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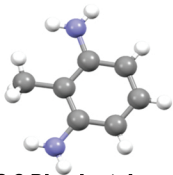
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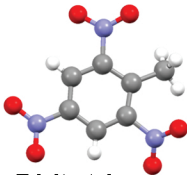
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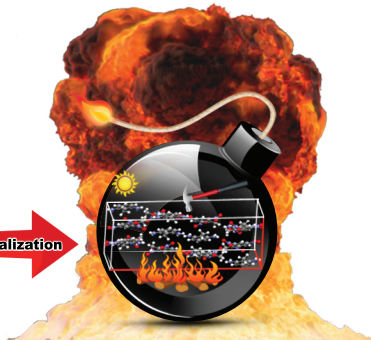
**2,6-Diaminotoluene**

+



**Trinitrotoluene**

**Cocrystalization**



# Characterization and Properties of a New Energetic Co-Crystal Composed of Trinitrotoluene and 2,6-diaminotoluene

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**Abstract:** A 1:1 co-crystal of TNT and 2,6-diaminotoluene were prepared by solvent evaporation method. The structure of the co-crystal was determined via single crystal and powder X-ray diffraction techniques. The diffraction data analysis revealed that the co-crystal is mainly formed by hydrogen bonding (amino-nitro) and donor-acceptor  $\pi$ - $\pi$  stacking. Besides, Hirshfeld surfaces and associated fingerprint plots of the co-crystal were examined and the results showed that the structures are stabilized by H...H, O...H, O...O and C...C ( $\pi$ - $\pi$ ) intermolecular interactions. The TNT: 2,6-diaminotoluene co-crystal shows significantly reduced impact sensitivity relative to pure TNT. The difference between the impact sensitivity of co-crystal and the impact sensitivity of TNT is due to having different intermolecular interactions observed in the co-crystal structure. This comprehensive study about the formation of co-crystal has resulted in alteration of vital properties including density, oxygen balance, melting point, decomposition temperature, crystal packing and detonation performance (sensitivity, velocity, pressure). The obtained results highlight that co-crystallization provides the newly discovered energetic material with attractive properties, and is an effective way to modify existing energetic material. As a consequence, the advanced and safer energetic material can be created without chemical synthesis.

**Keywords:** Trinitrotoluene, impact sensitivity, energetic co-crystal, detonation performance, crystal packing

## 1. Introduction

In material science, energetic materials including explosives, propellants and pyrotechnics which can be stored and quickly release too much amount of chemical energy on demand are important for both military and civilian purposes. Modern explosives are required to have high energy (pressure, velocity, and density), and low mechanical sensitivity [1]. In recent years, to achieve high energy output, high safety and low cost has been one of the targets of the development of explosives. Energy output and safety are the most important properties of explosives. They usually limit each other. In other words, the higher energy output generally goes with low safety [2]. The present trend is that co-crystallization is used as an alternative method to achieve explosives with better qualities [3]. Co-crystals are multi-component crystalline materials made up of two or more neutral co-formers, bonded by intermolecular forces such as hydrogen bonding,  $\pi$ -stacking and/or van der Waals forces. Co-crystallization is utilised to improve the physicochemical properties and performance of the composition for specific applications [4].

Co-crystals of TNT [5], 1, 3, 5, 7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) [6], and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) [7] have revealed the ability for altering materials properties with the help of co-crystallization by using energetic/non-energetic materials. Especially, 1:1 CL-20/BTF [8], 1:1 CL-20/TNT [9], and 2:1 CL-20/HMX [10] have brought about high-power and safe explosives.

Conventional energetic material, TNT, which has been utilized for a long time during military exercises, has highly negative ecological effect on the environment. And, this, at the same time, requires expensive and time consuming enhancement and detoxification operations. So, new, environmentally-friendly, non-toxic and highly energetic materials which require safe handling and storage have to be improved [11].

In this paper, non-energetic material 2,6-diaminotoluene was selected to form a co-crystal (TNT-ATL) with TNT. Also, crystal structure characterization, intermolecular interactions, thermal behaviour, detonation performance, crystal packing, impact sensitivity of the new co-crystal explosive are discussed. The aim of this study is not only to present advances of new co-crystal as energetic material, but also to provide new insights into future design of alternative TNT co-crystal in this field.

## 2. Experimental

### 2.1. Materials

TNT was synthesized from 2,4-dinitrotoluene (DNT) according to a known procedure [12]. 2,6-diaminotoluene was purchased from Sigma-Aldrich.

### 2.2. Preparation method

Crystallization was performed by dissolving a 1:1 molar ratio of TNT (1.57 mg), and 2,6-diaminotoluene (0.84 mg) in 85% anhydrous ethanol (approximately 3–5 mL) at 45 °C and stirring for 45 min. The solvent was allowed to evaporate at room temperature over a period of several days.

### 2.3. Optical microscopy

Optical micrographs of TNT and TNT-ATL crystals were taken under the SK2005A polarization microscope.

### 2.4. Single crystal X-ray diffraction

The single crystal X-ray diffraction data of the co-crystals was collected on an Agilent Technologies Super Nova diffractometer equipped with an Oxford Cryo systems. The crystal was kept at  $T = 120.0$  K during data collection. Using Olex2 [13], the structure was solved with the ShelXT [14] structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2017/1 of ShelXL [15] using Least Squares minimization.

### 2.5. Powder X-ray diffraction (PXRD)

PXRD patterns were recorded utilizing the D2 PHASER Advance instrument using Cu-K $\alpha$  radiation ( $\lambda = 1.54439$  Å), and an operating voltage and current 40 kV and 40 Ma, respectively. The data were collected over an angle range of  $2\theta = 5$ – $50^\circ$ . This technique provided an initial screening of samples for formation of co-crystals.

## 2.6. Differential scanning calorimetry

DSC was performed on a NETZSCH STA 449 F1 Differential Scanning Calorimeter. 1.58 mg of sample was placed in an aluminium pan, and the thermal behaviour of the samples was studied under a nitrogen purge (30.0 mL/min) at a heating rate of 10 °C/min over a range of 25-400 °C.

## 2.7. Infrared spectroscopy

The Infrared spectra were obtained by Fourier transform techniques with a Perkin-Elmer Spectrum 65 FT-IR spectrometer with ATR. Each spectrum was scanned in the range 500–4000  $\text{cm}^{-1}$ . Resolution ratio was 4  $\text{cm}^{-1}$ .

## 2.8. Impact sensitivity properties

The impact sensitivity was determined by using a BAM fall hammer device (BFH-12). Impact testing was conducted at the Cavendish Laboratory, Cambridge on the TNT and TNT-ATL co-crystal. A sample of 40  $\text{mm}^3$  was enclosed in anvil device consist of two coaxial steel cylinders. Anvil devices were disposed of along with sample after test. A load of 10 kg was dropped on to a sample from heights ranging from 10 cm to 100 cm. The ‘one-in-six’ test procedure was performed to obtain limiting impact energy for both tested sample. The method conducted throughout is the 30 trial Bruceton method [16].

## 3. Results and Discussion

### 3.1. The microscopic image of co-crystal

The macro-morphology of the crystals reflects its microscopic structure. The crystal morphologies are indicated in Figure 1. As seen in the Figure 1(b), the co-crystals which have a well-defined morphology, a regular structure, and a uniform size are dark red crystals. This differs from the crystal shape of TNT in the Figure 1(a), which are white plates. The dissimilarity in morphology also shows that co-crystal molecules have a different crystal structure.



(a)

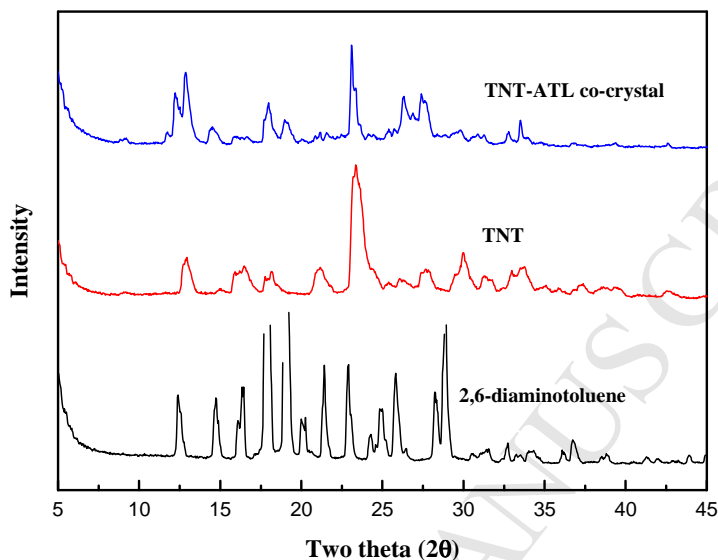


(b)

**Figure 1.** Microscope images of (a) TNT, (b) TNT-ATL.

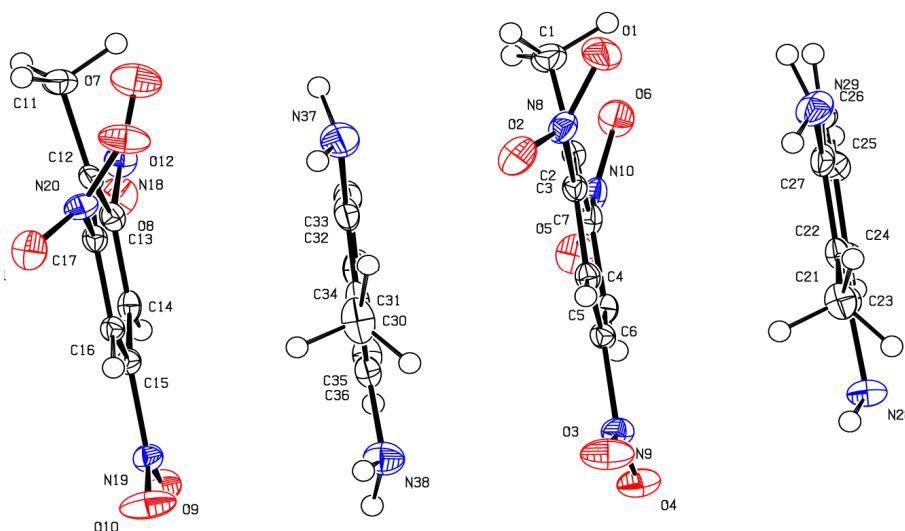
### 3.2. Structural characterization of TNT-ATL

The powder X-ray diffraction (PXRD) of the co-crystal, TNT and the co-former is indicated in Figure 2. The characteristic diffraction peaks of TNT and 2,6-diaminotoluene do not appear in the PXRD pattern. It is obvious that the diffraction pattern of the co-crystal is different from that of TNT and the co-former, demonstrating the formation of a new co-crystal.



**Figure 2.** Comparison of PXRD patterns with 2,6-diaminotoluene, TNT and TNT-ATL.

The crystal structure of the TNT-ATL co-crystal was determined by single-crystal X-ray diffraction data as indicated in Table 1. The ORTEP drawing of TNT-ATL co-crystal is indicated in Figure 3. The crystal data have been deposited in the Cambridge Crystallographic Data Centre; the CCDC number is 1845100.



**Figure 3.** ORTEP drawing of compound TNT-ATL

The main non-covalent interaction occurs between the electron-rich and electron-poor aromatic rings, as in between the electron-poor  $\pi$ -system of TNT and the electron-rich  $\pi$ -system of 2,6-diaminotoluene. When choosing electron-rich aromatic ring substances, COSMOtherm [17] software was used to predict the likelihood of co-crystal formation, by calculating the excess enthalpy of formation of the co-formers. The calculations were generated by the Turbomole package using the BP86 density functional with a TZVP34 basis set (BPTZVP-COSMO level of theory).

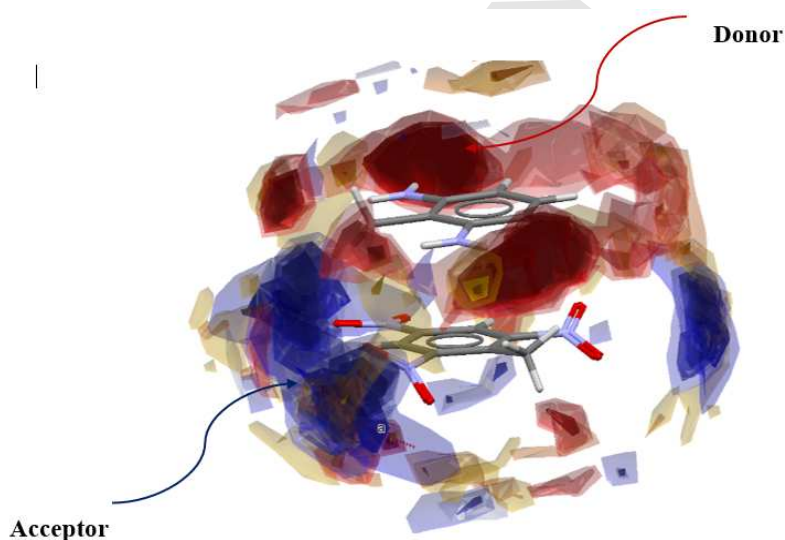
**Table 1.** Single-crystal X-Ray refinement factor for TNT-ATL.

Empirical formula	C <sub>14</sub> H <sub>15</sub> N <sub>5</sub> O <sub>6</sub>
Formula weight (g/mol)	349.31
Temperature/K	120.01(10)
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	9.5539 (4)
b/Å	28.8303 (14)
c/Å	11.1975 (5)
$\alpha$ /°	90
$\beta$ /°	99.451 (4)
$\gamma$ /°	90
Volume/Å <sup>3</sup>	3042.4 (2)
Z	8
$\rho_{\text{calc}}$ /g/cm <sup>3</sup>	1.525
$\mu$ /mm <sup>-1</sup>	0.122
F(000)	1456
Crystal size/mm <sup>3</sup>	0.518 × 0.242 × 0.074
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073)
2 $\theta$ range for data collection/°	5.618 to 59.532
Index ranges	-13 ≤ h ≤ 13, -37 ≤ k ≤ 38, -15 ≤ l ≤ 14
Reflections collected	53750
Independent reflections	8022 [R <sub>int</sub> = 0.0572, R <sub>sigma</sub> = 0.0468]
Data/restraints/parameters	8022/0/487
Goodness-of-fit on F <sup>2</sup>	1.032
Final R indexes [I ≥ 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0657, wR <sub>2</sub> = 0.1484
Final R indexes [all data]	R <sub>1</sub> = 0.0899, wR <sub>2</sub> = 0.1603

As can be understood from X-ray crystal structure data indicated in Figure 4 and Table 2, intermolecular hydrogen bonds occur between amino and nitro groups (N-H...O). The amino proton is located between the two oxygen of the neighbouring nitro group in a position where the proton could interact with both oxygen concurrently. The distances between the amino nitrogen and the nitro oxygens are distribution from 2.979 to 3.834 Å, and the two NH proton to nitro oxygen distances are distribution from 2.271 to 3.062 Å. The results showed that the hydrogen-bond strengths are weak, according to the expected weak proton-donating and accepting strengths. Cooperative effects originating from the conjugated nature of the hydrogen-bonded chains can contribute an additional stabilizing force to these chains. Furthermore, the strength of the hydrogen bond contributes to the stability of the crystals.

Mono-coordinated and bi-coordinated (three-centred) amino-nitro interactions can be clearly observed in Figure 5(a). The most common hydrogen-bond in amino-nitro interaction involves a three-centre hydrogen bond with the amino proton located between the two "inside" lone pairs of electrons of a single nitro group. Foremost, once a primary amino group donates one of its protons to a three-centre inside hydrogen bond, its second proton will form a two-centre bond to an intramolecular acceptor [18]. Utilization of  $\pi$ - $\pi$  stacking is of vital significance for the further development of supramolecular chemistry, and crystal structures prediction [19]. The electron donor-acceptor  $\pi$ - $\pi$  interactions carry great importance in the formation of TNT-ATL co-crystal. The distance between TNT and 2,6-diaminotoluene (stacked (facial) interlayers distance) has been measured as 3.509 Å as indicated in Figure 5 (b). The results of the new TNT-ATL co-crystal search are as follows: centroid-centroid contacts distance between two aromatic compounds slightly above 3.4 Å. Strong interactions are around 3.3 Å and weaker interactions between 3.6 Å and 3.8 Å being almost the maximum contact for which  $\pi$ - $\pi$  interactions are confirmed [20].

Both hydrogen bonding and  $\pi$ - $\pi$  stacking interactions are known as significant non-covalent intermolecular forces. As it is known close-packing is related with degree of intermolecular interactions; the higher the intermolecular interactions the higher close-packing.  $\pi$ - $\pi$  staking interactions causes formation of co-crystals but do not effect packing that much. As is evident from the x-rays data, packing is significantly affected from hydrogen bonds in these molecules.



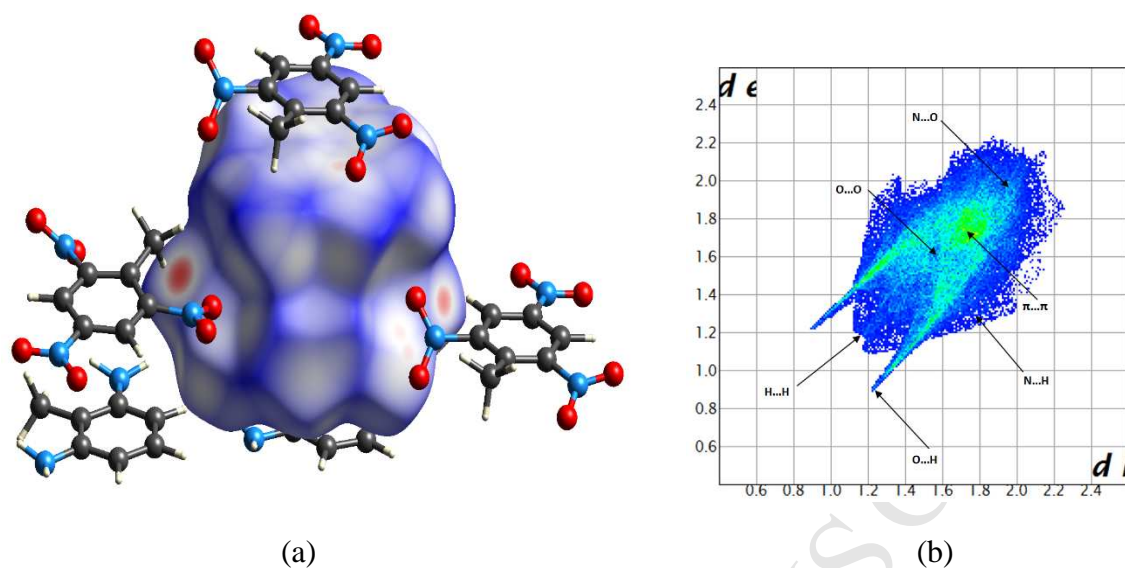
**Figure 4.** Full interaction maps between TNT and 2,6-diaminotoluene

**Table 2.** Hydrogen bond geometry (Å) of TNT-ATL co-crystal

Donor (D)	H	Acceptor (A)	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N	H	O				
N28	H28A	O3	0.87	2.271	3.047	147.05
N38	H38B	O10	0.88	2.275	2.979	136.87
N29	H29A	O12	0.88	2.777	3.545	146.65
N38	H38A	O5	0.88	2.773	3.483	138.7
N37	H37A	O2	0.88	3.062	3.834	147.61
N37	H37A	O1	0.88	2.703	3.533	157.75

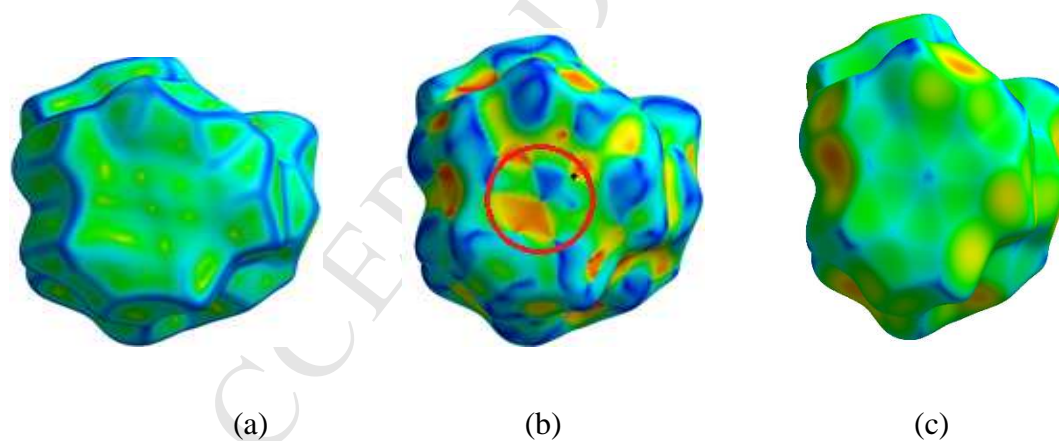






**Figure 6.** (a) Hirshfeld surface analysis of TNT-ATL, (b) the two-dimensional fingerprint plot of TNT-ATL.

Curvedness was always mapped on the Hirshfeld surfaces between  $-4.0$  (red) and  $+0.4$  (blue), and shape index between  $1.0$  (red) and  $+1.0$  (blue).  $d_e$  was mapped on the most appropriate scale for each group of compounds examined in order to maximize the information derived from this distance property and to make possible direct comparison between the related structures.

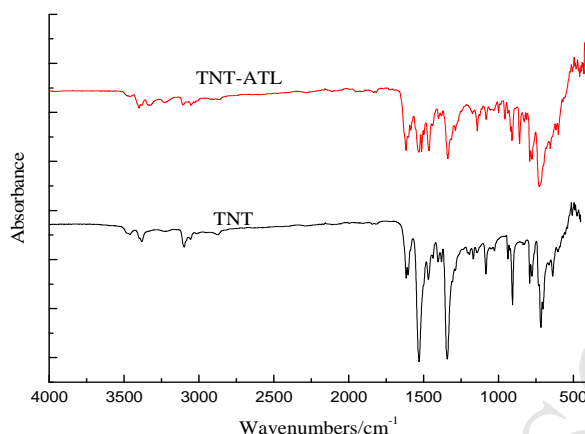


**Figure 7.** The molecule is shown with the Hirshfeld surface mapped with (a) curvedness, (b) shape index and (c)  $d_e$ .

### 3.4. Infrared spectroscopy

The formation of co-crystals with TNT changes both the  $\pi$ -stacking of the co-crystal former and reorients especially the nitro groups of the TNT molecule. Particularly, there exists a noteworthy alteration in the angle of the nitro group in the 4-position of TNT in the TNT-ATL co-crystal. As for the monoclinic TNT, these nitro groups of non-equivalent molecules make angles of  $33.5$  and  $23.5^\circ$  to the benzene ring. TNT-ATL co-crystal angles are  $30.48^\circ$

and  $28.70^\circ$ . The alteration in orientation of the nitro groups significantly affects the structural features of TNT in the co-crystal. The change during the orientation of the nitro groups in fact is sufficient. It outcomes in shifts in the vibrational spectra of this material. The IR spectra of TNT and TNT-ATL are indicated in Figure 8.

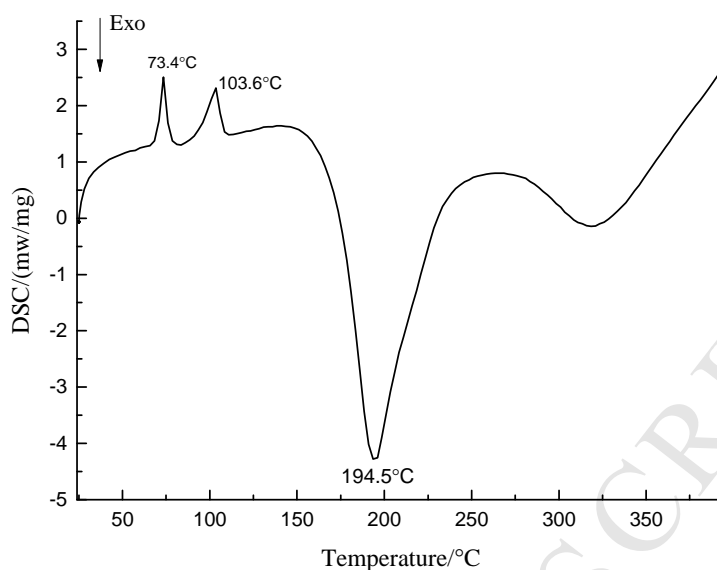


**Figure 8.** Comparison of infrared spectrum patterns for TNT and TNT-ATL.

Monoclinic TNT has an asymmetric nitro stretch ( $\nu_{as}$ ) at  $1532\text{ cm}^{-1}$  and a symmetric nitro stretch ( $\nu_s$ ) at  $1347\text{ cm}^{-1}$ . In the TNT-ATL co-crystal, the asymmetric nitro stretch ( $\nu_{as}$ ) is at  $1529\text{ cm}^{-1}$  and the symmetric nitro stretch ( $\nu_s$ ) at  $1336\text{ cm}^{-1}$ . Some peak shifts can lead to both the hydrogen bonding and the  $\pi$ - $\pi$  stacking, which alter the symmetry characteristics in the co-crystal structure.

### 3.5. Differential scanning calorimetry study of TNT-ATL

Differential scanning calorimetry (DSC) is a useful technique for determination of the thermal behaviour of materials. DSC thermogram is indicated in Figure 9, which contains two endotherms and one exotherm peaks. The first endotherm, that is  $73.4\text{ }^\circ\text{C}$ , it is supposed that TNT originated from the impurity. The TNT-ATL co-crystal was measured at melting point of  $103.6\text{ }^\circ\text{C}$ , which is higher melting point compared to TNT ( $82.1\text{ }^\circ\text{C}$ ) [25]. The melting point is a result of the lattice energy, namely different total intermolecular interaction occurred in a crystal cell [26]. The increase in melting point indicates to intermolecular interactions, while the TNT-ATL co-crystal formed  $\pi$ - $\pi$  stacking interaction, hydrogen bonding which leads the lattice energy to be much higher than TNT. In addition, increasing the melting point can be advantageous while creating munitions that resist deformation before detonation [5]. Co-crystallization can produce important alterations in another critical physical feature for energetic materials: the decomposition temperature. It was observed that exothermic peak at  $194.5\text{ }^\circ\text{C}$ , which might be attributed to some changes in the crystal phase.



**Figure 9.** DSC curve for TNT-ATL.

### 3.6. Energetic Performance

#### 3.6.1. Prediction Sensitivity

##### 3.6.1.1. Impact sensitivity

Impact sensitivity mainly depends on the chemical and physical properties. In this work, 10 kg drop weight was used. The  $h_{50}$  values of TNT and TNT-ATL were found to be 25.1 cm (impact energy 25.1 J) and 79.4 cm (impact energy 79.4 J), respectively. The outcomes of experiments imply that it is possible to reduce sensitivity significantly by crystallising TNT with non-energetic co-former.

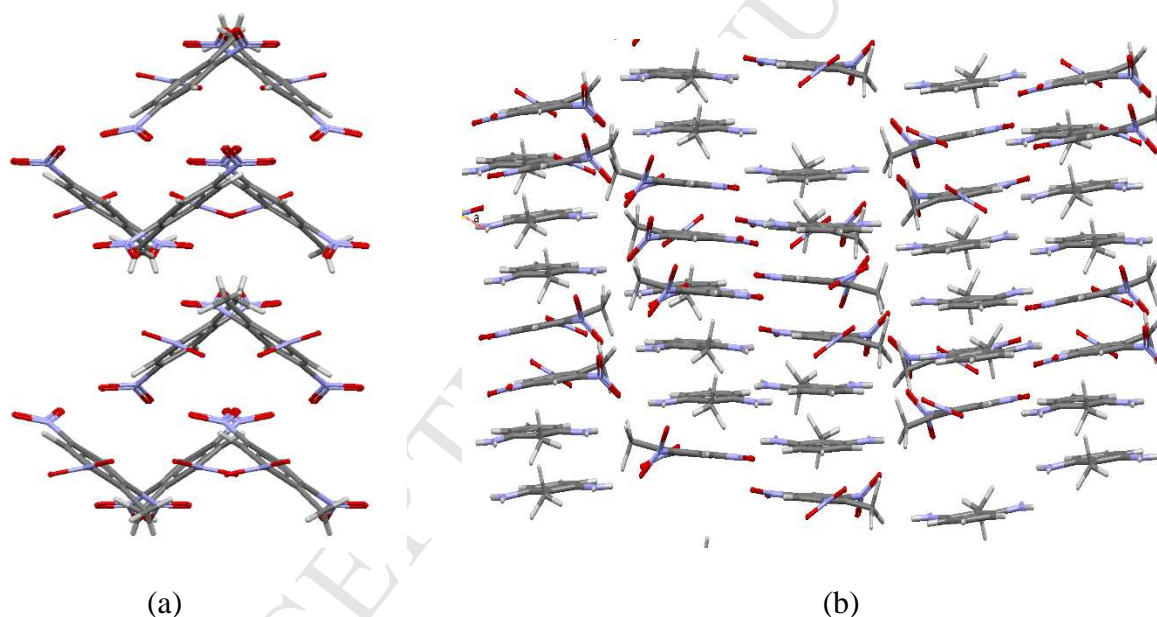
##### 3.6.1.1. Crystal packing effect on impact sensitivity

An organic energetic material is a metastable molecule, which is capable of releasing large amount of chemical energy quickly and highly with exothermic reactions. Therefore, prediction of its sensitivity is quite complex. Various techniques are used to measure an energetic sensitivity, including impact, shock, heat, electrostatic charge, friction etc. [28]. Earlier research indicated that numerous factors can affect these properties such as crystal packing, density, oxygen balance within the molecular structure, intermolecular hydrogen bonding,  $\pi \dots \pi$  staking, voids, defects, decomposition and molecular motion within a crystal lattice [29].

There should be a link between the packing structure and sensitivity, as performances and properties are always determined by structures. Nonetheless, there is no relationship discovered so far. Four types of stacking are used to clarify the crystal packing and to rationalize the effect of stacking on impact sensitivity. All  $\pi$ -stacking can be categorized as wavelike stacking, crossing stacking, mixed stacking, and face-to-face stacking [30]. The structures composed of parallel (face-to-face) or close to parallel layers are frequently less vulnerable to insensitive shear strain caused by impact or shock, since the layers may be able to slip/slide past each other easily [31]. This decreases the strain-induced localization of externally introduced energy, namely, the formation of hot spots. Indeed, perfect face-to-face

$\pi$ -stacked (layered) energetic materials are rarely seen, which potentially reduces impact sensitivity of energetic materials [32].

The possibility of structure having parallel or close to parallel layers is increased when the molecules are planar, especially if there is the likelihood of important intermolecular noncovalent interactions within the layers, such as hydrogen bonding and  $\pi\cdots\pi$  staking. Planar molecules also pack better in the crystal lattice, [33] resulting in desirably higher densities as well as less free space, which is often associated with lower sensitivity. It is interesting to compare 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and 1,1-diamino-2,2-dinitroethylene (FOX-7). They are both planar in their crystal structures and are involved in strong intermolecular hydrogen bonding between the  $-\text{NH}_2$  and the  $-\text{NO}_2$  [31a-31b-34b]. The hydrogen bonding helps  $\pi$ -stacking, which makes some energetic materials impact-insensitive. For example, TATB and FOX-7 have layered structures, however, the TATB layers are planar whereas those of FOX-7 are zigzag [31a-31b-34b]. TATB and FOX-7 impact energy is 120 J and 31 J, respectively. As in the examples above, in the structure of the new TNT-ATL co-crystal, face-to-face stacking occurs along the molecular planar and represents a facile sliding mechanism, as indicated in Figure 10, and suggests that this TNT-ATL co-crystal will exhibit low impact sensitivity compared to pure TNT.



**Figure 10.** (a) A comparison of the herringbone packing of TNT [34], (b) the face-to-face  $\pi$ -stacking of the TNT-ATL co-crystal

### 3.6.2. Calculation of detonation performance

Detonation parameters are essential for gaining a simple understanding of a material's energetic performance. Detonation performance includes two important parameters to calculate performance of explosive compounds; detonation pressure and detonation velocity. In this study, Kamlet-Jacobs empirical equations (1.1 and 1.2) were used to determine  $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$  (TNT: ATL and TNT) compounds [35-37].

$$D = 1.01 \cdot (N^{0.5}) \cdot (M_{\text{ave}} \cdot Q)^{0.25} \cdot (1 + 1.30 \cdot \rho) \quad (1.1)$$

$$P = 1.558 \cdot \rho^2 (N) \cdot (M_{\text{ave}} \cdot Q)^{0.5} \quad (1.2)$$

Where: D, detonation velocity (km/s); P, detonation pressure (GPa);  $\rho$ , density of a compound ( $\text{g}/\text{cm}^3$ ); N, moles of gaseous detonation products per gram of explosive;  $M_{\text{ave}}$ , average molecular weight of gaseous products; Q, chemical energy of detonation (kcal/g). The coefficient (0.239) of  $\Delta H^{\circ}\text{f}$  in the relations is a conversion factor from kJ/mol to kcal/mol. “M” is the molecular weight of the compound (in g/mol);  $\Delta H^{\circ}\text{f}$  is the standard heat of formation of the compound (in kJ/mol). The parameters N,  $M_{\text{ave}}$ , and Q are calculated according to the chemical composition of each explosive as revealed in literature (Table 3) [38].

**Table 3.** Stoichiometric relations key for calculations of the N,  $M_{\text{ave}}$  and Q parameters of the  $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$  explosives [38]

Stoichiometric relations			
Parameter	$c \geq 2a + b/2$	$2a + b > 2c \geq b/2$	$b/2 > c$
N	$(b + 2c + 2d)/4M$	$(b + 2c + 2d)/4M$	$(b + d)/2M$
$M_{\text{ave}}$	$4M/(b + 2c + 2d)$	$(56d + 88c - 8b)/(b + 2c + 2d)$	$(2b + 28d + 32c)/(b + d)$
$Q \times 10^{-3}$	$(28.8b + 94.05a + 0.239\Delta H^{\circ}\text{f})/M$	$[28.9b + 94.05(c/2 - b/4) + 0.239\Delta H^{\circ}\text{f}]/M$	$(57.8c + 0.239\Delta H^{\circ}\text{f})/M$

All theoretical calculations were carried out using the Gaussian G09W (revision B.01) program package. The enthalpies (H) and Gibbs free energies (G) were calculated using the complete basis set (CBS) method of Petersson and co-workers to get very accurate energies. The CBS models use the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated CBS limit. CBS-4 begins with an HF/3-21G(d) geometry optimization; the zero-point energy is computed at the same level. It uses a large basis set SCF calculation as a base energy, and an MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. An MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher order contributions. In this study, we applied the modified CBS-4M method (M referring to the use of minimal population localization), which is a reparametrized version of the original CBS-4 method and also includes some additional empirical corrections [39]-[40]. For a reference concerning the suitability and reliability of the applied CBS-4 M method see for example ref. [41]. For a  $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$  type explosive, %  $\square$  is calculated as  $1600(2a + b/2 - c)/M$ . The calculated oxygen balance ( $\square$ ), heat of formation ( $\Delta H^{\circ}\text{f}$ ), the chemical energy of detonation (Q), density ( $\rho$ ) and detonation velocity (D) and pressure (P) are listed in Table 4.

**Table 4.** Calculated detonation properties of TNT and TNT-ATL co-crystal

Molecule	$\square/\%$	$\Delta H^{\circ}\text{f}/$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )	Q/ ( $\text{kcal}\cdot\text{g}^{-1}$ )	$\rho/$ ( $\text{g}\cdot\text{cm}^{-3}$ )	D/ ( $\text{km}\cdot\text{s}^{-1}$ )	P/ GPa
TNT	-73.98	52	1417	1.64	7.11	19
TNT-ATL	-135.1	62.5	1594	1.525	7.08	18.5

## 4. Conclusion

Co-crystallization can be an effective technique for modification of the physicochemical properties of energetic materials. In this study, a novel co-crystal explosive including TNT and 2,6-diaminotoluene (in a 1:1 molar ratio) was synthesized and characterized. The formation of TNT-ATL co-crystal was found to result from both

intermolecular hydrogen bonding interactions (amino-nitro) and  $\pi$ - $\pi$  stacking. Besides, weak hydrogen bonds and  $\pi$ - $\pi$  stacking need to be taken into consideration in crystal engineering because they can affect crystal packing in unpredictable ways. The theoretical calculations verify that TNT-ATL co-crystal has almost equal energetic properties with TNT and lower impact sensitivity than its parent compound, which highlights its potential application as a novel energetic material. The co-crystallization technique showed in this study that the technique can be a favourable way to enhance safety of energetic materials by tuning crystal packing structure. Such a new energetic co-crystal reduces the impact sensitivity of accidental detonation. Hence, such formulations can be of vital importance for insensitive munitions. This new TNT co-crystal will provide a new and effective technique to modify the properties of certain compounds, and this will contribute to the production of enhanced explosives, which paves the way for future design of insensitive TNT co-crystals.

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**Highlights:**

- Co-crystallization of Trinitrotoluene
- Structure analysis and characterization of new formed co-crystal (TNT-ATL)
- Showed detonation performance of TNT-ATL co-crystal by calculation of theoretical method
- Explanation of Structure relationship with sensitivity

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