

## Journal Pre-proof

Experiments and simulations on interactions between 2,3-bis(hydroxymethyl)-2,3-dinitro-1,4-butanediol tetranitrate (DNTN) with some energetic components and inert materials

Pang Weiqiang , Wang Ke , Luigi T. DeLuca , Djalal Trache , Fan Xuezhong , Li Junqiang , Li Huan

PII: S2667-1344(21)00024-9  
DOI: <https://doi.org/10.1016/j.fpc.2021.06.001>  
Reference: FPC 20



To appear in: *FirePhysChem*

Received date: 6 April 2021  
Revised date: 13 May 2021  
Accepted date: 1 June 2021

Please cite this article as: Pang Weiqiang , Wang Ke , Luigi T. DeLuca , Djalal Trache , Fan Xuezhong , Li Junqiang , Li Huan , Experiments and simulations on interactions between 2,3-bis(hydroxymethyl)-2,3-dinitro-1,4-butanediol tetranitrate (DNTN) with some energetic components and inert materials, *FirePhysChem* (2021), doi: <https://doi.org/10.1016/j.fpc.2021.06.001>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2021 Xi'an Modern Chemistry Research Institute. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co. Ltd.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

## Experiments and simulations on interactions between 2,3-bis(hydroxymethyl)-2,3-dinitro-1,4-butanediol tetranitrate (DNTN) with some energetic components and inert materials

Pang Weiqiang<sup>1,2\*</sup>, Wang Ke<sup>1</sup>, Luigi T. DeLuca<sup>3</sup>, Djatal Trache<sup>4</sup>, Fan Xuezhong<sup>1</sup>, Li Junqiang<sup>1</sup>, Li Huan<sup>1</sup>

1. Xi'an Modern Chemistry Research Institute, Xi'an, Shaanxi, 710065, China; 2. Science and Technology on Combustion and Explosion Laboratory, Xi'an, Shaanxi, 710065, China; 3. Politecnico di Milano, Milan, 20156, Italy; 4. Energetic Materials Laboratory, Teaching and Research unit of Energetic Processes, Ecole Militaire

Polytechnique, BP 17, Bordj El-Bahri, 16046, Algiers, Algeria

**Abstract:** In order to survey the application prospects of 2,3-bis(hydroxymethyl)-2,3-dinitro-1,4-butanediol tetranitrate (DNTN, NEST-1, SMX) in high - energy solid rocket propellants and explosives, the interactions between DNTN with some energetic components and inert materials were investigated by means of differential scanning calorimetry (DSC) and molecular dynamic (MD) methods, where glycidyl azide polymer (GAP), cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitroamine (HMX), lead 3-nitro-1,2,4-triazol-5-onate (NTO-Pb), hexanitrohexaazaisowurtzitane (CL-20), aluminum powder (Al) and magnesium powder (Mg), 3,4-dinitrofurazanfuroxan (DNTF), N-guanylurea-dinitramide (GUDN), N-butyl-N-(2-nitroxy-ethyl)nitramine (Bu-NENA), bis(2,2-dinitropropyl) acetal (BDNPA)/bis(2,2-dinitropropyl) formal (BDNPF) mixture (A3), nitrocellulose - nitroglycerine (NC-NG) and ammonium dinitramide (ADN) were used as energetic components and hydroxyl terminated polybutadiene (HTPB), polyoxytetram ethylene-co- oxyethylene (PET), addition product of hexamethylene diisocyanate and water (N-100), 2,4-toluene diisocyanate (TDI), 1,3-dimethyl-1,3-diphenyl urea (C<sub>2</sub>), carbon black (C.B.), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), lead phthalate (-Pb), N-nitro-dihydroxyethylamine dinitrate (DINA), cupric 2,4-dihydroxy-benzoate (-Cu) were used as inert materials. The impact and friction sensitivities of DNTN and DNTN in combination with energetic materials were obtained. It was concluded that the binary systems of DNTN with RDX, HMX, NTO-Pb, Al, Mg, ADN, NC-NG, HTPB, PET, C<sub>2</sub>, C.B., -Cu and Al<sub>2</sub>O<sub>3</sub> are compatible, whereas systems of DNTN with GAP, CL-20, A3, N-100, TDI and DINA are slightly sensitive, and those containing DNTF and GUDN are incompatible. It is demonstrated that no consequential trend between sensitivity and compatibility is found. The mechanical properties and safety performance of GAP mixtures plasticized with three plasticizers decrease in the following order: [BTTN] > [TMETN] > [Bu-NENA].

**Keywords:** Interactions, compatibility, DNTN, DSC, molecular dynamic simulation, energetic components, inert materials,

### 1 Introduction

High-energy materials, which can increase the energy of solid propellants and explosives, have been an importantly developing orientation for powerful missions<sup>[1]</sup>. For many years, they have been widely utilized in civilian and military fields as construction, demolition, mining, safety equipment, gunpowder, missile and space propulsion applications<sup>[2]</sup>. While their drawbacks take much challenges to researchers, such as high sensitivity, low stability, high cost, *etc.* during their application. For example, aliphatic nitrate esters are currently the most widely used energetic ingredients in single-, double-, and triple-base propellants. While, these nitrate esters are unstable at ambient conditions, and stabilizing agents should be incorporated into the energetic compositions to inhibit and slow down the decomposition reactions that can occur<sup>[3]</sup>. 2,3-bis(hydroxymethyl)-2,3-dinitro-1,4-butanediol tetranitrate (C<sub>6</sub>H<sub>8</sub>N<sub>6</sub>O<sub>16</sub>, DNTN, the abbreviations in few literatures are NEST-1, SMX, DNTN, Fig. 1), as one of new energetic materials, which can be used as a main ingredient of high - energy solid propellants and explosives from the point of view of the high performance<sup>[4,5]</sup>.

\* Corresponding author. Tel. +86 02988291765

E-mail address: nwpu\_pwq@163.com

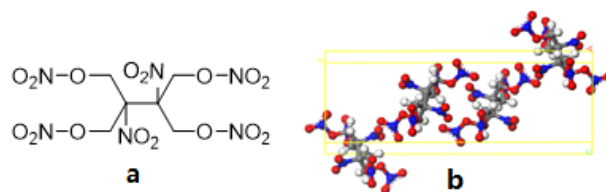


Fig.1 The structures of DNTN. a-chemical structure; b-crystal structure

In order to promote the practical application of DNTN, the interaction or compatibility of DNTN with some energetic components and inert materials in the propellants is one of the most stringent aspects. There are different techniques for the investigation of the compatibility of energetic materials such as microcalorimetry, vacuum stability test (VST), thermogravimetry (TG), differential scanning calorimetry (DSC), accelerating rate calorimeter (ARC) and chemical reactivity test (CRT). Among all the techniques, DSC measurement method was reported to be more convenient and popular for testing the compatibility of energetic materials in the fields of performance, stability, and compatibility energetic materials [6]. It has been shown that DSC method is able to show heat change during the phase transition, and consequently the phase boundaries can be determined [7]. For example, the compatibility of tetraethylammonium decahydrodecaborate (BHN), trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadacalin (TNAD), poly(3-nitromethyl-3-methyloxetane) (PNIMMO) and 3,3'-bisazidomethyloxetane-co-3-azidomethyl-3'-methyloxetane (BAMO-AMMO) with some energetic components and inert materials by means of DSC method were investigated [8-11]. Moreover, the interaction between 3,3'-bisazidomethyloxetane-co-glycidyl azide polymer (BAMO-GAP) and nano-sized cupric oxide (CuO), 1,3,3-trinitroazetidine (TNAZ) and N-oxidation-3,3'-azobis(6-diamino-1,2,4,5-tetrazi) (DATTO<sub>3,5</sub>) with main ingredients of solid propellant were studied by DSC, and the decomposition mechanism of the copolymer was obtained [12-16], and there are a few reports on the synthesis, thermal decomposition and evolutions of DNTN as high-energy filler [17-21], seldom, however, has the interactions between DNTN with some energetic components and inert materials used in solid propellants been reported. Moreover, theoretical simulation can help fully understand the relationships between performance and composition of system. As a result, much better and more efficient experimental preparation and application can be performed based on theoretical simulation [22]. Therefore, in this present work, the interactions between DNTN with some energetic components and inert materials were inspected by means of DSC and molecular dynamic (MD) simulation. In addition, the investigation on impact and friction sensitivity properties of the DNTN and its combination with the energetic materials was also carried out according to the existing methods.

## 2 Experimental

### 2.1 Materials and samples

2,3-bis(hydroxymethyl)-2,3-dinitro-1,4-butanediol tetranitrate (DNTN, 99.6%), glycidyl azide polymer (GAP, 99.8%), cyclotrimethylenetrinitramine (RDX, 99.6%), cyclotetramethylenetetranitroamine (HMX, > 99.5%), lead 3-nitro-1,2,4-triazol-5-onate (NTO-Pb, > 99.3%), hexanitrohexaazaisowurtzitane (CL-20, > 99.7%), aluminum powder (12 - 18  $\mu\text{m}$ , > 99.9%), magnesium powder (Mg, 44 - 74  $\mu\text{m}$ , > 99.9%), 3,4-dinitrofurazanfuroxan (DNTF, > 99.7%), and N-guanylurea-dinitramide (GUDN, > 99.7%), N-butyl-N-(2-nitroxy-ethyl)nitramine (Bu-NENA, > 99.8%), bis(2,2-dinitropropyl) acetal (BDNPA)/bis(2,2-dinitropropyl) formal (BDNPF) mixture

(A3, > 99.6 %), nitrocellulose - nitroglycerine (NC-NG, > 99.7 %) and ammonium dinitramide (ADN, > 99.8 %) were used as energetic components and hydroxyl terminated polybutadiene (HTPB), polyoxytetramethylene-co-oxyethylene (PET, M=4000), addition product of hexamethylene diisocyanate and water (N-100), 2,4-toluene diisocyanate (TDI), 1,3-dimethyl-1,3-diphenyl urea (C<sub>2</sub>, 99.0 %), carbon black (C.B., > 99.8 %), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>, 99.8 %), lead phthalate (-Pb, > 99.2 %), N-nitro-dihydroxyethylamine dinitrate (DINA), cupric 2,4-dihydroxybenzoate (-Cu, > 99.8 %) were used as inert materials were industrially procured. Mixtures of DNTN and energetic components or inert materials were prepared according to mass ratio 1:1.

All the sample systems involved in these experimental investigations, which were purified by different solvents and then dried for 48 h (at 60 °C), were premixed symmetrically and number defined as follows: DNTN (1); GAP (2); DNTN/GAP (3); RDX (4); DNTN/RDX (5); HMX (6); DNTN/HMX (7); NTO-Pb (8); DNTN/NTO-Pb (9); CL-20 (10); DNTN/CL-20 (11); Al (12); DNTN/Al (13); Mg (14); DNTN/Mg (15); DNTF (16); DNTN/DNTF (17); GUDN (18); DNTN/GUDN (19); Bu-NENA (20); DNTN/Bu-NENA (21); A3 (22); DNTN/A3 (23); NC-NG (24); DNTN/NC-NG (25); ADN (26); DNTN/ADN (27); HTPB (28); DNTN/HTPB (29); PET (30); DNTN/PET (31); N-100 (32); DNTN/N-100 (33); TDI (34); DNTN/TDI (35); C<sub>2</sub> (36); DNTN/C<sub>2</sub> (37); C.B. (38); DNTN/C.B. (39); Al<sub>2</sub>O<sub>3</sub> (40); DNTN/Al<sub>2</sub>O<sub>3</sub> (41); -Pb (42); DNTN/ -Pb (43); DINA (44); DNTN/DINA (45); -Cu (46); DNTN/ -Cu (47).

## 2.2 Equipment and experimentation

All the DSC measurements were carried out by NETZSCH DSC 204 HP instrument. The conditions of DSC were as follows: the sample mass of DNTN is 0.35 - 0.46 mg and the mixture system is 0.50 - 0.78 mg; the heating rate, 10 °C·min<sup>-1</sup>; atmosphere, dynamic atmosphere of nitrogen with a flow rate of 50 ml·min<sup>-1</sup> at 0.1 MPa. The DNTN, energetic component, inert material, mixture of DNTN/energetic component or DNTN/inert material was sealed in an aluminum cell, and all the samples were premixed symmetrically.

The impact sensitivity test was carried out on the drop-weight impact machine, which is based on the design of the Explosives Research Laboratory at Bruceton, Pennsylvania (USA) [23]. In the test, the sample is placed on a fixed roughened anvil. A hammer of known contact area is positioned above the sample and the weight is raised to a predetermined height and dropped. The conditions of this test were as follows: temperature, 18 °C; free-falling height, 25 cm; hammer weight, 2.0 kg; sample mass, about 40 mg; experiment repeat, 25 times for probability calculations.

The friction sensitivity test was carried out with the method of ABL (Above Base Line) [24]. In the ABL friction test, the sample is placed on an anvil, and a known force is applied hydraulically through a stationary wheel. A pendulum is used to propel the sliding anvil at any of several standard velocities perpendicular to the force vector. Sample initiation is detected by visual means (spark or flame). The conditions of this test were as follows: temperature, 18 °C; pendulum angle, 90 °; sample mass, about 50 mg; experiment repeat, 25 times for probability calculations.

## 2.3 Evaluated standard of compatibility for mixtures

The single system is defined as the pure energetic component, whose exothermic peak temperature is the smaller one between the two pure components. The temperature of maximum exothermic peak of single system is  $T_{p1}$ .  $T_{p2}$  stands for the maximum exothermic peak temperature of mixture system. The evaluated standards [25] of compatibility are listed in Table 1.

$$\Delta T_p = | T_{p2} - T_{p1} | \quad (1)$$

where  $\Delta T_p$  is the difference between  $T_{p2}$  and  $T_{p1}$ ;  $T_{p2}$  and  $T_{p1}$  are the maximum exothermic peak temperature of mixture system and single compound, respectively.

Table 1. Evaluated standards of compatibility for explosive and contacted materials

Criteria ( $\Delta T_p/^\circ C$ )		Rating*
Less than or equal to 2	A - Good	Compatible or good compatibility
3 - 5	B - Moderate	Slightly sensitized or moderate compatibility
6 - 15	C - Poor	Sensitized or poor compatibility
15 - above	D - Bad	Hazardous or bad compatibility

\*A - safe for use in any explosive design; B - safe for use in testing, when the device will be used in a very short period of time, not to be used as a binder material, or when long-term storage is desired; C - not recommended for use with explosive items; D - hazardous, do not use under any conditions.

#### 2.4 Theoretical simulation and calculation

The compositions of high-energy propellant ingredients were designed as GAP/Bu-NENA/Al/DNTN with 12/8/13/67 (the mole mass of GAP is 3700 g/mol), the same ratio of Bu-NENA was replaced by BTTN or TMETN, the correspondingly amorphous cells were constructed using amorphous cell module in Material Studio (MS) 8.0. The  $3 \times 1 \times 3$  supercell of DNTN was constructed based on its original cell, and then MD-NPT simulation was performed after supercell optimization. All cells were optimized using compass force field (Forcite Module), Van der Waals force, and the electrostatic interaction were calculated using the atom-based and Ewald methods, respectively.

The last 300 ps of equilibrium trajectory documents at 298 K were applied to calculate mechanical properties of three DNTN-based propellants. The elastic constants were obtained by the mechanical analysis in MS, and the related mechanical parameters could be evaluated. The generalized Hooke's law is written as:

$$\sigma_i = C_{ij} \varepsilon_j \quad (2)$$

where  $\sigma_i$  is the stress tensor (GPa),  $C_{ij}$  is the  $6 \times 6$  stiffness matrix of elastic constants, and  $\varepsilon_j$  is the strain tensor (GPa). Meanwhile, the stiffness matrix of the stress-strain behavior of isotropic material can be described by Lamé coefficients ( $\lambda$  and  $\mu$ ):

$$\begin{bmatrix} \lambda+2\mu & \lambda & \lambda & 0 & 0 & 0 \\ \lambda & \lambda+2\mu & \lambda & 0 & 0 & 0 \\ \lambda & \lambda & \lambda+2\mu & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu \end{bmatrix} \quad (3)$$

The elastic modulus of isotropic material can be calculated by the Lamé coefficients as follows [26]:

$$E = \mu \left( \frac{3\lambda + 2\mu}{\lambda + \mu} \right) \quad (4)$$

$$K = \lambda + \frac{2}{3}\mu \quad (5)$$

$$G = \mu \quad (6)$$

$$\gamma = \frac{\lambda}{2(\mu + \lambda)} \quad (7)$$

where,  $E$  is Young's modulus (GPa),  $K$  is Bulk modulus (GPa),  $G$  is Shear modulus (GPa), and  $\nu$  is Poisson's ratio, respectively.

### 3 Results and discussion

#### 3.1 Thermal decomposition of DNTN

The DSC and TG-DTG curves of pure DNTN sample at 0.1 MPa and heating rates of  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  are shown in Fig. 2. It can be found that there are one endothermic peak at  $86.8\text{ }^{\circ}\text{C}$  and one exothermic peak at  $185.1\text{ }^{\circ}\text{C}$  at 0.1MPa. The endothermic would be the melting of solid state of compound, indicating that this compound melt first from solid state to liquid state, then decomposition (Fig. 2a). There is only 0.32 % mass loss at  $86.4\text{ }^{\circ}\text{C}$ . There is 0.68% mass loss between  $86.4\text{ }^{\circ}\text{C}$  to  $134.7\text{ }^{\circ}\text{C}$ , which can be consult to the volatility of DNTN. With the temperature increasing, the decomposition velocity enhanced, and the maximum decomposed temperature is at  $205.1\text{ }^{\circ}\text{C}$  (Fig. 2b). Then DNTN was fully decomposed when the temperature is higher than  $400\text{ }^{\circ}\text{C}$ , and there is no residue.

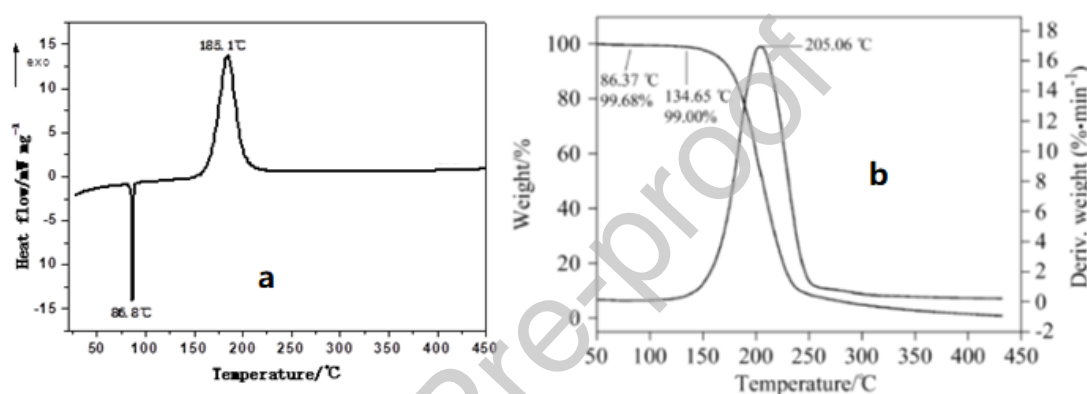
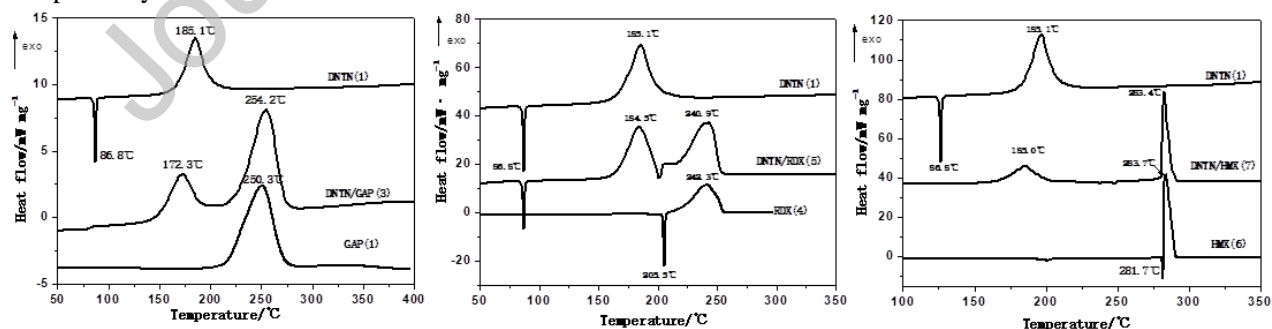


Fig. 2 The DSC (a) and TG-DTG (b) curves of DNTN at 0.1 MPa (heating rate:  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ ; sample mass: 0.35 - 0.46 mg)

#### 3.2 Compatibility of DNTN with propellant ingredients

##### 3.2.1 DNTN/energetic component systems

Typical DSC curves of systems (1) - (27) at 0.1 MPa at the heating rate of  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  and their maximum exothermic peak temperatures are shown in Figs. 3, and the evaluated standards of compatibility of mixtures are listed in Table 2.



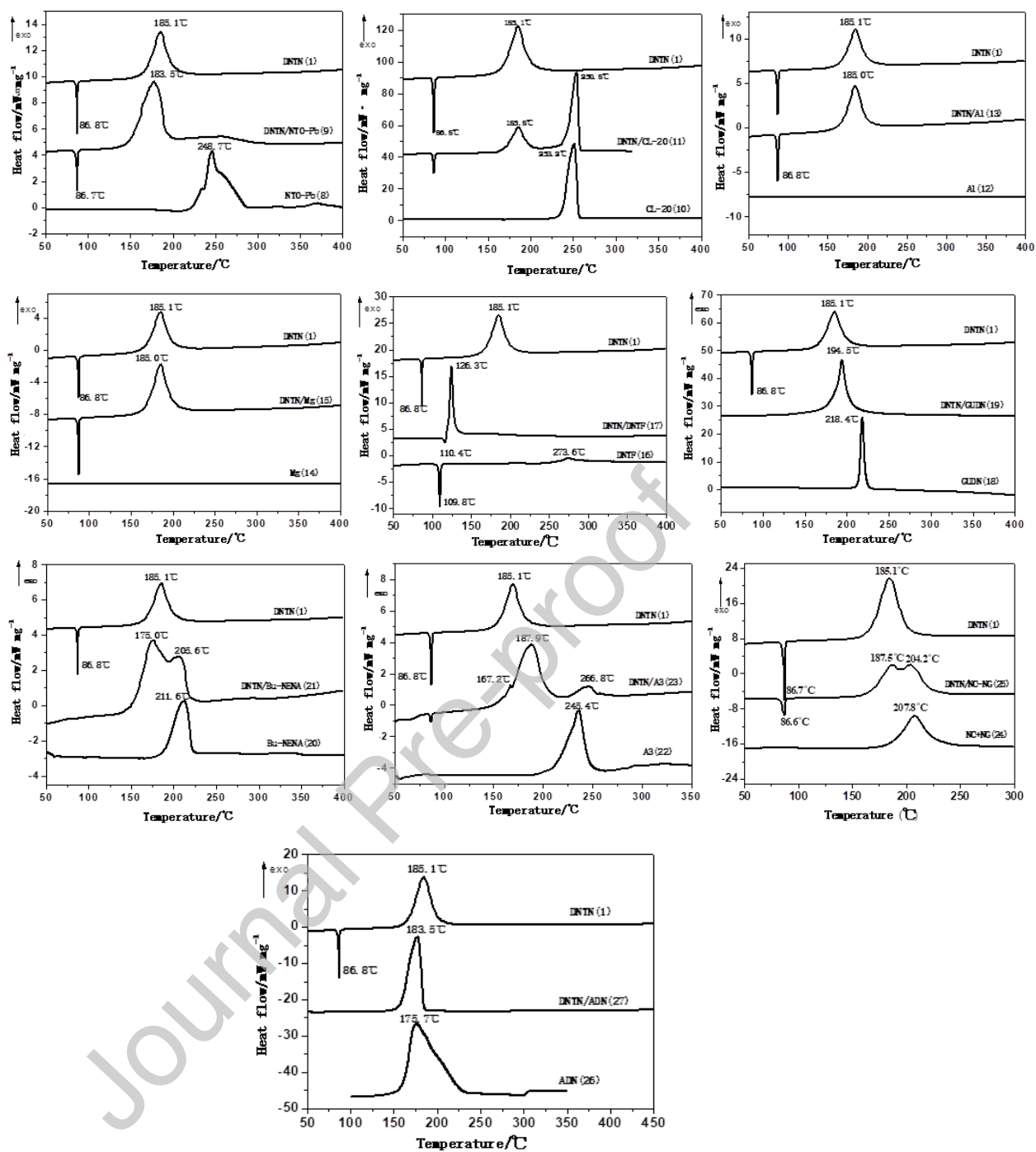


Fig. 3. The DSC curves of DNTN with some energetic components.

Table 2. The evaluations of compatibility with DSC peak temperatures (binary system of DNTN/energetic components with 1/1 mass ratio)

Systems		Peak temperatures			Rating
Mixture systems	Single systems	$T_{p1}/^{\circ}\text{C}$	$T_{p2}/^{\circ}\text{C}$	$\Delta T_p/^{\circ}\text{C}$	
DNTN/GAP (3)	GAP	250.3	254.2	3.9	B
DNTN/RDX (5)	DNTN	185.1	184.5	0.6	A
DNTN/HMX (7)	HMX	283.7	283.4	0.3	A
DNTN/NTO-Pb (9)	DNTN	185.1	183.5	1.6	A
DNTN/CL-20 (11)	CL-20	253.2	250.8	2.4	B

DNTN/Al (13)	DNTN	185.1	185.0	0.1	A
DNTN/Mg (15)	DNTN	185.1	185.0	0.1	A
DNTN/DNTF (17)	DNTN	185.1	126.3	58.5	D
DNTN/GUDN (19)	DNTN	185.1	194.5	9.4	C
DNTN/Bu-NENA (21)	DNTN	185.1	175.0	10.1	C
DNTN/A3(23)	DNTN	185.1	187.9	2.8	B
DNTN/NC-NG (25)	DNTN	185.1	187.5	2.4	B
DNTN/ADN (27)	DNTN	185.1	183.5	1.6	A

In the Table, mixture system, DNTN/energetic component binary system; single system, system of the pure energetic component, where exothermic peak temperature is smaller of the two pure components;

From the above data, the following observations can be obtained. The DSC curve of the DNTN/GAP mixture shows no endothermic change and two sharp exothermic changes. The exothermic peak temperature of GAP increases from 250.3 °C to 254.2 °C when DNTN is added, indicating that DNTN increases the exothermic decomposition temperature of GAP. The DSC curve of HMX consists of two endothermic peaks and one exothermic peak. The first peak temperature at 247.1 °C is due to the crystal transformation from  $\alpha$  to  $\beta$  [24]. The following endothermic peak at 281.7 °C is the phase change from solid to liquid, whereas the exothermic peak at 283.7 °C is caused by the rapid decomposition reaction. The exothermic peak temperature of the DNTN/HMX mixture is lower by 0.3 °C than that of pure HMX, suggesting that the presence of DNTN effectively stabilized HMX. Meanwhile, the exothermic peak temperature of the DNTN/ADN mixture is lower by 1.6 °C than that of pure DNTN and higher by 9.4 °C than that of pure ADN, which suggests that the presence of ADN effectively stabilized DNTN.

The maximum exothermic peak temperature difference between DNTN and DNTN/GAP mixture ( $\Delta T_p$ ) is 3.9 °C. The maximum exothermic peak temperature difference between DNTN and DNTN/NC-NG mixture is 2.4 °C. The value of  $\Delta T_p$  are 2.4 °C and 2.8 °C between DNTN/CL-20 mixture and DNTN/A3 mixtures, respectively. According to the standards of compatibility evaluated in Table 2, it could be shown that the binary systems DNTN/GAP, DNTN/NC-NG, DNTN/CL-20 and DNTN/A3 have moderate compatibility.

The values  $\Delta T_p$  between DNTN and DNTN/RDX, DNTN/HMX, DNTN/NTO-Pb, DNTN/Al, DNTN/Mg or DNTN/ADN mixtures are 0.6, 0.3, 1.6, 0.1, 0.1 and 1.6 °C, respectively, indicating that there is no chemical reaction between components of the mixture, and hence the mixture has good compatibility.

When DNTN and DNTF were mixed, the binary eutectic solid system came into being, where melting point is slightly higher than that of pure DNTF. Because the melting point of pure DNTF is 110.0 °C, and there are large quantity of heat emit, and there was no obvious endothermic peak before exothermic change. The endothermic peaks of DNTF are caused by the phase change from solid to liquid, and the endothermic peaks of binary system (17) are due to the melting process of DNTF.

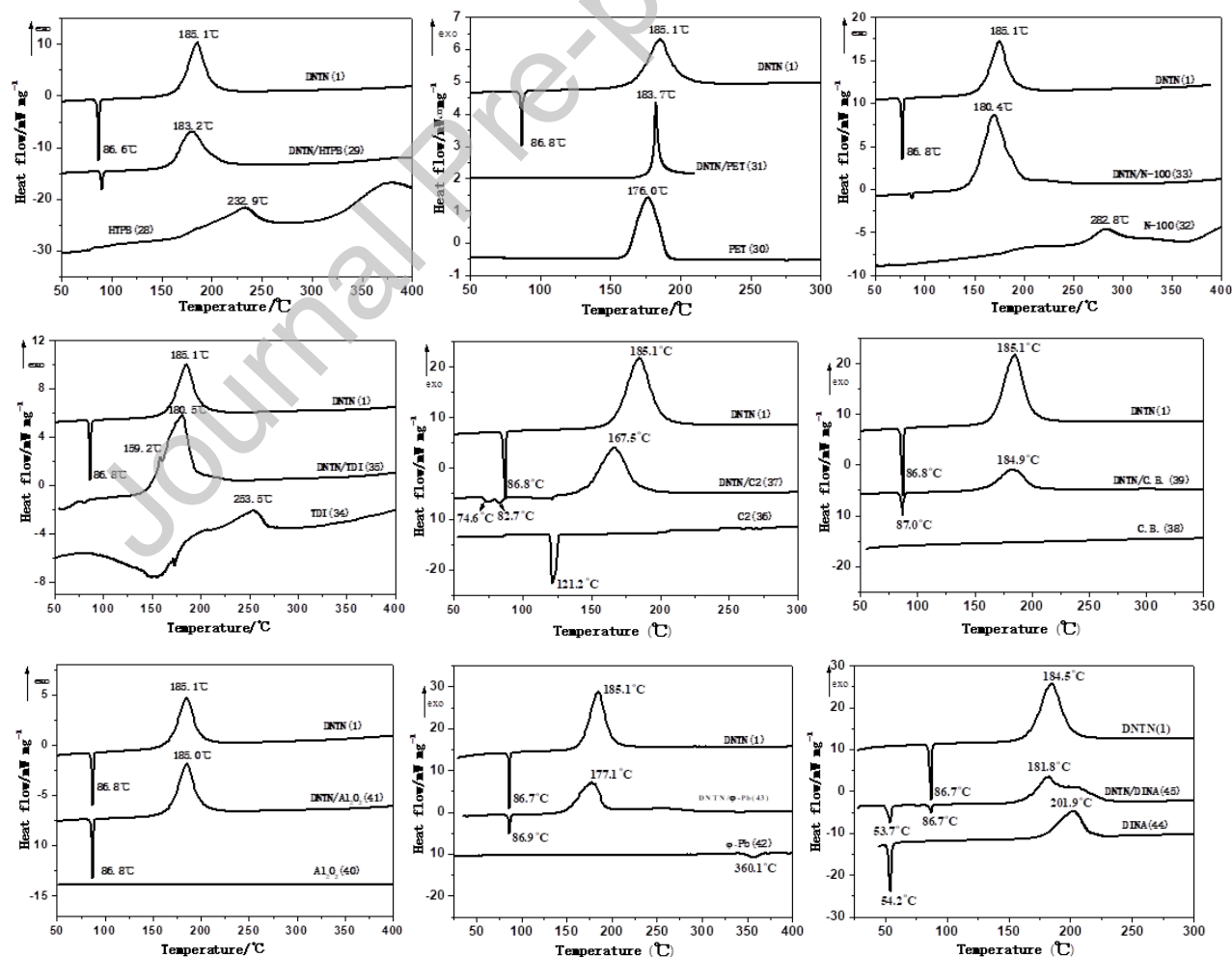
The value of  $\Delta T_p$  between DNTN and DNTN/Bu-NENA, DNTN/DNTF, DNTN/GUDN mixtures are 10.1 °C, 58.5 °C, 9.4 °C, respectively, which is consistent with the destabilization of Bu-NENA, DNTF and GUDN by the presence of DNTN. The compatibility of Bu-NENA, DNTF and GUDN with DNTN are incompatible, which may be assigned to the large quantity of heat of DNTN emitted. There was no endothermic peak before exothermic change for DNTN/Bu-NENA and DNTN/GUDN mixtures. The compatibility of binary systems DNTN/energetic component



decreases in the order: (13) = (15) > (7) > (5) > (9) = (27) > (25) = (11) > (23) > (3) > (19) > (21) > (17), and the relative thermal stability of binary systems DNTN/energetic component decreases in the order: (7) > (3) > (11) > (19) > (23) > (25) > (13) = (15) > (5) > (9) = (27) > (21) > (17).

### 3.2.2 DNTN/inert material systems

Typical DSC curves of (28) - (43) systems are shown in Figs. 4, and their maximum exothermic peak temperatures are shown in Table 3. The DSC curves of DNTN/HTPB, DNTN/N-100, DNTN/C.B., DNTN/Al<sub>2</sub>O<sub>3</sub> and DNTN/ -Pb mixtures show one endothermic peak each before their exothermic decomposition process. The endothermic peaks temperatures are from 86.8 °C to 92.4 °C are the eutectic points for these mixed systems DNTN/HTPB, DNTN/N-100, DNTN/C.B., DNTN/Al<sub>2</sub>O<sub>3</sub> and DNTN/ -Pb, respectively. While for the DNTN/DINA and DNTN/C<sub>2</sub> mixtures, there are two endothermic peaks at 74.6 °C/82.7 °C and 53.7 °C/86.7 °C, respectively. The values of  $\Delta T_p$  between DNTN and DNTN/HTPB, DNTN/PET, DNTN/C<sub>2</sub>, DNTN/C.B., DNTN/Al<sub>2</sub>O<sub>3</sub>, DNTN/ -Cu mixtures are all less than 2.0 °C, indicating that these binary systems have extremely good compatibility. While the values of  $\Delta T_p$  between DNTN and DNTN/N-100, DNTN/TDI, DNTN/DINA mixtures are all from 3.0 °C to 5.0 °C, indicating that these binary systems have moderate compatibility. The compatibility of binary systems DNTN/inert material decreases in the order: (41) > (39) = (37) > (47) > (31) > (29) > (45) > (35) > (33) > (43). The relative thermal stability of binary systems DNTN/inert material decreases in the order: (47) > (41) > (39) > (31) > (29) > (45) > (35) > (33) > (43) > (37).



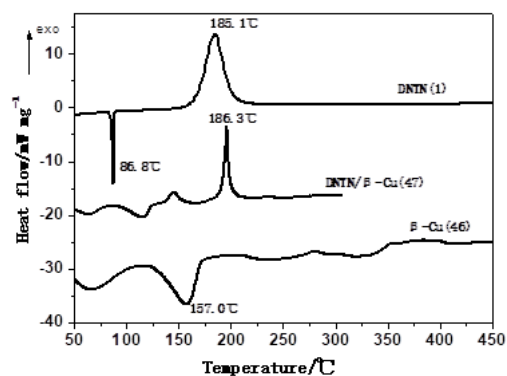


Fig. 4. The DSC curves of DNTN with some inert materials.

Table 3. The evaluations of compatibilities for DSC peak temperature (DNTN/inert materials DNTN with 1/1 mass ratio)

Systems	Peak temperatures				Rating
	Single systems	$T_{p1}/^{\circ}\text{C}$	$T_{p2}/^{\circ}\text{C}$	$\Delta T_p/^{\circ}\text{C}$	
Mixture systems	Single systems	$T_{p1}/^{\circ}\text{C}$	$T_{p2}/^{\circ}\text{C}$	$\Delta T_p/^{\circ}\text{C}$	
DNTN/HTPB (29)	DNTN	185.1	183.2	1.9	A
DNTN/PET (31)	DNTN	185.1	183.7	1.4	A
DNTN/N-100 (33)	DNTN	185.1	180.4	4.7	B
DNTN/TDI (35)	DNTN	185.1	180.5	4.6	B
DNTN/C <sub>2</sub> (37)	DNTN	185.1	167.5	0.2	A
DNTN/C.B. (39)	DNTN	185.1	184.9	0.2	A
DNTN/Al <sub>2</sub> O <sub>3</sub> (41)	DNTN	185.1	185.0	0.1	A
DNTN/ -Pb (43)	DNTN	185.1	177.1	8.0	C
DNTN/DINA (45)	DNTN	185.1	181.8	3.3	B
DNTN/ -Cu (47)	DNTN	185.1	186.3	0.8	A

Lastly, one point must be emphasized that when the system evaluated by DSC is incompatible, it cannot be affirmed indeed to be incompatible. Contrarily, when the system evaluated by DSC is compatible, it can be affirmed that it is compatible at ambient pressure. Because the samples were tested under the condition of high temperature, when it is compatible under that condition, it will be more compatible under the lower temperatures. Whereas, when the system evaluated by PDSC is incompatible, other evaluating methods such as DTA/TG or vacuum stability test (VST) may be used to confirm it [27-29].

### 3.3 Performance of DNTN/propellant ingredients

#### 3.3.1 The impact and friction sensitivities

There are many uses for knowing the sensitivity of energetic materials to impact and friction stimuli, which can propose the evaluation of energetic materials' *practical application over time*. The sensitivity of the systems between DNTN with some energetic materials was confirmed, and the results listed in Table 4. From the results depicted in Table 4, it can be seen that the tested mixtures are more sensitive to friction stimuli for which the values for most of the mixtures are 100 % under the investigated condition, while the impact sensitivity is lower than that of pure DNTN sample. From the impact sensitivity viewpoint, the DNTN in combination with some energetic materials are sensitive except for (5), (7) and (11). The RDX, HMX and CL-20 in systems (5), (7) and (11) are very sensible, and it makes the system more sensitive. Binary systems (9), (13) and (15) are of great compatibility and low sensitivity. Contrasting the sensitivity results with compatibility

experiments data that there was no consequential trend between the sensitivity and compatibility. Systems (17) and (19) are incompatible while their impact and friction sensitivities are very low. Binary system (11) displays a moderate compatibility, while its impact and friction sensitivity is very high. However, if the energetic materials can react with each other when they are mixed, they must be incompatible and very sensitive.

Table 4. Results of the impact and friction sensitivity of DNTN with some energetic materials

Samples	Impact/%	Friction/%	Samples	Impact/%	Friction/%
DNTN <sup>①</sup> (1)	10 cm ( $H_{50}$ )	100	DNTN/GAP (3)	62	92
GAP (2)	0	0	DNTN/RDX (5)	74	98
RDX (4)	0	0	DNTN/HMX (7)	74	100
HMX (6)	100	100	DNTN/NTO-Pb (9)	40	88
NTO-Pb (8)	0	0	DNTN/CL-20 (11)	78	100
CL-20 (10)	96	100	DNTN/Al (13)	38	87
Al <sup>②</sup> (12)	0	0	DNTN/Mg (15)	38	87
Mg <sup>③</sup> (14)	0	0	DNTN/DNTF (17)	54	100
DNTF (16)	100	90	DNTN/GUDN (19)	48	100
GUDN (18)	> 159 cm( $H_{50}$ )	0			

Note: The testing conditions of ①, ②, ③ and mixed samples are as follows: angle of pendulum = 90°; Falling weight = 5.0 kg; Total weight of testing sample = 50 mg. The others: Angle of pendulum = 66°; Falling weight = 2.0 kg; Total weight of testing sample = 30 mg.

### 3.3.2 Mechanical properties

The mechanical properties are important parameters for propellants, which relate to preparation, process and application of propellants. The elastic constants and related parameters of DNTN combine with main propellant ingredients are listed in Table 5. The densities of the designed three systems are 1.697, 1.752 and 1.741 g·cm<sup>-3</sup> when the plasticizers are, respectively, Bu-NENA, BTTN and TMETN. All diagonal elements  $C_{ii}$  and off-diagonal elements  $C_{ij}$  gradually decrease when the plasticizer changes from Bu-NENA to BTTN and TMETN, indicating that TMETN could better reduce the anisotropy of the system. It can also be seen that the *Young's modulus* ( $E$ ), the bulk modulus ( $K$ ), and the shear modulus ( $G$ ) of the GAP/Bu-NENA/Al/DNTN system are the highest values, while those of the GAP/BTTN/Al/DNTN system are the lowest (except for  $K$ ). It suggests that BTTN and TMETN can attenuate the stiffness better, improving the elasticity and decreasing the brittleness of DNTN-based propellants. Otherwise, the larger value of the Cauchy pressure ( $K/G$ ) is, the better of the ductility of the system is [30]. Furthermore, it is obvious that the ductility of the system with Bu-NENA is the best, and worst when the plasticizer is TMETN. The Poisson's ratios ( $\mu$ ) of the three systems are all within the range of 0.2 - 0.4, indicating all systems exhibit good plasticity and easy to be processed. The mechanical properties of the three system decreases in the order: [GAP/BTTN/Al/DNTN] > [GAP/TMETN/Al/DNTN] > [GAP/Bu-NENA/Al/DNTN].

Table 5 The elastic constants and related parameters of DNTN-based high-energy propellants

Systems	GAP/Bu-NENA/Al/DNTN	GAP/BTTN/Al/DNTN	GAP/TMETN/Al/DNTN
	3.5599	1.8915	1.6565
$\mu$	2.0547	1.5350	1.8222
$C_{11}$	7.9886	5.3382	7.0894
$C_{22}$	8.3879	4.3326	3.5067
$C_{33}$	6.6314	5.2136	5.3063

$C_{44}$	2.1567	2.1228	1.9968
$C_{55}$	2.3903	0.6192	1.5766
$C_{66}$	1.6172	1.8631	1.8931
$C_{12}$	3.7091	2.8278	2.5984
$C_{13}$	3.5070	2.7959	3.5113
$E/\text{GPa}$	5.412	3.945	4.512
$K/\text{GPa}$	4.930	3.078	2.873
$G/\text{GPa}$	2.055	1.535	1.822
$\nu$	0.317	0.286	0.238
$K/G$	2.399	2.005	1.577
$\rho/\text{g}\cdot\text{cm}^{-3}$	1.697	1.752	1.741

### 3.3.3 Safety

The bond lengths of trigger bonds of DNTN in three high-energy propellant compositions were calculated. The distribution curves are shown in Fig. 5, and the bond lengths of the average ( $\lambda_{\text{ave}}$ ) and the largest ( $\lambda_{\text{max}}$ ) trigger bonds are listed in Table 6. It can be seen that the lengths of the C–NO<sub>2</sub> bonds in each system are larger than those of the O–NO<sub>2</sub> bonds, indicating the C–NO<sub>2</sub> bond is more unstable and easier to be ruptured under the external stimulus. Compared with the DNTN supercell, the  $\lambda_{\text{ave}}$  and  $\lambda_{\text{max}}$  of the C–NO<sub>2</sub> bond and O–NO<sub>2</sub> bonds are shorter and no matter what the plasticizer is, which maybe resulted from the Van der Waals forces between DNTN and other components in the propellants. Otherwise, when the plasticizer is BTTN, the C–NO<sub>2</sub> bond lengths ( $\lambda_{\text{ave}} = 1.494 \text{ \AA}$ ,  $\lambda_{\text{max}} = 1.540 \text{ \AA}$ ) are both shorter than those of the other ones, indicating that propellant with BTTN possesses the better safety performance. In addition, when the plasticizer is Bu-NENA or TMETN, the lengths of the C–NO<sub>2</sub> and O–NO<sub>2</sub> bonds are almost equal. The safety of three system decreases in the order:  $[GAP/BTTN/Al/DNTN] > [GAP/TMETN/Al/DNTN] > [GAP/Bu-NENA/Al/DNTN]$ . Table 6. The average and the maximum bond lengths of C–NO<sub>2</sub> and O–NO<sub>2</sub> of DNTN in DNTN-based propellants and DNTN supercell

Systems	C–NO <sub>2</sub>		O–NO <sub>2</sub>	
	$\lambda_{\text{ave}}/\text{\AA}$	$\lambda_{\text{max}}/\text{\AA}$	$\lambda_{\text{ave}}/\text{\AA}$	$\lambda_{\text{max}}/\text{\AA}$
DNTN	1.498	1.620	1.478	1.525
GAP/Bu-NENA/Al/DNTN	1.495	1.580	1.442	1.475
GAP/BTTN/Al/DNTN	1.494	1.540	1.444	1.475
GAP/TMETN/Al/DNTN	1.496	1.580	1.442	1.475

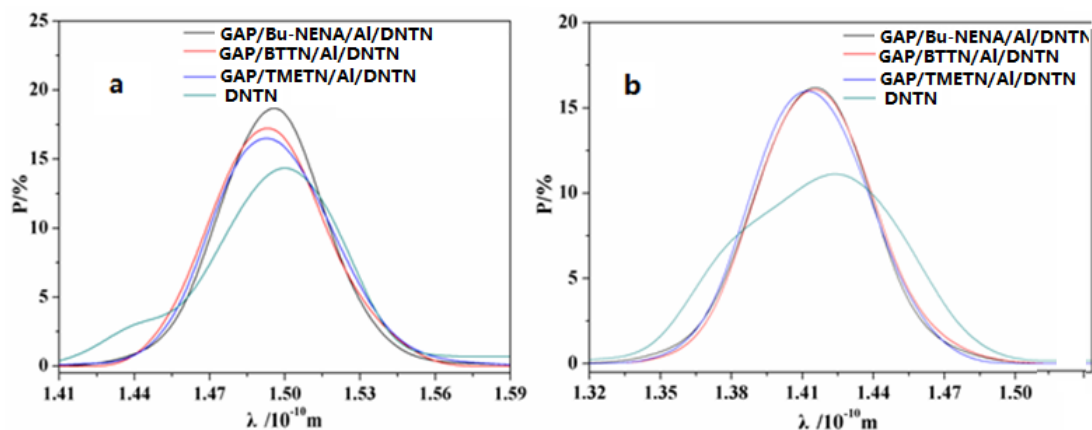


Fig. 5 The bond lengths ( $\lambda$ ) vs. percentages ( $P$ ) of DNTN in DNTN-based propellants and DNTN supercell. a- C–

NO<sub>2</sub> bond; b- N–NO<sub>2</sub> bond

#### 4 Conclusions

(1) The binary mixed systems of DNTN/RDX, DNTN/HMX, DNTN/NTO-Pb, DNTN/Mg, DNTN/Al, DNTN/ADN and DNTN/NC-NG have good compatibility, the system of DNTN/GAP, DNTN/CL-20 and DNTN/A3 have moderate compatibility, while the system of DNTN/GUDN, DNTN/DNTF and DNTN/Bu-NENA have bad compatibility according to the evaluated standard of compatibility.

(2) The inert mixed systems of DNTN/HTPB, DNTN/PET, DNTN/C<sub>2</sub>, DNTN/C.B., DNTN/ - Cu, and DNTN/Al<sub>2</sub>O<sub>3</sub> are compatible, the DNTN/N-100, DNTN/TDI and DNTN/DINA binary mixtures have moderate compatibility, while the DNTN/ -Pb binary mixtures have bad compatibility according to the evaluated standard of compatibility.

(3) The mechanical properties and safety performance of three system decrease in the order:  $[GAP/BTTN/Al/DNTN] > [GAP/METN/Al/DNTN] > [GAP/Bu-NENA/Al/DNTN]$

#### Acknowledgements

This work was supported by the foundation of Science and Technology on Combustion and Explosion Laboratory of China (2019SYSZCJJ). We would like to thank Lu HongLin of Analysis and Measuring Center of Xi'an Modern Chemistry Research Institute for their enthusiastic supports in DSC measurements and analysis.

#### References

- [1] Vladimir A. Sizov, Dmitriy V. Pleshakov, Andrey F. Asachenko, et al. Synthesis and study of the thermal and ballistic properties of SMX [J]. Cent. Eur. J. Energ. Mater. 2018, 15(1): 30-46.
- [2] Politzer P, Murray J S. Energetic materials: part 1. Decomposition, crystal and molecular properties. Elsevier, Amsterdam, 2003.
- [3] Djalal Trache, Ahmed Fouzi Tarchoun. Stabilizers for nitrate ester-based energetic materials and their mechanism of action: a state-of-the-art review [J]. Journal of Materials Science, 2018, 53, 100-123.
- [4] Jimmie C. Oxley, James L. Smith, Joseph E. Brady IV, et al. Characterization and analysis of tetranitrate esters [J]. Propellants Explos. Pyrotech. 2012, 37, 24-39.
- [5] David E. Chavez, Michael A. Hiskey, Darren L. Naud, et al. Synthesis of an energetic nitrate ester [J]. Angewandte Chemie International Edition, 2008, 47(43): 8307–8309.
- [6] Haifeng Huang, Yameng Shi, Jun Yang, et al. Compatibility Study of dihydroxylammonium 5,5'- bistetrazole-1,1'-diolate (TKX-50) with some energetic materials and inert materials [J]. Journal of Energetic Materials, 2015, 33: 66-72.
- [7] Djalal Trache, Kamel Khimeche, Mokhtar Benziane, Abdallah Dahmani. Solid-liquid phase equilibria for binary mixtures of propellant's stabilizers [J]. Journal of Thermal Analysis and Calorimetry, 2013, 112, 215-222.
- [8] Weiqiang Pang, Xuezhong Fan, Yunna Xue, et al. Study on the compatibility of tetraethylammonium decahydrodecaborate (BHN) with some energetic components and inert materials [J]. Propellants Explos. Pyrotech. 2013, 38, 278-285.
- [9] Q.-L. Yan, X.-J. Li, L.-Y. Zhang, et al. Compatibility study of trans-1,4,5,8-tetranitro- 1,4,5,8-tetraazadecalin (TNAD) with some energetic components and inert materials [J]. J. Hazard. Mater. 2008, 34, 529-534.
- [10] Pang Wei-Qiang, Fan XueZhong, Xu Hui-Xiang, et al. Fuelrich solid rocket propellants technology [M]. Xi'an: Northwestern Polytechnical University Press, 2016.
- [11] Wang Juan, Liu Da-bin, Zhou Xin-li. Influence of 2,4,6-trinitrotoluene on properties of 2,3-bis(hydroxymethyl)-2,3-dinitro-1,4-butanediol tetranitrate [J]. Journal of Nanjing University of Science and Technology, 2014, 38(1): 161-165.

- [12] Yu Jiankun. Preparation, structure characterization and properties of novel melt cast explosive 2,3-dihydroxymethyl-2,3-dinitro-1,4-butanediol tetranitrate [J]. *Chemical Propellants & Polymeric Materials*, 2012, 10(5): 21-27.
- [13] Li Jizhen, Fan Xuezhong, Fan Xiping, et al. Compatibility study of 1,3,3-trinitroazetidine components and inert materials[J]. *J. Therm. Anal. Cal.*, 2006, 85(6): 779-784.
- [14] E.L.M. Krabbendam-La Haye, W.P.C. de Klerk, M. Miszczak, et al. Compatibility testing of energetic materials at TNO-PML and MIAT [J]. *J. Therm. Anal. Cal.*, 2003, 72, 931-936.
- [15] J.A.F.F. Rocco, J.E.S. Lima, A.G. Frutuoso, et al. Thermal degradation of a composite solid propellant examined by DSC [J]. *J. Therm. Anal. Cal.*, 2004, 75, 551-557.
- [16] Ju Rong-hui, Li Ji-zhen, Fan Xue-zhong, et al. Interaction and compatibility of DATTO<sub>3.5</sub> with main compounds of CMDB propellant [J]. *Chinese Journal of Energetic Materials*, 2016, 24(3): 249-255.
- [17] David A.Reese, Lori J.Groven, Steven F.Son. Formulation and characterization of a new nitroglycerin-free double base propellant [J]. *Propellants, Explosives, Pyrotechnics*, 2013, 35, 42-46.
- [18] W.P.C. de Klerk, A.E.D.M. vander Heijden, W.H.M. Veltmans. Thermal analysis of the high - energetic material HNF [J]. *J. Therm. Anal. Cal.*, 2001, 64, 973-985.
- [19] Nikita V. Muravyev, Anatoly A. Bragin, Konstantin A. Monogarov, et al. 5- amino- 3,4- dinitropyrazole as a promising energetic material [J]. *Propellants, Explosives, Pyrotechnics*, 2016, 41(6): 999-1005.
- [20] Bi Fu-qiang, Fan Xue-zhong, Fu Xiao-long, et al. Interaction of dihydroxylammonium 5,5'- bistetrazole -1,1'- diolate with CMDB propellant components[J]. *Journal of Solid Rocket Technology*, 2014, 37 (2): 214-218.
- [21] David A.Reese, Steven F.Son, Lori J.Groven. Composite propellant based on a new nitrate ester [J]. *Propellants, Explosives, Pyrotechnics*, 2014, 39, 684-688.
- [22] Zhu Wei, Liu Dong-mei, Xiao Ji-jun, et al. Molecular dynamics study on sensitivity criterion, thermal expansion and mechanical properties multi-component high energy systems [J]. *Chinese Journal of Energetic Materials*, 2014, 22(5): 582-587.
- [23] Wei Lun, Wang Qiong-lin, Liu Shao-wu, et al. Application of high energy density compounds CL-20, DNTF and ADN in high energy propellant [J]. *Chinese Journal of Explosives & Propellants*, 2009, 32(1): 17-20.
- [24] M. Farber, R.D. Srivastava, thermal decomposition of HMX, in: 16th JANNAF Combustion Meeting, 308, CPIA Pub., 1979, pp. 723-729.
- [25] Liu Zi-ru. Thermal decomposition of energetic materials [M]. BeiJing: National Defense Industry Press, 2008.
- [26] Zhang Chao, Wang Ke, Li Jun-qiang, et al. Muti-scale simulation and experimental study of NC/TMETN bonding system [J]. *Chinese Journal of Explosives & Propellants*, 2019, 42(6): 589-596.
- [27] Tian Li, Tao Guo-hong, Cai Hua-qiang. Crystal structure and sensitivity properties of 2,3-bis(hydroxylmethyl)-2,3-dinitrobutane-1,4-diol tetranitrate[J]. *The 2nd national hazardous materials and safety technology proceeding*, 2013, 16-23.
- [28] Svatopluk Zeman. Some predictions in the field of the physical thermal stability of nitramines [J]. *Thermochim. Acta*, 1997, 302(1-2): 11-16.
- [29] Huang Meng, Ding Li, Chang Hai, et al. Study on interaction between component for HTPB/Al/AP/RDX composite propellant [J]. *Chinese Journal of Explosives & Propellants*, 2020, 43(2): 203-208.
- [30] Qi Xiao-fei, Zhang Xiao-hong, Guo Xin, et al. Molecular dynamics simulation on mechanical properties of NC/DIANP blends [J]. *Chinese Journal of Explosives & Propellants*, 2013, 36(2): 57-61,81.

#### Conflict of interest statement

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing

the position presented in, or the review of, the manuscript entitled. This manuscript was not submitted to any elsewhere, and it was not published before.

### Experiments and simulations on interactions between 2,3-bis(hydroxymethyl)-2,3-dinitro-1,4-butanediol tetranitrate (DNTN) with some energetic components and inert materials

Pang Weiqiang <sup>1,2\*</sup>, Wang Ke <sup>1</sup>, Luigi T. DeLuca <sup>3</sup>, Djalal Trache <sup>4</sup>, Fan Xuezhong <sup>1</sup>, Li Junqiang <sup>1</sup>, Li Huan <sup>1</sup>

1. Xi'an Modern Chemistry Research Institute, Xi'an, Shaanxi, 710065, China; 2. Science and Technology on Combustion and Explosion Laboratory, Xi'an, Shaanxi, 710065, China; 3. Politecnico di Milano, Milan, 20156,

Italy; 4. Energetic Materials Laboratory, Teaching and Research unit of Energetic Processes, Ecole Militaire

Polytechnique, BP 17, Bordj El-Bahri, 16046, Algiers, Algeria

**Abstract:** In order to survey the application prospects of 2,3-bis(hydroxymethyl)-2,3-dinitro-1,4-butanediol tetranitrate (DNTN, NEST-1, SMX) in high - energy solid rocket propellants and explosives, the interactions between DNTN with some energetic components and inert materials were investigated by means of differential scanning calorimetry (DSC) and molecular dynamic (MD) methods, where glycidyl azide polymer (GAP), cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitroamine (HMX), lead 3-nitro-1,2,4-triazol-5-onate (NTO-Pb), hexanitrohexaazaisowurtzitane (CL-20), aluminum powder (Al) and magnesium powder (Mg), 3,4-dinitrofurazanfuroxan (DNTF), N-guanylurea-dinitramide (GUDN), N-butyl-N-(2-nitroxy-ethyl)nitramine (Bu-NENA), bis(2,2-dinitropropyl) acetal (BDNPA)/bis(2,2-dinitropropyl) formal (BDNPF) mixture (A3), nitrocellulose - nitroglycerine (NC-NG) and ammonium dinitramide (ADN) were used as energetic components and hydroxyl terminated polybutadiene (HTPB), polyoxytetram ethylene-co- oxyethylene (PET), addition product of hexamethylene diisocyanate and water (N-100), 2,4-toluene diisocyanate (TDI), 1,3-dimethyl-1,3-diphenyl urea (C<sub>2</sub>), carbon black (C.B. ), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), lead phthalate ( -Pb), N-nitro-dihydroxyethylamine dinitrate (DINA), cupric 2,4-dihydroxy-benzoate ( -Cu) were used as inert materials. The impact and friction sensitivities of DNTN and DNTN in combination with energetic materials were obtained. . It was concluded that the binary systems of DNTN with RDX, HMX, NTO-Pb, Al, Mg, ADN, NC-NG, HTPB, PET, C<sub>2</sub>, C.B., -Cu and Al<sub>2</sub>O<sub>3</sub> are compatible, whereas systems of DNTN with GAP, CL-20, A3, N-100, TDI and DINA are slightly sensitive, and those containing DNTF and GUDN are incompatible. It is demonstrated that no consequential trend between sensitivity and compatibility is found. The mechanical properties and safety performance of GAP mixtures plasticized with three plasticizers decrease in the following order: [BTTN] > [TMETN] > [Bu-NENA].

**Keywords:** Interactions, compatibility, DNTN, DSC, molecular dynamic simulation, energetic components, inert materials,

## 1 Introduction

High-energy materials, which can increase the energy of solid propellants and explosives, have been an importantly developing orientation for powerful missions <sup>[1]</sup>. For many years, they have been widely utilized in civilian and military fields as construction, demolition, mining, safety equipment, gunpowder, missile and space propulsion applications <sup>[2]</sup>. While their drawbacks take much challenges to researchers, such as high sensitivity, low stability, high cost, *etc.* during their application. For example, aliphatic nitrate esters are currently the most widely used energetic ingredients in single-, double-, and triple-base propellants. While, these nitrate esters are unstable at ambient conditions, and stabilizing agents should be incorporated into the energetic compositions to inhibit and slow down the decomposition reactions that can occur <sup>[3]</sup>. 2,3-bis(hydroxymethyl)-2,3-dinitro-1,4-butanediol tetranitrate (C<sub>6</sub>H<sub>8</sub>N<sub>6</sub>O<sub>16</sub>, DNTN, the abbreviations in few literatures are NEST-1, SMX, DNTN, Fig. 1), as one of new energetic materials, which can be used as a main ingredient of high - energy solid propellants and explosives from the point of view of the high

\* Corresponding author. Tel. +86 02988291765

E-mail address: nwpu\_pwq@163.com

performance [4,5].

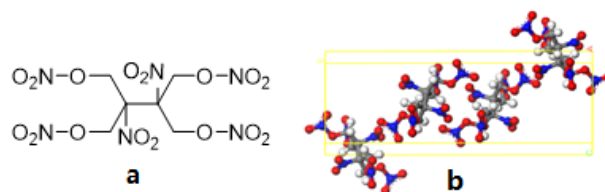


Fig.1 The structures of DNTN. a-chemical structure; b-crystal structure

In order to promote the practical application of DNTN, the interaction or compatibility of DNTN with some energetic components and inert materials in the propellants is one of the most stringent aspects. There are different techniques for the investigation of the compatibility of energetic materials such as microcalorimetry, vacuum stability test (VST), thermogravimetry (TG), differential scanning calorimetry (DSC), accelerating rate calorimeter (ARC) and chemical reactivity test (CRT). Among all the techniques, DSC measurement method was reported to be more convenient and popular for testing the compatibility of energetic materials in the fields of performance, stability, and compatibility energetic materials [6]. It has been shown that DSC method is able to show heat change during the phase transition, and consequently the phase boundaries can be determined [7]. For example, the compatibility of tetraethylammonium decahydrodecaborate (BHN), trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadacalin (TNAD), poly(3-nitromethyl-3-methyloxetane) (PNIMMO) and 3,3'-bisazidomethyloxetane-co-3-azidomethyl-3'-methyloxetane (BAMO-AMMO) with some energetic components and inert materials by means of DSC method were investigated [8-11]. Moreover, the interaction between 3,3'-bisazidomethyloxetane-co-glycidyl azide polymer (BAMO-GAP) and nano-sized cupric oxide (CuO), 1,3,3-trinitroazetidene (TNAZ) and N-oxidation-3,3'-azobis(6-diamino-1,2,4,5-tetrazin) (DATTO<sub>3.5</sub>) with main ingredients of solid propellant were studied by DSC, and the decomposition mechanism of the copolymer was obtained [12-16], and there are a few reports on the synthesis, thermal decomposition and evolvments of DNTN as high-energy filler [17-21], seldom, however, has the interactions between DNTN with some energetic components and inert materials used in solid propellants been reported. Moreover, theoretical simulation can help fully understand the relationships between performance and composition of system. As a result, much better and more efficient experimental preparation and application can be performed based on theoretical simulation [22]. Therefore, in this present work, the interactions between DNTN with some energetic components and inert materials were inspected by means of DSC and molecular dynamic (MD) simulation. In addition, the investigation on impact and friction sensitivity properties of the DNTN and its combination with the energetic materials was also carried out according to the existing methods.

## 2 Experimental

### 2.1 Materials and samples

2,3-bis(hydroxymethyl)-2,3-dinitro-1,4-butanediol tetranitrate (DNTN, 99.6%), glycidyl azide polymer (GAP, 99.8%), cyclotrimethylenetrinitramine (RDX, 99.6%), cyclotetramethylenetetranitroamine (HMX, > 99.5%), lead 3-nitro-1,2,4-triazol-5-onate (NTO-Pb, > 99.3%), hexanitrohexaazaisowurtzitane (CL-20, > 99.7%), aluminum powder (12 - 18  $\mu\text{m}$ , > 99.9%), magnesium powder (Mg, 44 - 74  $\mu\text{m}$ , > 99.9%), 3,4-dinitrofurazanfuroxan (DNTF, > 99.7%), and N-guanylurea-dinitramide (GUDN, > 99.7%), N-butyl-N-(2-nitroxy-ethyl)nitramine (Bu-NENA, >



99.8 %), bis(2,2-dinitropropyl) acetal (BDNPA)/bis(2,2-dinitropropyl)formal (BDNPF) mixture (A3, > 99.6 %), nitrocellulose - nitroglycerine (NC-NG, > 99.7 %) and ammonium dinitramide (ADN, > 99.8 %) were used as energetic components and hydroxyl terminated polybutadiene (HTPB), polyoxytetramethylene-co-oxyethylene (PET, M=4000), addition product of hexamethylene diisocyanate and water (N-100), 2,4-toluene diisocyanate (TDI), 1,3-dimethyl-1,3-diphenyl urea (C<sub>2</sub>, 99.0 %), carbon black (C.B., > 99.8 %), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>, 99.8 %), lead phthalate (-Pb, > 99.2 %), N-nitro-dihydroxyethylamine dinitrate (DINA), cupric 2,4-dihydroxybenzoate (-Cu, >99.8 %) were used as inert materials were industrially procured. Mixtures of DNTN and energetic components or inert materials were prepared according to mass ratio 1:1.

All the sample systems involved in these experimental investigations, which were purified by different solvents and then dried for 48 h (at 60 °C), were premixed symmetrically and number defined as follows: DNTN (1); GAP (2); DNTN/GAP (3); RDX (4); DNTN/RDX (5); HMX(6); DNTN/HMX (7); NTO-Pb (8); DNTN/NTO-Pb (9); CL-20 (10); DNTN/CL-20 (11); Al (12); DNTN/Al (13); Mg (14); DNTN/Mg (15); DNTF (16); DNTN/DNTF (17); GUDN (18); DNTN/GUDN (19); Bu-NENA (20); DNTN/Bu-NENA (21); A3 (22); DNTN/A3 (23); NC-NG (24); DNTN/NC-NG (25); ADN (26); DNTN/ADN (27); HTPB (28); DNTN/HTPB (29); PET (30); DNTN/PET (31); N-100 (32); DNTN/N-100 (33); TDI (34); DNTN/TDI (35); C<sub>2</sub> (36); DNTN/C<sub>2</sub> (37); C.B. (38); DNTN/C.B. (39); Al<sub>2</sub>O<sub>3</sub> (40); DNTN/Al<sub>2</sub>O<sub>3</sub> (41); -Pb (42); DNTN/ -Pb (43); DINA (44); DNTN/DINA (45); -Cu (46); DNTN/ -Cu (47).

## 2.2 Equipment and experimentation

All the DSC measurements were carried out by NETZSCH DSC 204 HP instrument. The conditions of DSC were as follows: the sample mass of DNTN is 0.35 - 0.46 mg and the mixture system is 0.50 - 0.78 mg; the heating rate, 10 °C·min<sup>-1</sup>; atmosphere, dynamic atmosphere of nitrogen with a flow rate of 50 ml·min<sup>-1</sup> at 0.1 MPa. The DNTN, energetic component, inert material, mixture of DNTN/energetic component or DNTN/inert material was sealed in an aluminum cell, and all the samples were premixed symmetrically.

The impact sensitivity test was carried out on the drop-weight impact machine, which is based on the design of the Explosives Research Laboratory at Bruceton, Pennsylvania (USA) [23]. In the test, the sample is placed on a fixed roughened anvil. A hammer of known contact area is positioned above the sample and the weight is raised to a predetermined height and dropped. The conditions of this test were as follows: temperature, 18 °C; free-falling height, 25 cm; hammer weight, 2.0 kg; sample mass, about 40 mg; experiment repeat, 25 times for probability calculations.

The friction sensitivity test was carried out with the method of ABL (Above Base Line) [24]. In the ABL friction test, the sample is placed on an anvil, and a known force is applied hydraulically through a stationary wheel. A pendulum is used to propel the sliding anvil at any of several standard velocities perpendicular to the force vector. Sample initiation is detected by visual means (spark or flame). The conditions of this test were as follows: temperature, 18 °C; pendulum angle, 90 °; sample mass, about 50 mg; experiment repeat, 25 times for probability calculations.

## 2.3 Evaluated standard of compatibility for mixtures

The single system is defined as the pure energetic component, whose exothermic peak temperature is the smaller one between the two pure components. The temperature of maximum exothermic peak of single system is  $T_{p1}$ .  $T_{p2}$  stands for the maximum exothermic peak temperature of mixture system. The evaluated standards [25] of compatibility are listed in Table 1.

$$\Delta T_p = | T_{p2} - T_{p1} | \quad (1)$$

where,  $\Delta T_p$  is the difference between  $T_{p2}$  and  $T_{p1}$ ;  $T_{p2}$  and  $T_{p1}$  are the maximum exothermic peak temperature of mixture system and single compound, respectively.

Table 1. Evaluated standards of compatibility for explosive and contacted materials

Criteria ( $\Delta T_p/^\circ\text{C}$ )		Rating*
Less than or equal to 2	A - Good	Compatible or good compatibility
3 - 5	B - Moderate	Slightly sensitized or moderate compatibility
6 - 15	C - Poor	Sensitized or poor compatibility
15 - above	D - Bad	Hazardous or bad compatibility

\*A - safe for use in any explosive design; B - safe for use in testing, when the device will be used in a very short period of time, not to be used as a binder material, or when long-term storage is desired; C - not recommended for use with explosive items; D - hazardous, do not use under any conditions.

#### 2.4 Theoretical simulation and calculation

The compositions of high-energy propellant ingredients were designed as GAP/Bu-NENA/Al/DNTN with 12/8/13/67 (the mole mass of GAP is 3700 g/mol), the same ratio of Bu-NENA was replaced by BTTN or TMETN, the correspondingly amorphous cells were constructed using amorphous cell module in Material Studio (MS) 8.0. The  $3 \times 1 \times 3$  supercell of DNTN was constructed based on its original cell, and then MD-NPT simulation was performed after supercell optimization. All cells were optimized using compass force field (Forcite Module), Van der Waals force, and the electrostatic interaction were calculated using the atom-based and Ewald methods, respectively.

The last 300 ps of equilibrium trajectory documents at 298 K were applied to calculate mechanical properties of three DNTN-based propellants. The elastic constants were obtained by the mechanical analysis in MS, and the related mechanical parameters could be evaluated. The generalized Hooke's law is written as:

$$\sigma_i = C_{ij} \varepsilon_j \quad (2)$$

where,  $\sigma_i$  is the stress tensor (GPa),  $C_{ij}$  is the  $6 \times 6$  stiffness matrix of elastic constants, and  $\varepsilon_j$  is the strain tensor (GPa). Meanwhile, the stiffness matrix of the stress-strain behavior of isotropic material can be described by Lamé coefficients ( $\lambda$  and  $\mu$ ):

$$\begin{bmatrix} \lambda + 2\mu & \lambda & \lambda & 0 & 0 & 0 \\ \lambda & \lambda + 2\mu & \lambda & 0 & 0 & 0 \\ \lambda & \lambda & \lambda + 2\mu & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu \end{bmatrix} \quad (3)$$

The elastic modulus of isotropic material can be calculated by the Lamé coefficients as follows [26]:

$$E = \mu \left( \frac{3\lambda + 2\mu}{\lambda + \mu} \right) \quad (4)$$

$$K = \lambda + \frac{2}{3} \mu \quad (5)$$

$$G = \mu \quad (6)$$

$$\gamma = \frac{\lambda}{2(\mu + \lambda)} \quad (7)$$

where,  $E$  is Young's modulus (GPa),  $K$  is Bulk modulus (GPa),  $G$  is Shear modulus (GPa), and  $\nu$  is Poisson's ratio, respectively.

### 3 Results and discussion

#### 3.1 Thermal decomposition of DNTN

The DSC and TG-DTG curves of pure DNTN sample at 0.1 MPa and heating rates of  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  are shown in Fig. 2. It can be found that there are one endothermic peak at  $86.8\text{ }^{\circ}\text{C}$  and one exothermic peak at  $185.1\text{ }^{\circ}\text{C}$  at 0.1MPa. The endothermic would be the melting of solid state of compound, indicating that this compound melt first from solid state to liquid state, then decomposition (Fig. 2a). There is only 0.32 % mass loss at  $86.4\text{ }^{\circ}\text{C}$ . There is 0.68% mass loss between  $86.4\text{ }^{\circ}\text{C}$  to  $134.7\text{ }^{\circ}\text{C}$ , which can be consult to the volatility of DNTN. With the temperature increasing, the decomposition velocity enhanced, and the maximum decomposed temperature is at  $205.1\text{ }^{\circ}\text{C}$  (Fig. 2b). Then DNTN was fully decomposed when the temperature is higher than  $400\text{ }^{\circ}\text{C}$ , and there is no residue.

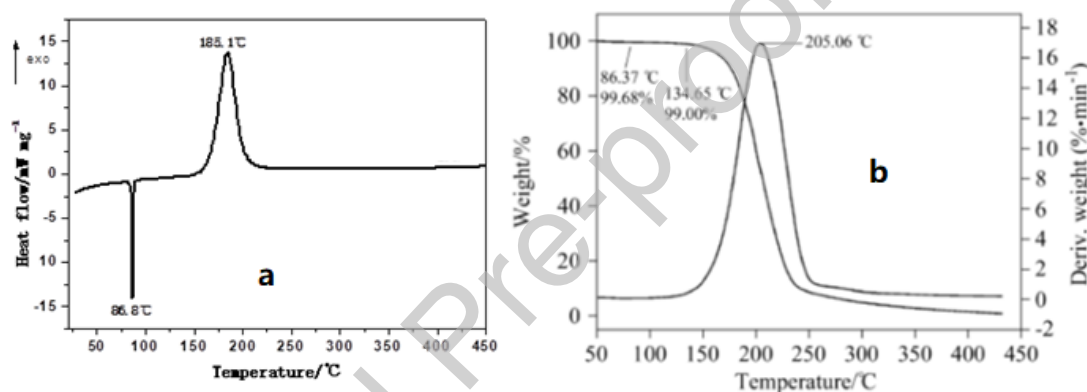
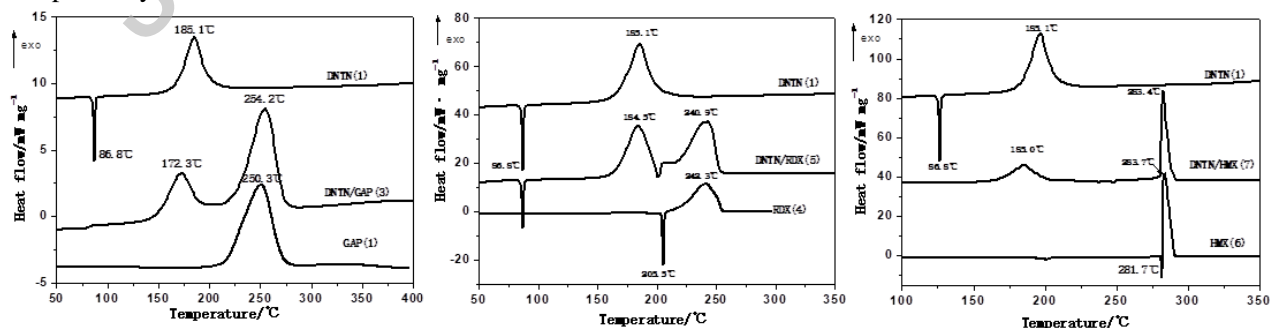


Fig. 2 The DSC (a) and TG-DTG (b) curves of DNTN at 0.1 MPa (heating rate:  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ ; sample mass: 0.35 - 0.46 mg)

#### 3.2 Compatibility of DNTN with propellant ingredients

##### 3.2.1 DNTN/energetic component systems

Typical DSC curves of systems (1) - (27) at 0.1 MPa at the heating rate of  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  and their maximum exothermic peak temperatures are shown in Figs. 3, and the evaluated standards of compatibility of mixtures are listed in Table 2.



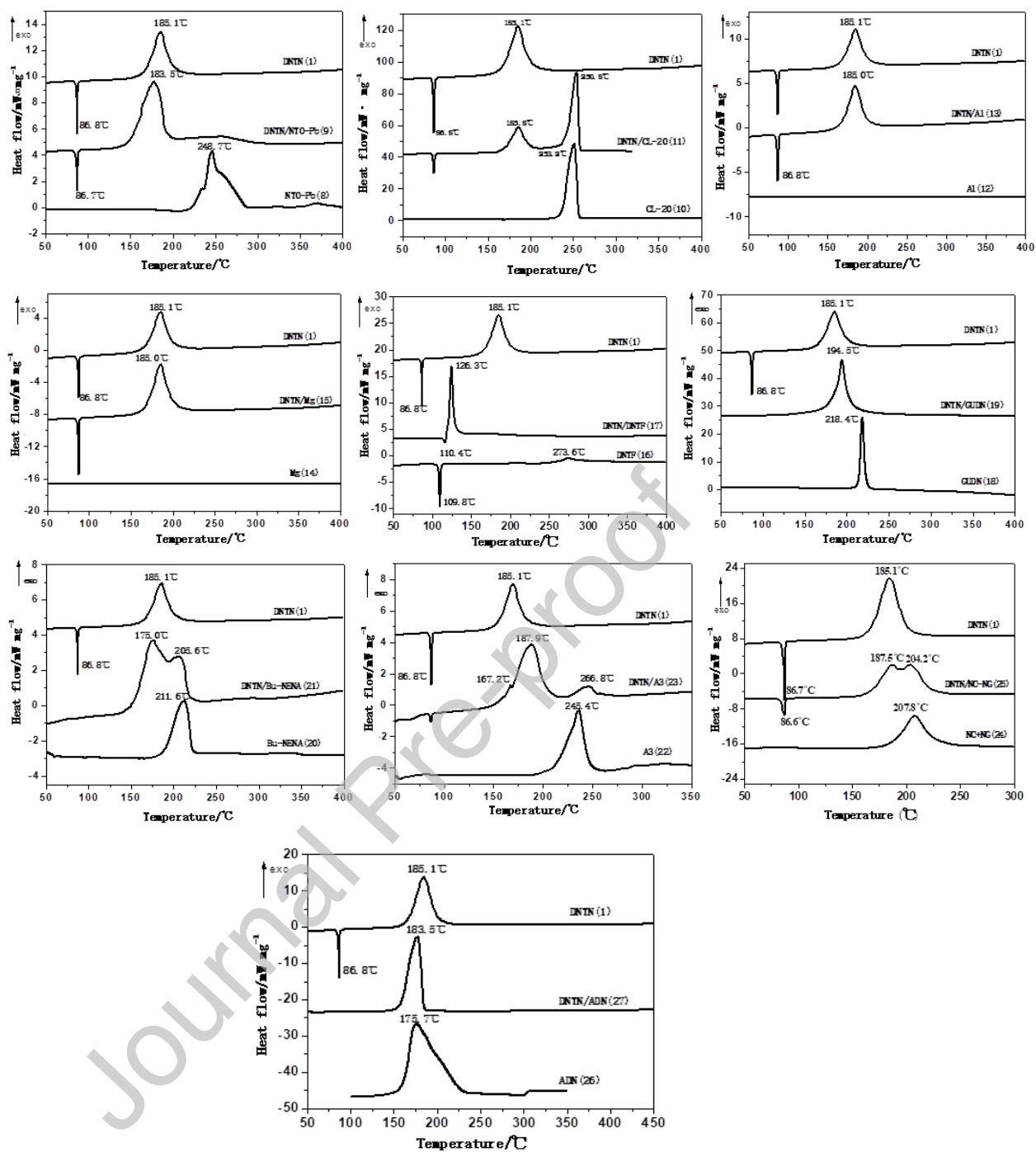


Fig. 3. The DSC curves of DNTN with some energetic components.

Table 2. The evaluations of compatibility with DSC peak temperatures (binary system of DNTN/energetic components with 1/1 mass ratio)

Systems		Peak temperatures			Rating
Mixture systems	Single systems	$T_{p1}/^{\circ}\text{C}$	$T_{p2}/^{\circ}\text{C}$	$\Delta T_p/^{\circ}\text{C}$	
DNTN/GAP (3)	GAP	250.3	254.2	3.9	B
DNTN/RDX (5)	DNTN	185.1	184.5	0.6	A
DNTN/HMX (7)	HMX	283.7	283.4	0.3	A
DNTN/NTO-Pb (9)	DNTN	185.1	183.5	1.6	A
DNTN/CL-20 (11)	CL-20	253.2	250.8	2.4	B

DNTN/Al (13)	DNTN	185.1	185.0	0.1	A
DNTN/Mg (15)	DNTN	185.1	185.0	0.1	A
DNTN/DNTF (17)	DNTN	185.1	126.3	58.5	D
DNTN/GUDN (19)	DNTN	185.1	194.5	9.4	C
DNTN/Bu-NENA (21)	DNTN	185.1	175.0	10.1	C
DNTN/A3(23)	DNTN	185.1	187.9	2.8	B
DNTN/NC-NG (25)	DNTN	185.1	187.5	2.4	B
DNTN/ADN (27)	DNTN	185.1	183.5	1.6	A

In the Table, mixture system, DNTN/energetic component binary system; single system, system of the pure energetic component, where exothermic peak temperature is smaller of the two pure components;

From the above data, the following observations can be obtained. The DSC curve of the DNTN/GAP mixture shows no endothermic change and two sharp exothermic changes. The exothermic peak temperature of GAP increases from 250.3 °C to 254.2 °C when DNTN is added, indicating that DNTN increases the exothermic decomposition temperature of GAP. The DSC curve of HMX consists of two endothermic peaks and one exothermic peak. The first peak temperature at 247.1 °C is due to the crystal transformation from  $\alpha$  to  $\beta$  [24]. The following endothermic peak at 281.7 °C is the phase change from solid to liquid, whereas the exothermic peak at 283.7 °C is caused by the rapid decomposition reaction. The exothermic peak temperature of the DNTN/HMX mixture is lower by 0.3 °C than that of pure HMX, suggesting that the presence of DNTN effectively stabilized HMX. Meanwhile, the exothermic peak temperature of the DNTN/ADN mixture is lower by 1.6 °C than that of pure DNTN and higher by 9.4 °C than that of pure ADN, which suggests that the presence of ADN effectively stabilized DNTN.

The maximum exothermic peak temperature difference between DNTN and DNTN/GAP mixture ( $\Delta T_p$ ) is 3.9 °C. The maximum exothermic peak temperature difference between DNTN and DNTN/NC-NG mixture is 2.4 °C. The value of  $\Delta T_p$  are 2.4 °C and 2.8 °C between DNTN/CL-20 mixture and DNTN/A3 mixtures, respectively. According to the standards of compatibility evaluated in Table 2, it could be shown that the binary systems DNTN/GAP, DNTN/NC-NG, DNTN/CL-20 and DNTN/A3 have moderate compatibility.

The values  $\Delta T_p$  between DNTN and DNTN/RDX, DNTN/HMX, DNTN/NTO-Pb, DNTN/Al, DNTN/Mg or DNTN/ADN mixtures are 0.6, 0.3, 1.6, 0.1, 0.1 and 1.6 °C, respectively, indicating that there is no chemical reaction between components of the mixture, and hence the mixture has good compatibility.

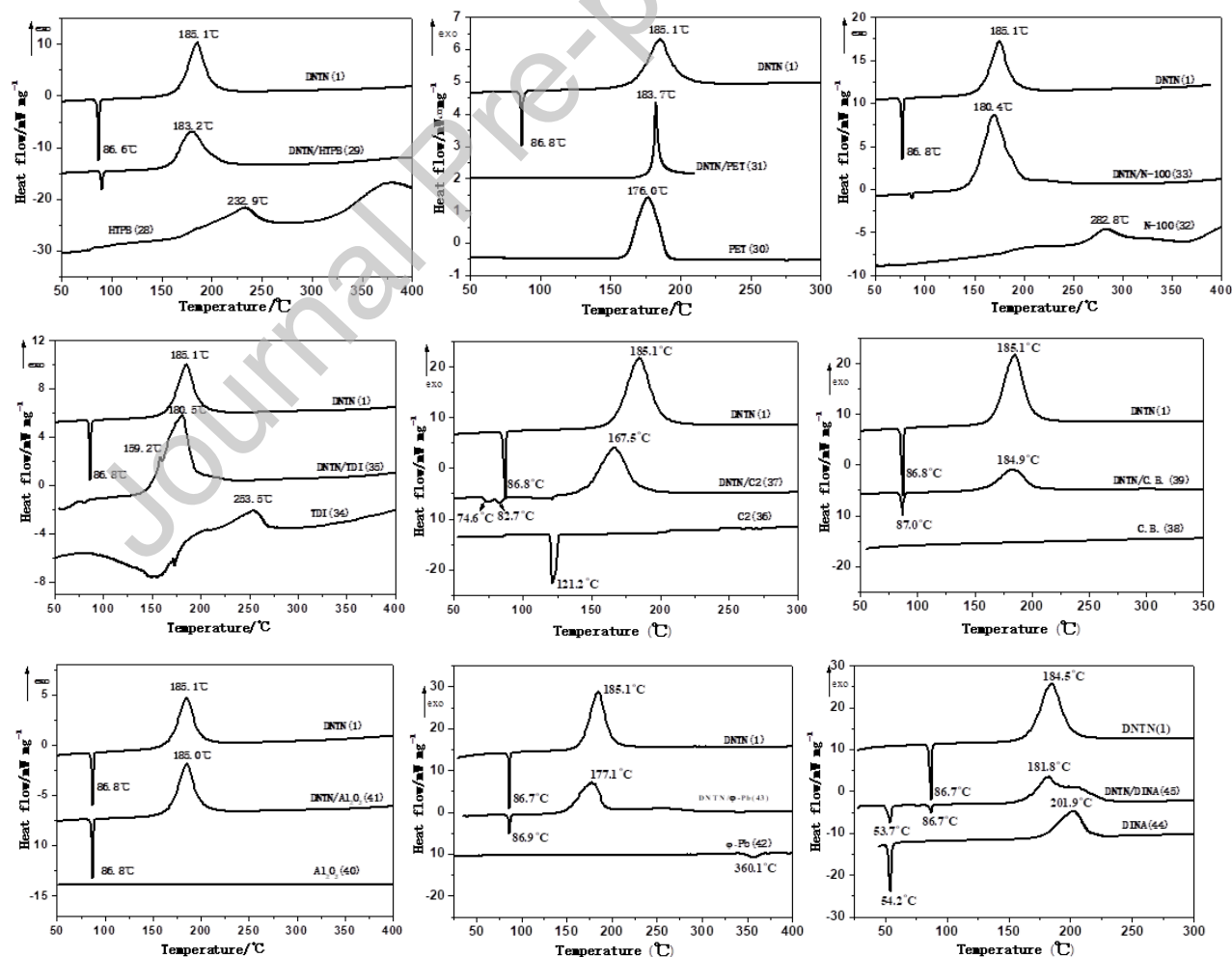
When DNTN and DNTF were mixed, the binary eutectic solid system came into being, where melting point is slightly higher than that of pure DNTF. Because the melting point of pure DNTF is 110.0 °C, and there are large quantity of heat emit, and there was no obvious endothermic peak before exothermic change. The endothermic peaks of DNTF are caused by the phase change from solid to liquid, and the endothermic peaks of binary system (17) are due to the melting process of DNTF.

The value of  $\Delta T_p$  between DNTN and DNTN/Bu-NENA, DNTN/DNTF, DNTN/GUDN mixtures are 10.1 °C, 58.5 °C, 9.4 °C, respectively, which is consistent with the destabilization of Bu-NENA, DNTF and GUDN by the presence of DNTN. The compatibility of Bu-NENA, DNTF and GUDN with DNTN are incompatible, which may be assigned to the large quantity of heat of DNTN emitted. There was no endothermic peak before exothermic change for DNTN/Bu-NENA and DNTN/GUDN mixtures. The compatibility of binary systems DNTN/energetic component

decreases in the order: (13) = (15) > (7) > (5) > (9) = (27) > (25) = (11) > (23) > (3) > (19) > (21) > (17), and the relative thermal stability of binary systems DNTN/energetic component decreases in the order: (7) > (3) > (11) > (19) > (23) > (25) > (13) = (15) > (5) > (9) = (27) > (21) > (17).

### 3.2.2 DNTN/inert material systems

Typical DSC curves of (28) - (43) systems are shown in Figs. 4, and their maximum exothermic peak temperatures are shown in Table 3. The DSC curves of DNTN/HTPB, DNTN/N-100, DNTN/C.B., DNTN/ $\text{Al}_2\text{O}_3$  and DNTN/ -Pb mixtures show one endothermic peak each before their exothermic decomposition process. The endothermic peaks temperatures are from 86.8 °C to 92.4 °C are the eutectic points for these mixed systems DNTN/HTPB, DNTN/N-100, DNTN/C.B., DNTN/ $\text{Al}_2\text{O}_3$  and DNTN/ -Pb, respectively. While for the DNTN/DINA and DNTN/ $\text{C}_2$  mixtures, there are two endothermic peaks at 74.6 °C/82.7 °C and 53.7 °C/86.7 °C, respectively. The values of  $\Delta T_p$  between DNTN and DNTN/HTPB, DNTN/PET, DNTN/ $\text{C}_2$ , DNTN/C.B., DNTN/ $\text{Al}_2\text{O}_3$ , DNTN/ -Cu mixtures are all less than 2.0 °C, indicating that these binary systems have extremely good compatibility. While the values of  $\Delta T_p$  between DNTN and DNTN/N-100, DNTN/TDI, DNTN/DINA mixtures are all from 3.0 °C to 5.0 °C, indicating that these binary systems have moderate compatibility. The compatibility of binary systems DNTN/inert material decreases in the order: (41) > (39) = (37) > (47) > (31) > (29) > (45) > (35) > (33) > (43). The relative thermal stability of binary systems DNTN/inert material decreases in the order: (47) > (41) > (39) > (31) > (29) > (45) > (35) > (33) > (43) > (37).



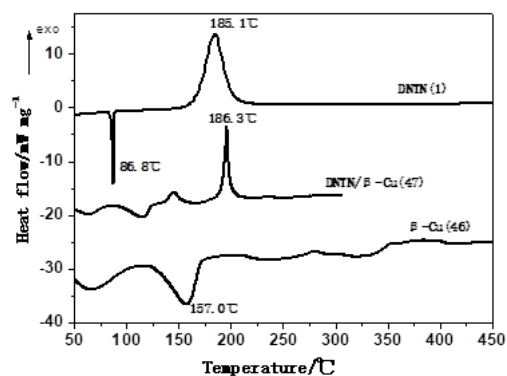


Fig. 4. The DSC curves of DNTN with some inert materials.

Table 3. The evaluations of compatibilities for DSC peak temperature (DNTN/inert materials with 1/1 mass ratio)

Systems		Peak temperatures			Rating
Mixture systems	Single systems	$T_{p1}/^{\circ}\text{C}$	$T_{p2}/^{\circ}\text{C}$	$\Delta T_p/^{\circ}\text{C}$	
DNTN/HTPB (29)	DNTN	185.1	183.2	1.9	A
DNTN/PET (31)	DNTN	185.1	183.7	1.4	A
DNTN/N-100 (33)	DNTN	185.1	180.4	4.7	B
DNTN/TDI (35)	DNTN	185.1	180.5	4.6	B
DNTN/C <sub>2</sub> (37)	DNTN	185.1	167.5	0.2	A
DNTN/C.B. (39)	DNTN	185.1	184.9	0.2	A
DNTN/Al <sub>2</sub> O <sub>3</sub> (41)	DNTN	185.1	185.0	0.1	A
DNTN/ -Pb (43)	DNTN	185.1	177.1	8.0	C
DNTN/DINA (45)	DNTN	185.1	181.8	3.3	B
DNTN/ -Cu (47)	DNTN	185.1	186.3	0.8	A

Lastly, one point must be emphasized that when the system evaluated by DSC is incompatible, it cannot be affirmed indeed to be incompatible. Contrarily, when the system evaluated by DSC is compatible, it can be affirmed that it is compatible at ambient pressure. Because the samples were tested under the condition of high temperature, when it is compatible under that condition, it will be more compatible under the lower temperatures. Whereas, when the system evaluated by PDSC is incompatible, other evaluating methods such as DTA/TG or vacuum stability test (VST) may be used to confirm it [27-29].

### 3.3 Performance of DNTN/propellant ingredients

#### 3.3.1 The impact and friction sensitivities

There are many uses for knowing the sensitivity of energetic materials to impact and friction stimuli, which can propose the evaluation of energetic materials' *practical application over time*. The sensitivity of the systems between DNTN with some energetic materials was confirmed, and the results listed in Table 4. From the results depicted in Table 4, it can be seen that the tested mixtures are more sensitive to friction stimuli for which the values for most of the mixtures are 100 % under the investigated condition, while the impact sensitivity is lower than that of pure DNTN sample. From the impact sensitivity viewpoint, the DNTN in combination with some energetic materials are sensitive except for (5), (7) and (11). The RDX, HMX and CL-20 in systems (5), (7) and (11) are very sensible, and it makes the system more sensitive. Binary systems (9), (13) and (15) are of great compatibility and low sensitivity. Contrasting the sensitivity results with compatibility experiments data that there was no consequential trend between the sensitivity and compatibility.

Systems (17) and (19) are incompatible while their impact and friction sensitivities are very low. Binary system (11) displays a moderate compatibility, while its impact and friction sensitivity is very high. However, if the energetic materials can react with each other when they are mixed, they must be incompatible and very sensitive.

Table 4. Results of the impact and friction sensitivity of DNTN with some energetic materials

Samples	Impact/%	Friction/%	Samples	Impact/%	Friction/%
DNTN <sup>①</sup> (1)	10 cm ( $H_{50}$ )	100	DNTN/GAP (3)	62	92
GAP (2)	0	0	DNTN/RDX (5)	74	98
RDX (4)	0	0	DNTN/HMX (7)	74	100
HMX (6)	100	100	DNTN/NTO-Pb (9)	40	88
NTO-Pb (8)	0	0	DNTN/CL-20 (11)	78	100
CL-20 (10)	96	100	DNTN/Al (13)	38	87
Al <sup>②</sup> (12)	0	0	DNTN/Mg (15)	38	87
Mg <sup>③</sup> (14)	0	0	DNTN/DNTF (17)	54	100
DNTF (16)	100	90	DNTN/GUDN (19)	48	100
GUDN (18)	> 159 cm( $H_{50}$ )	0			

Note: The testing conditions of ①, ②, ③ and mixed samples are as follows: angle of pendulum = 90°; Falling weight = 5.0 kg; Total weight of testing sample = 50 mg. The others: Angle of pendulum = 66°; Falling weight = 2.0 kg; Total weight of testing sample = 30 mg.

### 3.3.2 Mechanical properties

The mechanical properties are important parameters for propellants, which relate to preparation, process and application of propellants. The elastic constants and related parameters of DNTN combine with main propellant ingredients are listed in Table 5. The densities of the designed three systems are 1.697, 1.752 and 1.741 g·cm<sup>-3</sup> when the plasticizers are, respectively, Bu-NENA, BTTN and TMETN. All diagonal elements  $C_{ii}$  and off-diagonal elements  $C_{ij}$  gradually decrease when the plasticizer changes from Bu-NENA to BTTN and TMETN, indicating that TMETN could better reduce the anisotropy of the system. It can also be seen that the *Young's modulus* ( $E$ ), the bulk modulus ( $K$ ), and the shear modulus ( $G$ ) of the GAP/Bu-NENA/Al/DNTN system are the highest values, while those of the GAP/BTTN/Al/DNTN system are the lowest (except for  $K$ ). It suggests that BTTN and TMETN can attenuate the stiffness better, improving the elasticity and decreasing the brittleness of DNTN-based propellants. Otherwise, the larger value of the Cauchy pressure ( $K/G$ ) is, the better of the ductility of the system is [30]. Furthermore, it is obvious that the ductility of the system with Bu-NENA is the best, and worst when the plasticizer is TMETN. The Poisson's ratios ( $\mu$ ) of the three systems are all within the range of 0.2 - 0.4, indicating all systems exhibit good plasticity and easy to be processed. The mechanical properties of the three system decreases in the order: [GAP/BTTN/Al/DNTN] > [GAP/TMETN/Al/DNTN] > [GAP/Bu-NENA/Al/DNTN].

Table 5 The elastic constants and related parameters of DNTN-based high-energy propellants

Systems	GAP/Bu-NENA/Al/DNTN	GAP/BTTN/Al/DNTN	GAP/TMETN/Al/DNTN
	3.5599	1.8915	1.6565
$\mu$	2.0547	1.5350	1.8222
$C_{11}$	7.9886	5.3382	7.0894
$C_{22}$	8.3879	4.3326	3.5067
$C_{33}$	6.6314	5.2136	5.3063
$C_{44}$	2.1567	2.1228	1.9968



$C_{55}$	2.3903	0.6192	1.5766
$C_{66}$	1.6172	1.8631	1.8931
$C_{12}$	3.7091	2.8278	2.5984
$C_{13}$	3.5070	2.7959	3.5113
$E/\text{GPa}$	5.412	3.945	4.512
$K/\text{GPa}$	4.930	3.078	2.873
$G/\text{GPa}$	2.055	1.535	1.822
$\nu/\text{GPa}$	0.317	0.286	0.238
$K/G$	2.399	2.005	1.577
$\rho/\text{g}\cdot\text{cm}^{-3}$	1.697	1.752	1.741

### 3.3.3 Safety

The bond lengths of trigger bonds of DNTN in three high-energy propellant compositions were calculated. The distribution curves are shown in Fig. 5, and the bond lengths of the average ( $\lambda_{\text{ave}}$ ) and the largest ( $\lambda_{\text{max}}$ ) trigger bonds are listed in Table 6. It can be seen that the lengths of the C–NO<sub>2</sub> bonds in each system are larger than those of the O–NO<sub>2</sub> bonds, indicating the C–NO<sub>2</sub> bond is more unstable and easier to be ruptured under the external stimulus. Compared with the DNTN supercell, the  $\lambda_{\text{ave}}$  and  $\lambda_{\text{max}}$  of the C–NO<sub>2</sub> bond and O–NO<sub>2</sub> bonds are shorter and no matter what the plasticizer is, which maybe resulted from the Van der Waals forces between DNTN and other components in the propellants. Otherwise, when the plasticizer is BTTN, the C–NO<sub>2</sub> bond lengths ( $\lambda_{\text{ave}} = 1.494 \text{ \AA}$ ,  $\lambda_{\text{max}} = 1.540 \text{ \AA}$ ) are both shorter than those of the other ones, indicating that propellant with BTTN possesses the better safety performance. In addition, when the plasticizer is Bu–NENA or TMETN, the lengths of the C–NO<sub>2</sub> and O–NO<sub>2</sub> bonds are almost equal. The safety of three system decreases in the order: [GAP/BTTN/Al/DNTN] > [GAP/TMETN/Al/DNTN] > [GAP/Bu–NENA/Al/DNTN].

Table 6. The average and the maximum bond lengths of C–NO<sub>2</sub> and O–NO<sub>2</sub> of DNTN in DNTN-based propellants and DNTN supercell

Systems	C–NO <sub>2</sub>		O–NO <sub>2</sub>	
	$\lambda_{\text{ave}}/\text{\AA}$	$\lambda_{\text{max}}/\text{\AA}$	$\lambda_{\text{ave}}/\text{\AA}$	$\lambda_{\text{max}}/\text{\AA}$
DNTN	1.498	1.620	1.478	1.525
GAP/Bu–NENA/Al/DNTN	1.495	1.580	1.442	1.475
GAP/BTTN/Al/DNTN	1.494	1.540	1.444	1.475
GAP/TMETN/Al/DNTN	1.496	1.580	1.442	1.475

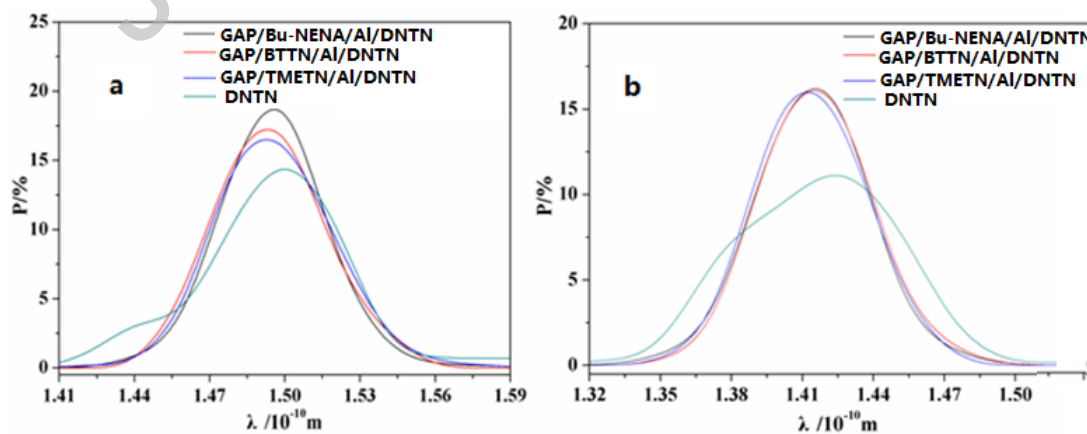


Fig. 5 The bond lengths ( $\lambda$ ) vs. percentages ( $P$ ) of DNTN in DNTN-based propellants and DNTN supercell. a- C–NO<sub>2</sub> bond; b- O–NO<sub>2</sub> bond

#### 4 Conclusions

(1) The binary mixed systems of DNTN/RDX, DNTN/HMX, DNTN/NTO-Pb, DNTN/Mg, DNTN/Al, DNTN/ADN and DNTN/NC-NG have good compatibility, the system of DNTN/GAP, DNTN/CL-20 and DNTN/A3 have moderate compatibility, while the system of DNTN/GUDN, DNTN/DNTF and DNTN/Bu-NENA have bad compatibility according to the evaluated standard of compatibility.

(2) The inert mixed systems of DNTN/HTPB, DNTN/PET, DNTN/C<sub>2</sub>, DNTN/C.B., DNTN/ - Cu, and DNTN/Al<sub>2</sub>O<sub>3</sub> are compatible, the DNTN/N-100, DNTN/TDI and DNTN/DINA binary mixtures have moderate compatibility, while the DNTN/ -Pb binary mixtures have bad compatibility according to the evaluated standard of compatibility.

(3) The mechanical properties and safety performance of three system decrease in the order: [GAP/BTTN/Al/DNTN] > [GAP/METN/Al/DNTN] [GAP/Bu-NENA/Al/DNTN]

#### Acknowledgements

This work was supported by the foundation of Science and Technology on Combustion and Explosion Laboratory of China (2019SYSZCJJ). We would like to thank Lu HongLin of Analysis and Measuring Center of Xi'an Modern Chemistry Research Institute for their enthusiastic supports in DSC measurements and analysis.

#### References

- [1] Vladimir A. Sizov, Dmitriy V. Pleshakov, Andrey F. Asachenko, et al. Synthesis and study of the thermal and ballistic properties of SMX [J]. Cent. Eur. J. Energ. Mater. 2018, 15(1): 30-46.
- [2] Politzer P, Murray J S. Energetic materials: part 1. Decomposition, crystal and molecular properties. Elsevier, Amsterdam, 2003.
- [3] Djalal Trache, Ahmed Fouzi Tarchoun. Stabilizers for nitrate ester-based energetic materials and their mechanism of action: a state-of-the-art review [J]. Journal of Materials Science, 2018, 53, 100-123.
- [4] Jimmie C. Oxley, James L. Smith, Joseph E. Brady IV, et al. Characterization and analysis of tetranitrate esters [J]. Propellants Explos. Pyrotech. 2012, 37, 24-39.
- [5] David E. Chavez, Michael A. Hiskey, Darren L. Naud, et al. Synthesis of an energetic nitrate ester [J]. Angewandte Chemie International Edition, 2008, 47(43): 8307–8309.
- [6] Haifeng Huang, Yameng Shi, Jun Yang, et al. Compatibility Study of dihydroxylammonium 5,5'- bistetrazole-1,1'-diolate (TKX-50) with some energetic materials and inert materials [J]. Journal of Energetic Materials, 2015, 33: 66-72.
- [7] Djalal Trache, Kamel Khimeche, Mokhtar Benziane, Abdallah Dahmani. Solid-liquid phase equilibria for binary mixtures of propellant's stabilizers [J]. Journal of Thermal Analysis and Calorimetry, 2013, 112, 215-222.
- [8] Weiqiang Pang, Xuezhong Fan, Yunna Xue, et al. Study on the compatibility of tetraethylammonium decahydrodecaborate (BHN) with some energetic components and inert materials [J]. Propellants Explos. Pyrotech. 2013, 38, 278-285.
- [9] Q.-L. Yan, X.-J. Li, L.-Y. Zhang, et al. Compatibility study of trans-1,4,5,8-tetranitro- 1,4,5,8-tetraazadecalin (TNAD) with some energetic components and inert materials [J]. J. Hazard. Mater. 2008, 34, 529-534.
- [10] Pang Wei-Qiang, Fan XueZhong, Xu Hui-Xiang, et al. Fuelrich solid rocket propellants technology [M]. Xi'an: Northwestern Polytechnical University Press, 2016.
- [11] Wang Juan, Liu Da-bin, Zhou Xin-li. Influence of 2,4,6-trinitrotoluene on properties of 2,3-bis(hydroxymethyl)-2,3-dinitro-1,4-butanediol tetranitrate [J]. Journal of Nanjing University of Science and Technology, 2014, 38(1): 161-165.
- [12] Yu Jiankun. Preparation, structure characterization and properties of novel melt cast explosive 2,3-

- dihydroxymethyl-2,3-dinitro-1,4-butanediol tetranitrate [J]. *Chemical Propellants & Polymeric Materials*, 2012, 10(5): 21-27.
- [13] Li Jizhen, Fan Xuezhong, Fan Xiping, et al. Compatibility study of 1,3,3-trinitroazetidine components and inert materials [J]. *J. Therm. Anal. Cal.*, 2006, 85(6): 779-784.
- [14] E.L.M. Krabbendam-La Haye, W.P.C. de Klerk, M. Miszczak, et al. Compatibility testing of energetic materials at TNO-PML and MIAT [J]. *J. Therm. Anal. Cal.*, 2003, 72, 931-936.
- [15] J.A.F.F. Rocco, J.E.S. Lima, A.G. Frutuoso, et al. Thermal degradation of a composite solid propellant examined by DSC [J]. *J. Therm. Anal. Cal.*, 2004, 75, 551-557.
- [16] Ju Rong-hui, Li Ji-zhen, Fan Xue-zhong, et al. Interaction and compatibility of DATTO<sub>3.5</sub> with main compounds of CMDB propellant [J]. *Chinese Journal of Energetic Materials*, 2016, 24(3): 249-255.
- [17] David A.Reese, Lori J.Groven, Steven F.Son. Formulation and characterization of a new nitroglycerin-free double base propellant [J]. *Propellants, Explosives, Pyrotechnics*, 2013, 35, 42-46.
- [18] W.P.C. de Klerk, A.E.D.M. vander Heijden, W.H.M. Veltmans. Thermal analysis of the high - energetic material HNF [J]. *J. Therm. Anal. Cal.*, 2001, 64, 973-985.
- [19] Nikita V. Muravyev, Anatoly A. Bragin, Konstantin A. Monogarov, et al. 5- amino- 3,4- dinitropyrazole as a promising energetic material [J]. *Propellants, Explosives, Pyrotechnics*, 2016, 41(6): 999-1005.
- [20] Bi Fu-qiang, Fan Xue-zhong, Fu Xiao-long, et al. Interaction of dihydroxylammonium 5,5'- bistetrazole -1,1'- diolate with CMDB propellant components [J]. *Journal of Solid Rocket Technology*, 2014, 37 (2): 214-218.
- [21] David A.Reese, Steven F.Son, Lori J.Groven. Composite propellant based on a new nitrate ester [J]. *Propellants, Explosives, Pyrotechnics*, 2014, 39, 684-688.
- [22] Zhu Wei, Liu Dong-mei, Xiao Ji-jun, et al. Molecular dynamics study on sensitivity criterion, thermal expansion and mechanical properties multi-component high energy systems [J]. *Chinese Journal of Energetic Materials*, 2014, 22(5): 582-587.
- [23] Wei Lun, Wang Qiong-lin, Liu Shao-wu, et al. Application of high energy density compounds CL-20, DNTF and ADN in high energy propellant [J]. *Chinese Journal of Explosives & Propellants*, 2009, 32(1): 17-20.
- [24] M. Farber, R.D. Srivastava, thermal decomposition of HMX, in: 16th JANNAF Combustion Meeting, 308, CPIA Pub., 1979, pp. 723-729.
- [25] Liu Zi-ru. Thermal decomposition of energetic materials [M]. BeiJing: National Defense Industry Press, 2008.
- [26] Zhang Chao, Wang Ke, Li Jun-qiang, et al. Muti-scale simulation and experimental study of NC/TMETN bonding system [J]. *Chinese Journal of Explosives & Propellants*, 2019, 42(6): 589-596.
- [27] Tian Li, Tao Guo-hong, Cai Hua-qiang. Crystal structure and sensitivity properties of 2,3-bis(hydroxylmethyl)-2,3-dinitrobutane-1,4-diol tetranitrate [J]. *The 2nd national hazardous materials and safety technology proceeding*, 2013, 16-23.
- [28] Svatopluk Zeman. Some predictions in the field of the physical thermal stability of nitramines [J]. *Thermochim. Acta*, 1997, 302(1-2): 11-16.
- [29] Huang Meng, Ding Li, Chang Hai, et al. Study on interaction between component for HTPB/Al/AP/RDX composite propellant [J]. *Chinese Journal of Explosives & Propellants*, 2020, 43(2): 203-208.
- [30] Qi Xiao-fei, Zhang Xiao-hong, Guo Xin, et al. Molecular dynamics simulation on mechanical properties of NC/DIANP blends [J]. *Chinese Journal of Explosives & Propellants*, 2013, 36(2): 57-61,81.