1,2,4]-triazine (TZTN) in a molar ratio 1:1 to form a novel cocrystal explosive. Structure determination showed that the cocrystal is formed by strong intermolecular hydrogen bond interaction. Optical microscopy demonstrated that crystal morphology of the cocrystal was significantly improved in contrast to the crystal of NTO and TZTN. The differential scanning calorimetry (DSC) showed that the cocrystal exhibited the enhancement of thermal stability and became less sensitive to impact, compared with the TZTN. Moreover, the results suggested that the NTO/TZTN cocrystal not only has unique performance itself, but also effectively alters the properties of NTO and TZTN.

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1. Introduction

Recently, energetic materials are not only widely studied for civilian application but for military use¹⁻³. These materials must possess properties that allow them to be handled safely and avoid accidents during transport and storage⁴⁻⁶. There are admirable amount of research programs worldwide to pursue novel energetic materials with higher potential energy and enhanced insensitivity^{7, 8}. However, achieving a fine balance between high detonation performance and low sensitivity is challenging task, as the energy and sensitivity of explosives usually conflict with each other, few of these materials have proven suitable for explosives application⁹⁻¹¹. A good approach is to introduce co-crystallization techniques to obtain explosives with excellent comprehensive performance¹²⁻¹⁵.

Co-crystallization is an effective method to improve the solubility, bioavailability physical and chemical stability properties of drugs without changing their chemical structure, and it is widely used for the pharmaceutical chemicals¹⁶⁻¹⁹. The cocrystal as a novel technology, is generally consisting of two or more components bonded hydrogen bonding, π -stacking and Van der Waal's forces²⁰⁻²². Therefore, co-crystallization may provide a new method to modify the performance of energetic materials, since cocrystal has different compositions and structures relative to its pure components²³⁻²⁶.

The compound 3-nitro-1,2,4-triazol-5-one (NTO), provides a greater margin of safety against reaction to unplanned stimuli and exhibits excellent physical properties, including a high crystal density of 1.93 g/cm³. In addition, its calculated detonation velocity and pressure equivalent to those of RDX, making it a current candidate of choice for propellant and explosives applications²⁷⁻²⁹. However, because of the strong acidity, the use of NTO is strongly restricted. The nitrogen-rich compounds based on C-N and N-N heteroaromatic rings normally exhibit high energetic performances, especially for the condensed ring compounds. A nitrogen-rich compound 5,6,7,8-tetrahydrotetrazolo[1,5-*b*] [1,2,4]-triazine (TZTN) containing tetrazole ring

and triazine ring, is a conjugated structure with acceptable density and good stability. Furthermore, TZTN can only be protonated by strong acid, and its energetic salts show high detonation performance¹⁵. By cocrystallizing with weak base TZTN, it could neutralize acidity of NTO to some extent and without obviously decreasing the energy and make NTO with a better integrated performance.

Here we present a novel energetic-energetic cocrystal composed of NTO and TZTN with a molar ratio of 1:1. The crystal structure as well as explosive performance of the new cocrystal explosive were analyzed and compared.

2. Experimental section

2.1 Materials and Sample Preparation

NTO and TZTN(Fig. 1) were synthesized according to literatures^{15, 28} and anhydrous methanol were provided by Sinopharm Chemical Reagent Beijing Co., Ltd.

Crystallization experiments was conducted by dissolving a molar ratio of 1:1 mixture of NTO (0.26 g) and TZTN (0.25g) in anhydrous methanol (20 mL) at 45°C and stirring for 30min. The solvent was evaporated over a period of several hours at room temperature, and a new energetic cocrystal of NTO/TZTN was formed. In addition, and its crystal structure was determined by single-crystal X-ray diffraction.

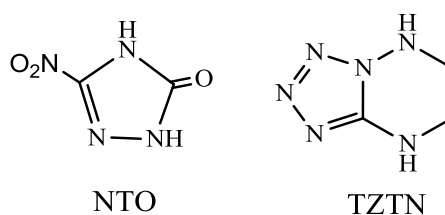


Fig. 1 Chemical structures of NTO and TZTN

2.2 Optical microscopy

Optical micrographs of the crystals were taken under the OLYMPUS BX51 microscope.

2.3 Powder X-ray diffraction (PXRD)

Powder X-ray diffraction patterns were recorded on a Bruker D8Advance with a Cu K α radiation ($\lambda = 1.54439 \text{ \AA}$), the voltage and current applied were 40 kV and 40

mA, respectively. The data were collected over an angle range from 5° to 50°.

2.4 Single crystal X-ray diffraction

The single-crystal X-ray diffraction data of the cocrystal was collected on a Rigaku Saturn 724+ CCD diffractometer (Mo K α radiation, graphite mono-chromator). The crystal was kept at 293.15 K during data collection. Crystal structures were solved by direct method using SHELXS-97³⁰, structure solution program using direct method and refined with the SHELXL-97³¹. Hydrogen atoms were added theoretically and refined with riding model position parameters and fixed isotropic thermal parameters.

2.5 Dynamic Scanning Calorimetry (DSC)

DSC were carried out with a model Pyris-1 differential scanning calorimeter. 0.2-0.5mg of were placed in aluminum pans and thermal behavior of samples at a heating rate of 5 °C/min over a range from 40 to 500 °C.

2.6 Infrared spectroscopy (IR)

The infrared spectra were obtained by Fourier transform techniques with a Bruker Equinox55 spectrometer with KBr pellets. Each spectrum was scanned in the range of 400–4000 cm⁻¹. Resolution ratio is 4 cm⁻¹.

2.7 Impact Sensitivity Properties

The impact sensitivity was determined by using a BAM fall hammer apparatus with 5kg and 2kg drop weight on ~15 mg samples. Depending on the result of previous, the level of impact energy is decreased after ignition for the next trial and increased after “no reaction”.

2.8 Computational Methods

The geometric optimization of the structures and frequency analyses carried out using Gaussian 03 suite of programs³². The geometries of NTO, TZTN and the cocrystal have been optimized using the hybrid DFT-B3LYP method with 6-311++g(3d,2p) basis set³³.

Enthalpy of formation is the most important parameter for energetic compounds. The enthalpies of formation of the three compounds at 298 K were calculated straightforwardly using the atomization energies method³⁴.

3. Results and discussion

3.1 The microscope images of cocrystal

The microscope images of NTO, TZTN and the NTO/TZTN cocrystal explosive are shown in Fig. 2. The differences in morphology among them are obvious. It can be found that the cocrystal was a white prism-like transparent crystal with well-defined morphology, regular structure, uniform size and smooth surface with the comparison of NTO and TZTN. Experiments showed that cocrystal become more compact and smooth. The above results reveal that the cocrystal has a different crystal structure compared with NTO and TZTN, and can be preliminarily implied as cocrystal method can not only change the shape and particle size of energetic materials.

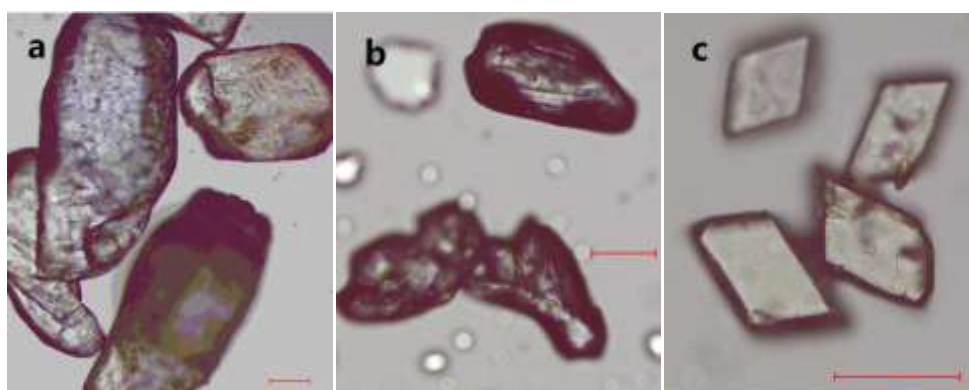


Fig. 2 Microscope images of NTO (a), TZTN(b) and NTO/TZTN(c) cocrystal(scale bar is 10μm)

3.2 The results of XRD

The analysis of XRD approved the formation of cocrystal, and XRD patterns of cocrystal and co-formers are sketched in Fig. 3. As illustrated in this figure, the powder X-ray diffraction (PXRD) pattern of the cocrystal is evidently different from co-formers, which identifies the cocrystal as a new material rather than product of crystal transformation.

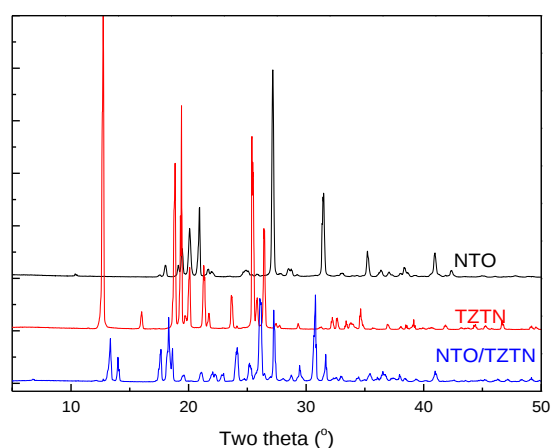


Fig. 3 XRD patterns for NTO, TZTN and NTO/TZTN cocrystal

3.3 Structure of the Cocrystal

The crystallographic data of the NTO/TZTN cocrystal obtained by X-ray single-crystal diffraction are presented in Table 1. It confirms that the cocrystal belongs to monoclinic system with space group $P2(1)/c$. It can be seen from Fig. 4 that the cocrystal consists of NTO and TZTN molecules in a 1:1 molar ratio. The 3-D packing structures showed that the NTO and TZTN molecules are arranged like zigzag chains (Fig. 5).

In the crystal structure, the strong intermolecular hydrogen bond interactions between nitro groups, ketone groups and adjacent hydrogen are the primary drive forces for the formation of cocrystal (Fig. 6). The formation of NTO/TZTN cocrystal is mainly rely on the strong intermolecular hydrogen bonding interactions to bring the two kind of molecules together.

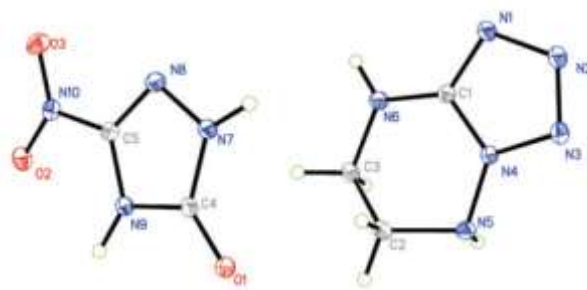


Fig. 4 The molecular structure of NTO/TZTN cocrystal

Table 1. Crystallographic data for cocrystal

Empirical formula	C5H8N10O3		
Formula mass	256.21	D_c (g·cm ⁻³)	1.665
Temperature (K)	153(2)	M (Mo K_α) (mm ⁻¹)	0.71073
Crystal system	Monoclinic	$F(000)$	528
Space group	$P2(1)/c$	θ (°)	2.77~31.51
Z	4	Reflection measured	9599
a (Å)	13.532(5)	Independent reflection [R_{int}]	3341 [R_{int} =0.0227]
b (Å)	5.1339(18)	S	1.001
c (Å)	14.727(5)	$R_1, wR_2[I>2\sigma(I)]$	0.0371, 0.0983
β (°)	92.242(4)	$R_1, wR_2(all)$	0.0448, 0.1041
V (Å ³)	1022.4(6)	CCDC	1042895

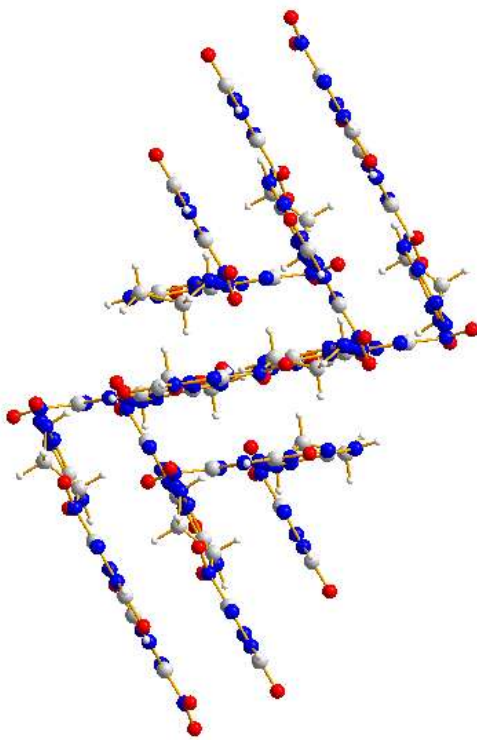


Fig. 5 3D-packing structures of cocrystal

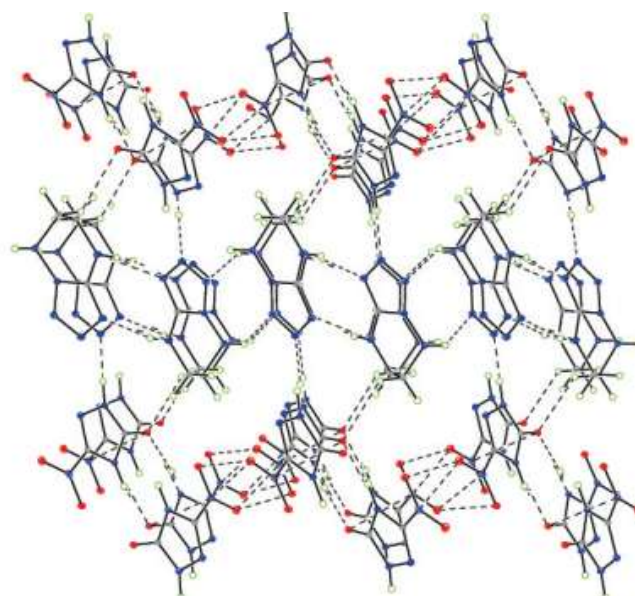


Fig. 6 The cocrystal were connected by the possible intermolecular hydrogen bonds along the b-axis

3.4 DSC study of cocrystal

Differential Scanning Calorimeter is helpful in studies on the thermal behaviour of the cocrystal, and the DSC results are illustrated in Fig. 7. It was evident from the curves that the thermal behaviour of cocrystal is obviously different from their co-formers, and the differences in thermal stability of these substances further suggest the formation of a new cocrystal. The NTO/TZTN crystal show melt at 156.6°C and increases 12.3°C comparing with TZTN, which can be attributed to the hydrogen bonding in the structure. The exothermic peak of NTO/TZTN cocrystal shift to lower temperature with two continuous sharp exothermic process at the temperatures of 177.5°C , 197.9°C , which indicates some changes may have occurred in the crystal phase.

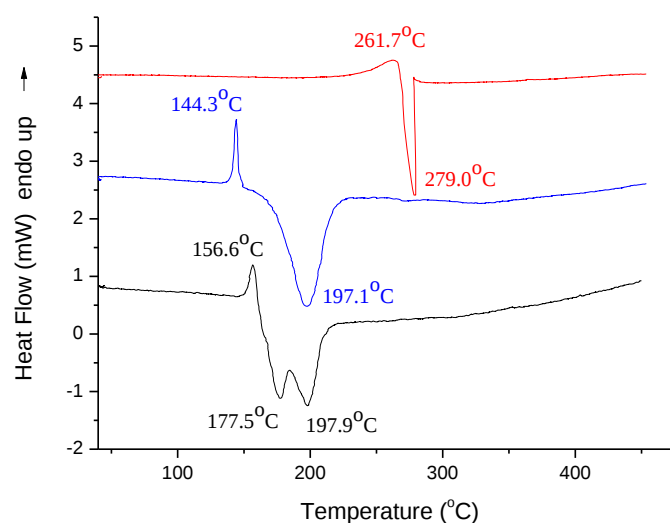


Fig.7 DSC curves for NTO, TZTN and NTO/TZTN

3.5 IR Spectroscopy

IR spectroscopy works well in determination of the predominant phase and can be used for the characterization of cocrystals³⁵. The IR spectra of NTO, TZTN and cocrystal are presented in Fig. 8. The assignments for the most characteristic vibrational bands are listed in Table 2. It can be concluded from the table that a group of low intensity bands assigned to C-H stretching vibration of TZTN increased from the region of 3280.3–3289.2 cm^{-1} to 3227.5–3264.4 cm^{-1} . While, the C-H stretching of NTO shifted from the region of 3212.3 cm^{-1} to 3227.5 cm^{-1} , and the C=O stretching vibration decreased from 1714.8 cm^{-1} to 1707.7 cm^{-1} . Simultaneously, some peak shift also takes place for bonds of both TZTN and NTO. These shifts can be attributed to the hydrogen-bonding, which changed the symmetry characteristic in cocrystal structure.

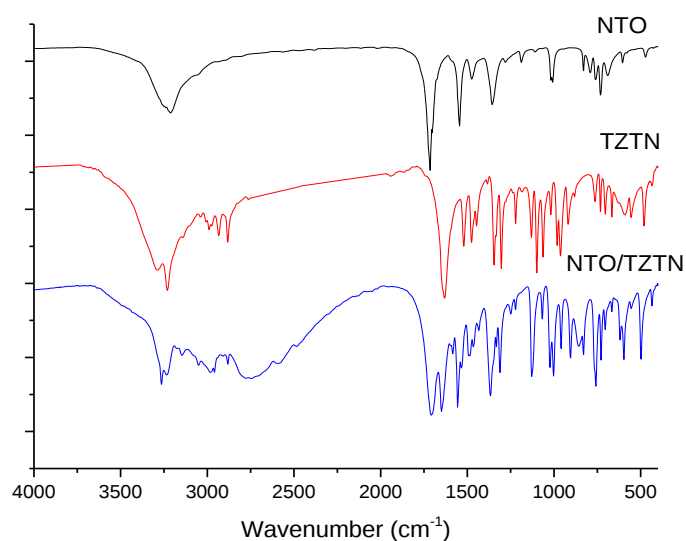


Fig. 8 IR spectra of NTO, TZTN and NTO/TZTN cocrystal.

Table 2 Assignments of the Major Bands of the IR spectra of NTO, TZTN, and NTO/TZTN cocrystal.

assignment	NTO	cocrystal	TZTN	assignment
		3264.4	3289.2	N-H stretching vibration
N-H stretching vibration	3212.3	3227.5	3230.3	N-H stretching vibration
		2983.1	2933.7	-CH ₂ - asymmetric stretching vibration
		2881.7	2882.1	-CH ₂ - stretching vibration
C=O stretching vibration	1714.8	1707.7		
NO ₂ asymmetric stretching vibration	1544.9	1555.9		
		1534.2	1520.5	N-N stretching vibration
		1485.7	1475.5	-CH ₂ - scissor bending vibration
NO ₂ symmetric stretching vibration	1356.6	1366.4		
C-N stretching vibration	1188.3	1128.5		

3.6 Impact Sensitivity Properties

Impact sensitivity is largely dependent on the physical property and the chemical properties. The results revealed that cocrystal relative insensitive nature towards mechanical stimuli, the impact sensitive of 11 J, which is higher than those of NTO (>40J), but which shows a satisfactory than that of TZTN (IS= 6 J). As a result, the cocrystal can significantly reduce the sensitivity of a sensitive explosive.

3.7 Detonation Properties

Cocrystallization can produce some changes in important physical properties of energetic materials, such as the density, which is helpful to evaluate their detonation properties. The cocrystal has a crystallographic density of $1.665 \text{ g}\cdot\text{cm}^{-3}$, which is lower than that of NTO ($1.93 \text{ g}\cdot\text{cm}^{-3}$)³⁶ but somewhat higher than that of TZTN ($1.577 \text{ g}\cdot\text{cm}^{-3}$). The heats of formation was calculated by using Gaussian 03 suite of programs. Detonation velocity, detonation pressure are the key parameters to evaluate the performance of explosives. Detonation velocity and detonation pressure can be estimated by empirical Kamlet–Jacobs formula³⁷. We can find from Table 3, in comparison with the pure TZTN, there is a little improvement of the detonation properties through cocrystallizing it with another much more powerful energetic compound, such as NTO.

Table 3. Detonation Properties for NTO NTO/TZTN Cocrystals

samples	Density/ $\text{g}\cdot\text{cm}^{-3}$	$\Delta H_f/\text{kJ}\cdot\text{mol}^{-1}$	D/ $\text{m}\cdot\text{s}^{-1}$	P/GPa
NTO	1.930^{36}	-6.3	8446	33.0
TZTN	1.577	499.2	7272	21.6
NTO/TZTN	1.665	481.4	7458	23.5

4. Conclusion

A novel NTO/TZTN cocrystal with the molar ratio of 1:1 has been synthesized and characterized. The microscope images and X-ray single-crystal diffraction results showed that the cocrystal with prism shaped morphology belong to the monoclinic system with space group $P2(1)/c$. The formation of cocrystal is mainly influenced by a number of strong intermolecular hydrogen bonds. The changes in structure

ultimately yield unique properties in the cocrystal compared with the pure components. In particular, NTO/TZTN cocrystal affords a reduction of sensitivity in comparison with pure TZTN according to the drop weight impact data and decreases the strong acidity of NTO to some extent. The detonation velocity and detonation pressure of NTO/TZTN cocrystal are 7458 km/s and 23.5 GPa, respectively, a little lower than those of NTO. Our investigations on the energetic-energetic cocrystal of the NTO/TZTN provide a promising way to tune the performances of the existing explosives.

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A novel binary cocrystal explosive of NTO was discovered and it exhibits strong intermolecular hydrogen bond interaction in crystal structure.

