

## Article

# Small Deviations in Geometries Affect Detonation Velocities and Pressures of Nitroaromatic Molecules

Danijela S. Kretić , Marija I. Maslarević and Dušan Ž. Veljković \* 

University of Belgrade, Faculty of Chemistry, Studentski trg 12–16, 11000 Belgrade, Serbia;  
danijela@chem.bg.ac.rs (D.S.K.); majamaslarevic@gmail.com (M.I.M.)

\* Correspondence: vdusan@chem.bg.ac.rs

**Abstract:** Understanding the factors that affect the detonation performance of high-energy molecules (HEMs) is crucial for the design of novel explosives and fuels with desirable characteristics. While molecular factors, such as the presence of specific functional groups that give organic molecules explosive properties, are key determinants of detonation characteristics, other factors like the geometry of molecules in crystal structures can also affect the high-energy properties of materials. Although it is known that slight deviations in the crystal structure geometry affect the sensitivity of nitroaromatic explosives, the influence of these variations on detonation performance remains unknown. In this study, we extracted different crystal structures of the same high-energy nitroaromatic molecules from the Cambridge Structural Database and calculated their detonation velocities and pressures using the Kamlet–Jacobs equations. Results indicated that different geometries of the same crystal structure can lead to non-negligible differences in detonation velocities and pressures. In the case of the 2,4,6-triamino-1,3,5-trinitrobenzene molecule, discrepancies in detonation pressures among different crystal structures were calculated to be 7.68%. Analysis of geometrical arrangements showed that these differences are mainly the consequence of diverse non-covalent bonding patterns that affect crystal densities.

**Keywords:** crystal structures; high-energy material; Cambridge Structural Database; detonation velocity; detonation pressure



Received: 13 November 2024

Revised: 21 February 2025

Accepted: 31 March 2025

Published: 9 April 2025

**Citation:** Kretić, D.S.; Maslarević, M.I.; Veljković, D.Ž. Small Deviations in Geometries Affect Detonation Velocities and Pressures of Nitroaromatic Molecules. *Organics* **2025**, *6*, 17. <https://doi.org/10.3390/org6020017>

**Copyright:** © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Controlling the detonation properties of high-energy materials (HEMs) is the focus of numerous theoretical and experimental studies [1–8]. To achieve control over the detonation features of high-energy molecules, it is necessary to reveal and understand all the factors that affect different aspects of the detonation process. The two most important characteristics of high-energy molecules are detonation performance and sensitivity towards external stimuli. The main goal of the high-energy material design is to achieve low sensitivity and high detonation performance for newly developed explosives. Unfortunately, these objectives are often conflicting since in most cases low sensitivity of explosives is coupled with low performance and vice versa [4].

Detonation performance is usually expressed in terms of detonation velocity (D) and detonation pressure (P). While there is no reliable procedure for precise calculation of the sensitivity towards detonation of HEMs, detonation velocities and pressures of organic CHNO explosives could be successfully calculated using Kamlet–Jacobs Equations (1) and (2) [9–11]:

$$D \text{ (km/s)} = 1.01 \varphi^{0.5} (1 + 1.30 \rho) \quad (1)$$

$$P_D \text{ (kbar)} = 15.58 \varphi \rho^2 \quad (2)$$

In these equations,  $\rho$  represents density (in g/cm<sup>3</sup>) while  $\varphi$  is the Kamlet–Jacobs parameter. This parameter is defined by Equation (3):

$$\varphi = N M_{\text{ave}}^{0.5} Q^{0.5} \quad (3)$$

where  $N$  is the number of moles of detonation products in the gas phase per gram of HEM,  $M_{\text{ave}}$  is the average molecular mass of products in the gas phase (in g/mol), and  $Q$  is total heat release (in calories per gram of HEM). According to these equations, detonation velocity and pressure of HEM are determined by four quantities: loading density, number of moles of gaseous products, molecular mass of gaseous products, and total heat release. Since loading density is defined as the mass of the explosive per volume unit, which depends on particular circumstances, it is common to use crystal density ( $d$ ) instead of loading density [12]. Crystal density itself may be affected by multiple factors like the planarity of HEMs that constitute the crystal, and hydrogen bonds [4]. Although molecular planarity is not a necessary precondition for the high crystal density of HEMs, it was found that planar HEMs have to some extent higher density compared to non-planar molecules. This phenomenon raises the question of the influence of geometry on the detonation characteristics of these HEMs.

As already mentioned, several factors affect the sensitivity and detonation performance of explosives. However, there are some factors that can affect both of these characteristics of HEMs. One of these factors is hydrogen bonding. Hydrogen bonding may alter the sensitivity of HEMs towards detonation, both by increasing it and decreasing it [4,13]. While intramolecular hydrogen bonds usually decrease the sensitivity of HEMs by preventing nitro groups from leaving the molecule, intermolecular hydrogen bonds through their stabilizing effect decrease HEMs' heat of formation [4,14]. Furthermore, hydrogen bonding may affect the density of HEMs, a feature that according to the Kamlet–Jacobs equation significantly contributes to the detonation performance of the explosives.

It is known that HEM polymorphs with the same chemical composition but different crystal packing possess different detonation characteristics [8,15]. A study of the relationship between charge distribution on nitro-groups and detonation properties of selected HEMs showed that different values of torsion angles of nitro groups in HEM polymorphs lead to differences in detonation characteristics [16].

Recently, it was shown that small differences in geometries between different crystal structures of the same nitroaromatic molecules significantly affect their sensitivities towards detonation [8,17,18]. However, it is still unknown how these differences affect detonation pressure and detonation velocities of nitroaromatic molecules. In this study, we compared detonation pressures and velocities calculated for the series of crystal structures of trinitroaromatic molecules with small differences in geometries to reveal the influence of deviations in geometries on detonation performance. The results obtained in this way were explained in the context of crystal density and non-covalent bonding patterns in crystal structures of selected HEMs.

## 2. Materials and Methods

Crystal structures of five common trinitroaromatic explosives were chosen for analysis (1,3,5-trinitrobenzene (TNB), 2,4,6-trinitrophenol (TNP), 2,4,6-trinitrotoluene (TNT), 2,4,6-triamino-1,3,5-trinitrobenzene (TATNB), and 2,4,6-trinitrophenylmethylnitramine (TETRYL)), based on a previously performed study investigating the influence of geometric parameters on the sensitivity of high-energy nitroaromatic compounds [8]. All crystal structures were extracted from the Cambridge Structural Database (CSD) [19]. Only those structures in which no other molecules (except for the studied HEM) were present have

been selected for further analysis. A special focus was on the structure obtained by neutron diffraction experiment, since in this structure the positions of all atoms (including hydrogens) were reliable. All structures with differences in geometries were selected for further analysis, regardless of the underlying cause for the geometry differences (polymorphism, experimental errors, or variations in crystallographic determination methodologies). Detonation velocities and pressures were calculated using the DEPRO calculator which is part of the Atomistica.online software (version 1.20) [20,21]. All DEPRO calculations of detonation velocities and pressures were based on the Kamlet–Jacobs equations. Crystal densities necessary for detonation velocity and pressure calculations were extracted from CSD, too. Three-dimensional structures were visualized and non-covalent interactions were analyzed using Mercury software (version 2023.3.1.) [22].

### 3. Results

#### 3.1. Calculations of Detonation Velocity and Detonation Pressure

Three-dimensional representations of nitroaromatic high-energy molecules that were studied in the frame of this research are given in Figure 1.

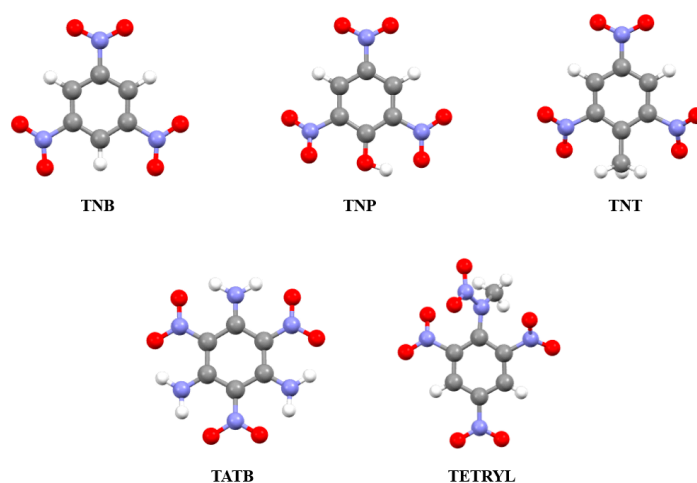


**Figure 1.** Three-dimensional structures of TNB, TNP, TNT, TATNB, and TETRYL molecules.

For all studied molecules, the Cambridge Structural Database was searched according to criteria given in Methodology section, and extracted geometries were used for calculations of detonation performance and velocity. In the case of the TNB molecule, five crystal structures that contained only the TNB molecule were extracted and studied (Figure 2).

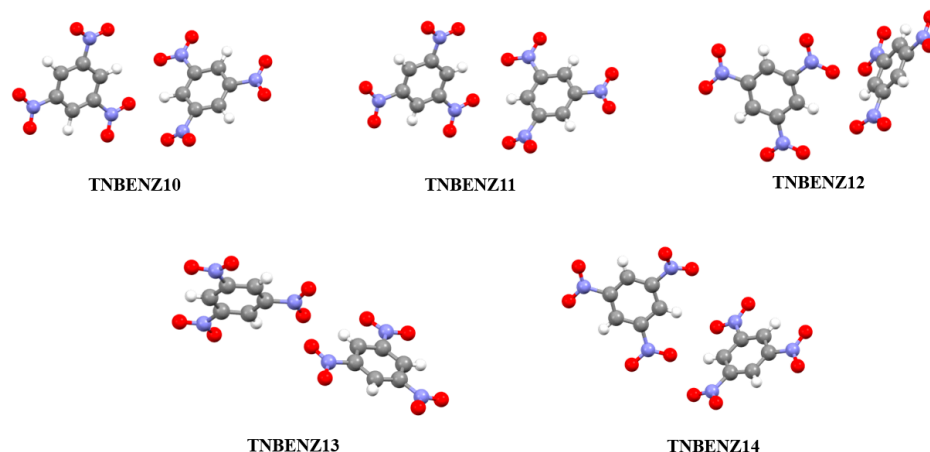


**Figure 2.** Fragments of crystal structures TNBENZ10, TNBENZ11, TNBENZ12, TNBENZ13 and TNBENZ14 that contain the trinitrobenzene molecule.

An experimental heat of formation for 1,3,5-trinitrobenzene ( $-37.0$  kJ/mol) necessary for the calculation of D and P values was taken from the literature [23]. The calculated values of D and P for different crystal structures of TNB are given in Table 1.

**Table 1.** Calculated detonation velocities (D) and detonation pressures (P) for selected crystal structures containing 1,3,5-trinitrobenzene molecules. Experimental crystal densities ( $\rho$ ) were also provided.

| CSD REFCODE | $\rho$ (g/cm <sup>3</sup> ) | D (km/s) | P (kbar) |
|-------------|-----------------------------|----------|----------|
| TNBENZ10    | 1.676                       | 7.2789   | 224.9444 |
| TNBENZ12    | 1.688                       | 7.3146   | 228.1770 |
| TNBENZ13    | 1.717                       | 7.4009   | 236.0846 |
| TNBENZ11    | 1.729                       | 7.4366   | 239.3961 |
| TNBENZ14    | 1.737                       | 7.4575   | 241.3384 |

Analysis of calculated D and P values showed that there are non-negligible differences in these values for different crystal structures of the same HEM. The lowest values of D and P were calculated for the TNBENZ10 crystal structure ( $D = 7.2789$  km/s and  $P = 224.9444$  kbar). This is the structure with the lowest crystal density ( $\rho = 1.676$  g/cm<sup>3</sup>). On the other hand, the highest values of D and P were calculated for the TNBENZ14 crystal structure ( $D = 7.4575$  km/s and  $P = 241.3384$  kbar), which also has the highest value of crystal density ( $\rho = 1.737$  g/cm<sup>3</sup>).

In the case of the TNP molecule, 10 crystal structures containing only TNP molecules were extracted from the CSD (Figure 3).

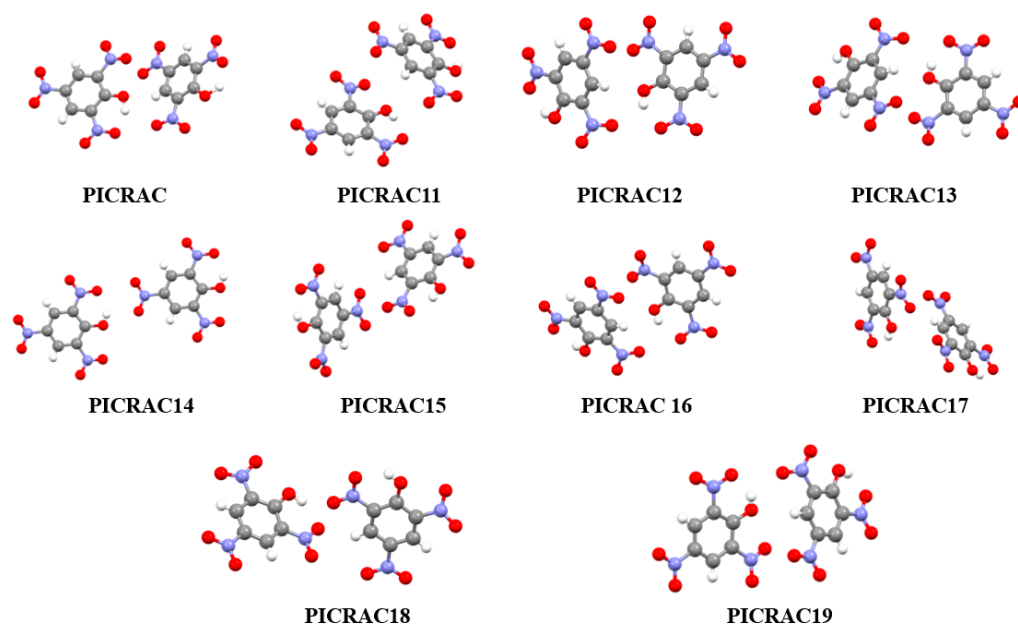


**Figure 3.** Fragments of crystal structures PICRAC, PICRAC11, PICRAC12, PICRAC13, PICRAC14, PICRAC15, PICRAC16, PICRAC17, PICRAC18 and PICRAC19 that contain the 2,4,6-trinitrophenol molecule.

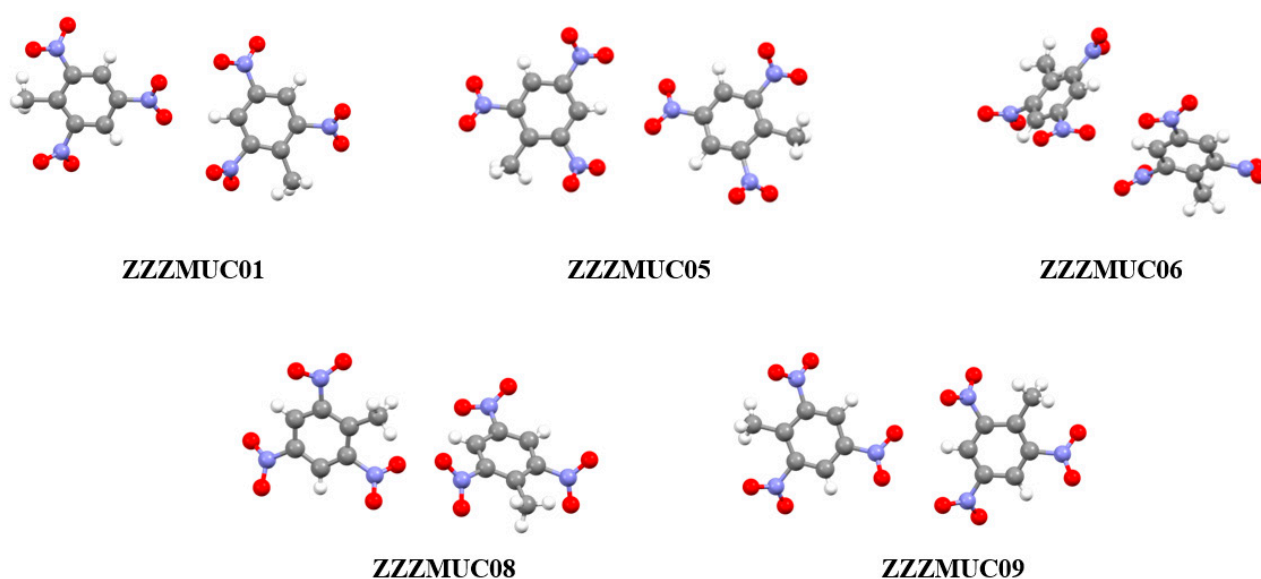
An experimental heat of formation for 2,4,6-trinitrophenol ( $-217.9$  kJ/mol) necessary for the calculation of D and P values was taken from the literature [24]. Calculated values of D and P for the TNP molecule are given in Table 2.

**Table 2.** Calculated detonation velocities (D) and detonation pressures (P) for selected crystal structures containing 2,4,6-trinitrophenol molecules. Experimental crystal densities ( $\rho$ ) were also provided.

| CSD REFCODE | $\rho$ (g/cm <sup>3</sup> ) | D (km/s) | P (kbar) |
|-------------|-----------------------------|----------|----------|
| PICRAC19    | 1.761                       | 7.5504   | 249.5617 |
| PICRAC11    | 1.768                       | 7.5713   | 251.5496 |
| PICRAC      | 1.771                       | 7.5803   | 252.4040 |
| PICRAC18    | 1.774                       | 7.5892   | 253.2599 |
| PICRAC17    | 1.789                       | 7.6340   | 257.5609 |
| PICRAC12    | 1.794                       | 7.6489   | 259.0026 |
| PICRAC16    | 1.801                       | 7.6698   | 261.0277 |
| PICRAC15    | 1.812                       | 7.7026   | 264.2260 |
| PICRAC14    | 1.819                       | 7.7235   | 266.2714 |
| PICRAC13    | 1.822                       | 7.7324   | 267.1505 |

In the case of 2,4,6-trinitrophenol fragments, analysis of calculated D and P values showed that differences in these values for different crystal structures of the same HEM are also significant. The lowest values of D and P were calculated for the PICRAC19 crystal structure (D = 7.5504 km/s and P = 249.5617 kbar). This is the structure with the lowest crystal density ( $\rho$  = 1.761 g/cm<sup>3</sup>). The highest values of D and P were calculated for the PICRAC13 crystal structure (D = 7.7324 km/s and P = 267.1505 kbar), which has the highest value of crystal density ( $\rho$  = 1.822 g/cm<sup>3</sup>).

Search of the CSD according to the criteria mentioned in the Methodology section resulted in the extraction of five structures containing solely 2,4,6-trinitrotoluene fragment (Figure 4).

**Figure 4.** Fragments of crystal structures ZZZMUC01, ZZZMUC05, ZZZMUC06, ZZZMUC08, and ZZZMUC09, that contain the 2,4,6-trinitrotoluene molecule.

Similar to previous cases, an experimental heat of formation for 2,4,6-trinitrotoluene (−63.2 kJ/mol) was found in the literature [24]. Calculated values of D and P for the TNT molecule are given in Table 3.

**Table 3.** Calculated detonation velocities (D) and detonation pressures (P) for selected crystal structures containing 2,4,6-trinitrotoluene molecules. Experimental crystal densities ( $\rho$ ) were also provided.

| CSD REFCODE | $\rho$ (g/cm <sup>3</sup> ) | D (km/s) | P (kbar) |
|-------------|-----------------------------|----------|----------|
| ZZZMUC05    | 1.648                       | 7.0024   | 205.9722 |
| ZZZMUC06    | 1.650                       | 7.0082   | 206.4724 |
| ZZZMUC01    | 1.655                       | 7.0227   | 207.7257 |
| ZZZMUC09    | 1.704                       | 7.1646   | 220.2082 |
| ZZZMUC08    | 1.713                       | 7.1907   | 222.5404 |

Differences in values of D and P for crystal structures containing the TNT molecules were not as significant as in previous cases, but still non-negligible. The lowest values of D and P were calculated for the ZZZMUC05 structure (D = 7.0024 km/s and P = 205.9722 kbar), while the highest values were calculated for the ZZZMUC08 structure (D = 7.1907 km/s and P = 222.5404 kbar). It is interesting to notice that D and P values calculated for crystal structures containing TNT were significantly lower than for TNB and TNP crystal structures.

Only two crystal structures containing the 2,4,6-triamino-1,3,5-trinitrobenzene molecule were extracted from the CSD (Figure 5).

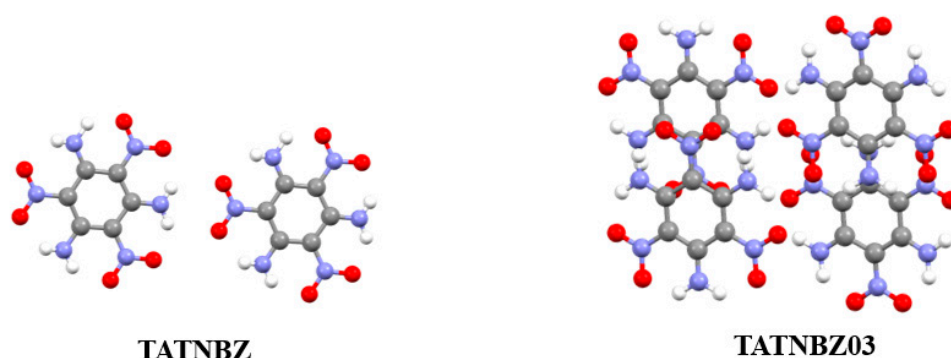


**Figure 5.** Fragments of crystal structures TATNBZ and TATNBZ03, that contain the 2,4,6-triamino-1,3,5-trinitrobenzene molecule.

While 2,4,6-triamino-1,3,5-trinitrobenzene is known for very moderate impact sensitivity due to the network of intramolecular hydrogen bonds that prevent the rupture of the C-N bonds, detonation velocity and pressure for this HEM are very high compared to other nitroaromatic explosives like TNT [25]. Calculations showed that the TATNBZ structure has D value of 8.0555 km/s and P value of 300.4390 kbar (Table 4). These values are even higher for the TATNBZ03 crystal structure: calculations showed that for this structure D value is 8.2907 km/s and P value is 325.4453 kbar. For the purpose of this study, an experimental heat of formation for 2,4,6-triamino-1,3,5-trinitrobenzene (−74.7 kJ/mol) was found in the literature [26].

**Table 4.** Calculated detonation velocities (D) and detonation pressures (P) for selected crystal structures containing 2,4,6-triamino-1,3,5-trinitrobenzene molecules. Experimental crystal densities ( $\rho$ ) were also provided.

| CSD REFCODE | $\rho$ (g/cm <sup>3</sup> ) | D (km/s) | P (kbar) |
|-------------|-----------------------------|----------|----------|
| TATNBZ      | 1.937                       | 8.0555   | 300.4390 |
| TATNBZ03    | 2.016                       | 8.2907   | 325.4453 |

It should be noted that both TATNBZ and TATNBZ03 crystal structures have very high crystal densities (1.937 and 2.016 g/cm<sup>3</sup>, respectively).

Similar as in previous case, only two crystal structures containing solely the 2,4,6-trinitrophenylmethylnitramine molecule were found in the CSD (Figure 6).

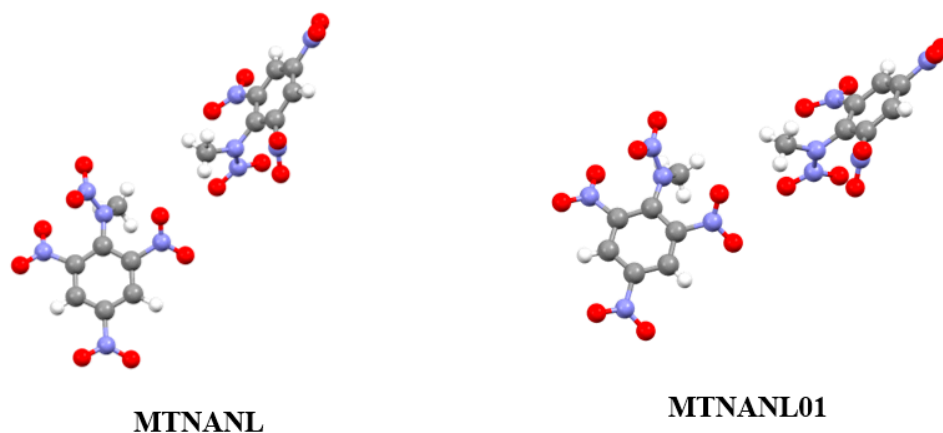


**Figure 6.** Fragments of crystal structures MTNANL and MTNANL01, that contain the 2,4,6-trinitrophenylmethylnitramine (TETRYL) molecule.

Calculated detonation velocities and pressures for these crystal structures are more similar to the TNT than to TATNB crystal structures. In the case of the MTNANL structure, D was calculated to be 7.7101 km/s, while P was calculated to be 257.5120 kbar (Table 5). For the MTNANL01 structure, the calculated D value was 7.7040 km/s, while P was 256.9173 kbar. For the purpose of these calculations, an experimental heat of formation for 2,4,6-trinitrophenylmethylnitramine (−41.0 kJ/mol) was found in the literature [27].

**Table 5.** Calculated detonation velocities (D) and detonation pressures (P) for selected crystal structures containing 2,4,6-trinitrophenylmethylnitramine molecules. Experimental crystal densities ( $\rho$ ) were also provided.

| CSD REFCODE | $\rho$ (g/cm <sup>3</sup> ) | D (km/s) | P (kbar) |
|-------------|-----------------------------|----------|----------|
| MTNANL      | 1.731                       | 7.7101   | 257.5120 |
| MTNANL01    | 1.729                       | 7.7040   | 256.9173 |

### 3.2. Analysis of Non-Covalent Interactions in Crystal Structures

Since D and P values are dependent on crystal density, which is on the other hand affected by non-covalent bonding patterns and strengths, non-covalent interactions were analyzed in crystal structures with highest and lowest values of crystal density.

The comparison of non-covalent bonding patterns for crystal structures TNBENZ10 (the lowest value of crystal density among the crystals containing TNB) and TNBENZ14 (the highest value of crystal density among the crystals containing TNB) was performed in the context of C-H $\cdots$ O interactions and stacking interactions between nitroaromatic molecules (Figure 7). In the TNBENZ10 crystal structure, C-H $\cdots$ O interactions ranging in length from 2.281 to 2.969 Å were identified. However, these contacts were mainly monofurcated (interacting hydrogen atom bonded to one oxygen atom). In the TNBENZ14 crystal structure, C-H $\cdots$ O interactions with O $\cdots$ H distances between 2.325 and 3.119 Å were detected. Compared to the TNBENZ10 structure, in TNBENZ14 C-H $\cdots$ O interactions were mainly bifurcated (two hydrogen atoms interacting with one oxygen atom) or simultaneous (two oxygen atoms interacting with one hydrogen atom). Previous studies have showed that although longer, bifurcated C-H $\cdots$ O interactions are stronger than monofurcated interactions in the case of aromatic C-H donors [27].

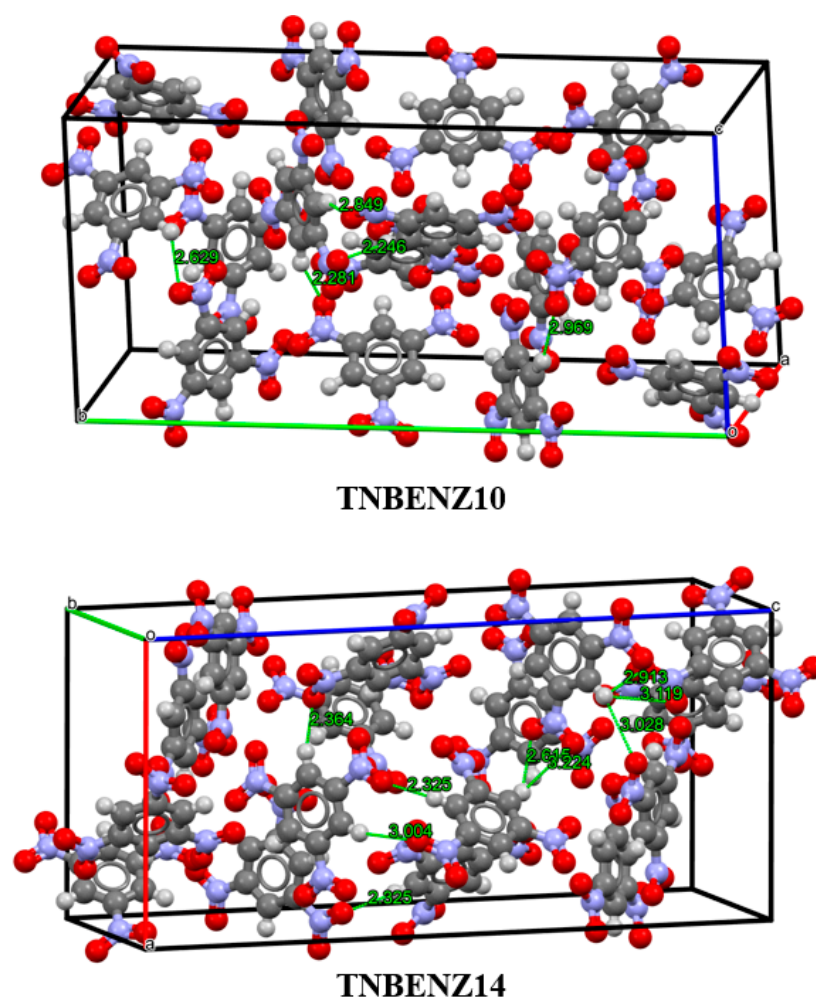


**Figure 7.** Important C-H $\cdots$ O contacts in fragments of TNBENZ10 and TNBENZ14 crystal structures.

While in the crystal structure TNBENZ10 stacking interactions were not detected due to the T-shaped crystal packing, in the case of the TNBENZ14 structure visual analysis showed that stacking interactions between nitroaromatic fragments were present.

Similar situation was observed in crystal structures of 2,4,6-trinitrophenol (Figure 8). In the case of the PICRAC19 structure (which has the lowest value of crystal density among the crystals containing TNP), C-H $\cdots$ O interactions are rare and monofurcated, with O $\cdots$ H distances of 2.434 Å. On the other hand, in the crystal structure PICRAC13 (which has the highest value of crystal density among the crystals containing TNP) numerous C-H $\cdots$ O interactions were identified, including bifurcated interactions. The O $\cdots$ H distances in C-H $\cdots$ O interactions detected in the PICRAC13 crystal structure had values between 2.352 and 2.638 Å.

The non-covalent bonding patterns in crystal structures containing the TNT molecule are more complicated (Figure 9).

Among the structures that contain the TNT molecule, the structure ZZZMUC05 has the lowest value of crystal density, while the structure ZZZMUC08 has the highest value (Table 3). Although both crystal structures contain mainly monofurcated C-H $\cdots$ O interactions, the ZZZMUC08 structure contains  $\pi$ - $\pi$  stacking interactions between nitroaromatic fragments, too (Figure 8). The distance between centroids of two parallelly oriented trinitro aromatic fragments is 5.832 Å, with the angle between the ring planes of 15.92°.

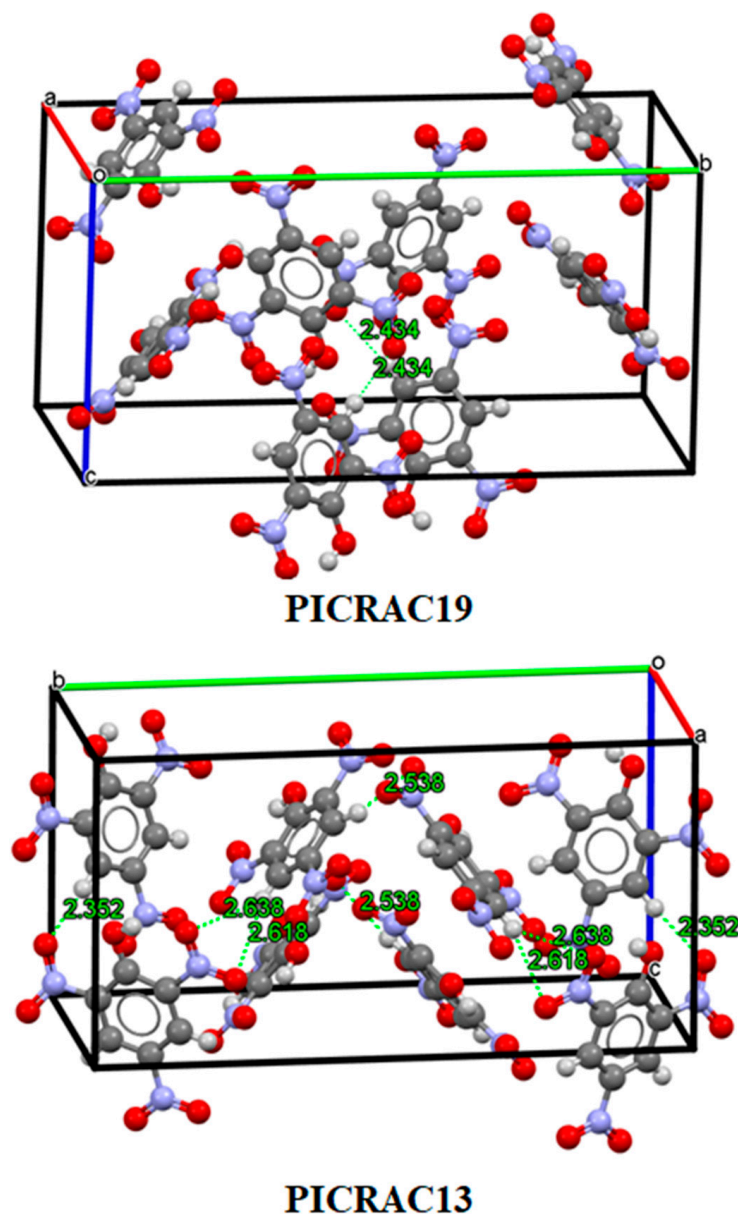


**Figure 8.** Important C-H $\cdots$ O contacts in fragments of PICRAC19 and PICRAC13 crystal structures.

In the case of TATNB and TETRYL molecules, only two crystal structures were extracted for each of these molecules (TATNBZ and TATNBZ03 containing the TATNB molecule and MTNANL and MTNANL01 containing TETRYL molecule).

Three-dimensional structures for both molecules are given in Figures S1 and S2. Calculations showed that the TATNBZ crystal structure have significantly lower detonation pressure value (more than 25 kbar) and moderately lower detonation velocity value compared to the TATNBZ03 structure. From the analysis of crystal structures, it could be seen that stacking interactions and N-H $\cdots$ O hydrogen bonds between aromatic rings exist in both crystal structures (C-H $\cdots$ O interactions were not present since in the TATNB molecule there are no C-H fragments). It could also be noticed that distances between centroids of nitroaromatic rings are shorter in TATNBZ03 (5.040 Å) than in the TATNBZ (5.101 Å) crystal structure. In terms of N-H $\cdots$ O interactions, in both structures patterns of these contacts are similar.

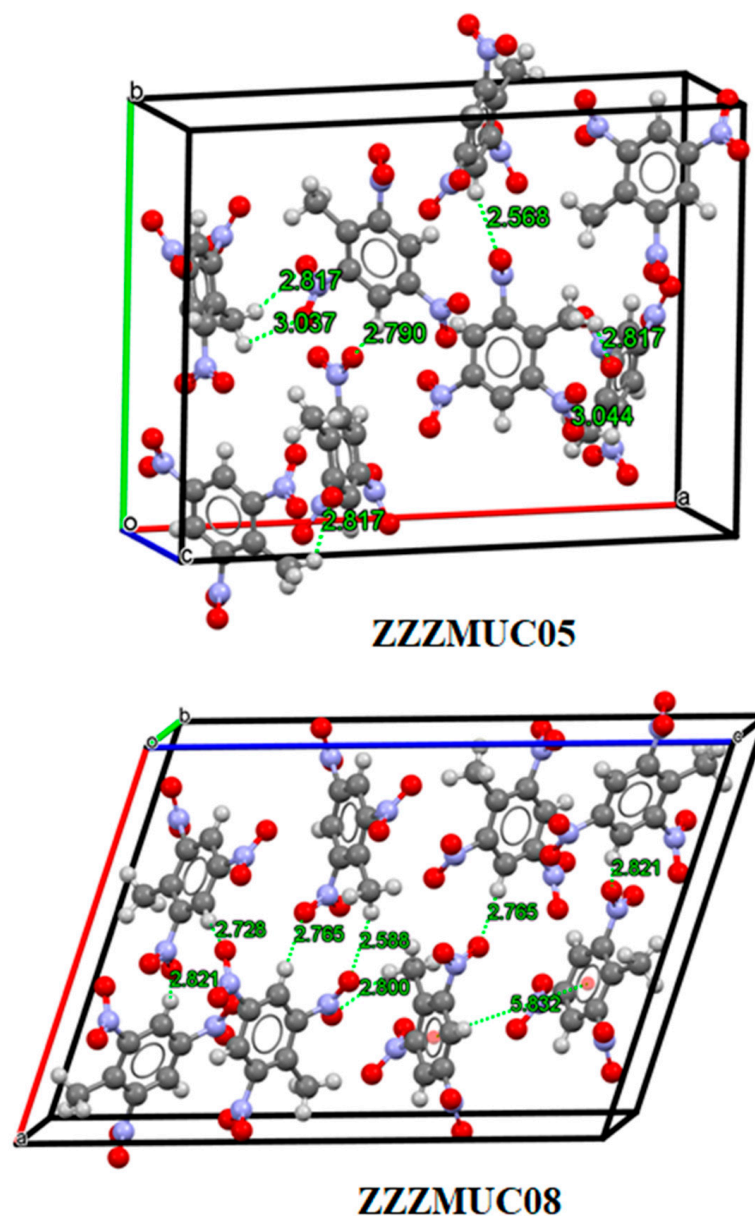


**Figure 9.** Important C-H $\cdots$ O and  $\pi$ - $\pi$  stacking interactions in fragments of ZZZMUC05 and ZZZMUC08 crystal structures.

In the case of MTNANL and MTNANL01 crystal structures, calculations showed that both structures have similar D and P values. Analysis of crystal structures indicates that in both structures similar patterns of monofurcated C-H $\cdots$ O interactions could be recognized.

#### 4. Discussion

Analysis of the calculated detonation velocities and pressures reveals that subtle geometric variations within nitroaromatic molecules can lead to substantial differences in detonation performance. The most pronounced discrepancies in D and P values were observed between non-identical crystal structures of TATNB. The detonation pressure disparity between TATNBZ and TATNBZ03 was calculated to be 25.01 kbar (7.68%), while the detonation velocity difference was 2.84%. According to the Kamlet-Jacobs equations, these variations primarily stem from differences in crystal densities. The underlying cause of these crystal density differences can be attributed to variations in non-covalent interaction patterns within the crystal structures. Analysis of non-covalent interactions in

the TATNBZ and TATNBZ03 structures shows that  $\pi$ - $\pi$  stacking interactions are shorter in the TATNBZ03 structure (centroid-centroid distance of 5.040 Å) than in the TATNBZ structure (centroid-centroid distance of 5.101).

The second most significant difference was detected between two crystal structures containing TNT molecules, ZZZMUC08 and ZZZMUC05. The difference in calculated P values for these two structures was 16.57 kbar (7.45%), and D values were 2.62%. Analysis of non-covalent contacts showed that in the ZZZMUC08 structure  $\pi$ - $\pi$  stacking interactions were present (centroid-centroid distance of 5.832 Å), while in ZZZMUC05 nitroaromatic fragments are mostly T-shape arranged without the possibility for energetically stable  $\pi$ - $\pi$  stacking interactions. This discrepancy is the most likely cause for different crystal density values. In addition, in both crystal structures, similar networks of monofurcated C-H $\cdots$ O interactions were noticed.

In the case of the TNB molecule, the difference in detonation pressure values between the TNBENZ10 and TNBENZ14 structures (structures with the lowest and highest D and P values) is 16.39 kbar (6.79%). At the same time, the difference between detonation velocity values for these two structures was smaller, 2.39%. It should be pointed out that the crystal structure TNBENZ10 was obtained by a very precise neutron diffraction experiment. Analysis of non-covalent interaction patterns for these two structures shows significant discrepancies between non-covalent bonding patterns of these structures both in terms of  $\pi$ - $\pi$  stacking and C-H $\cdots$ O interactions. Interactions of  $\pi$ - $\pi$  type in the TNBENZ14 structure (centroid-centroid distance of 5.793 Å) were significantly shorter than similar contact in the TNBENZ10 structure (centroid-centroid distance of 5.907 Å). The combined effect of shorter  $\pi$ - $\pi$  distances and the presence of multiple bifurcated C-H $\cdots$ O interactions is the most probable reason for higher crystal density values for the TNBENZ14 structure.

A similar situation with respect to C-H $\cdots$ O interactions bonding patterns was recognized in crystal structures containing TNP molecules. The difference in P value between the PICRAC19 (lowest crystal density) and PICRAC13 structures (highest crystal density) was calculated to be 17.59 kbar (6.58%), while the difference in calculated D values was 2.35%. Analysis of non-covalent bonding patterns showed the network of C-H $\cdots$ O interactions in both crystal structures. However, in the PICRAC structure, a few monofurcated C-H $\cdots$ O interactions were detected (O $\cdots$ H distance in the shortest C-H $\cdots$ O interaction was measured to be 2.434 Å), while in PICRAC13 numerous C-H $\cdots$ O interactions were detected including bifurcated interactions (O $\cdots$ H distance in the shortest C-H $\cdots$ O interaction was measured to be 2.352 Å).

Analysis of the two crystal structures containing the TETRYL molecule also provided interesting results with respect to the influence of geometry variations on the detonation performance of nitroaromatic HEMs. In both MTNANL and MTNANL01 structures, very similar non-covalent bonding patterns consisting of monofurcated C-H $\cdots$ O interactions were identified (O $\cdots$ H distance in the shortest C-H $\cdots$ O interaction was measured to be around 2.4 Å in both structures). On the other hand, experimental crystal density values, as well as calculated D and P values were also very similar. The difference in calculated P values was 0.23%, while the difference in calculated D values was only 0.08%. Results showing that similar bonding patterns result in similar crystal density, D and P values further confirm our conclusion that differences in non-covalent bonding led to different detonation performance values. It should be noted that due to the empirical nature of the Kamlet-Jacobs equations, the calculated values of detonation parameters may exhibit a slight level of uncertainty.

## 5. Conclusions

Results obtained within this study show that small deviations in crystal structure geometries may alter the detonation velocity (D) and pressure (P) of high-energy nitroaromatic molecules. The differences in detonation pressure values for different crystal structures of the TATNB molecule were calculated to be 7.68%. Similar values were obtained in cases of all the other studied nitroaromatic HEMs except for the TETRYL molecule, where these differences were very small. The main reason for these differences in detonation performance is different values of crystal densities, which are mainly the consequence of specific non-covalent bonding patterns characteristic for every crystal structure. The  $\pi$ - $\pi$  stacking and C-H $\cdots$ O interactions were identified as the most significant non-covalent interactions in crystal structures of nitroaromatic HEMs. The presence of bifurcated C-H $\cdots$ O interactions usually leads to higher values of crystal densities, compared to the structures containing monofurcated C-H $\cdots$ O interactions. Structures in which similar patterns of non-covalent interactions were recognized (like MTNANL and MTNANL01 structures containing TETRYL molecule) also had very similar values of D and P. These results may be of great importance for the design of new high-energy materials since they show that even in the case of the same HEM, detonation performance could be improved by preparing crystal structures with different molecular arrangements.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/org6020017/s1>, Figure S1: Important C-H $\cdots$ O contacts in fragments of TATNBZ and TATNBZ03 crystal structures; Figure S2: Important C-H $\cdots$ O contacts in fragments of ZZZMUC05 and ZZZMUC08 crystal structures.

**Author Contributions:** Conceptualization, D.Ž.V.; methodology, D.Ž.V.; validation, D.Ž.V. and D.S.K.; formal analysis, D.S.K., M.I.M. and D.Ž.V.; investigation, D.S.K., M.I.M. and D.Ž.V.; resources, D.Ž.V.; data curation, D.S.K. and M.I.M.; writing—original draft preparation, D.Ž.V.; writing—review and editing, D.S.K. and D.Ž.V.; visualization, D.S.K. and D.Ž.V.; project administration, D.Ž.V.; funding acquisition, D.Ž.V. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work is supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Contract numbers: 451-03-66/2024-03/200168 and 451-03-136/2025-03/200168), and it contributes to the achievement of Sustainable Development Goals 9 (Industry, Innovation, and Infrastructure) and 12 (Responsible Consumption and Production). This research was supported by the Science Fund of the Republic of Serbia, PROMIS, #6066886, CD-HEM.

**Data Availability Statement:** The original contributions presented in this study are included in this article/Supplementary Materials. Further inquiries can be directed to the corresponding author.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References

1. Born, M.; Karaghiosoff, K.; Klapötke, T.M.; Voggenreiter, M. Oxetane Monomers Based on the Powerful Explosive LLM-116: Improved Performance, Insensitivity, and Thermostability. *ChemPlusChem* **2022**, *87*, e202200049. [CrossRef] [PubMed]
2. Born, M.; Plank, J.; Klapötke, T.M. Energetic Polymers: A Chance for Lightweight Reactive Structure Materials? *Prop. Explos. Pyrotech.* **2022**, *47*, e202100368. [CrossRef]
3. Agrawal, J.P.; Dodke, V.S. Some Novel High Energy Materials for Improved Performance. *Z. Anorg. Allg. Chem.* **2021**, *647*, 1856–1882. [CrossRef]
4. Politzer, P.; Murray, J.S. High Performance, Low Sensitivity: Conflicting or Compatible? *Propellants Explos. Pyrotech.* **2016**, *41*, 414–425. [CrossRef]
5. Politzer, P.; Murray, J.S. Detonation Performance and Sensitivity: A Quest for Balance. In *Advances in Quantum Chemistry*; Academic Press: Cambridge, MA, USA, 2014; Volume 69, pp. 1–30.
6. Nešić, J.; Cvijetić, I.N.; Bogdanov, J.; Marinković, A. Synthesis and Characterization of Azido Esters as Green Energetic Plasticizers. *Prop. Explos. Pyrotech.* **2021**, *46*, 1537–1546. [CrossRef]

7. Kretić, D.S.; Veljković, I.S.; Veljković, D.Ž. Tris(3-nitropentane-2,4-dionato- $\kappa^2$  O,O') Complexes as a New Type of Highly Energetic Materials: Theoretical and Experimental Considerations. *Chemistry* **2023**, *5*, 1843–1854. [[CrossRef](#)]
8. Kretić, D.S.; Medaković, V.B.; Veljković, D.Ž. How Do Small Differences in Geometries Affect Electrostatic Potentials of High-Energy Molecules? Critical News from Critical Points. *Crystals* **2022**, *12*, 1455. [[CrossRef](#)]
9. Kamlet, M.J.; Jacobs, S.J. Chemistry of Detonations. I. A Simple Method for Calculating Detonation Properties of C–H–N–O Explosives. *J. Chem. Phys.* **1968**, *48*, 23–35.
10. Politzer, P.; Murray, J.S. The Kamlet-Jacobs Parameter  $\varphi$ : A Measure of Intrinsic Detonation Potential. *Propellants Explos. Pyrotech.* **2019**, *44*, 844–849. [[CrossRef](#)]
11. Wang, Y.; Zhang, J.; Su, H.; Li, S.; Zhang, S.; Pang, S. A Simple Method for the Prediction of the Detonation Performances of Metal-Containing Explosives. *J. Phys. Chem. A* **2014**, *118*, 4575–4581. [[CrossRef](#)]
12. Politzer, P.; Murray, J.S. Perspectives on the crystal densities and packing coefficients of explosive compounds. *Struct. Chem.* **2016**, *27*, 401–408. [[CrossRef](#)]
13. Kretić, D.S.; Radovanović, J.I.; Veljković, D.Ž. Can the sensitivity of energetic materials be tuned by using hydrogen bonds? Another look at the role of hydrogen bonding in the design of high energetic compounds. *Phys. Chem. Chem. Phys.* **2021**, *23*, 7472–7479. [[CrossRef](#)]
14. Shoaf, A.L.; Bayse, C.A. Trigger Bond Analysis of Nitroaromatic Energetic Materials Using Wiberg Bond Indices. *J. Comput. Chem.* **2018**, *39*, 1236–1248. [[CrossRef](#)]
15. Liu, G.; Gou, R.; Li, H.; Zhang, C. Polymorphism of Energetic Materials: A Comprehensive Study of Molecular Conformers, Crystal Packing, and the Dominance of Their Energetics in Governing the Most Stable Polymorph. *Cryst. Growth Des.* **2018**, *18*, 4174–4186. [[CrossRef](#)]
16. Aina, A.A.; Misquitta, A.J.; Phipps, M.J.S.; Price, S.L. Charge Distributions of Nitro Groups Within Organic Explosive Crystals: Effects on Sensitivity and Modeling. *ACS Omega* **2019**, *4*, 8614–8625. [[CrossRef](#)]
17. Christopher, I.L.; Pulham, C.R.; Michalchuk, A.A.L.; Morrison, C.A. Is the impact sensitivity of RDX polymorph dependent? *J. Chem. Phys.* **2023**, *158*, 124115. [[CrossRef](#)] [[PubMed](#)]
18. Dunitz, J.D.; Filippini, G.; Gavezzotti, A. A Statistical Study of Density and Packing Variations Among Crystalline Isomers. *Tetrahedron* **2000**, *56*, 6595–6601. [[CrossRef](#)]
19. Groom, C.R.; Bruno, I.J.; Lightfoot, M.P.; Ward, S.C. The Cambridge Structural Database. *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.* **2016**, *72*, 171–179. [[CrossRef](#)]
20. Armaković, S.; Armaković, S.J. Atomistica.online—Web Application for Generating input Files for ORCA Molecular Modelling Package Made with the Anvil Platform. *Mol. Simul.* **2022**, *49*, 117–123. [[CrossRef](#)]
21. Armaković, S.; Armaković, S.J. Online and desktop graphical user interfaces for xtb programme from Atomistica.online platform. *Mol. Simul.* **2024**, *50*, 560–570. [[CrossRef](#)]
22. Macrae, C.F.; Sovago, I.; Cottrell, S.J.; Galek, P.T.A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G.P.; Stevens, J.S.; Towler, M.; et al. Mercury 4.0: From visualization to analysis, design and prediction. *J. Appl. Cryst.* **2020**, *53*, 226–235. [[CrossRef](#)] [[PubMed](#)]
23. Finch, A.; Smith, A.E. Thermochemistry of Nitrophenols. V. Enthalpies of formation of 2,4- and 2,6-dinitrophenols. *Thermochim. Acta* **1983**, *69*, 375–378. [[CrossRef](#)]
24. Rouse, P.E., Jr. Enthalpies of formation and calculated detonation properties of some thermally stable explosives. *J. Chem. Eng. Data* **1976**, *21*, 16–20. [[CrossRef](#)]
25. Boddu, V.M.; Viswanath, D.S.; Ghosh, T.K.; Damavarapu, R. 2,4,6-Triamino-1,3,5-Trinitrobenzene (TATB) and TATB-based formulations: A review. *J. Hazard. Mater.* **2010**, *181*, 1–8. [[CrossRef](#)] [[PubMed](#)]
26. Krien, G.; Licht, H.H.; Zierath, J. Thermochemical investigation of nitramines. *Thermochim. Acta* **1973**, *6*, 465–472. [[CrossRef](#)]
27. Veljković, D.Ž.; Janjić, G.V.; Zarić, S.D. Are C–H–O interactions linear? The case of aromatic CH donors. *CrystEngComm* **2011**, *13*, 5005–5010. [[CrossRef](#)]

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.