

Article

Regulation of Crystal Packing and Energetic Performance of TNT Derivatives by Bromine Substitution

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Abstract

Improving the energetic performance of established explosives through rational structural modification provides an alternative strategy for the development of entirely new energetic molecules. In this work, bromine substitution was employed to regulate the solid-state properties of TNT derivatives, and two compounds, 3-bromo-2,4,6-trinitrotoluene (3-BrTNT) and 3,5-dibromo-2,4,6-trinitrotoluene (3,5-BrTNT), were synthesized and characterized. Single-crystal X-ray diffraction revealed that different bromination patterns lead to distinct crystal structures and packing characteristics. Electrostatic potential analysis and Hirshfeld surface analysis further revealed that bromine substitution modifies molecular surface characteristics and intermolecular contact distributions within the crystals. Compared with 3-BrTNT, 3,5-BrTNT exhibits a higher crystal density of 2.312 g cm^{-3} and improved calculated detonation performance, with a detonation velocity of 7915 m s^{-1} and a detonation pressure of 31.86 GPa. Meanwhile, both brominated derivatives exhibit reduced impact sensitivity compared with TNT. These results demonstrate that the bromination pattern, rather than bromine incorporation alone, plays an important role in regulating crystal structures and energetic properties. This study provides insight into substitution-pattern-controlled crystal engineering as a strategy for optimizing TNT-based energetic materials.

Keywords: brominated TNT derivatives; crystal engineering; crystal packing; high-density energetic materials; Hirshfeld surface analysis; detonation performance

1. Introduction

Designing entirely new energetic molecules is not the only way to improve explosive performance. For many well-established explosives, relatively small structural modifications can alter the way molecules pack in the solid state, leading to measurable changes in density and detonation behavior without sacrificing the advantages of the parent compound [1–6]. This strategy is particularly attractive for materials that already possess proven stability, mature manufacturing processes and practical value but whose performance is constrained by intrinsic structural characteristics [7].

Among these materials, 2,4,6-trinitrotoluene (TNT) remains one of the most widely used aromatic explosives [8–11]. Its chemical stability, melt-cast processability and long history of industrial production continue to make it an important component of both military and civilian explosive formulations [8,9]. Despite these advantages, the relatively low crystal density of TNT limits its detonation performance [8,10]. Recent studies have demonstrated that crystal engineering strategies based on TNT frameworks, including molecular modification and crystal packing regulation, can effectively tune energetic



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performance and safety characteristics [12]. Since crystal density is determined by both molecular structure and the efficiency of crystal packing, modifying the substituent pattern of the TNT framework provides an effective approach to investigate how molecular-level changes are translated into solid-state packing characteristics and macroscopic energetic properties [3,10,11,13].

Substituent effects on crystal packing are often more significant than might be expected from the molecular structure alone [1,3,5,14,15]. Changing the size, shape or electronic distribution of a substituent can alter intermolecular contacts, resulting in different packing arrangements and, ultimately, different bulk properties [16–18]. Bromine is an attractive substituent in this context because its relatively large atomic radius and high polarizability have the potential to modify intermolecular interactions while introducing only a simple structural change to the aromatic framework [16,19]. Although brominated nitroaromatic compounds have been reported, previous studies have mainly emphasized molecular synthesis and energetic evaluation, whereas the influence of bromination patterns on solid-state packing remains less systematically explored [10,12,19]. How different bromination patterns influence crystal packing and how these structural changes are reflected in density and detonation performance have received much less attention [5,14,17]. A systematic understanding of these relationships remains limited.

In this work, two brominated TNT derivatives, 3-BrTNT and 3,5-BrTNT, were selected as representative mono- and dibrominated derivatives to systematically investigate how increasing bromine substitution influences molecular structure, crystal packing, intermolecular interactions, and energetic performance. The selection of these two derivatives allows the effect of substitution degree to be evaluated while maintaining the fundamental TNT framework. Bromine incorporation is expected to modify molecular polarizability, steric effects, and intermolecular interaction patterns, thereby providing a potential strategy for regulating the crystal engineering of TNT-based energetic materials. Although halogen substitution has been explored in energetic molecular design, the relationship between bromine-induced structural modification and the resulting changes in crystal packing characteristics and energetic behavior remains unclear. Therefore, this study combines experimental synthesis, single-crystal X-ray diffraction, Hirshfeld surface analysis, electrostatic potential analysis, and theoretical calculations to establish a comprehensive structure–property relationship between bromine substitution, molecular packing, and energetic performance.

2. Experimental Section

2.1. Experiments and Instruments

Reagents included: bromotoluene and 3,5-dibromotoluene (analytically pure), Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China; concentrated sulfuric acid (mass fraction 98%), Chengdu Kelong Chemical Co., Ltd., Chengdu, China; fuming nitric acid (mass fraction 95%), Chengdu Kelong Chemical Co., Ltd., Chengdu, China; and ethyl acetate (analytically pure), Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China. Instruments included: Bruker D8 VENTURE single-crystal diffractometer (Bruker AXS GmbH, Karlsruhe, Germany); automatic melting point tester ZRD-1, Tianjin Xintianguang Analytical Instrument Co., Ltd., Tianjin, China; and differential scanning calorimeter HCT-1, Beijing Hengjiu Technology Co., Ltd., Beijing, China.

2.2. Synthesis Route

As shown in the diagram, trinitrobromotoluene and 3,5-dibromotrinitrotoluene were synthesized by one-step nitration using bromotoluene and 3,5-dibromotoluene as raw materials and a mixed acid system as the nitration system.

2.2.1. Synthesis of Trinitrotrinitrotoluene

The synthetic route of trinitrotrinitrotoluene is shown in Figure 1. The synthesis steps are as follows: Under ice bath conditions, 56 mL of 98% concentrated sulfuric acid was added to the three-necked flask, and 28 mL of fuming nitric acid was slowly added. After the addition was completed, the stirring was maintained for 20 min, and 4.8 mL of bromotoluene was slowly added dropwise. The reaction system was always kept below 10 °C. During the addition process, the solution changed from colorless to reddish-brown. After the addition was completed, the temperature was raised to 130 °C and the reaction was performed for 3 h. After the completion of the reaction, the reaction was cooled to room temperature, quenched with ice water, filtered, washed and dried to obtain white solid products.

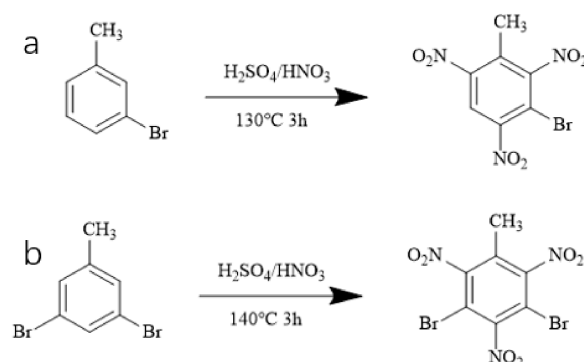


Figure 1. The synthetic route of 3-BrTNT (a) and 3,5-BrTNT (b).

2.2.2. Synthesis of 3,5-Dibromotrinitrotoluene

The synthetic route of trinitrodibromotoluene is shown in Figure 1. The synthesis steps are as follows: Under the condition of an ice-water bath, 28 mL of 98% concentrated sulfuric acid was added to the three-necked flask, and 10 mL of fuming nitric acid was slowly added dropwise. After the addition was completed, the mixture was stirred for 20 min, and 1.25 g of 3,5-dibromotoluene was slowly added. The system was always lower than 10 °C. During the addition process, the solution changed from colorless to reddish-brown. After the addition was completed, the temperature was increased to 140 °C and the reaction was performed for 3 h. After the reaction was completed, the product was obtained by cooling to room temperature, quenching with ice water, filtering, washing and drying.

2.3. Characterization and Single-Crystal X-Ray Diffraction

The synthesized compounds were characterized by nuclear magnetic resonance (NMR) spectroscopy, Fourier-transform infrared (FT-IR) spectroscopy and single-crystal X-ray diffraction (SCXRD).

NMR spectra were recorded on a 500 MHz spectrometer using tetramethylsilane (TMS) as the internal reference. FT-IR spectra were collected in the range of 4000–400 cm^{−1}. The corresponding NMR and FT-IR spectra are provided in the Supplementary Materials (Figures S1–S6). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of ethyl acetate solutions. Diffraction data were collected on a Bruker D8 VENTURE single-crystal diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) using Cu Kα radiation (λ = 1.54178 Å). The crystal structures were solved with SHELXT and refined with SHELXL using full-matrix least-squares procedures [20,21]. Crystallographic data and refinement parameters are provided in Table 1.

Table 1. Crystallographic data and structure refinement parameters for 3-BrTNT and 3,5-BrTNT.

Compound	3-BrTNT	3,5-BrTNT
Empirical formula	C ₇ H ₄ BrN ₃ O ₆	C ₇ H ₃ Br ₂ N ₃ O ₆
Formula weight	306.03	384.94
Temperature/K	193 K	193 K
Crystal system	monoclinic	triclinic
Space group	P2 ₁ /n	P-1
a/Å	13.2082 (7)	5.5902 (10)
b/Å	5.7359 (3)	8.9330 (16)
c/Å	14.3201 (8)	11.692 (2)
α/°	90	77.201 (8)
β/°	113.835 (3)	85.657 (8)
γ/°	90	76.474 (8)
Volume/Å ³	992.38 (10)	553.39 (18)
Z	4	2
ρ/g·cm ⁻³	2.048	2.312
μ/mm ⁻¹	5.963	9.604
F(000)	600.0	368.0
R1 [I > 2σ(I)]	0.0423	0.0395
wR2 (all data)	0.1116	0.1201
Goodness-of-fit	1.0918	1.075
Reflections collected	1918	2186
Parameters	170	171
Largest diff. peak/e Å ⁻³	0.448	0.604
Deepest diff. hole/e Å ⁻³	−0.542	−0.864

2.4. Computational Methods and Energetic Calculations

Density functional theory (DFT) calculations were performed using Gaussian 16, Revision A.03 (Gaussian, Inc., Wallingford, CT, USA). The molecular geometries of 3-BrTNT, 3,5-BrTNT and the reference molecules used for thermochemical calculations were optimized using the B3LYP functional [22,23] with the 6-31+G(d',p') basis set. Tight convergence criteria were applied during geometry optimization, and frequency calculations were subsequently carried out at the same level of theory to verify the optimized structures as stationary points.

The gas-phase heats of formation were calculated using an isodesmic reaction approach. The reference molecules, including methane, ethane, benzene, bromomethane and nitromethane, were optimized at the same theoretical level.

Zero-point energy corrections obtained from frequency calculations were included in the thermochemical evaluation. The calculated heats of formation together with the crystal densities obtained from single-crystal X-ray diffraction were used as input parameters for EXPLO5 (version 6.05; M. Sućeska, Zagreb, Croatia) to estimate the detonation velocity and detonation pressure. The calculated energetic parameters were used for comparative evaluation of the energetic performance of the brominated TNT derivatives.

3. Results and Discussion

3.1. Crystal Structures and Molecular Packing

Single-crystal X-ray diffraction (SCXRD) was carried out to determine the molecular structures and investigate the solid-state packing characteristics of 3-BrTNT and 3,5-BrTNT [20,21]. The corresponding crystallographic parameters and refinement details are summarized in Table 1, and the molecular structures together with crystal packing arrangements are presented in Figure 2.

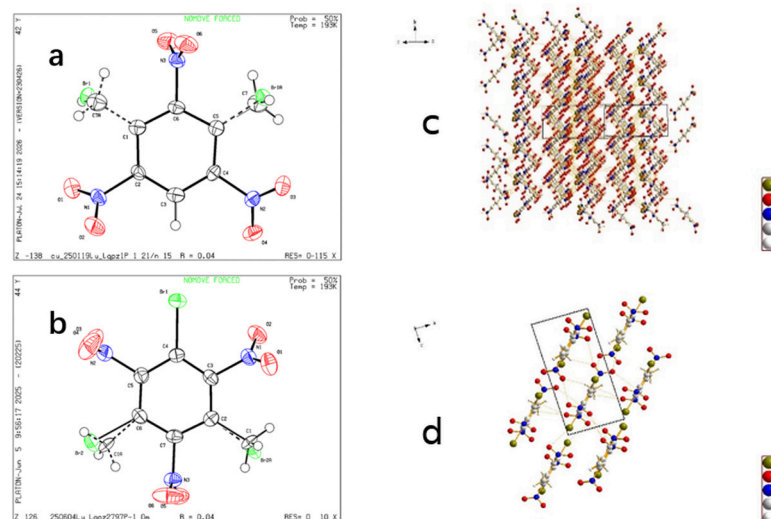


Figure 2. Molecular structures of (a) 3-BrTNT and (b) 3,5-BrTNT, and crystal packing arrangements of (c) 3-BrTNT and (d) 3,5-BrTNT. In (a,b), C, H, N, O, and Br atoms are shown in gray, white, blue, red, and green, respectively; in (c,d), the atom colors are identified by the legend at the right of each packing panel, and the black boxes denote unit-cell boundaries.

Both compounds maintain the characteristic nitroaromatic framework of TNT derivatives; however, the different bromination patterns result in distinct crystal structures and packing behaviors [3,10].

3-BrTNT crystallizes in the monoclinic crystal system with the space group $P2_1/n$. The molecule adopts a relatively planar aromatic skeleton, and the bromine substituent is accommodated within the nitro-substituted benzene framework without significant distortion of the molecular geometry. The crystal density of 3-BrTNT is 2.048 g cm^{-3} , suggesting a relatively compact solid-state structure within the crystal lattice.

In comparison, 3,5-BrTNT obtained from 3,5-dibromotoluene crystallizes in the triclinic crystal system with the space group $P-1$. The introduction of an additional bromine atom leads to an increase in molecular weight and polarizability, while also modifying the molecular surface and intermolecular packing mode. Notably, 3,5-BrTNT exhibits a higher crystal density of 2.312 g cm^{-3} , which is significantly increased compared with that of 3-BrTNT.

The difference in crystal density between the two derivatives suggests that the solid-state properties of brominated TNT derivatives are influenced not only by molecular mass but also by the arrangement of molecules within the crystal lattice [1,3,5,14]. The symmetric substitution pattern of 3,5-BrTNT provides a more balanced distribution of bromine atoms around the aromatic framework, which may contribute to a more favorable molecular arrangement and enhanced intermolecular interactions [16,19]. The enhanced polarizability introduced by bromine atoms may further contribute to closer molecular contacts within the lattice.

As shown in Figure 2, both compounds exhibit ordered packing arrangements involving the nitroaromatic cores. Compared with 3-BrTNT, the crystal structure of 3,5-BrTNT shows a more compact molecular arrangement, consistent with its higher crystal density. The contribution of specific intermolecular contacts to these structural differences is further analyzed by Hirshfeld surface and ESP analyses. These structural differences demonstrate that rational control of bromine substitution provides an effective approach for regulating the crystal packing and density of energetic molecular frameworks [1,5].

3.2. Intermolecular Interactions: ESP and Hirshfeld Surface Analysis

To understand the influence of bromine substitution on the molecular surface characteristics and intermolecular contact distribution, electrostatic potential (ESP) mapping and Hirshfeld surface analysis were performed for 3-BrTNT and 3,5-BrTNT [24–26]. As shown in Figure 3, both compounds exhibit similar electrostatic potential distributions due to their common TNT-derived nitroaromatic framework. The negative potential regions are mainly located around the nitro-oxygen atoms, whereas the aromatic ring regions and hydrogen-containing sites show relatively positive potentials. These polarized regions indicate the potential sites involved in intermolecular interactions within the crystal structures, particularly through nitro-group-related electrostatic interactions. However, the different bromination patterns modify the molecular surface environment and polarizability, resulting in variations in the intermolecular contact distribution.

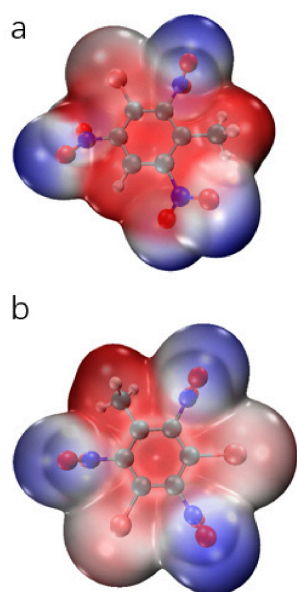


Figure 3. Electrostatic potential (ESP) maps of (a) 3-BrTNT and (b) 3,5-BrTNT. Red and blue surface regions represent relatively negative and positive electrostatic potentials, respectively.

The two-dimensional fingerprint plots derived from Hirshfeld surface analysis (Figure 4a,b) provide a visual comparison of the overall intermolecular contact characteristics of the two crystals. Although both compounds show similar distribution features owing to their structural similarity, differences in the shape and spread of the fingerprint plots reveal that bromine substitution modifies the relative contribution of intermolecular contacts within the crystal lattice. This observation is consistent with the different crystal packing arrangements identified by single-crystal X-ray diffraction [17,25].

Quantitative analysis of the Hirshfeld surface contacts further reveals the influence of bromine substitution on the intermolecular contact network. For 3-BrTNT, Br $\cdots$ O and O $\cdots$ O contacts contribute 17.7% and 21.5% of the total surface contacts, respectively, demonstrating that halogen-related and nitro-group-related interactions represent major components of its crystal contact environment. In comparison, 3,5-BrTNT exhibits a different contact distribution, with O $\cdots$ H and O $\cdots$ O contacts contributing 21.3% and 14.1%, respectively. The increased contribution of O $\cdots$ H contacts and the variation in O $\cdots$ O contacts suggest that the introduction of an additional bromine atom modifies the balance of intermolecular contacts within the crystal lattice. These changes indicate a redistribution of intermolecular interactions that favors more efficient molecular packing and contributes to the increased crystal density of 3,5-BrTNT.

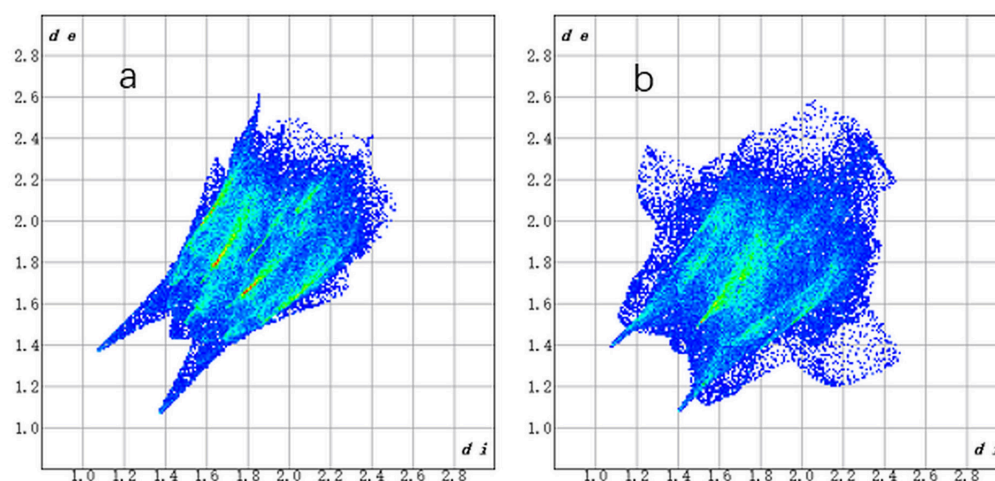


Figure 4. Two-dimensional Hirshfeld fingerprint plots of (a) 3-BrTNT and (b) 3,5-BrTNT. The axes represent the distances from the Hirshfeld surface to the nearest external (d_e) and internal (d_i) nuclei; the color scale from blue through green to red indicates increasing relative contact frequency.

Overall, the Hirshfeld surface analysis demonstrates that bromine substitution does not simply increase the molecular mass of TNT derivatives but also modifies the intermolecular contact environment through changes in molecular surface characteristics. The different fingerprint distributions and contact contributions between 3-BrTNT and 3,5-BrTNT are consistent with their distinct crystal structures and densities obtained from single-crystal X-ray diffraction. These results indicate that the bromination pattern plays an important role in regulating the solid-state packing behavior of TNT derivatives. The modified intermolecular contact environment provides structural insight into the differences in crystal density and energetic performance observed for the two derivatives.

3.3. Energetic Performance and Sensitivity

The energetic performances of 3-BrTNT and 3,5-BrTNT were evaluated based on their calculated heats of formation, crystal densities, detonation velocities, detonation pressures, and mechanical sensitivities. The corresponding parameters are summarized in Table 2. Compared with TNT, both brominated derivatives exhibit enhanced energetic characteristics, which can be attributed to the combined effects of increased crystal density, positive heats of formation, and bromination-induced changes in molecular structure and intermolecular interactions [8,11]. The calculated densities of 3-BrTNT and 3,5-BrTNT are 2.048 and 2.312 g cm^{−3}, respectively, both higher than that of TNT (1.640 g cm^{−3}). Meanwhile, the calculated heats of formation increase from −63.00 kJ mol^{−1} for TNT to 32.11 and 40.53 kJ mol^{−1} for 3-BrTNT and 3,5-BrTNT. The positive HOF values indicate that bromine substitution alters the molecular composition and increases the stored chemical energy relative to TNT.

Table 2. Energetic performance and sensitivity parameters of TNT, 3-BrTNT and 3,5-BrTNT.

Compound	ρ (g·cm ^{−3})	ΔH_f (kJ·mol ^{−1})	V_D (m·s ^{−1})	P (GPa)	IS (J)	FS (N)
TNT	1.64	−63	6881	22.8	15	>360
3-BrTNT	2.048	32.11	7055	23.15	50	>360
3,5-BrTNT	2.312	40.53	7915	31.86	62	>360

The enhanced density and positive heat of formation are reflected in the calculated detonation performance [3,5]. 3-BrTNT exhibits a detonation velocity of 7055 m s^{−1} and

a detonation pressure of 23.15 GPa, slightly exceeding those of TNT (6881 m s^{−1} and 22.80 GPa). In comparison, 3,5-BrTNT achieves a significantly higher detonation velocity of 7915 m s^{−1} and detonation pressure of 31.86 GPa, demonstrating the beneficial effect of the 3,5-dibromo substitution pattern on energetic output. This improvement is consistent with the structural differences discussed above, where 3,5-BrTNT exhibits a higher crystal density and modified intermolecular contact distribution induced by the 3,5-dibromo substitution pattern. These results suggest that the energetic performance of brominated TNT derivatives is influenced not only by molecular composition but also by crystal structural characteristics [14,27]. Therefore, bromine substitution should not be considered merely as a strategy for increasing molecular mass, but rather as a means of regulating the solid-state arrangement that governs macroscopic energetic properties.

The mechanical sensitivities of the brominated TNT derivatives were further evaluated to assess their safety characteristics. The impact sensitivities of 3-BrTNT and 3,5-BrTNT are 50 and 62 J, respectively, while both compounds exhibit friction sensitivities higher than 360 N. Compared with TNT (15 J), the brominated derivatives show reduced impact sensitivity, indicating improved resistance to mechanical stimuli after bromine substitution. These results suggest that bromine incorporation can simultaneously improve energetic performance and reduce mechanical sensitivity under the investigated conditions [1,5,7].

The variation in mechanical sensitivity is likely related to the changes in crystal structure and intermolecular contact distribution induced by bromine substitution [28]. Single-crystal X-ray diffraction and Hirshfeld surface analysis reveal that the two derivatives possess different molecular arrangements and intermolecular interaction patterns. These structural differences may contribute to the different responses toward mechanical stimuli observed for the brominated derivatives [27]. Therefore, 3,5-BrTNT exhibits a favorable balance between energetic performance and mechanical safety, suggesting that controlling the bromination pattern provides an effective approach for tuning the properties of TNT-based energetic materials.

4. Conclusions

In summary, the effects of bromine substitution on the crystal structures, intermolecular interactions, and energetic properties of TNT derivatives were systematically investigated. The comparison between 3-BrTNT and 3,5-BrTNT demonstrates that the substitution pattern plays an important role in regulating molecular packing characteristics and solid-state properties. Single-crystal X-ray diffraction analysis revealed that 3,5-BrTNT adopts a distinct crystal structure with a higher crystal density of 2.312 g cm^{−3} compared with 3-BrTNT. ESP and Hirshfeld surface analyses further indicated that bromine substitution modifies the electrostatic distribution and intermolecular contact characteristics, resulting in different intermolecular interaction patterns within the crystal lattice. Benefiting from the combined effects of higher crystal density, increased heat of formation, and modified intermolecular interactions, 3,5-BrTNT exhibits enhanced detonation performance with a detonation velocity of 7915 m s^{−1} and a detonation pressure of 31.86 GPa, while maintaining acceptable mechanical sensitivity. These findings demonstrate that rational control of substitution patterns provides an effective crystal engineering strategy for developing high-density energetic materials with balanced energetic output and safety characteristics [1,5].

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/cryst16090585/s1>, Figure S1: ¹H NMR spectrum of 3-BrTNT; Figure S2: ¹³C NMR spectrum of 3-BrTNT; Figure S3: The infrared spectrum of 3-BrTNT; Figure S4: ¹H NMR spectrum of 3,5-BrTNT; Figure S5: ¹³C NMR spectrum of 3,5-BrTNT; Figure S6: The infrared spectrum of 3,5-BrTNT.

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