Three Insensitive Energetic Co-crystals of 1-Nitronaphthalene, with 2,4,6-Trinitrotoluene (TNT), 2,4,6-Trinitrophenol (Picric Acid) and D-Mannitol Hexanitrate (MHN)

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Abstract: Co-crystallization is proposed as an effective method to alter the physico-chemical properties of energetic materials, *e.g.* density, sensitivity and solubility. As reported in this paper, it was found that 1-nitronaphthalene could form co-crystals with TNT, picric acid and MHN in a 1:1 molecular ratio. The sensitivity and thermal stability of the 1-nitronaphthalene co-crystals was greatly improved compared with that of pure TNT, picric acid and MHN. In addition, the melting points of TNT, picric acid and MHN were lowered through co-crystallization with 1-nitronaphthalene. The electrostatic potential surface of 1-nitronaphthalene, calculated by the DFT method, showed that the electron-rich 1-nitronaphthalene has a tendency to be a proton donor and to co-crystallize with other energetic materials. The structures of the co-crystals of 1-nitronaphthalene with TNT and picric acid were characterized by single crystal X-ray diffraction (SXRD). The 1-nitronaphthalene/MHN co-crystal was studied by powder X-ray diffraction (PXRD), differential scanning calorimetry (DSC) and FTIR.

Keywords: co-crystal, insensitive energetic material, crystal structure, explosive properties

1 Introduction

Since co-crystal engineering is actively applied in the pharmaceutical industry to alter pharmaceutical properties, such as improvement in solubility [1-3] to assist

in drug absorption, it has attracted the interest of energetic materials researchers [4-9] and has emerged as an effective way of preparing novel explosives, in addition to synthesis.

Sensitivity, which relates to safety, is an increasingly important consideration for energetic materials and this is leading to the development of high energy-insensitive explosives. The modern evolution of explosives is so slow that it can hardly meet the functionally distinguishable needs in civilian and military applications. Even so, many efforts have been made to synthesize novel energetic materials in recent decades and few novel energetic materials have satisfied the stringent performance criteria. The currently used military explosives are still explosives which were invented decades ago, including TNT (2,4,6-trinitrotoluene), HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane) *etc*. There are only a few new energetic materials which have been synthesized and applied in recent decades, such as TATB (1,3,5-triamino-2,4,6-trinitrobenzene) and CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane). Co-crystal engineering provides an opportunity to improve the properties of existing energetic materials at the molecular level, in order to achieve their potential applications. Though many energetic-energetic co-crystals have been reported in the literature, *e.g.* co-crystals of CL-20/BTF (benzotrifuroxan) [9], CL-20/HMX [4], and TNT/CL-20 [8], the universal principles for designing energetic-energetic co-crystals are still unclear.

1-Nitronaphthalene is an intermediate product in the manufacture of drugs and dyestuffs, and is used as an insensitive energetic component in composite explosives [10] due to its low oxygen balance and molecular structure. Although it was synthesized long ago, we could not find any crystallographic information on 1-nitrophthalene, or MHN, in the Cambridge Structural Database (CSD), probably due to their poor crystallization behavior. Only one ternary super molecular structure of (G)$_2$BPDS*NN with (G = guanidinium ion; BPDS = 4,4'-bipehnyldisulfonate; NN = 1-nitronaphthalene) [11, 12], was found in the CSD.

The 1-nitronaphthalene molecule contains a wide ranging positive electrostatic potential surface, so it is likely to attract electron-poor energetic molecules. After a number of experiments, we proved that 1-nitronaphthalene can co-crystallize with TNT, picric acid and MHN. Three co-crystals of 1-nitronaphthalene, with TNT, picric acid and MHN, were obtained. As is well known, TNT and picric acid are explosives with low sensitivity and MHN is a high density explosive with a positive oxygen balance and extremely high sensitivity, which limits its applications. The properties of these co-crystals were studied and it was found that the explosive characteristics of the co-crystals differ

markedly from the original compounds, especially in terms of sensitivity. This study has enriched the range of energetic co-crystals and will probably provide new insight into designing insensitive energetic co-crystals.

2 Materials and Methods

2.1 Materials
TNT and 2,4,6-trinitrophenol (picric acid) were provided by Liaoning Qingyang Chemical Industry Co., Ltd. D-mannitol and naphthalene (starting material) were obtained from Guangdong Xilong Chemical Co., Ltd. MHN (D-mannitol hexanitrate) [13] and 1-nitronaphthalene [14] were synthesized by treatment of the starting materials with nitric acid in our laboratory. The other chemicals and reagents used in the present study were purchased from trade sources and used without further purification.

2.2 Crystallization
A 1:1 mixture of TNT (227 mg, 1 mmol) and 1-nitronaphthalene (173 mg, 1 mmol) was added to methanol (30 mL) in an open beaker (100 mL) and stirred until complete dissolution. The solution was then allowed to evaporate slowly at 25 °C over several days. Yellow needles of the 1:1 1-nitronaphthalene/TNT co-crystal (co-crystal I) were obtained.

A 1:1 mixture of picric acid (229 mg, 1 mmol) and 1-nitronaphthalene (173 mg, 1 mmol) was added to dichloromethane (30 mL) in an open beaker (100 mL) and stirred until complete dissolution. The solution was then allowed to evaporate slowly at 25 °C over several days. Yellow blades of the 1:1 1-nitronaphthalene/picric acid co-crystal (co-crystal II) were obtained.

2.3 Melting-process
A 1:1 mixture of TNT (227 mg, 1 mmol) and 1-nitronaphthalene (173 mg, 1 mmol) was added in a test-tube and heated till both compounds were melted completely at 85 °C, then the mixture natural cooling to room temperature over several hours.

A 1:1 mixture of picric acid (229 mg, 1 mmol) and 1-nitronaphthalene (173 mg, 1 mmol) was added in a test-tube and heated till both compounds were melted completely at 125 °C, then the mixture natural cooling to room temperature over several hours.

A 1:1 mixture of MHN (452 mg, 1 mmol) and 1-nitronaphthalene (173 mg, 1 mmol) was added in a test-tube and heated till both compounds were melted

completely at 110 °C, then the mixture natural cooling to room temperature over several hours.

2.4 Single Crystal X-ray Diffraction (SXRD)

The SXRD experiments for co-crystal I and co-crystal II were performed on a Bruker Smart APEX II–CCD single-crystal X-ray diffractometer using graphite monochromated MoKa radiation ($\lambda = 0.71073$ Å) at 296 K. The structures were solved by direct methods and refined on F2 by the full-matrix least-squares method using SHELXTL [15], version 5.1.S3. Anisotropic thermal parameters were refined for non-hydrogen atoms within the main backbone of the molecules. Except for the solvent molecules, hydrogen atoms were localized in their calculated positions and refined using a riding model.

2.5 Powder X-ray diffraction (PXRD)

The crystal structure of 1-nitronaphthalene/MHN co-crystal was identified by powder X-ray diffraction because single crystals could not be obtained with a size suitable for single crystal X-ray analysis. PXRD data were collected on a Bruker D8 Advance diffractometer using Cu-Kα radiation ($\lambda = 1.54056$ Å) at 35 kV and 40 mA. The sample was placed on a circular glass sample holder and pressed with a glass slide. The sample was scanned with a range $2\theta = 5\text{-}40°$ continuous scan with a step size of $0.015°$ and a scan speed of 0.2 s per step.

2.6 Differential scanning calorimetry (DSC)

DSC experiments were performed on a DSC823e instrument, using 0.5 mg samples in the sample pan. The sample was heated from 50 to 300 °C at a heating rate of 10 °C /min. The sample was purged with a stream of nitrogen at 20 mL/min.

2.7 Impact sensitivity test

The impact sensitivities of the co-crystals were determined using an in-house-constructed drop-weight test at room temperature. Samples of 20 ± 0.05 mg were enclosed in aluminum pans and impacted with a 10 kg or 2 kg weight. Referred to the Chinese military specification GJB Z377A-1994, the Bruceton method [16] for sensitivity testing gives the calculated heights of 50% probability to detonate ($h_{50\%}$).

2.8 Detonation velocity test

The detonation velocities of the co-crystals were determined using a ZBS-10A 100 MHz intelligent ten segments of detonation velocity measuring instrument

at room temperature. Samples of 2 ± 0.5 g were loaded into Φ 6 mm iron tubes and initiated with 200 mg $Pb(N_3)_2$. Data were collected with sensors.

3   Results and Discussion

3.1 Structure of 1-nitrophthalene co-crystals

The following co-crystals were obtained: 1-nitrophthalenewithTNT (co-crystal I), with 2,4,6-trinitrophenol (picric acid) (co-crystal II), and with D-mannitol hexanitrate (MHN) (co-crystal III) in 1:1 molecular ratios. The crystallographic data for co-crystals I and II are presented in Table 1.

Table 1.   Crystallographic Information for co-crystals I and II[a]

Co-crystal	I	II
Formula	$C_{10}H_7NO_2 \cdot C_7H_5N_3O_6$	$C_{10}H_7NO_2 \cdot C_6H_3N_3O_7$
Formula weight	400	402
Stoichiometry	1:1	1:1
Morphology	needles	blades
Solvent	methanol	dichloromethane
Space group	P-1	P 2 (1)
CCDC number	902325	902326
a, [Å]	7.611 (3)	8.181 (14)
b, [Å]	7.880 (3)	8.061 (14)
c, [Å]	14.602 (6)	13.23 (2)
α, [deg]	91.062 (4)	90
β, [deg]	93.555 (5)	90.29 (2)
γ, [deg]	98.664 (5)	90
Cell vol., [Å^3]	863.8	873
ρ_{calc}, [g/cm^3]	1.539	1.53
Mu, [mm^{-1}]	0.125	0.129
Z	2	2
$h_{min, max}$	-6, 9	-9, 9
$k_{min, max}$	-9, 9	-9, 9
$l_{min, max}$	-17, 17	-13, 15
data/restraints/param	4252/0 49X/263	2287/0 -129X/263
R_1, wR_2	5.27 (for 1942 data), 14.49 (for 2991 data)	15.74 (for 1259 data), 44.39 (for 2646 data)
GOF	1.033	1.082

[a] All structural data were collected at 296 K.
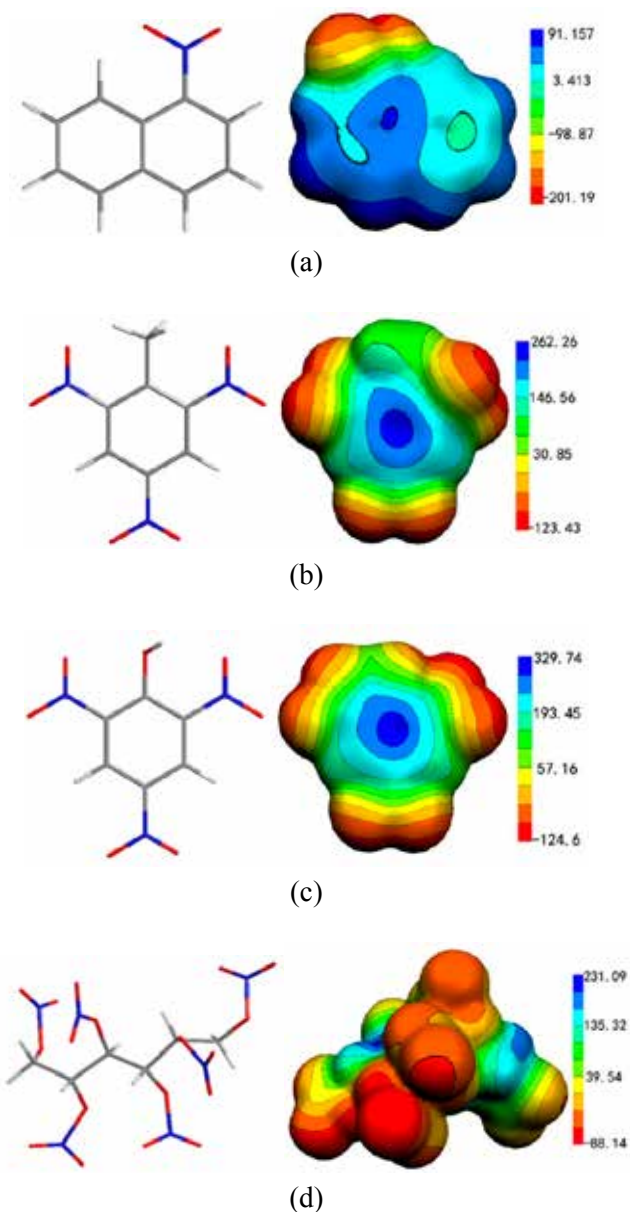
(a)

(b)

(c)

(d)

Figure 1. The electrostatic potential surfaces of 1-nitronaphthalene (a), TNT (b), picric acid (c) and MHN (d), calculated by the DFT (B3LYP/6-311G(d,p)) method. The ESPs are drawn at isosurface electron density values of 0.001. The numerical values marked in the figures have units kJ/mol.

   Figure 1 shows the electrostatic potential surfaces of 1-nitronaphthalene (a), TNT (b), picric acid (c) and MHN (d). Figure 2 and Figure 3 show the ORTEP diagrams for co-crystal I and co-crystal II respectively with thermal ellipsoids of 50% probability. In co-crystals I, one nitro group of TNT attracts a hydrogen atom on the aromatic ring of 1-nitronaphthalene and forms a C11-H11···O1 weak interaction, the bond length being 2.646 Å and the bond angle C11-H11···O1 being 149.72°. The benzene ring of TNT is almost parallel with the aromatic rings of 1-nitronaphthalene, with a dihedral angle of 2.37°. The formation of co-crystal I significantly affects the nitro groups of the TNT molecule, especially the angle of the plane of the nitro group (N2O3O4) compared to the ring planes, which is changed to 3.15°. Simultaneously, the angle of the plane of the nitro group (N4O7O8) of 1-nitronaphthalene in co-crystal I is 53° compared to the aromatic ring.
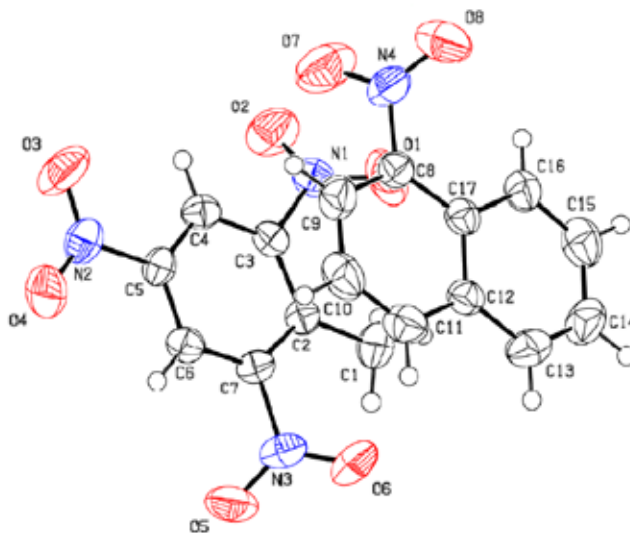

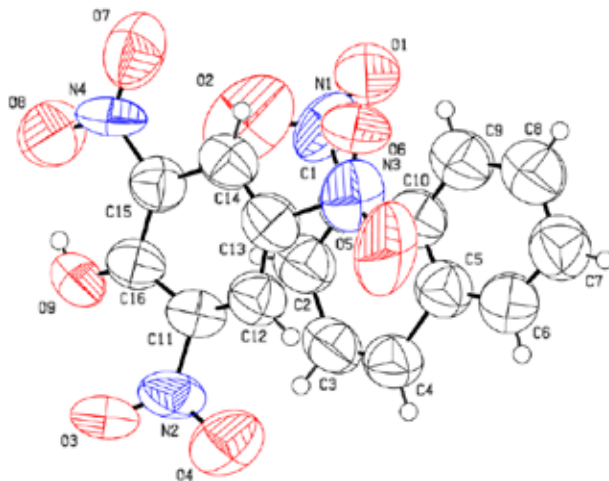**Figure 2.**   ORTEP diagram for co-crystal I with thermal ellipsoids of 50% probability.

Figure 3.   ORTEP diagram for co-crystal II with thermal ellipsoids of 50% probability.

Figure 4 shows the crystal structure of co-crystal I. When viewed along the a-axis in Figure 4a it can be seen that each TNT molecule overlaps with one 1-nitronaphthalene molecule. This also occurs for other co-crystals of TNT [5], where π···π stacking interactions are assumed to be the main driving force for the formation of the layered structure. In co-crystal I, homogeneous layers of TNT alternate with layers of 1-nitronaphthalene. The layered structure is similar to those of FOX-7 [17] and TATB [18], and is believed to disperse impact energy, leading to the insensitivity of these energetic materials.
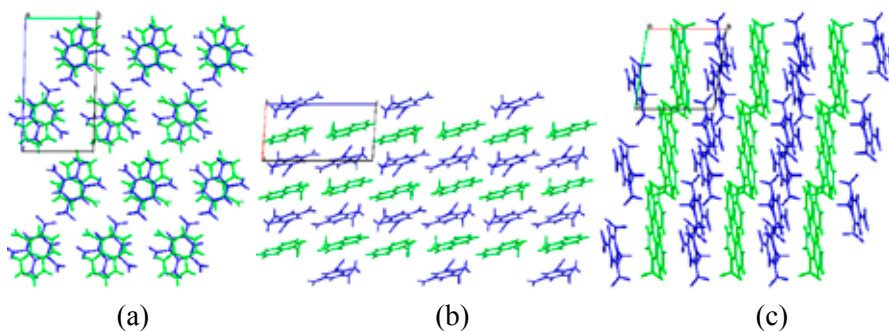

(a)   (b)   (c)

Figure 4. Crystal structure of co-crystal I; (a), (b) and (c) represent views along the a-, b- and c-axis, respectively; the parallelograms represent the unit cells.

The molecular structure of co-crystal II is shown in Figure 3. As in the structure of co-crystal I, the benzene ring of picric acid is almost parallel with the aromatic rings of 1-nitronaphthalene, with a dihedral angle of 2.07°. The structure of 1-nitronaphthalene in co-crystal II is significantly different from that in co-crystal I, with the angle of the plane of the nitro group (N1O1O2) of 1-nitronaphthalene is 23.3° compared to the aromatic ring and a weak intramolecular hydrogen bond, C2-H2···O2 (2.477 Å) existing.

The molecular structure of TNT is similar to that of picric acid, both of them being trinitro derivatives of substituted benzenes. The similar electrostatic potential surfaces of TNT and picric acid provides a common driving force in their co-crystal formation. The electrostatic potential of the nitro groups in TNT is -123.43 kJ/mol, compared to -124.6 kJ/mol in picric acid. Compared to co-crystal I, co-crystal II exhibits similar crystal layers, as shown in Figure 5.
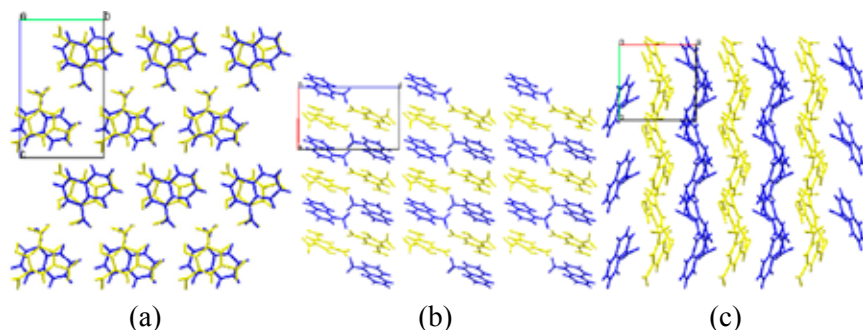

(a)　　　　　　　　(b)　　　　　　　　(c)

Figure 5.　Crystal structure of co-crystal II; (a), (b) and (c) represent views along the a-, b- and c-axis respectively; the parallelograms represent the unit cells.

3.3 Powder X-ray diffraction (PXRD)

Figure 6 shows the PXRD patterns of the co-crystals and their pure components. The powder of the 1-nitronaphthalene co-crystals was prepared by the melting method. The experimental results showed that the melting method was more efficient and convenient than the solvent evaporation method and the powder obtained was more suitable for the drop-weight impact sensitivity test and the explosive performance test.
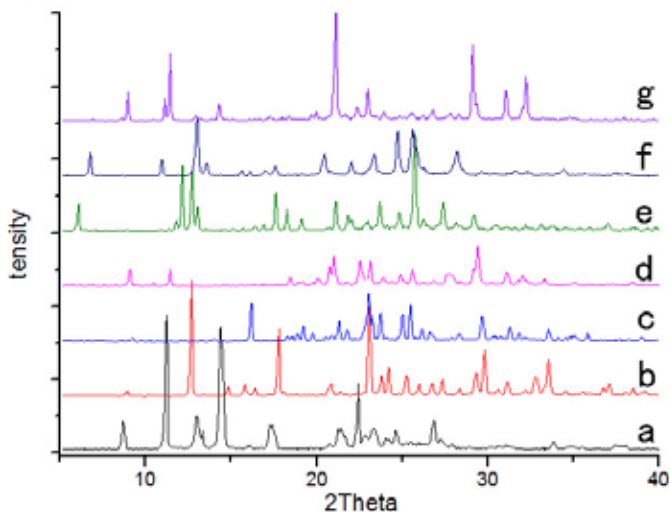
Figure 6. Powder X-ray diffraction patterns for 1-nitronaphthalene (a), TNT (b), picric acid (c), MHN (d), co-crystal I (e), co-crystal II (f), co-crystal III (g).

The cell parameters of the co-crystals are significantly different from those of the pure components, and the angles of X-ray diffraction are modified dramatically. As a result, the PXRD peak positions of the co-crystals were significantly different from those of their pure components. As is shown in Figure 6, the powder X-ray diffraction pattern of 1-nitronaphthalene co-crystals were significantly different from those of their components.

3.4 Structural influences on 1-nitronaphthalene co-crystal properties

Correlations between the structures formed and the observed material properties are important considerations in engineering novel 1-nitronaphthalene co-crystals. The properties considered in this work include density, packing coefficient, thermal properties, impact sensitivity and explosive power.

Ideal energetic materials should have high densities and packing coefficients (PCs). Therefore, enhancing these parameters is crucial for creating novel energetic material co-crystals. Density and PC data for the pure components and the co-crystals are presented in Table 3, except for the cases of 1-nitronaphthalene, MHN and co-crystal III due to the absence of relevant crystallographic information.

Table 2.   Density (ρ) and packing coefficient (PC) data for pure components and co-crystals

Compound	Molecular volume[a] [Å³]	Cell volume [Å³]	ρ_{calc} [g/cm³]	ρ_{meas}[b] [g/cm³]	PC [%]
1-Nitronaphthalene	202.89	--	--	1.434	--
TNT	199.66	1837	1.643	1.636	86.95
Picric acid	192.4	1726.8	1.763	1.835	89.14
MHN	415.08	--	--	1.834	--
Co-crystal I	402.55	863.746	1.539	1.569	93.2
Co-crystal II	395.29	872.469	1.530	1.728	90.6
Co-crystal III	617.97	--	--	1.822	--

[a]Calculated by the DFT (B3LYP/6-311G(d,p)) method, [b]Measured by Micromeritics AccuPyc II 1340 V1.01 gas displacement density analyzer at room temperature.

Table 3.   Thermal properties and impact sensitivities of the 1-nitronaphthalene co-crystals and their pure components

Compound	Melting point [°C]*	Decomposition temperature [°C]*
1-Nitronaphthalene	56	184 (evaporated)
TNT	79	225 (evaporated)
Picric acid	120	274 (evaporated)
MHN	106	186
Co-crystal I	62	240 (evaporated)
Co-crystal II	67	260 (evaporated)
Co-crystal III	92	194

*Measured by DSC at a heating rate of 10 °C/min.

The low density of 1-nitronaphthalene (1.434 g/cm³) leads to a slight loss of densities of the 1-nitronaphthalene co-crystals compared with the pure components. The PCs of co-crystals I and II are slightly increased relative to the pure components due to strong intermolecular interactions in these compounds. Improvement in the PCs leads to a higher density of the 1-nitronaphthalene co-crystals compared to mechanical mixtures of the components.

The intermolecular interactions in the 1-nitronaphthalene co-crystals greatly affect their thermal properties, especially melting points and decomposition temperatures. Figure 7 shows the DSC curves of the three co-crystals and their pure components are listed. The thermal properties of the 1-nitronaphthalene co-crystals and of their pure components are listed in Table 4.
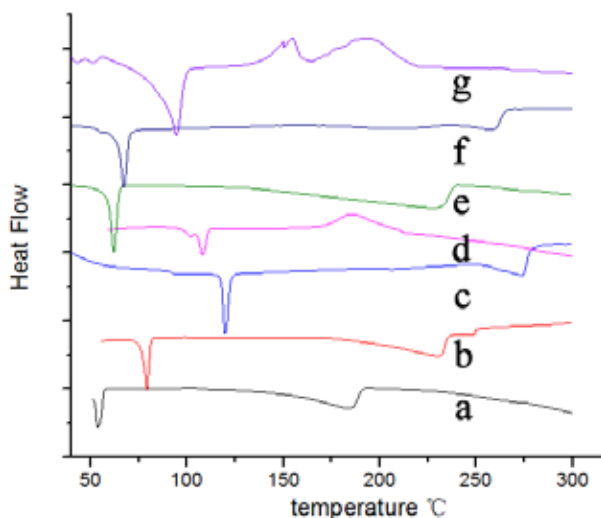
Figure 7. DSC thermograms for 1-nitronaphthalene (a), TNT (b), picric acid (c), MHN (d), co-crystal I (e), co-crystal II (f), co-crystal III (g).

1-nitronaphthalene melts at 56 °C, and evaporates at 184 °C before decomposition. The unique molecular structure makes 1-nitronaphthalene stable at a temperature of 184 °C. The low melting point and high thermal stability of 1-nitronaphthalene were reflected in the co-crystal systems, with melting points of 62 °C (I), 67 °C (II) and 92 °C (III). At the same time, the decomposition temperatures of the co-crystals were increased compared to those of the pure components, leading to the stability of the 1-nitronaphthalene co-crystals.

Table 4. Drop-weight impact sensitivity test data for 1-nitronaphthalene co-crystals and components. (2 kg weight for sensitivity testing of MHN and a 10 kg weight for the others)

Sample	$h_{50\%}$, [cm]
1-Nitronaphthalene	>100[a]
TNT	88.4[a]
Picric acid	52.9[a]
MHN	39[b]
Co-crystal I	>100[a]
Co-crystal II	>100[a]
Co-crystal III	63.6[a]

[a]Test drop weight 10 kg, [b]Test drop weight 2 kg.

3.5 Impact sensitivity

The impact sensitivity of the 1-nitronaphthalene co-crystals and their pure components are summarized in Table 4. It can be seen from Table 4 that even with a 10 kg drop weight, the h_{50} of co-crystals I and II is over 100 cm. The h_{50} of pure MHN is 39 cm with a 2 kg drop weight. After co-crystallizing with 1-nitronaphthalene, the h_{50} of co-crystal III is greatly increased to 63.6 cm with a 10 kg drop weight. Thus, impact sensitivity of energetic materials can be greatly decreased through co-crystallization with 1-nitronaphthalene.

3.6 Explosive power of the 1-nitronaphthalene co-crystals

Explosives are utilized in engineering by explosive release of chemical energy. Explosive power is the major consideration for application in engineering.

Table 5.   Explosive properties of 1-nitronaphthalene co-crystals and their components

Polymorph or co-crystal	Measured detonation velocity [m/s] (loading density ρ, [g/cm³])	Enthalpy of formation HOFs, [kJ/mol]	Calculated detonation velocity, [m/s]	Calculated detonation pressure, [GPa]	Calculated blasting heat, [kJ/mol]	Oxygen balance, [%]
1-Nitronaphtha-lene	not initiated	45.7	4336.7	7.1506	3059.94	-198.8
TNT	6900 (1.62)	63.2	7152.5	21.4235	5975.42	-74
Picric acid	7260 (1.7)	217.9	8175.5	29.3501	7261.08	-52.4
MHN	8260 (1.72)	675.5	9599.8	40.8787	8858.09	7.08
Co-crystal I	not initiated	108.9	5318.6	13.5841	4883.53	-127.9
Co-crystal II	not initiated	263.6	6024.6	17.965	5621.34	-115.4
Co-crystal III	7000 (1.68)	721.2	8130.8	33.0429	7990.97	-49.9

*Initiated by 200 mg $Pb(N_3)_2$ in a Φ 6 mm iron tube.

The detonation properties for the co-crystals, including detonation velocity, detonation pressure and blasting heat at maximum theoretical density (MTD), were estimated by the Kamlet-Jacobs equations [19] and listed in Table 5:

$$D = 1.01 \left(N \overline{M}^{\frac{1}{2}} Q^{\frac{1}{2}} \right)^{\frac{1}{2}} (1 + 1.30\rho_0) \tag{1}$$

$$P = 1.558 N \overline{M}^{1/2} Q^{1/2} \tag{2}$$

where each term in Equations (1) and (2) are defined as follows: D, the detonation velocity (km/s); P, the detonation pressure (GPa); N, the moles of detonation gases per gram of explosive; M, the average molecular weight of these gases; Q, the heat of detonation (J/g); and ρ_0, the loading density of the explosive (g/cm^3). Q was evaluated by the HOF differences between the products and explosives according to the principle of exothermic reactions.

The detonation velocity of the 1-nitronaphthalene co-crystals was decreased compared to their pure components. The insensitivity and low oxygen balance of co-crystals I and II lead them hardly initiated by 200 mg $Pb(N_3)_2$. Although MHN is extremely sensitive, after co-crystallization with 1-nitronaphthalene, its sensitivity was greatly decreased and the detonation velocity was reduced to 7000 m/s (1.68 g/cm^3). The detonation velocity of co-crystal III would be over 7000 m/s at a higher loading density. Thus, co-crystal III is an attractive candidate for replacing the current military explosive TNT.

4 Conclusions

Three novel insensitive energetic co-crystals were prepared through co-crystallization of 1-nitronaphthalene with TNT, picric acid and MHN. The sensitivity and melting point of TNT, picric acid and MHN were dramatically decreased. The low melting point, insensitivity and good explosive properties, indicate that these 1-nitronaphthalene co-crystals could be utilized as melt-cast explosives. Co-crystal III, which melts at 92 °C and is more powerful than TNT, is especially interesting.

The electrostatic potential surface of 1-nitronaphthalene shows that this insensitive material contains a wide range of positive electrostatic potential. This insensitive material would probably co-crystallize with other high energy density, electron-poor energetic materials, *e.g.* CL-20, HMX, and thus modify their sensitivity. Besides insensitivity, 1-nitronaphthalene also exhibits low density and low oxygen balance, properties which are inevitably introduced to the co-crystal systems.

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