

Fused Triazole-Tetrazine Assembled with Different Functional Moieties: Construction of Multipurpose Energetic Materials

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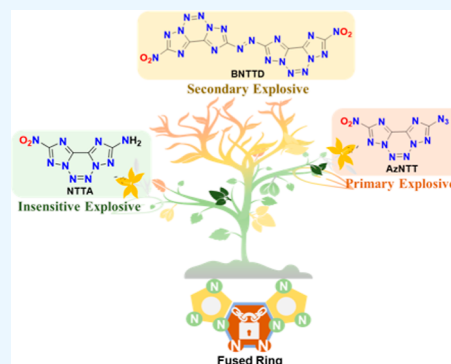


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Supporting Information

ABSTRACT: Azido, amino, and azo functionalities were introduced into tetrazine backbones to access multifunctional energetic materials. AzNTT demonstrates effective initiation capability (MPC = 50 mg), whereas NTTA balances well between the energy and stability. Azo-functionalized BNTTD has a high density of 1.908 g cm⁻³, with performance comparable to that of the benchmark material HMX. This work underscores the scope of energetic functionalization and the outstanding comprehensive performance of polycyclic tetrazines.



INTRODUCTION

Originating from the invention of black powder, the history of energetic materials spans several millennia. The evolution of these materials has largely been propelled by the demand from both the military and civilian sectors. Energetic materials are characterized by their capacity to rapidly release vast amounts of energy,^{1,2} rendering them indispensable for explosives, propellants, and pyrotechnics.^{3–6} Traditional pathways to new energetic materials are often limited by a few molecular backbones. With this context, the academic community is interested in seeking new energetic systems for balanced stability and performance. However, basic principles of structure–property relationships are necessary for rational design of novel compounds with tailored properties.^{7,8} The inherent conflict between energy and stability poses challenges for both safe synthesis and efficient application.⁹

Compared with other nitrogen-rich heterocycles, triazole-based compounds generally have higher positive heats of formation, more modifiable sites and better environmental compatibility.^{10–15} For instance, 5-amino-3-nitro-1,2,4-triazole is a high energy insensitive material;¹⁶ 3-nitro-1,2,4-triazolo-5-one (NTO) possesses the characteristics of insensitivity, compactness, and high enthalpy. Its measured detonation performance is close to that of cyclotrimethylenetrinitramine (RDX).^{17–19} 5,5'-Dinitro-3,3'-azo-1,2,4-triazole has already been investigated and shown remarkably high decomposition temperatures.²⁰ Besides, 3,3'-dinitro-5,5'-bis(1H-1,2,4-triazole) has a high density and thermal decomposition temperature, acceptable sensitivity.²¹ Meanwhile, 5-(5-amino-1H-1,2,4-triazol-3-yl)3-nitro-1H-1,2,4-triazole, 5-(5-azido-1H-1,2,4-triazol-3-yl)-3-nitro-1H-1,2,4-triazole had also been

systematically studied.²² However, regarding the density and detonation performance of bis-1,2,4-triazole compounds, there is still a gap in comparison to those of the classic energetic compounds. As a unique backbone, nitrogen-rich fused rings feature considerably many N=N, N–N, and C–N bonds with high bond energy and ring-strain energy. Furthermore, the coplanar structures facilitate electron delocalization and resonance, contributing to enhanced thermal stability and low mechanical sensitivity.^{23,24} We envisage that incorporating an azo bridge into bistriazole will not only be valuable to access fused triazole-tetrazine²⁵ but also expand the reaction scope for diversified functionalizations (Figure 1A).

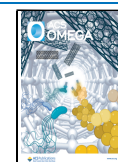
Further commonly used modifications include explosophores such as nitro, amino, nitramino, azido groups, etc.^{11,27} Established on the dominant fused skeleton, the rational assembly of different explosophores could further tailor the specific properties for various applications. Among these, the azide group, which has a high heat of formation but poor mechanical sensitivity, is often used in primary explosive formulations.^{23,27–30} In comparison, the amino groups can be introduced as hydrogen bond donors to enhance hydrogen bonding interaction toward high-performance materials with low sensitivity.³¹ The azo bond can play a bridging role and increase the enthalpy of the formation, which further amplifies

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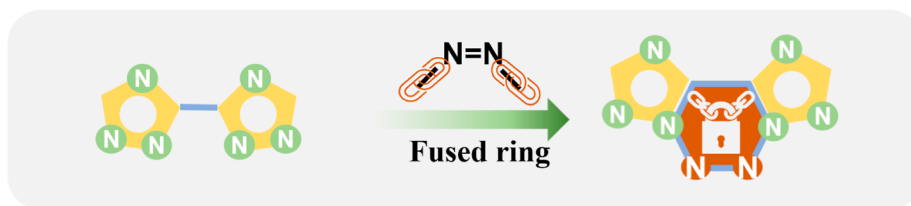
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A. Our strategy



B. This work

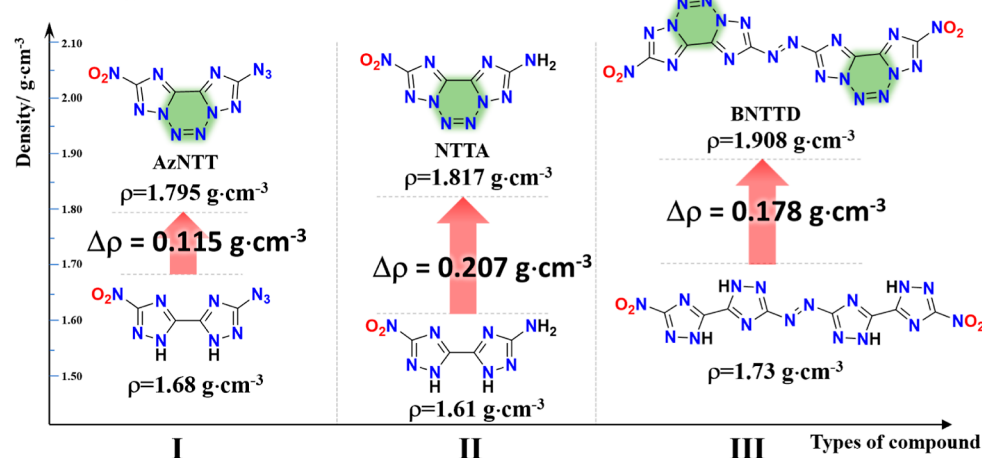
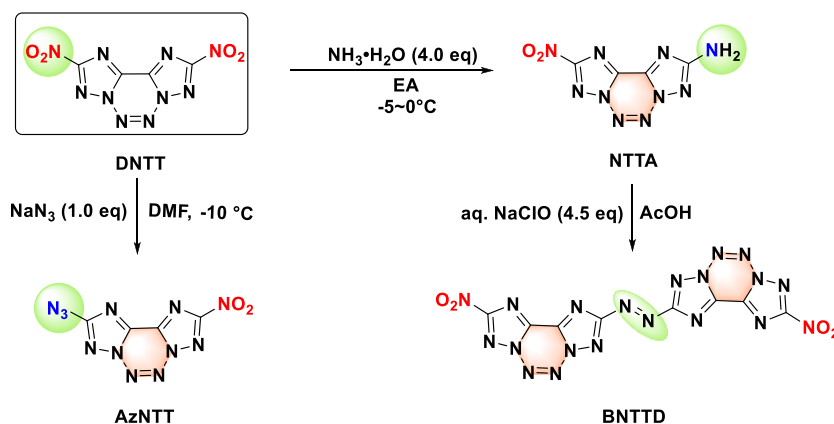


Figure 1. Comparison of fused tetrazine-triazole with bistriazoles (density from X-ray diffraction analysis recalculated to 298 K: $\rho_{298\text{K}} = \rho_{\text{T}}/[1 + \alpha_{\text{V}}(298\text{ K} - \text{T})]$, where $\alpha_{\text{V}} = 1.6 \times 10^{-4} \text{ K}^{-1.26}$).

Scheme 1. Synthetic Routes of Compounds AzNTT, NTTA, and BNTTD



the detonation performance.³² In our continuous effort to study fused nitrogen-rich heterocycles, herein diversified functionalized explosives were assembled into the fused triazole-tetrazole. By a comparative study with bistriazole analogous compounds, the remarkably increased density and detonation performance highlight the advances of tricyclic fused triazole-tetrazine backbones. Furthermore, the influence of functional moieties on the function of energetic materials was summarized to guide the design and synthesis of the new generation of high-energy-density materials (Figure 1B).

EXPERIMENTAL SECTION

Caution! In this work, all new compounds are potentially energetic materials that tend to explode under certain external mechanical actions. All experimental manipulations of those compounds must be carried out using safety precautions. Eye protection and leather gloves must be worn at all times.

The start material, 2,9-dinitrobis([1,2,4]triazolo)[1,5-*d*:5',1'-*f*][1,2,3,4]tetrazine, was synthesized according to the literature.^{21,25} The selectivity of monosubstitution was achieved by controlling the reaction temperature and the stoichiometric ratio of ammonia. Then, the equivalent of sodium azide as a nucleophile reacted with DNTT at $-10\text{ }^{\circ}\text{C}$ to give rise to the single-side azide substituted compound 2-azido-9-nitrobis([1,2,4]triazolo)[1,5-*d*:5',1'-*f*][1,2,3,4]tetrazine (AzNTT). Subsequently, several attempts were made to selectively reduce the nitro group of DNTT to prepare single amino compounds 9-nitrobis([1,2,4]triazolo)[1,5-*d*:5',1'-*f*][1,2,3,4]tetrazin-2-amine (NTTA). Different reagents, including Pd/C, $\text{NH}_4\text{Cl}/\text{Fe}$, and NaBH_4 , were chosen to reduce the nitro groups. Unfortunately, the reductions gave mixtures without the target molecules. Further investigation showed that aminolysis of DNTT was an alternative feasible pathway. After solvent screening, it was found that ethyl

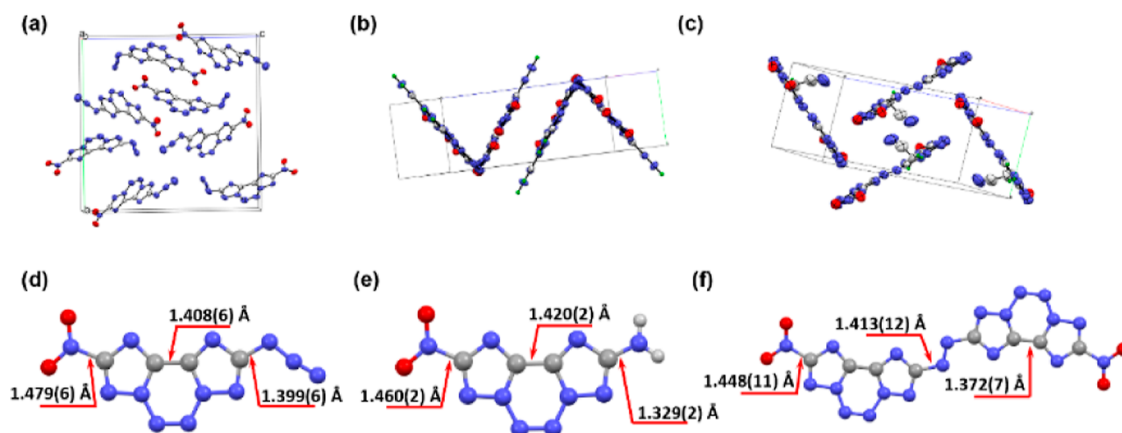


Figure 2. Crystal packing diagram and bond length of AzNTT (a,d), NTTA (b,e), and BNTTD (c,f).

Table 1. Physicochemical and Energetic Properties of New Compounds Compared with RDX, HMX, $\text{Pb}(\text{N}_3)_2$, and DDNP

comp	ρ^a ($\text{g}\cdot\text{cm}^{-3}$)	T_d^b ($^\circ\text{C}$)	ΔH_f^c ($\text{kJ}\cdot\text{mol}^{-1}$)/($\text{kJ}\cdot\text{g}^{-1}$)	V_D^d ($\text{m}\cdot\text{s}^{-1}$)	P^e (GPa)	IS^f (J)	FS^g (N)
AzNTT	1.795	195.5	1170.60/4.72	8855	31.7	<2.0	<5.0
NTTA	1.82	178.2	808.94/3.64	8544	29.1	35	288
BNTTD	1.908 ^h	165.6	2011.94/4.57	9197	35.6	8	60
RDX ⁱ	1.8	204	70.30/0.32	8801	33.6	7.4	120
HMX ⁱ	1.905	279	74.80/0.25	9144	39.2	7	120
$\text{Pb}(\text{N}_3)_2^j$	4.8	315	450.10/1.55	5920	33.8	2.5–4	0.1–1
DDNP ^j	1.72	157	321.00/1.52	6900	24.2	1	24.2

^aCrystal density. ^bDecomposition temperature (onset). ^cCalculated heat of formation. ^dDetonation velocity (calculated with Explo5 v6.05). ^eDetonation pressure (calculated with Explo5 v6.05). ^fImpact sensitivity. ^gFriction sensitivity. ^hDensity measured by gas pycnometer at 25 $^\circ\text{C}$, $\text{g}\cdot\text{cm}^{-3}$. ⁱReference 37. ^jReference 28.

acetate is the most effective solvent for yielding the monoaminate product NTTA at low temperatures. There were many methods to construct azo bridge, but for the construction of large molecules, in complement to the efficiency of the reaction, a simple purification method should be considered.³³ Here, after different oxidants were tried, the azo-bridged compound BNTTD was synthesized by further derivation of NTTA with sodium hypochlorite as an oxidant. While the reaction was completed, the target compound could be obtained by adding an appropriate amount of water. Multinuclear NMR, infrared spectroscopy, and single-crystal X-ray diffraction analysis fully characterized all of the newly synthesized compounds (Scheme 1). In addition, aiming to compare the performance changes of the compounds, we prepared (*E*)-1,2-bis(5'-nitro-2*H*,2'*H*-[3,3'-bi(1,2,4-triazol)-5-yl]diazene according to the oxidation conditions of the C=N=C bridge (Scheme S1).³⁴

RESULTS AND DISCUSSION

We analyzed the crystal structure of all the new compounds in detail to understand the structural characteristics. Single crystals of the compounds AzNTT, BNTTD, and NTTA suitable for single-crystal X-ray diffraction were obtained by slowly evaporating saturated acetonitrile and methanol solutions (Figure 2a–c). The compound AzNTT crystallizes with the $P2_12_12_1$ space group, and the density is $1.832\text{ g}\cdot\text{cm}^{-3}$ at 170 K. The crystal structures of NTTA belongs to the $C2/c$ space group, exhibits mixed packing and has a density of $1.855\text{ g}\cdot\text{cm}^{-3}$ at 170 K. Furthermore, each crystal contains one molecule of BNTTD and a couple of cocrystallized acetonitrile molecules, reveals wave packing, and compound BNTTD·2MeCN crystallizes in the $P2_1/c$ space group. The density of

all the newly prepared fused ring compounds was higher than that of the corresponding C–C asymmetric substituted energetic compounds: 5-(5-azido-1*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (AzNBT, $1.68\text{ g}\cdot\text{cm}^{-3}$), 5-(5-amino-1*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (ANBT, $1.61\text{ g}\cdot\text{cm}^{-3}$),²² and (*E*)-1,2-bis(5'-nitro-2*H*, 2'*H*-[3,3'-bi(1,2,4-triazol)]-5-yl)diazene (BNBTD, $1.73\text{ g}\cdot\text{cm}^{-3}$).

Because of the conjugated fused rings, all of the structures of the neutral compounds are nearly planar. The amino and nitro group connected by the tetrazine fused ring of NTTA could be confirmed from their horizontal view [C2–N2–C1–N, $-179.19(15)$, O1–N10–C4–N9, $-4.2(2)$]. Interestingly, the planes of two tetrazine fused rings in BNTTD's structure are linked by an azo bridge and run parallel to each other; the layer spacing is 0.229 \AA . The molecular planarity parameter (MPP) of BNTTD is 0.077705 \AA , far less than the MPP (0.089949 \AA) of DNTT,³⁵ this suggests that BNTTD maintains better planarity. Moreover, BNTTD has a slightly shorter C–NO₂ bond [C–NO₂, $1.447(11)\text{ \AA}$] than that of NTTA (C–NO₂, $1.460(2)\text{ \AA}$) and DNTT [C–NO₂ (α, β), $1.454\text{ \AA} \sim 1.466\text{ \AA}$] (Figure 2d–f). In the study of complexity science and material diversity, the molecular dimension is also an important indicator. Different sizes may lead to qualitative differences in the material properties and principles of motion. Using Multiwfn software, the molecular length of a single BNTTD was 21.63 \AA and the unit cell volume was $1018(8)\text{ \AA}^3$.^{35,36} This is rare in molecules of organic energetic materials.

All new compounds' physicochemical and detonation properties were investigated to evaluate their application potential as high-energy materials. From the differential scanning calorimetry curve of AzNTT, there was a minor endotherm signal followed by an intense exothermic peak. Its

higher onset temperature of exothermic peak is 195.5 °C. Fused rings' heat of formation ($\Delta_f H$) was computed using the Gaussian 09 suite of programs. All polycyclic ring compounds, benefiting from the nitrogen-rich fused ring skeleton, have positive heat of formation values above 3.0 kJ·g⁻¹, exceeding the values for RDX (0.36 kJ·g⁻¹) and CL-20 (0.90 kJ·g⁻¹). Relying on the measured density and calculated heats of formation in hand, the detonation performances of AzNTT, NTTA, and BNTTD were obtained by employing the EXPLO_05 (v 6.05). As can be seen in Table 1, the calculated detonation velocities and pressures were found in the range from 8544 to 9196.5 m·s⁻¹, 29.1 to 35.6 GPa, respectively. Among them, the value of BNTTD was superior to those of HNS (V_D , 7612 m·s⁻¹; P , 24.3 GPa) and RDX (V_D , 8795 m·s⁻¹; P , 34.9 GPa) and comparable with those of HMX (V_D , 9144 m·s⁻¹; P , 39.6 GPa). It could be used as a promising second explosive from its advancement.

The sensitivities toward impact and friction were also determined. The impact sensitivities (ISs) were tested to be less than 2 J, and the friction sensitivities (FSs) were less than 5N for AzNTT. The better detonation performance and particular sensitivity, plus the environmentally benign syntheses that could be an alternative to toxic lead azide, contribute to the practical application of AzNTT as a bright primary explosive. In the single-side amino substitution compounds, NTTA, not surprisingly, demonstrated a lower sensitivity (IS = 35 J, FS = 288 N). The azo compound BNTTD was acceptably sensitive (IS = 8 N; FS = 60 N). The relatively lower friction sensitivity should reduce the likelihood of accidents caused by slight friction. The moderate sensitivities nearly guarantee the possibility of production, handling, and transportation safety and retain competitive detonation performance simultaneously.

To verify the potential of the compound for practical application, we tested the detonation ability in accordance with the physicochemical properties of compound AzNTT. As shown in Figure 3a, the experimental work was performed by using a different amount of AzNTT to detonate 70 mg of secondary explosive (RDX) against a 2 mm lead block. The apparatus was fired by an electric igniter, and when the amount of AzNTT was less than 50 mg, secondary explosives (RDX) could not be initiated. Furthermore, reducing the amount has a slight influence on the diameters of the blasted holes, which

stay at around 8.0 mm (Figure 3b,c). The experiment results demonstrate that AzNTT is a promising initiating explosive with an MPC of 50 mg, which is superior to that of the reported ICM-103 (60 mg) and DDNP (70 mg).²⁷ In comparison to traditional heavy metal-based primary explosives, AzNTT, as an organic primary explosive, exhibits greater environmental friendliness and enhanced initiation capability.

CONCLUSIONS

Several new fused tricyclic dinitrazolo-1,2,3,4-tetrazine derivatives were simply and effectively synthesized by adopting versatile explosives. Benefited from the significant fused ring frame and ring tension, these compounds derived from asymmetric substitution fused cyclic possess high heats of formation above 3.0 kJ·g⁻¹, superior to the values of RDX (0.36 kJ·g⁻¹) and CL-20 (0.90 kJ·g⁻¹). The compound AzNTT has unique sensitivity (FS < 2 J, IS < 5 N) because of the addition of azide moieties. Its initiation capability was evaluated by a notably low MPC of 50 mg and could become a potential organic primary explosive. The incorporation of amino with nitro groups gave NTTA a relatively low mechanical sensitivity (FS = 35 J, IS = 288 N); it balances well with energy and stability. The BNTTD has a higher density of 1.908 g·cm⁻³, with excellent detonation property (V_D , 9196.5 m·s⁻¹; P , 35.6 GPa), superior to those of HNS (V_D , 7612 m·s⁻¹; P , 24.3 GPa) and RDX (V_D , 8795 m·s⁻¹; P , 34.9 GPa) and comparable with those of HMX (V_D , 9144 m·s⁻¹; P , 39.6 GPa). It would be used as a promising second explosive. Taking the unique fused ring skeleton to assemble functional groups with different functions, further exerting the advantages of the skeleton, specific energetic materials can be prepared, which also guides the future design of advanced energetic materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.4c01261>.

Experimental procedures; computational details; characterization data; and crystallographic data for compounds AzNTT, NTTA, and BNTTD (PDF)

Crystallographic data for AzNTT (CIF)

Crystallographic data for NTTA (CIF)

Crystallographic data for BNTTD (CIF)

checkCIF report for NTTA (PDF)

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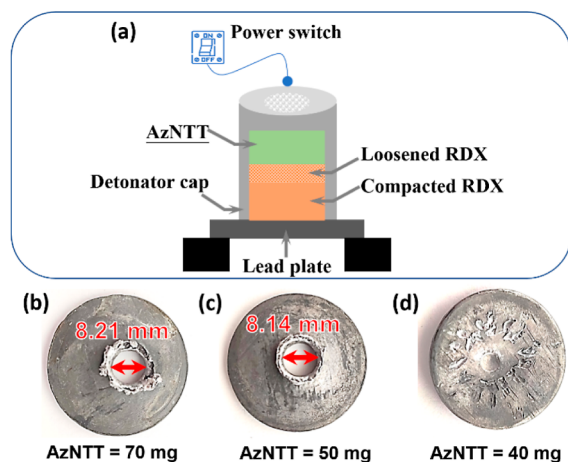


Figure 3. Illustration of the test setup and result of the detonation test of compound AzNTT.

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Notes

The authors declare no competing financial interest.

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