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Investigation of TNB/NNAP cocrystal synthesis, molecular interaction and formation process

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ABSTRACT

A novel cocrystal of 1,3,5-trinitrobenzene (TNB) and 1-nitronaphthalene (NNAP) was synthesized by solution and mechanochemical method, respectively. The crystal structure was characterized by single crystal X-ray diffraction (SXRD). Then the intermolecular interaction was illustrated quantitatively by Hirshfeld surface analysis accordingly. Two other isostructural cocrystals, TNT (2,4,6-trinitrotoluene)/NNAP and TNP (2,4,6-trinitrophenol)/NNAP were also calculated for comparison. Among the three cocrystals, TNB/NNAP cocrystal has the largest proportion of π-π stacking interaction (12.7%). While TNP/NNAP cocrystal has a greater percentage of hydrogen bonding than the other two cocrystals, which is 43.2% of the total interactions. These results indicate electronic effect has an influence on the intermolecular interaction in the cocrystal. The IR spectra of the intermediate products provide more information about the formation process of hydrogen bonding and π-π stacking. We can tell from the differential scanning calorimetry (DSC) thermograms that a eutectic mixture was generated first after TNB and NNAP were physically mixed without grinding, and then turned into the cocrystal and finally transformed completely.

1. Introduction

Cocrystallization, which is recognized as a promising way to enhance the performance of energetic materials, has attracted much attention in recent years [1–5]. Though many cocrystal explosives were synthesized, the formation mechanism of the cocrystal explosive is still unclear. The research of same set cocrystal is beneficial for the cocrystal explosive study [6,7]. For instance, the cocrystals of DADP (diacetone diperoxide) and three halo-substituted nitrobenzenes show the influence of substituent group on the molecular arrangement [8,9]. Moreover, these studies also found the dynamic effect in the cocrystals formation by the comparison of two structurally similar compounds, which is vital for the cocrystallization mechanism [10]. Therefore, preparation and analysis of a series of cocrystals is an effective way to make a deeper understanding of the cocrystal explosive formation mechanism. NNAP is often used as an insensitive component in the composite explosive. Our previous work demonstrated that NNAP can cocrystallize with TNT and TNP both in a molar ratio of 1:1 [11]. Structural characterization of the two cocrystals indicates that they show a similar layer structure. Weak hydrogen bonding and π-π stacking are the main driving forces for the cocrystal formation [12–14]. Thus, we anticipated that another common explosive TNB, which has a similar molecular structure to TNT and TNP, could also cocrystallize with NNAP. The molecular structures of TNB, TNT, TNP, and NNAP are presented in Fig. 1. As expected, after several attempts, TNB/NNAP cocrystal was synthesized successfully.

Unlike pharmaceutical cocrystals, the approach to obtain the energetic cocrystal is limited, mostly by solvent evaporation, which is time-consuming and environmentally unfriendly [15,16]. Solid synthesis by mechanochemistry is recognized as a more efficient approach for the synthesis of cocrystals than traditional solution methods. Moreover, grinding synthesis provides direct information about the products or the intermediates for the understanding cocrystal formation mechanism from the perspective of chemical reaction processes. In this paper, liquid-assisted grinding (LAG) was performed to confirm the possibility of the cocrystal synthesis by mechanochemistry [17,18]. PXRD, FTIR, and DSC were utilized to provide a better understanding of the formation mechanism of the cocrystal via cogrinding process [19–21]. The substituent group effect and kinetic factor are involved, and some useful guidance for cocrystal explosive design and synthesis is instructive and worthy

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of attention. Because of the hazard of the explosive, special measures must be taken during the experiments.

2. Experimental section

2.1. Materials

TNB and NNAP were synthesized by literature methods [22,23]. The products were identified by ^{1}H NMR and FTIR microspectroscopy. Both materials were vacuum-dried at 40 °C for 24 h before use. The ethanol was purchased from Sinopharm Chemical Regent Co. Ltd and used as received.

2.2. Synthesis

We added 0.0213 g TNB and 0.0173 g NNAP to 5 ml ethanol with the stiring for 30 min. The solution was filtered and then the filtrate was evaporated at room temperature until faint yellow crystals appeared.

Both TNB and NNAP were ground into powder before mechanochemical synthesis. After that, 0.0213 g TNB and 0.0173 g NNAP were physically mixed and then ground with a mortar and pestle. During the grinding, a small quantity of sample was taken out at the prescribed intervals and kept in 25 °C/40%RH storage condition for further examination.

2.3. Measurements

The single-crystal X-ray diffraction data of the cocrystal was collected on Bruker SMART APEX II diffractometer by using Mo Kα X-ray radiation ($\lambda = 0.71069$ Å) and a graphite monochromator.

PXRD patterns for all the samples were taken from a Bruker D8 Advance (Cu Kα radiation, voltage 40 kV, and current 40 mA). The data were collected over an angle ranging from 5° to 40° with a scanning speed of 0.02° per second.

FTIR spectra of all the samples were collected on a Thermo Scientific Nicolet⟨SUP⟩TM⟨/SUP⟩ IS10 FT-IR Spectrometer, in the range 4000–550 cm^{-1}.

DSC thermograms were recorded on a METTLER TOLEDO DSC822^e calorimeter with typical sample weights of 0.3–0.5 mg. Each sample was placed in pierced-lid 40 μL aluminium pan. Measurements were performed in a dynamic atmosphere of nitrogen with a flow of 50 cm^3/min, at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Crystal structure

The crystal structure was solved by the direct methods within SHELXTS-97 program, and further refinements were carried out in SHELXTL-97 program [24,25]. The crystal data has been deposited in the Cambridge Crystallographic Data Center, CCDC reference number 1033991. The crystallographic data for TNB/NNAP cocrystal is summarized in Table 1. The asymmetric unit of the cocrystal consists of one NNAP molecule and half of TNB molecule. As is depicted in Fig. S2 (Supplementary), hydrogen bonding and π-π stacking can be observed in the crystal packing.

Table 1
Crystal data and structure refinements for cocrystal of TNB/NNAP.

Parameters	Data
Empirical formula	$C_{13}\,H_{8.5}\,N_{2.5}\,O_5$
Formula weight	279.72 g/mol
Temperature	293 (2)·K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Cell parameters	$a = 17.785$ (4) Å
	$b = 8.639$ (17) Å
	$c = 16.498$ (3) Å
	$\alpha = 90°$
	$\beta = 100.65°(3)$
	$\gamma = 90°$
Volume	2491.2 (9) Å^3
Z	8
Calculated density	1.492 g/cm^3
Absorption coefficient	0.118 mm^{-1}
F (000)	1152
Crystal size	0.30 × 0.20 × 0.10 mm
Theta ranges for data collection	2.33–25.37°
Max. and min. transmission	0.9883 and 0.9656
Data/restraints/parameters	2281/0/187
Goodness-of-fit on F^2	1.003
Final R indices [I > 2sigma(I)]	R1 = 0.0631, wR2 = 0.1550
R indices (all data)	R1 = 0.1022, wR2 = 0.1766
Largest diff. peak and hole	0.203 and −0.226 e Å^{-3}

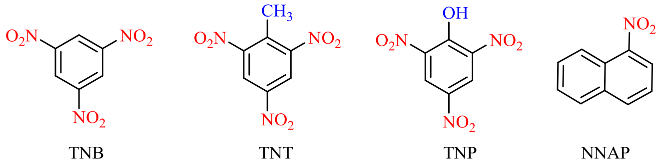

Fig. 1. Molecular structures of TNB, TNT, TNP, and NNAP.

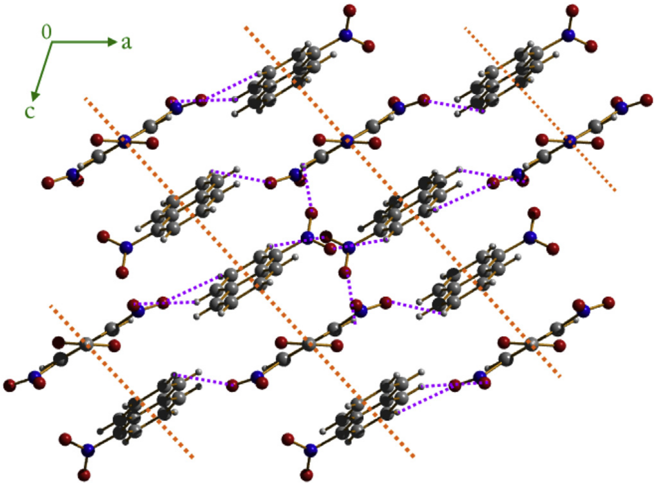

Fig. 2. Crystal packing of TNB/NNAP cocrystal with a view along the b axis. Orange dash line represents π–π stacking interaction, and purple dash line represents hydrogen bonding. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

As is noted in Fig. 2, nitro group of TNB forms weak hydrogen bonding with −CH of NNAP, the bond lengths are 2.672 Å and 2.678 Å, respectively. However, another stronger −CHċO interaction occurs between the nitro group of NNAP and H in the benzene ring of TNB, which has a bond length of 2.539 Å and angle of 122°. Numerous similar contacts were found in the cocrystal, indicating the fact that weak hydrogen bonding plays a leading role in the assembling of the cocrystal. The typical hydrogen bonding and π-π stacking interactions of TNB/NNAP cocrystal are listed in Table 2. The shortest distance of C–C in respective benzene ring is 3.621 Å, and the shortest distance between ring centroids is 3.705 Å. Usually, when the vertical distance between two rings is in the region of 3.3–3.8 Å, the π-π stacking interaction formed [26]. Therefore, π-π stacking is another driving force for the cocrystal formation. It