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Exploring Application of 1,2,4-Triazole Energetic Salts: Gas Generating Agent, Propellant and Explosive Compositions

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Abstract: High-nitrogen energetic salts as the functional materials could be applied to formulate second explosives, gas-generating agents, and propellants due to their large gas and energy release after combustion. Herein, a series of the insensitive and highly gas productive 1,2,4-triazole derivatives including 4,5,5′-triamine-3,3′-bi-1,2,4-triazole (**1**) and 4,5′-dinitramino-5-amine-3,3′-bi-1,2,4-triazole (**4**) as well as corresponding salts were synthesized and characterized. The crystal structures of 4,5,5′-triamine-3,3′-bi-1,2,4-triazole (**1**), nitrate salt (**2**), 4,5′-dinitramino-5-amine-3,3′-bi-1,2,4-triazole (**4**) and triaminoguanidine salt (**9**) were determined by X-ray diffraction. For explosives candidates, energetic salts of ammonium (**5**), hydrazinium (**6**), hydroxylammonium (**7**), and triaminoguanidine (**9**) not only display the outstanding detonation performance (D, 8657–9120 m s^{-1}, P, 27.78–33.39 GPa), but also show low mechanical sensitivities (IS $\geq$ 20 J, FS $\geq$ 216 N). Furthermore, the constant-volume combustion experiment results reveal that **5**, **6**, **7**, and **9** show excellent gas productivity (P$_{max}\geq$ 12.8 MPa) and pressure-up rate (dP/dt$_{max}\geq$ 164 GPa s^{-1}). These compounds could be the efficient components of gas-generating agents and propellants based on the calculated combustion parameters from EXPLO 5 software.

Keywords: high-nitrogen energetic material · second explosive · gas-generating agent · propellant

1 Introduction

Since the 18th century, the industrial revolution has gradually entered a stage of rapid development with the advent of safe nitroglycerin. The employment of energetic materials (EMs) opens a new era in the development of human society [1–3]. "Good detonation performance, non-toxicity on the environment, safety during transportation, stability during storage…" are essential properties to attain applied standards for modern advanced energetic materials [4,5]. Thus, its environmental friendliness and sensitivity are also significant properties when pursuing high energy in the application of EMs.

EMs as a functional material can rapidly release large gas and energy when external energy input, which could be applied to formulate explosives, gas generating agents, and propellants [6–8]. The commonly used gas generating agent is sodium azide (NaN₃) [9], but the primary challenge for NaN₃ in the application is its high toxicity (LD*$_{50}$ = 27 mg kg^{-1}) [10] that increase obstacles of the filtration system and environment. Therefore, environment-friendly EMs are being explored and applied to the fields of gas generating agents, propellants, and explosives [11].

The burning performance of advanced energetic materials is one of the important parameters to dominate its potential [12,13]. Although guanidine nitrate (GN) was widely used for gas generators due to its excellent gas production, an evident issue for GN is its slow burning behavior which is related to the slow of breakage of the relatively strong C-NH₂ bonds [14]. Because compounds with high formation enthalpy and high nitrogen content can be rapidly decomposed after external energy input, like azo, azide, and azole derivatives, etc [15], this property attracted the attention of researchers in the fields of EMs. Triaminoguanidinium azotetrazolate (TAGZT) [16] and 4,5-bis(1H-tetrazol-5-yl)-2H-1,2,3-triazole (BTTZ) [17] containing tetrazole ring have been studied as eco-friendly gas generating candidates. Their excellent gas production (V = 934 L kg^{-1} and 730 L kg^{-1}, respectively) can ensure to yield more gas during combustion progress. Meanwhile, the gas generating component combing bistetrazole (BT) as fuel and phase-stabilized ammonium nitrate (PSAN) as oxidant also be explored [13]. Unfortunately, those tetrazole derivatives are sensitive to external mechanical stimulus, which limits their application. Besides, Guanidinium azotetrazolate (GZT) can be applied gas generating candidate owing to the low sensitivity (IS = 32J, FS > 360N) and good gas production (V = 890 L kg^{-1}) [18–20]. As a result, the highly gas-productive and insensitive energetic salts play an important role in the application of novel agents. The performances of those fuels are listed in Figure 1.

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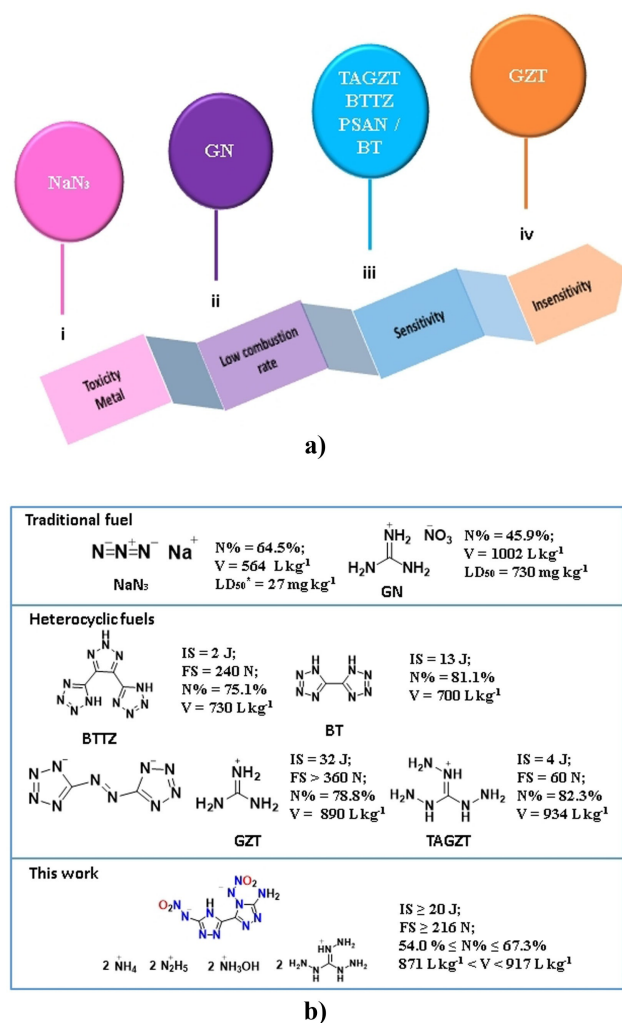*gcheng@mail.njust.edu.cn*

Figure 1. a) The exploration of gas generating fuels; b) Comparison of properties and parameters of this work and previous work. "V" is the volume of gas at STP of single composition using EXPLO 5.

In this work, we successfully prepare a series of insensitive (IS ≥ 20 J, FS ≥ 216 N) and high gas productive (V, 871–917 L kg^{-1}) energetic salts. The combustion performances of novel compounds are tested by an equal volume combustion experiment. Meanwhile, the detonation performances of novel compounds are investigated and the propulsion performances of HTPB based propellant formula using compound **7** as fuel are evaluated.

2 Experimental Section

Caution! All triazole compounds are energetic materials. They should be handled on small scale. The experimental operation should be carried out behind blast shields and with proper protective equipment.

2.1 Syntheses

The synthetic pathway is shown in Figure 2. 4,5,5′-triamine-3,3′-bi-1,2,4-triazole (**1**) was obtained by the cyclization reaction of 2-amino-5-carboxy-1,2,4-triazole and one equivalent diaminoguanidine hydrochloride at 120 °C after adjusting the pH of the mixture to 8. Then, nitrate salt **2** or perchlorate salt **3** was formed by an acid-base reaction of **1** and nitric acid or perchloric acid in water at 60 °C for 3 h.

To introduce the explosive group into **1**, the nitration of **1** was realized by using 100 % HNO$_3$ to afford 4,5′-dinitramino-5-amine-3,3′-bi-1,2,4-triazole (**4**). Then, the nitrogen-rich energetic salts **5**, **6**, **7**, and **8** were obtained via the acid-base reaction of ammonium hydroxide, hydrazine hydrate, hydroxylamine solution, 4,5,5′-triamine-3,3′-bi-1,2,4-triazole and compound **4** in hot water. It was worth noted that triamineguandine salt **9** was prepared through the reaction of a sodium salt of **4** instead of **4** as intermediate and triaminoguanidine hydrochloride based on the metathesis reaction in hot water. Interestingly, compounds **1** and **4** showed poor solubility in hot water. Those target salts were obtained with high purity because these compounds can be recrystallized by cooling the hot solution.

2.1.1 4, 5, 5′-Triamine-3, 3′-bi-1, 2, 4-Triazole (1)

Phosphorus pentoxide (40 g, 281 mmol) was slowly dissolved in phosphoric acid (80 g, 816 mmol) preheated to 50 °C. A finely ground mixture of 2-amino-5-carboxy-1, 2, 4-triazole (12.8 g, 100 mmol, 1.0 equiv.) and diaminoguanidine monohydrochloride (16 g, 128 mmol, 1.28 equiv.) was slowly added to the preheated solution. After the complete addition, the viscous mixture was slowly heated to 120 °C and kept for 4 h. The residue was poured into ice water (300 mL) and then adjusted to pH = 8 with concentrated NaOH solution, changing the color of the suspension from white to brown. The precipitate was filtered, washed repeatedly with water, and air-dried to obtain the crude compound **1** as a solid. Yield: 4.2 g, 23.2 mmol, 23.2 %. DSC (5 °C min^{-1}): T_{onset} = 329 °C. ^{1}H NMR (d_6-DMSO, 25 °C): δ = 12.40 (s, H), 6.149 (s, 2H), 5.801 (s, 2H), 5.7177 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO, 25 °C): δ = 157.48, 154.25, 148.84, 142.12 ppm. IR (KBr): v = 3735, 3416, 3159, 2624, 1627, 1556, 1473, 1367, 1309, 1257, 1126, 1050, 983, 889, 752,712 cm^{-1}.

2.1.2 General Procedures for Synthesis of Energetic Salts 2–3

Compound **1** (0.362 g, 2.0 mmol) was added to a solution of the corresponding acid (2.0 mmol) in a mixture of water (5 mL), the reaction mixture was stirred at 60 °C for 3 h. The solution was then dried by air and the residue was recrystallized from water to give the pure product.
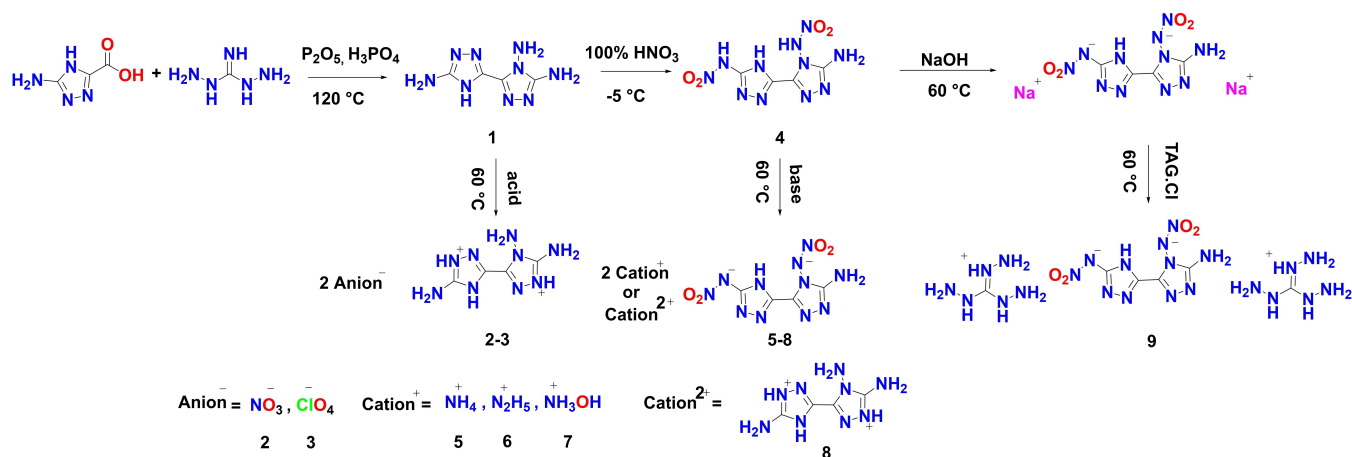
Figure 2. Synthesis of 4, 5, 5′-triamine-3, 3′-bi-1, 2, 4-triazole and corresponding energetic salt.

2.1.2.1 4, 5, 5′-Triamine-3, 3′-bi-1, 2, 4-Triazolium Dinitrate (2)

White solid (0.46 g, yield: 75%). DSC (5 °C min⁻¹): $T_{onset} =$ 173 °C. ¹H NMR (d_6-DMSO, 25 °C): δ = 8.44 (s, 2H), 7.34 (br s, 4H) ppm. ¹³C NMR (d_6-DMSO, 25 °C): δ = 154.57, 151.92, 142.26, 140.83 ppm. IR (KBr): ν = 3566, 3398, 3300, 3165, 2688, 1694, 1435, 1387, 1291, 1091, 1035, 963, 823, 781, 758, 715, 673 cm⁻¹.

2.1.2.2 4, 5, 5′-Triamine-3, 3′-bi-1, 2, 4-Triazolium Diperchlorate (3)

White solid (0.6 g, yield: 80%). DSC (5 °C min⁻¹): $T_{onset} =$ 271 °C. ¹H NMR (d_6-DMSO, 25 °C): δ = 8.36 (s, 2H), 5.19 (br s, 4H) ppm. ¹³C NMR (d_6-DMSO, 25 °C): δ = 154.51, 151.79, 142.31, 140.76 ppm. IR (KBr): ν = 3466, 3350, 3086, 2464, 1690, 1616, 1536, 1491, 1397, 1085, 965, 893, 749, 710, 658 cm⁻¹.

2.1.2.3 5-Amino-4, 5′-Dinitroamino-3, 3′-bi-1, 2, 4-Triazole (4)

HNO₃ (100%, 10 mL) was placed in a 50 mL three-neck round-bottom flask and cooled to −5 °C. Next, **1** (1.5 g, 8.28 mmol) was slowly added when the temperature of the mixture was kept below 0 °C. After the complete addition, the reaction temperature was maintained below −5 °C with stirring. Afterward, the solution was poured into 100 g of ice and stirred for precipitating yellow solid from the solution. The precipitate was filtered off and washed with ice-cooled water to give pure **4** as a slightly yellowish powder. Yield: 1.41 g (5.2 mmol, 63%). DSC (5 °C min⁻¹): $T_{onset} =$ 136 °C. ¹H NMR (d_6-DMSO, 25 °C): δ = 8.45 (s, 2H), 5.12 (br s, 4H) ppm. ¹³C NMR (d_6-DMSO, 25 °C): δ = 152.73, 149.96, 140.56, 139.36 ppm. IR (KBr): ν = 3589, 3392, 3231, 3144, 2707, 1694, 1644, 1584, 1500, 1406, 1336, 1265, 1221, 1093, 996, 958, 878, 840, 776, 731 cm⁻¹.

2.1.3 General Procedures for Synthesis of Energetic Salts 5–9

Compound **4** (0.542 g, 2.0 mmol) was added to a solution of the corresponding base (2.0 mmol) in a mixture of water (5 mL), the reaction mixture was stirred at 60 °C for 3 h. The solution was then dried by air and the residue was re-crystallized from water to give the pure product.

2.1.3.1 Diammonium 5-Amino-4, 5′-Dinitroamino-3, 3′-bi-1, 2, 4-Triazolate (5)

White solid (0.4 g, yield: 60%). DSC (5 °C min⁻¹): $T_{onset} =$ 190 °C, ¹H NMR (d_6-DMSO, 25 °C): δ = 7.41 (br s, 8H), 5.91 (s, 2H) ppm. ¹³C NMR (d_6-DMSO, 25 °C): δ = 157.16, 153.31, 149.23, 141.91 ppm. IR (KBr): ν = 3044, 1682, 1621, 1560, 1524, 1383, 1222, 1138, 1083, 1041, 974, 882, 765, 712, 674, 624 cm⁻¹.

2.1.3.2 Dihydrazinium 5-Amino-4, 5′-Dinitroamino-3, 3′-bi-1, 2, 4-Triazolate (6)

Yellow solid (0.33 g, yield: 50%). DSC (5 °C min⁻¹): $T_{onset} =$ 212 °C, ¹H NMR (d_6-DMSO, 25 °C): δ = 7.285 (br s, 10H), 5.91 (s, 2H) ppm. ¹³C NMR (d_6-DMSO, 25 °C): δ = 157.36, 153.13, 148.62, 141.75 ppm. IR (KBr): ν = 3149, 2700, 1500, 1434, 1343, 1260, 1121, 1082, 1008, 970, 866, 787, 762, 730, 669 cm⁻¹.

2.1.3.3 Dihydroxylammonium 5-Amino-4, 5′-Dinitroamino-3, 3′-bi-1, 2, 4-Triazolate (7)

White solid (0.4 g, yield: 59%). DSC (5 °C min⁻¹): $T_{onset} =$ 200 °C, ¹H NMR (d_6-DMSO, 25 °C): δ = 9.3 (s, 8H), 7.07 (br s, 2H) ppm. ¹³C NMR (d_6-DMSO, 25 °C): δ = 157.36, 151.83, 147.34, 141.96 ppm. IR (KBr): ν = 3413, 3330, 2903, 2703, 1674, 1631, 1524, 1450, 1391, 1285, 1203, 1089, 1008, 968, 872, 769, 671 cm⁻¹.

Exploring Application of 1,2,4-Triazole Energetic Salts: Gas Generating Agent, Propellant and Explosive Compositions

2.1.3.4 4, 5, 5′-Triamine-3, 3′-bi-1, 2, 4-Triazolium 5-Amino-4, 5′-Dinitroamino-3, 3′-bi-1, 2, 4-Triazolate (8)

White solid (0.7 g, yield: 80%). DSC (5 °C min⁻¹): $T_{onset} =$ 224 °C, ¹H NMR (d_6-DMSO, 25 °C): δ = 8.29 (s, 2H), 8.05(s, 2H), 7.51(s, 2H), 6.99(s, 2H) ppm. ¹³C NMR (d_6-DMSO, 25 °C): δ = 157.82, 157.49, 151.97, 150.05, 147.87, 147.09, 143.08, 142.62 ppm. IR (KBr): ν = 3466, 3214, 2631, 1680, 1526, 1443, 1399, 1281, 1235, 1142, 1086, 1045, 960, 876, 770, 693 cm⁻¹.

2.1.3.5 Ditriaminoguanidine 5-Amino-4, 5′-Dinitroamino-3, 3′-bi-1, 2, 4-Triazolate (9)

White solid (0.7 g, yield: 70%).DSC (5 °C min⁻¹): $T_{onset} =$ 191 °C, ¹H NMR (d_6-DMSO, 25 °C): δ = 13.02(s, 1H), 8.61(s, 6H), 5.61(s, 2H), 4.51(s, 12H) ppm. ¹³C NMR (d_6-DMSO, 25 °C): δ = 159.09, 157.20, 152.94, 149.34, 142.18 ppm. IR (KBr): ν = 3390, 3224, 1673, 1611, 1516, 1454, 1413, 1281, 1221, 1132, 1076, 999, 969, 877, 771, 733, 619 cm⁻¹.

3 Results and Discussion

3.1 X-Ray Crystallography

To acquire the three-dimensional information of target compounds, the single crystals of **1**, **2**, **4**, and **9** were obtained by the slow evaporation of water at room temperature and measured by X-ray diffraction. The crystallographic data were collected in supporting information (Table S2).

Neutral compound **1**·1/2 H₂O crystallizes in the triclinic P-1 space group with a moderate density of 1.631 g cm⁻³ at 170 K (Figure 3), which has four molecules per unit cell (Z = 4). Compound **1** exhibits excellent coplanar based on the

torsion angles (N1-C1-N4-N5 = 176.3(5)°, N2-N3-C2-C3 = 1.0(5)°, N7-C4-N6-C3 = 176.8(5)°). The face-to-face packing mode of **1** in Figure 3c contributes to reducing sensitivity by transforming it into layer sliding to absorb the kinetic energy induced by mechanical stimulation [21]. Dinitrate salt **2**·H₂O belongs to the triclinic space group P-1, which has two molecules per unit cell. With the introduction of nitrate anions, the density of **2**·H₂O is effectively increased to 1.746 g cm⁻³ at 298 K from 1.631 g cm⁻³ at 173 K. The hydrogen bonds between nitrogen and oxygen atoms resulted in the hydrogen bonding network of **2** being more complex than that of **1**. As shown in Figure 3d, **2** (3.28 Å) has a larger interlayer distance than compound **1** (3.165 Å), and the nitrate anion is orderly arranged in each layer.

Molecular **4**·3H₂O crystallizes in the monoclinic P₂₁/c space group with a density of 1.760 g cm⁻³ at 170 K and contains one neutral molecule and three water molecules. The nitramino group at the C4 position is nearly coplanar with 1,2,4-triazole skeleton, which is explained by torsion angles of C4-N10-N11-O6 (−2.6°), C4-N10-N11-O7 (177.62°), N8-N9-C4-N10 (−177.16°) and C3-N7-C4-N10 (178.04°). However, another nitramino group, located at the N4 position, has a certain angle (72.8°) with the plane of 1,2,4-triazole (torsion angles: C1-N4-N5-N6 = 107.22°, C2-N4-N5-N6 = −75.6°, N4-N5-N6-O3 = 4.9°, and N4-N5-N6-O4 = −176.63°). Figure 4b shows the layer distances of cross stacking packing for **4** are 3.37 Å and 2.98 Å in the horizontal and vertical directions, respectively. Both distances are less than 4 Å, indicating that the stronger intermolecular π-π interaction and more tightly packing [6]. Triaminoguanidine salt **9**, which is composed of two triaminoguanidine and one 4,5′-dinitramino-5-amine-3,3′-bi-1,2,4-triazoliate, crystallizes in the monoclinic space group P₂₁/n and has a molecular density of 1.71 g cm⁻³ at 170 K. According to Figure 4d, the packing mode of **9** reveals that the 3D-tube stacking was

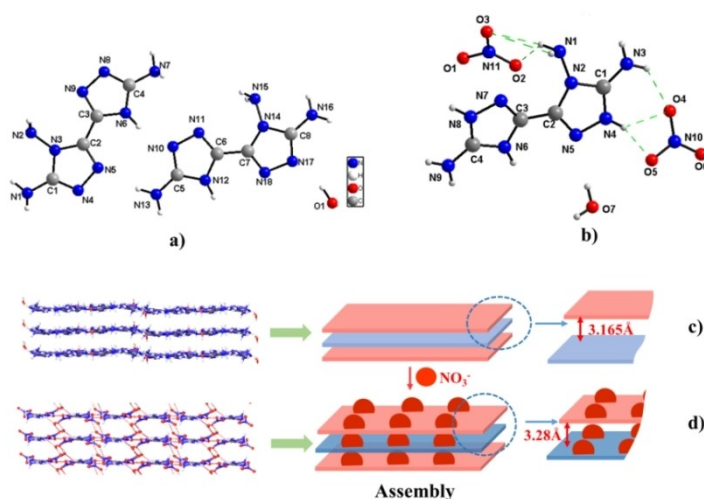**Figure 3.** a) Single-crystal X-ray structure of **1**·1/2 H₂O; b) Single-crystal X-ray structure of **2**·H₂O; c) face-to-face crystal packing for **1**·1/2 H₂O; d) face-to-face packing for **2**·H₂O.
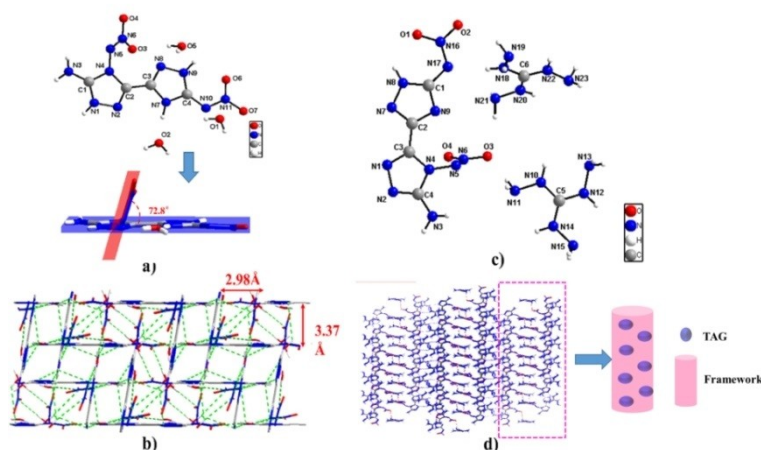
Figure 4. a) Single-crystal X-ray structure of **4**·3H₂O; b) Crossing packing for **4**·3H₂O; c) Single-crystal X-ray structure of **9**; d) 3D – tube layers stacking for **9**.

constructed from triaminoguanidine and triazole framework [22]. After external stimulation, the force of this packing mode is mostly dispersed in the layer plane, which plays a decisive role in reducing the sensitivity of energetic molecules.

3.2 Physicochemical and Energetic Properties

Herein, the differential scanning calorimetry (DSC) was employed to determine the thermal behaviors of compounds **1**–**9** with a heating rate of 5 °C min⁻¹ under a nitrogen atmosphere. The results are shown in Figure 5 and Table 1. Neutral compound **1** starts to decompose at 329 °C, which is comparable to that of traditional heat-resistant explosive

hexanitrostibene HNS ($T_{onset} = 318$ °C, D = 7612 m s⁻¹) [23]. Thermal stabilities of salt **3** (271 °C) are comparable with TNT ($T_{onset} = 295$ °C).

The introduction of the nitramino group into **4** leads to poor thermal decomposition ($T_{onset} = 136$ °C). The extrapolated onset temperatures of these energetic salts **5**–**9** range from 190 °C up to 224 °C. Among them, the decomposition of **5**, **7**, and **9** commenced at 190 °C, 200 °C, and 191 °C, respectively. Compounds **6** and **8** have higher thermal stability than RDX ($T_{onset} = 204$ °C) and decompose at 212 °C and 224 °C, respectively.
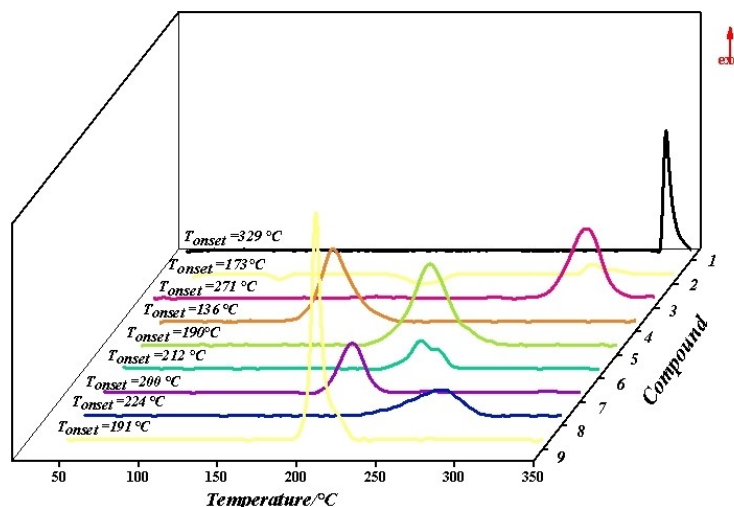

Figure 5. DSC curves of compounds **1**–**9** measured at 5 °C min⁻¹.

Exploring Application of 1,2,4-Triazole Energetic Salts: Gas Generating Agent, Propellant and Explosive Compositions

Table 1. Physical and detonation properties of the synthesized compounds in comparison with TNT and RDX.

Compound	T_{onset}[a] [°C]	ρ[b] [g cm^{-3}]	$\Delta_f H_m$[c] [kJ mol^{-1}/kJ g^{-1}]	D[d] [m s^{-1}]	P[e] [GPa]	V[f] [L kg^{-1}]	IS[g] [J]	FS[h] [J]
1	329	1.62	602/3.33	8190	22.9	788.8	>40	>360
2	173	1.76	−202/−0.66	7937	24.0	802.3	30	>360
3	271	1.88	−64/−0.168	8240	30.0	770.4	15	240
4	136	1.77	700/2.58	8526	27.5	786.8	10	120
5	190	1.69	522/1.71	8657	27.8	885.9	20	240
6	212	1.69	821/2.45	9069	30.7	908.7	20	240
7	200	1.76	663/1.97	9120	33.4	871.5	20	216
8	224	1.77	728/1.61	8177	24.0	797.5	>40	>360
9	191	1.66	1200/2.50	9077	30.0	917.3	27	288
TNT[i]	295	1.65	−295/−0.30	6881	19.5	/	15	353
RDX[i]	204	1.80	70.3/0.34	8795	34.9	/	7.5	120

[a] Thermal decomposition temperature (T_{onset}); [b] Density measured by gas pycnometer (25 °C); [c] Calculated heat of formation; [d] Calculated detonation velocity; [e] Calculated detonation pressure; [f] Volume of gas at STP; [g] Impact sensitivity; [h] Friction sensitivity; [i] Reference [28].

3.3 Energy and Physical Properties

Detonation performances of novel compounds are related to their density and heat of formation (HOF). In general, the high density and HOF have a positive effect on the performance of explosives. The results of physical and detonation performance are shown in Table 1.

The densities of new compounds fall in the range 1.62–1.88 g cm^{-3}. Perchlorate salt (3) possesses the highest density among all compounds. The HOF of 1–9 are far higher than trinitrotoluene (TNT, −295 kJ mol^{-1}) [24]. Except for nitrate salt (−202 kJ mol^{-1}) and perchlorate salt (−64 kJ mol^{-1}), other compounds show positive heat of formation from 522 kJ mol^{-1} to 1200 kJ mol^{-1}. In particular, the HOFs of 6 and 9 show 821 kJ mol^{-1} and 1200 kJ mol^{-1}, respectively, which are superior to that of other salts. Taking the calculated enthalpy and molecular density as elements of computation, the detonation parameters include detonation velocity (*D*), gas volume at standard temperature-pressure (*V*), and detonation pressure (*P*) is calculated by EXPLO 5 (version 6.05) [25].

The data of physicochemical and energetic properties are listed in Table 1. Lying in the range of 22.9–33.4 GPa and 7937–9120 m s^{-1}, respectively, the detonation pressures and velocities of these compounds are much better than those of TNT (D = 6881 m s^{-1}, P = 19.5 GPa). The sensitive parameters include impact (IS) and friction (FS) of 1–9 was investigated by the BAM method [26]. These novel samples show impact sensitivity over 15 J and friction sensitivity over 216 N. Even more, the detonation velocity (D = 9120 m s^{-1}) of compound 7 is higher than RDX and detonation pressure (P = 33.4 GPa) is comparable with RDX (D = 8795 m s^{-1}, P = 34.9 GPa), but its mechanical sensitivities (IS = 20 J, FS = 216 N) are much lower than RDX (IS = 7.5 J, FS = 120 N). Therefore, compound 7 exhibits great potential as the second explosives based on the physicochemical and energetic properties.

3.4 Constant-Volume Combustion Experiment

As the gas generating component, the gas production of triazole derivatives during the chemical reaction is considered. Therefore, the volumes of detonation gases of these candidate compounds at standard temperature pressure were calculated by EXPLO5 (version 6.05) software. Among them, 5, 6, 7, and 9 have pretty high gas production (871.5–917.3 L kg^{-1}) and positive HOF (522–1200 kJ mol^{-1}) with the introduction of energetic ions. Furthermore, the combustion law of pressure changes measured by the constant-volume combustion experiment plays an important role in the application of gas generating agents [27, 28]. Ignition charge (B/KNO$_3$, 0.5 mg) and energetic salts (6 mg) were loaded into the closed explosive equipment (12.56 µL) containing the nickel-chromium wire, which was completely covered by the ignition charge, and the combustion experiment was proceeded by introducing 24 A electricity to heat the nickel-chromium wire (duration 110 ms). The experimental setup is listed in Figure 6.
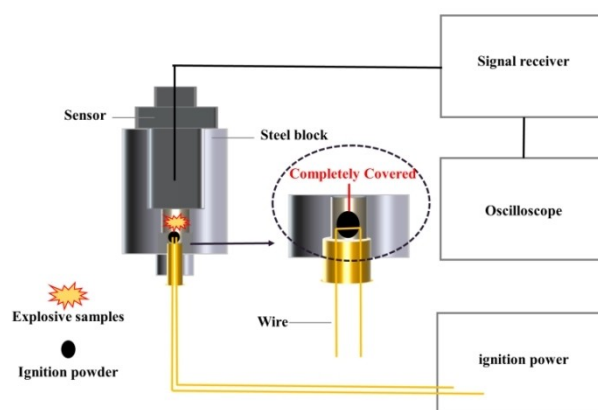
Figure 6. Sectional view of combustion experiment device.

The constant-volume combustion results of new energetic salts and guanidine nitrate (GN), the commonly used gas-generating component [10], are shown in Figure 7 and Table 2. Compared with GN, all of these samples show the more excellent performance of releasing gas ($P_{max} \geq$ 12.8 MPa) and the maximum pressure-up rate (dP/dt_{max}, 164–690 GPa s^{-1}) than GN ($P_{max} = 4$ MPa, $dP/dt_{max} =$ 82.1 GPa s^{-1}). There is no doubt that compound **9** possesses prominent gas productivity ($P_{max} > 13.4$ MPa) and the maximum pressure-up rate ($dP/dt_{max} = 690$ GPa s^{-1}) during the combustion process. The pressure value of **7** also exceeds the maximum value by 13.4 MPa, but dP/dt_{max} (485 GPa s^{-1}) is inferior to **9**. Diammonium salt **6** boosts P_{max} to 12.8 MPa after a pressure-up time of 285 μs, while the dP/dt_{max} is 164 GPa s^{-1}. The gas productivity and maximum pressure

rate of sample **5** ($P_{max} = 13.2$ MPa, $dP/dt_{max} = 240$ GPa s^{-1}) are more 3 times than those of GN ($P_{max} = 4$ MPa, $dP/dt_{max} =$ 82 GPa s^{-1}). Hence, these results suggest that the novel compounds have a faster energy release and pressurization rate than GN.

3.5 Propellant Performances

For the solid propellant, specific impulse (I_{sp}) as an essential parameter is closely related to the combustion temperature and mole number of gaseous products, which determined the efficiency of propulsion. Explosives, like RDX, HMX, etc, can be used as the fuels of solid propellants to improve combustion efficiency [8], Compound **7** exhibits excellent properties than RDX for sensitivity and detonation performance. To further evaluate the potential of compound **7** as fuel in solid propellant formulations, the propulsion performances of HTPB based propellant formula are calculated by EXPLO5 (version 6.05) using compound **7** as fuel (Table 3). The basic propellant formulation consists of 14 wt% HTPB, 15 wt% Aluminium, 71 wt% AP. The specific impulse (I_{sp}), combustion temperature (T_c), and mole number of gaseous products (M_c) are calculated as 262 s, 3336 K, and 36.7 mol kg^{-1}, respectively. When 5 wt%–20 wt% of compound **7** is added to the basic propellant, the values of I_{sp} are not a significant change from 262 s to 264 s, but I_{sp} starts slightly decrease from 264 s to 260 s with as compound **7** up to 25 wt%. Besides, the combustion temperature of the novel formula is reduced from 3336 K to 2924 K with the increases content of compound **7**. Therefore, compound **7** has great promise as high-energy fuel components in solid propulsion formulations.
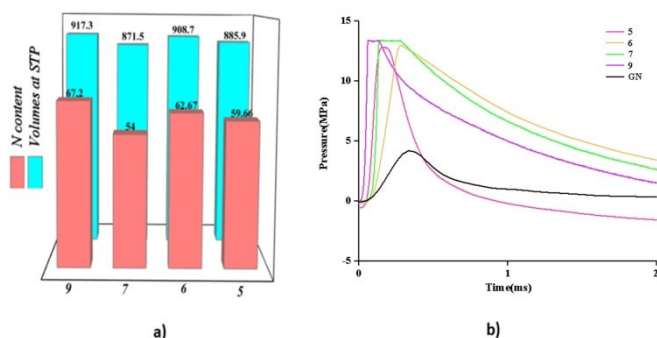

Figure 7. a) The nitrogen content and volumes of detonation gases at STP of novel compounds; b) The P-t relationship of novel compounds (**5**, **6**, **7**, and **9**) and GN.

4 Conclusion

In summary, a series of 1,2,4-triazole derivatives with high nitrogen content are successfully synthesized via facile pathways and investigated by spectroscopy (multinuclear NMR spectra, infrared), elemental analysis, differential scanning calorimetry measurements. Among them, the crystal information of **1**, **2**, **4**, and **9** are collected for investigating

Table 2. Constant-volume experiment results of **5**, **6**, **7**, **9** and GN.

Sample	P_{max}[a] [MPa]	Pressurization time[b] [μs]	dP/dt_{max}[c] [GPa s^{-1}]
5	13.2	151	240
6	12.8	285	164
7	>13.4[d]	148	485
9	>13.4	95	690
GN	4	332	82.1

[a] Maximum pressure; [b] Pressure-up time; [c] Maximum pressure-up rate; [d] Maximum value of oscilloscope.

Table 3. Propellants performances.

Formula	Al/%	AP/%	HTPB/%	Fuels/%	T[a]/K	M[b]/mol kg^{-1}	I_{sp}[c]/s
P1	15	71	14	0	3336	36.7	262
P2	15	66	14	5	3277	37.7	263
P3	15	61	14	10	3214	38.7	263
P4	15	55	14	15	3142	39.8	264
P5	15	51	14	20	3053	40.9	263
P6	15	46	14	25	2924	41.8	260

[a] Isobaric combustion temperature in the combustion chamber; [b] Mole number of gaseous products in the combustion chamber; [c] Specific impulse.

various packing modes and intermolecular interaction. All of these compounds possess good denotation performance (D, 8177 m s⁻¹–9120 m s⁻¹; P, 22.9 Gpa–33.4 Gpa). Compound **7** not only displays the outstanding detonation performance (D, 9120 m s⁻¹, P: 33.39 GPa), but also shows lower mechanical sensitivities (IS ≥ 20 J, FS ≥ 216 N) than RDX (IS = 7.5 J, FS = 120 N). Moreover, these samples of **5, 6, 7, 9** with excellent gas-generating capability ($P_{max} \geq$ 12.8 MPa) and high pressure-up rate ($dP/dt_{max} \geq$ 164 GPa s⁻¹) show the promising potential to become replacement of the typical gas-generating component GN (P_{max} = 4 MPa, dP/dt_{max} = 82.1 GPa s⁻¹). Meanwhile, the performance of propellant formulations reveals that compound **7** is the potential candidate as fuel based on the commonly used HTPB propellant. All these desire results demonstrate that 1,2,4-trizole energetic salts show great potential for the further application of agents, explosives, and propellants.

Acknowledgements

Data Availability Statement

No Data available.

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