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High Energy Density Material (HEDM) – Progress in Research Azine Energetic Compounds

Synthesis, properties and applications of high energy density material (HEDM) –azine energetic compounds

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In recent years, the application of high-nitrogen containing azine energy materials has been one of the hot spots in the field of energy materials in China and elsewhere. This paper reviews domestic and foreign studies into high-nitrogen azine energetic materials. The synthetic methods, structural and theoretical analysis, physical and chemical properties, sensitivity properties, thermal properties and detonation properties of some typical pyrazine energetic compounds are summarised, including: 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) of diazines, 4,4′,6,6′-tetra(azido)azo-1,3,5-triazine (TAAT) of triazines, 3,6-dihydrazino-1,2,4,5-tetrazine (DHT), 3,6-bis(1H-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine (BTATz) and 3,3′-azobis(6-amino-1,2,4,5-tetrazine) (DAAT) of tetrazine and their respective applications and potential value are described. The results of published studies reviewed here show that the application of azine energetic compounds in propellants can effectively improve the burning rate and reduce the characteristic signal; the application of azine energetic compounds in mixed explosives can reduce the sensitivity and improve the detonation performance; the application of azine energetic compounds in gas generators can reduce the combustion temperature and increase the gas content. Therefore, this class of compounds has a broad application prospect in energetic materials.

1. Introduction

High energy density material (HEDM) is a new concept formed in recent years. There is no unified definition so far, although it is generally composed of a high energy density compound (HEDC) and other components (such as an oxidiser, combustible agent, binder, plasticiser and insensitive agent). The general requirements for energy and stability are as follows: density $\rho \approx 1.9$ g cm^{-3}, detonation velocity $D \approx 9.0$ km s^{-1}, detonation pressure $P \approx 40.0$ GPa and bond dissociation energy (BDE) ≈ 80–120 kJ mol^{-1}. This type of material can be used as a propellant, explosive and pyrotechnic composition (1).

The new high energy density materials include five types of substances: acyclic compounds, strained and caged compounds, nitrogen heterocyclic compounds (azine compounds, azole compounds, furazan compounds), nitrogen clusters and oxygen cluster molecules and excited state materials. Among these, nitrogen heterocyclic compounds have high enthalpy of formation, high density, insensitivity and thermal stability. The high nitrogen and low hydrocarbon content of the molecule make it easier to achieve oxygen balance and increase the density. Most of the decomposition products are nitrogen (N$_2$) with the lowest energy level, they are of great environmental friendliness and have attracted attention from domestic and foreign researchers (2).

The basic skeleton of azine compounds is the aromatic hexagonal ring of the nitrogen

heterocycle. On the one hand, aromaticity makes the whole molecule more stable, thus having lower sensitivity to friction, impact and sparks and being safer to use; on the other hand, N atoms replace the CH group in the benzene ring system, which gives the system a higher enthalpy of formation, higher heat of combustion and makes it more likely to achieve oxygen balance. At present, the research on azine compounds mainly focuses on tetrazines (DHT, BTATz) and polynitro- or amino-substituted diazines (such as LLM-105). The study of polyazide azo triazines (such as TAAT) and other triazines mainly focuses on medical aspects. Only a small number of theoretical studies have been conducted on pentazine and total nitrogen substituted benzene, but there has been no breakthrough in experiment.
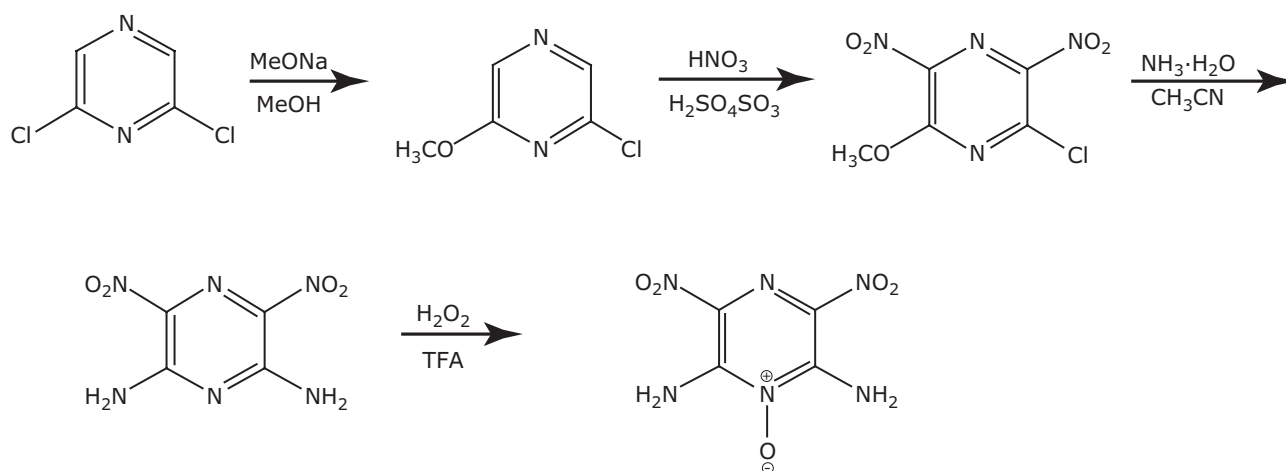
2. 2,6-Diamino-3,5-dinitropyrazine-1-oxide (LLM-105)

The chemical name of LLM-105 is 2,6-diamino-3,5-dinitropyrazine-1-oxide. According to the literature, LLM-105 was first synthesised by the Lawrence Livermore National Laboratory (LLNL), USA in 1995. Pagoria *et al.* studied its various physical properties in the laboratory and preliminarily explored its applicability. Due to its superior performance, LLM-105 quickly attracted the attention of the global explosives division (3–5).

2.1 Synthesis of LLM-105

LLM-105 was initially synthesised by oxidation of 2,6-diamino-3,5-dinitropyrazine (ANPZ) using trifluoroacetic acid (TFA) at room temperature by Pagoria *et al.* (3) of LLNL, USA. 10 g was

synthesised for the first time. However, it is difficult to synthesise the precursor ANPZ. In 1998, Pagoria *et al.* (4) improved the method for synthesising ANPZ. Using commercially available 2,6-dichloropyrazine as a starting material, 400 g of LLM-105 was successfully prepared through a four-step reaction and the total yield reached 48%. The Fraunhofer Institute for Chemical Technology, Germany (6) also used 2,6-dichloropyrazine as the starting material to synthesise LLM-105 in four steps. The total reaction yield reached 41%, the final product purity reached 93% and it contained a small amount of ANPZ byproduct. In 2009, Pagoria *et al.* (7) provided a method for the synthesis of LLM-105 including nitration of 2,6-diaminopyrazine-1-oxide (DAPO) that had a good effect. In 2010, Pagoria *et al.* (8) provided a method for synthesising a pyrazine-containing material, in which the iminodiacetonitrile derivative is contacted with hydroxylamine or a hydroxylamine salt for forming DAPO, further comprising contacting the DAPO with nitric acid in the presence of sulfuric acid for forming LLM-105. In 2015, an investigation by Zuckerman *et al.* (9) focused on optimising flow nitration conditions for cost effective preparation of DAPO. Synthesising LLM-105 using a flow microreactor system has the advantages of safety, decreased reaction time and improved product purity. In 2018, Pagoria *et al.* (10) described various approaches to the synthesis of LLM-105 developed over the past 20 years. The method of synthesising LLM-105 from different starting materials including 2,6-dimethoxypyrazine (DMP), 2-chloro-6-methoxypyrazine (CMP) and DAPO is described and the synthesis method is optimised. The classic synthetic route of LLM-105 is shown in **Scheme I**.

Scheme I. Synthetic process of 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105)

In China in 2006, Guo *et al*. (11) optimised the reaction conditions on the basis of this synthetic route, using 2,6-dichloropyrazine as starting material. LLM-105 was synthesised through the four steps of substitution, nitrification, ammonification and oxidation. The total yield was more than 36% and the purity of the product was more than 98% after the recrystallisation from dimethyl sulfoxide (DMSO). In the same year, Liu *et al*. (12) synthesised LLM-105 with 2,6-dichloropyrazine as the starting reactant *via* a four-step reaction. In 2012, Yu *et al*. (13) continued to improve the technology. They provided a method where LLM-105 was prepared by methoxylation, nitration, amination and oxidation using 2,6-dichloropyrazine as starting material, the total yield reached 54%. In order to reduce the manufacturing costs, Deng *et al*. (14) synthesised LLM-105 using ANPZ as the starting material and high-concentration hydrogen peroxide (H_2O_2) solution as an oxidising agent. The amount of TFA was reduced by 50% compared to the original method, which greatly reduced the LLM-105 synthesis cost. In order to further reduce the cost of LLM-105, Deng (15) also recovered the TFA in the waste liquid from the LLM-105 production process through strong alkali neutralisation, concentration, acidification and distillation processes. The results show that the recovery rate of TFA was more than 80% and the purity was more than 98%. In 2012, Zhou *et al*. (16) explored a new broken azeotropic technique to recover TFA by adding solvent A and then employing atmospheric distillation to recover TFA for the synthesis of LLM-105. Wang (17) provided a method in which spherical or cubic crystals of LLM-105 were prepared using solvent-nonsolvent recrystallisation technology. Zhang *et al*. (18) reviewed research progress in synthesis methods, properties, crystal structures and thermochemical properties of LLM-105 and its application in explosives. In 2016, Wang *et al*. (19) provided the technology for synthesising LLM-105 through the oxidation of ANPZ on the kilogram scale, the yield of LLM-105 was 98.3% and its purity 96.4%. The dosage of TFA was reduced compared to previous methods. In 2016, Wang (20) improved the synthetic process of LLM-105, using commercially available iminodiacetonitrile as the starting material, through a three-step reaction of nitrosation, ring formation and nitration. The total yield of LLM-105 was 44% and the new technology has the advantages of simple synthesis, low synthesis cost and little environmental pollution.

2.2 Structure and Theoretical Analysis of LLM-105

According to the quantitative calculations in the literature (21, 22), there is a strong delocalisation among the amino and nitro group and the six-membered ring of pyrazine and the hydrogen bond existing between $-NH_2$ and $-NO_2$ which are stronger than the ordinary hydrogen bond, thus enhancing the stability of the whole molecule. All the atoms in the molecule are in the same plane and multiple intermolecular hydrogen bonds are formed in the crystal, which makes the whole system similar to the layered structure of graphite, which is not only conducive to the formation of higher density crystals, but also slides easily and makes it more insensitive (23). Wang *et al*. (24) used density functional theory (DFT) with B3LYP/6-31G(d,p) level to optimise the geometric structure of LLM-105 and found that there was no imaginary frequency. The configuration and atomic numbering of LLM-105 after geometry optimisation are shown in **Figure 1**. It can be seen that all atoms on the triazole ring in LLM-105 are basically in the same plane. Due to the formation of π-conjugated systems, the C–N bond length (0.131 nm ~ 0.142 nm) on the ring is longer than the standard double bond (0.122 nm), shorter than the standard single bond (0.146 nm) and tends towards the average. This is consistent with the discovery of He *et al*. (25, 26), who optimised the stable geometry of LLM-105 at the level of B3LYP/6-31G**. He (25, 26) believed that all
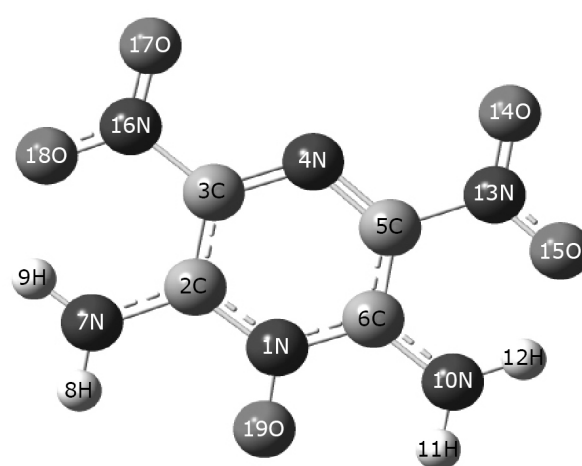

Fig. 1. Optimised structure of 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) at B3LYP/6-31G(d,p) level. Reprinted from (24). Copyright (2013), with permission from *Chinese Journal of Explosives & Propellants*

atoms of LLM-105 belong to the same plane and there are hydrogen bonds and large conjugated structures in the molecule.

2.3 The Performance of LLM-105

2.3.1 Physical Properties of LLM-105

The molecular formula of LLM-105 is $C_4H_4N_6O_5$, relative molecular mass M_r = 216.04, density ρ = 1.913 g cm^{-3}, oxygen equilibrium (OB) = −37.03%, heat of formation (HOF) = −12 kJ mol^{-1}. It is a needle-like bright yellow crystal. It is insoluble in commonly used organic solvents, but soluble in DMSO (27).

2.3.2 Sensitivity of LLM-105

Pagoria and Kennedy *et al*. (4, 28) measured LLM-105 by differential scanning calorimetry (DSC). The DSC curve showed that the thermal stability was the same as trinitrotoluene (TNT). The friction sensitivity of LLM-105 was greater than 0.36 N. The impact sensitivity was 117 cm. The shock sensitivity was close to triamino-trinitrobenzene (TATB) and was better than high melting explosive (HMX) and hexanitrostilbene (HNS). Tarver *et al*. (29) conducted a special study on the sensitivity of LLM-105 and the results showed that the thermal sensitivity and impact sensitivity of LLM-105 were between TATB and HMX. Cutting *et al*. (30) studied the thermal sensitivity of LLM-105 using a one-dimensional thermal explosion delay period and the results showed that the delay period of thermal explosion of LLM-105 is between HMX and TATB, which is superior to HNS-IV and equivalent to TNT. Comparing with HMX and research department explosive (RDX), all reactions of LLM-105 are relatively mild. The explosive reaction of LLM-105 was not observed at the critical temperature of HMX. It is estimated that the critical temperature of LLM-105 is about 15°C higher than that of HMX, between 190°C and 214°C. It can be seen that the above studies are in good agreement with one another.

2.3.3 Energy and Detonating Performance of LLM-105

The energy released by LLM-105 is 112% of the explosive TATB and its theoretical detonation velocity at the crystal density is D = 8560 m s^{-1}

(4, 31). Cutting *et al*. (30) tested the detonation velocity of 7980 m s^{-1} when the relative density of RX-55-AA was 93%.

2.3.4 Thermal Stability of LLM-105

The DSC exothermic peak of LLM-105 measured at 10°C min^{-1} heating rate was 342°C (3, 4). The DSC exothermic peaks for TATB and HNS-IV were 355°C and 320°C, respectively. The compatibility of LLM-105 with some common high explosives by the use of thermal techniques (DSC and vacuum stability test) and supplementary nonthermal techniques (Fourier transform infrared and X-ray diffraction) shows that LLM-105 has good compatibility with HMX, DNTF and CL-20 (32). LLM-105 has good thermal stability.

2.4 The Use and Potential Value of LLM-105

Due to the high cost of LLM-105 synthesis, there is currently no mass production. It is known that LLM-105 is a promising explosive with potential. The thermal stability and shock wave sensitivity, which are close to TATB and superior to HMX and HNS, make it suitable for potential application as new booster materials that approach HMX in performance (31). LLM-105 can be potentially applied to booster explosives, detonator charges, main charges and other explosives to make eutectic explosives to improve the performance of other explosives (32, 33). At present, the research on LLM-105 mainly focuses on improving the synthesis route, reducing the cost of synthesis, process amplification and further evaluating its performance for formulation verification (18, 34–38).

3. 4,4',6,6'-Tetra(azido)azo-1,3,5-triazine (TAAT)

4,4',6,6'-Tetra(azido)azo-1,3,5-triazine (TAAT) is a typical polyazido heterocyclic system, which contains many azido groups which can decompose exothermically. The nitrogen content of TAAT is very high, up to 79.55%. It has good stability, high decomposition temperature and low friction sensitivity. The heat of formation is as high as 2171 kJ mol^{-1}. The heat of formation is the highest among all reported polynitro compounds, polyazide compounds and high-nitrogen compounds (39, 40).
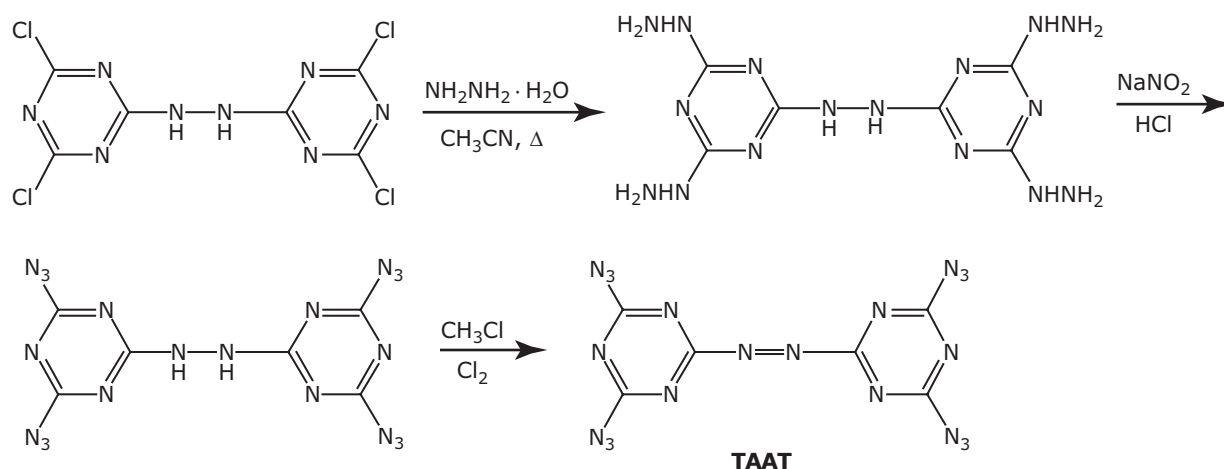
3.1 Synthesis of TAAT

In 1921, Ott *et al*. (41) synthesised 2,4,6-triazido-1,3,5-triazine (TAT) from 2,4,6-trichloro-1,3,5-triazine (TCT) and sodium azide (NaN$_3$). However, due to the limitation of knowledge at that time, the structure of the azide group was not properly analysed. In 1976, a series of hydrazine triazine and azotriazine compounds were synthesised by Loew *et al*. (42), but they were not used as energetic materials. In 2000, Gillan (43) showed that TAT had a high heat of formation (1053 kJ mol^{-1}) through experimental measurement, but its stability was extremely poor and it was very sensitive to collision, friction and sparks, therefore it did not have practical value. In order to reduce the sensitivity of TAT and seek its practical application, Hiskey and Huynh (39, 44) connected TAT with hydrazine bonds and azo bonds to form a symmetric molecule with a double heterocyclic ring of four azides. TAAT and 4,4′,6,6′-tetra(azido)hydrazo-1,3,5-triazine (TAHT) were obtained respectively. Some performance parameters of TAT, TAHT and TAAT are shown in **Table I** (45). By

comparing the enthalpy of formation of TAT, TAHT and TAAT in **Table I**, it is found that the enthalpy is significantly increased after the introduction of azo bonds (above 300 kJ mol^{-1}) and that using azo bridges connects two azide triazines to form a large conjugate system that can effectively improve the stability and decomposition temperature, reduce friction sensitivity and significantly enhance the stability. Huynh *et al*. (39) reported that TAAT could be synthesised by reacting 4,4′,6,6′-tetrachloro-dihydro-azo-1,3,5-triazine in acetonitrile with hydrazine hydrate to obtain 4,4′,6,6′-tetrahydro-dihydro-azo-1,3,5-triazine, followed by azide reaction in the presence of sodium nitrate (NaNO$_2$)/hydrochloric acid (HCl) and finally dehydrogenation in chloroform (CHCl$_3$)/water (H$_2$O) mixed solvent by chlorine oxidation to obtain TAAT (**Scheme II**). In 2007, TAAT was synthesised from cyanuric chloride and hydrazine hydrate as starting materials by Li (46). This synthesis was a four-step process including coupling, hydrazinolysis, diazotisation and oxidation. Compared with the triazine compounds synthesised earlier, TAAT has higher decomposition temperature, lower friction sensitivity, higher stability and higher heat of formation. The investigation indicates that chlorine can transform 4,4′,6,6′-tetra(azido)hydrazo-1,3,5-triazine into TAAT at 94%, but *N*-bromosuccinimide transforms only to 84%. In 2011, TAAT was synthesised from TAHT by Li (47) through oxidative reaction with trichloroisocyanuric acid (TCI), dichloroisocyanuric acid (DCI), sodium dichloroisocyanurate (SDCI), sodium dibromoisocyanurate (SDBI), *N*-chlorosuccinimide (NCS), *N*-bromosuccinimide (NBS), Cl$_2$, Br$_2$ and sodium hypochlorite (NaClO) with yields of 72% ~ 93%.

Table I Some Performance Parameters of TAT, TAHT and TAAT			
Performance	**TAT**	**TAHT**	**TAAT**
Density, g cm^{-3}	1.72	1.65	1.724
Enthalpy of formation, kJ mol^{-1}	1053	1753	2171
NHOF, kJ mol^{-1}	72.20	62.61	83.50
BAM friction sensitivity, kg	<0.5	2.9	2.4
Impact sensitivity, cm	6.2	18.3	6.2

Scheme II. Synthetic process of 4,4′,6,6′-tetra(azido)azo-1,3,5-triazine (TAAT)

3.2 Structure and Theoretical Analysis of TAAT

Although the stability of triazines is usually low, the use of azo bridges to connect two triazines to form a large conjugated system can effectively improve the stability. For example, TAAT with a nitrogen content of 79.55% has good stability, high decomposition temperature, low friction sensitivity and high heat of formation up to 2171 kJ mol^{-1} (39, 40). In 2009, Yu *et al*. (48) optimised the molecular geometry of TAAT at the level of DFT-B3LYP/6-31G* by using quantum chemical methods. The results were compared with experimental measurements. It was proven that the introduction of azo bonds could enhance the stability of the title compounds from both experimental and theoretical aspects. In 2012, Geng *et al*. (49) calculated the geometric optimisation of TAAT at B3LYP/6-31+G(d) level. The optimised configuration of TAAT is shown in **Figure 2**. The vibration analysis results have no imaginary frequency, indicating that it is a stable point on the potential energy surface and a stable geometric configuration is obtained. Natural bond orbital (NBO) analysis of the compound was carried out. The results showed that the compound has weak conjugation and the bond between the azide group and the ring is relatively weak, making it easy to break when thermally decomposed. All the C–N, C2–N24, C11–N15 bond lengths on the triazine ring are between C–N single bond (0.147 nm) and C=N double bond (0.127 nm). Wiberg bond order is between 1.0254 and 1.9519 and between the bond levels of standard single

bond (1.0) and standard double bond (2.0). Due to the wide distribution range, the conjugation of the target compound TAAT is weak. Two triazine rings are each connected to two azide groups, which are connected by an azo group. Due to the steric hindrance effect, the configuration has a certain torsion in the space and the torsion angle is 33.8°. The system energy calculated at the B3LYP/6-31+G(d) level is -3.48×10^{-6} kJ mol^{-1}, the thermal energy is 483.90 kJ mol^{-1} and the molar heat capacity at constant volume is 251.70 kJ mol^{-1} K^{-1}. The entropy is 548.26 kJ mol^{-1} K^{-1} (pressure is 1.01×10^5 Pa, temperature is 298.15 K).

3.3 The Performance of TAAT

3.3.1 Physical Properties of TAAT

The molecular formula of TAAT is $C_6H_4N_{20}$, relative molecular mass $M_r \approx 356$, density $\rho = 1.724$ g cm^{-3}, OB = -62.00%, HOF = 2171 kJ mol^{-1} (39).

3.3.2 Sensitivity of TAAT

The DSC indicates a fast decomposition temperature of TAAT at 185°C, the impact sensitivity of TAAT is 6.2 cm, the friction sensitivity of TAAT is 2.4 kg, the spark sensitivity is <0.36 J (39).

3.3.3 Energy and Detonating Performance of TAAT

TAAT theoretical detonation velocity $D = 8498.72$ m s^{-1}, HOF = 2171 kJ mol^{-1}. Vacuum constant volume detonation heat is 6092 kJ kg^{-1}.
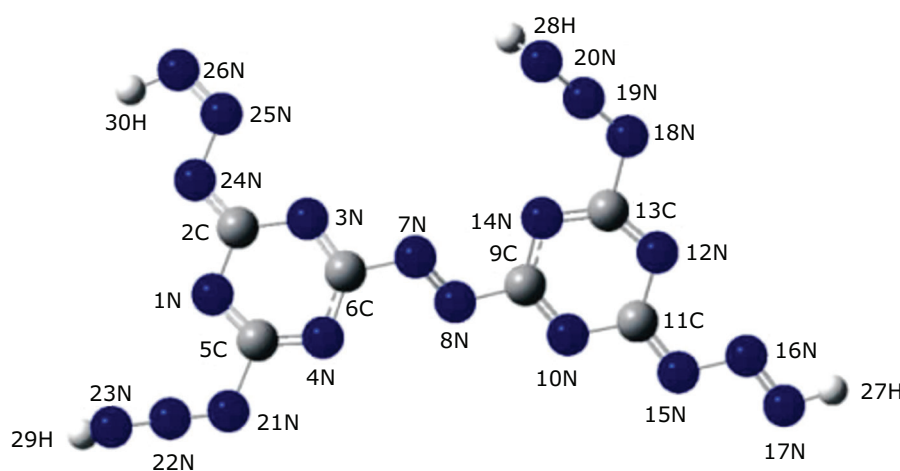

Fig. 2. Optimised structure of 4,4',6,6'-tetra(azido)azo-1,3,5-triazine(TAAT). Reprinted from (49). Copyright (2012), with permission from *Journal of Northwest Normal University*

The heat of decomposition for TAAT is about 2607 J g^{-1}, twice that of TAHT (50).

3.3.4 Thermal Stability of TAAT

The synthesised TAAT was subjected to thermal analysis by DSC. Under dynamic nitrogen protection, the heating rate was >20°C min^{-1} and the sample dosage was 0.70 mg. The experimental results are shown in **Figure 3**. From **Figure 3**, it can be seen that TAAT has a strong endothermic peak at 153.78°C, which corresponds to the melting peak of TAAT, that is, its melting point. However, TAAT begins to decompose exothermically near 200°C, the decomposition rate of TAAT reaches a maximum at 221.74°C and the exothermic end occurs at 238°C, which indicates that there is no other heat change until the end of the test. Under
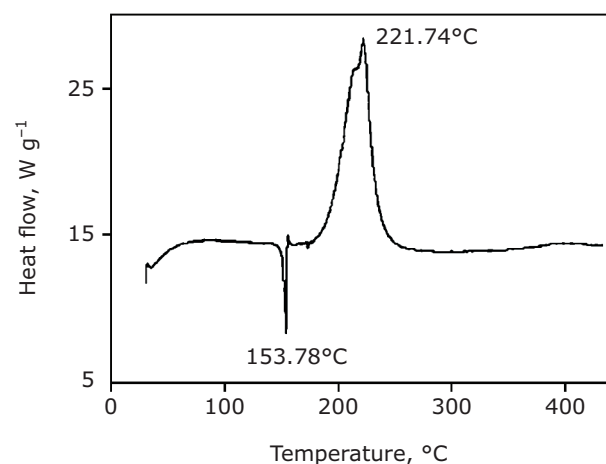

Fig. 3. DSC curve of 4,4′,6,6′-tetra(azido)azo-1,3,5-triazine(TAAT). The temperatures indicated in the figure are the temperatures of the weight loss steps. Reprinted from (47). Copyright (2011), with permission from *Chinese Journal of Organic Chemistry*

fast heating conditions, TAAT has completely decomposed (47).

3.4 The Use and Potential Value of TAAT

TAAT is a typical example of polyazido-azo-heterocyclic systems, which possesses high nitrogen content (79.5%) and the largest heat of formation (2171 kJ mol^{-1}) among all reported energetic materials (39). As a natural consequence of its chemical structure, it will generate large amounts of N_2 gas when it decomposes. This decomposition pathway is highly desirable for energetic materials in order to avoid environmental pollution and health risks, as well as untraceable signatures (51). Among the polyazide heterocyclic compounds, TAAT has a higher decomposition temperature, low friction sensitivity and strong stability. In addition to being used as energetic materials, TAAT can be pyrolysed to prepare nitrogen rich C/N nanotubes and nanospheres and is expected to be used in biocompatible materials, battery electrodes, corrosion protection, sensors, propellants and fuels (39, 52–54).

4. 3,6-Dihydrazino-1,2,4,5-tetrazine (DHT)

There are three isomers of tetrazine: 1,2,3,4-tetrazine (as shown in **Figure 4(a)**), 1,2,3,5-tetrazine (**Figure 4(b)**), 1,2,4,5-tetrazine (homotetrazine or *S*-tetrazine) (**Figure 4(c)**). The chemical name of DHT is 3,6-dihydrazino-1,2,4,5-tetrazine, which belongs to all tetrazines (*S*-tetrazine). The most current research is on pyridine and its synthesis method is also mature. Only Russia and the USA have reported a small amount of 1,2,3,4-tetrazine compounds and these studies are mainly related to the synthesis and properties of benzo-1,2,3,4-tetrazine oxides and
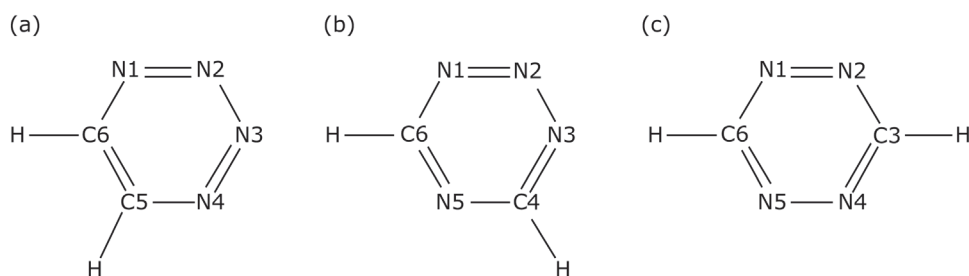

Fig. 4. Structural formula of three isomers of tetrazine: (a) 1,2,3,4-tetrazine; (b) 1,2,3,5-tetrazine; (c) 1,2,4,5-tetrazine

their derivatives (50, 55, 56). There are few reports on 1,2,3,5-tetrazine (57, 58). At present, the first method for synthesising tetrazine compounds is to synthesise 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (BT) and then carry out nucleophilic substitution for 3,5-dimethylpyrazole groups in BT to produce a series of four azine compounds.

4.1 Synthesis of DHT

DHT was originally established in 1966 by Marcus *et al*. (59). DHT and its derivatives were prepared by the reaction of 3,6-diamino-*s*-tetrazine (DATZ) with hydrazine. DATZ is formed by the amination of BT. In the process of amination the replacement is not complete, part of the DATZ is monosubstituted and the yield is low (60–62). In 1998, Chavez *et al*. (63) obtained DHT with BT and hydrazine hydrate when studying the dual heterocyclic system 1,2,4-triazolo[4,3-*b*][1,2,4,5] tetrazine. In 1998, Chavez *et al*. (64) described the synthesis and properties of several new energetic 1,2,4,5-tetrazine derivatives. Hiskey *et al*. (65) from the Los Alamos National Lab (LANL), USA, studied a new synthesis route of DHT for the synthesis of the tetrazine-type explosive LAX-112. In acetonitrile, the precursor 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydro-1,2,4,5-tetrazine (BDT) was reacted with hydrazine hydrate to obtain DHT. Talawar *et al*. (66) mixed BDT with hydrazine hydrate in acetonitrile at low temperature to obtain DHT in yield 92%, which further shortened the synthetic route. Cutivet *et al*. (67) found that dihydrotetrazines have more advantages than tetrazines in the nucleophilic substitution reaction of amines, which saves the BDT oxidation step. Therefore, the reaction time is shorter and the reaction conditions milder. However, Cutivet (67) did not study the nucleophilic substitution of ruthenium on the precursor. In 2003, Klapötke *et al*. (68) proposed a method in which 3,6-bishydrazino-1,2,4,5-tetrazine was synthesised as described by hydrazinolysis of 3,6-bis-(3,5-dimethylpyrazolyl)-1,2,4,5-tetrazine. In China, Wang *et al*. (69) proposed a method for the synthesis of BDT and its salts from triaminoguanidine nitrate and 2,4-pentanedione after condensation, oxidation and neutralisation. In 2006, Pan *et al*. (70) used a literature method (36) to scale up the synthesis of DHT to 100 g and the yield was 77%. In 2013, Jia *et al*. (71) optimised a literature method (37), using 3,6-bis(3,5-dimethylpyrazole)-1,2,4,5-tetrazine as

starting material. DHT was obtained by hydrazine substitution reaction and the synthesis conditions of 3-DHT were optimised. The purity of DHT was 98.5% and the yield was 92%. In the same year, He (72) used lanthanum nitrate, hydrazine hydrate and acetylacetone as the starting materials. BT was prepared by hydrosilylation condensation and oxidative dehydrogenation, using BT as the intermediate and DHT was synthesised by nucleophilic substitution reaction.

4.2 Structure and Theoretical Analysis of DHT

Zhang (73) *et al*. studied the stability and intramolecular interactions of the energetic salts of DHT using dispersion corrected DFT. The geometric optimisation of DHT was calculated by the Gaussian 09 program at DFT-B3LYP/6-31G(d,p) level. The vibration analysis has no virtual frequency and is a relatively stable structure. The configuration of DHT after geometry optimisation and atom numbering is shown in **Figure 5(a)**. As can be seen from **Figure 5(a)**, the DHT molecule is symmetrical in the centre and all atoms in the tetrazine ring in DHT are basically in the same plane. The tetrazine ring forms a
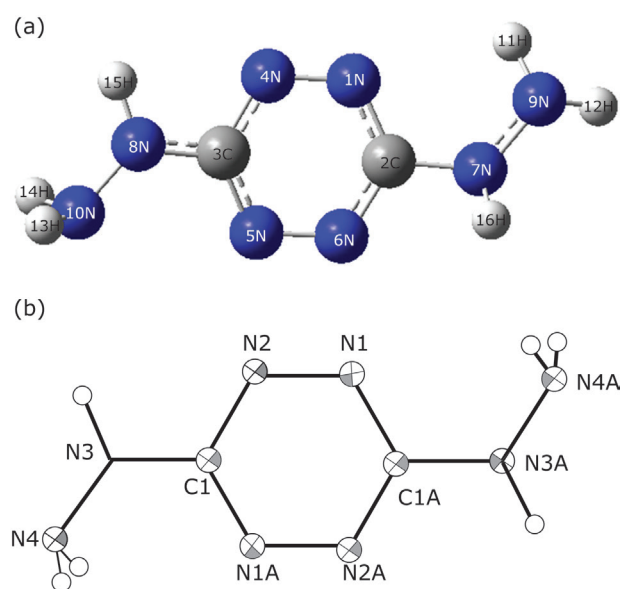

Fig. 5. Optimised structure of 3,6-dihydrazino-1,2,4,5-tetrazine (DHT): (a) the structure optimised after B3LYP/6-31G(d,p) level of DHT; (b) the structure optimised after B3LYP/6-311G* level of DHT. Reprinted from (74). Copyright (2011), with permission from *Chemical Journal of Chinese Universities*

conjugated system, both C2–N7 and C3–N8 have p–π hyperconjugation. As shown in **Figure 5(b)**, the geometric optimisation of DHT was calculated by the Gaussian 03 program at DFT-B3LYP/6-31G(d,p) level by Feng (74) who proposed that the DHT molecule presents a symmetrical structure with the centre of symmetry being the centre of tetrazine. The introduction of hydrazide influenced the conjugated system of the tetrazine ring and the groups C1–N3 and C1A–N3A on both sides of the molecule exist in p–π hyperconjugation. It can be seen in **Figures 5(a)** and **5(b)** that the structures of the DHTs in the two figures are similar, therefore, it may be considered that the DHT molecule is a symmetrical structure at the centre and there exists a conjugated system.

4.3 The Performance of DHT

4.3.1 Physical Properties of DHT

The molecular formula of DHT is $C_2N_8H_6$, the relative molecular mass M_r = 142 and the nitrogen content is 78.8%. Kerth *et al*. (75) measured the density ρ = 1.69 g cm^{-3} by experiment and velocity and detonation pressure were 10.65 km s^{-1} and 39.02 GPa respectively at a density of 1.69 g cm^{-3}, the melting point was 158°C ~ 160°C. Feng *et al*. (74) theoretically calculated that the density is 1.64 g cm^{-3}, the K-J equation is used when the density is 1.64 g cm^{-3}. It is estimated that the detonation velocity and detonation pressure of DHT are 9.27 km s^{-1} and 36.02 GPa respectively. It can be seen that the theoretical estimate is close to the experimental value.

4.3.2 Sensitivity of DHT

The drop weight sensitivity is H_{50} = 70 cm and the friction sensitivity is >36 N (74). According to GJB772A-97 method 601.2 and method 602.1, Zhang *et al*. (76) measured an impact sensitivity of H_{50} = 70 cm and friction sensitivity P = 8%. Pan *et al*. (70) measured that the percent of explosion was 0% and the impact sensitivity of DHT was H_{50}>50 cm, under the conditions: hammer weight of 2 kg, sample weight of 0.2 g, 10 kg drop hammer of 50 cm height (reference standard QJ3039-98). At a test angle of 90° and a test pressure of 4.0 MPa (reference standard QJ2913-97), the percent of explosion is 0% and the friction sensitivity is 8%. It can be seen that these three groups of tests have good consistency.

4.3.3 Energy and Detonating Performance of DHT

DHT theoretical detonation velocity D = 10.15 km s^{-1} and HOF = 536 kJ mol^{-1} (75). Vacuum constant volume detonation heat is 7710.0 kJ kg^{-1} (reference standard QJ1359-88) (70). Jia *et al*. (71) measured the detonation velocity of DHT D = 9234 m s^{-1} and the enthalpy ΔH_f = 535 kJ mol^{-1}. It can be seen that the theoretical performance is good.

4.3.4 Thermal Stability of DHT

The thermal behaviour of DHT was studied with DSC and thermogravimetric analysis (TGA)-differential thermal gravimetric (DTG) methods and can be divided into two exothermic decomposition stages. DHT has good thermal stability and does not begin to decompose until 140°C. DSC analysis shows that there is an exothermic peak at 161°C and the exothermic value is 1660 J g^{-1}. TGA analysis shows that DHT decomposed at 140°C ~ 160°C and lost 64.9% of its mass. Its thermodynamic properties indicate that it can be added to propellants or explosives as an energy enhancing component (66, 77). Zhang *et al*. (76) and Jia *et al*. (71) studied and analysed the DSC (in **Figure 6(a)**) and TGA-DTG (in **Figure 6(b)**) spectra of DHT. The DHT has a sharp exothermic decomposition peak at 162.9°C, with a smaller span and larger heat release. When the temperature is lower than 146°C, the weight loss of DHT is lower. Rapid weight loss occurs during a temperature rise of 164.33°C ~ 179.42°C. The decomposition is basically completed at 204.36°C and there is also some residue.

4.4 The Use and Potential Value of DHT

Due to DHT being both a high-nitrogen and a high-hydrogen compound, it burns violently in the air, generating nitrogen and water and releasing enormous energy. These characteristics can be used in such fields as explosives, gas generators, solid propellants, pyrotechnic technology and more. Burns *et al*. conducted a large number of experimental studies using high-nitrogen compounds such as BHT, BTA and DHT instead of sodium azide as an airbag gas generator component for automotive airbags. In the literature (78), BHT non-metallic salt was used as fuel and the formulation was no longer used with high
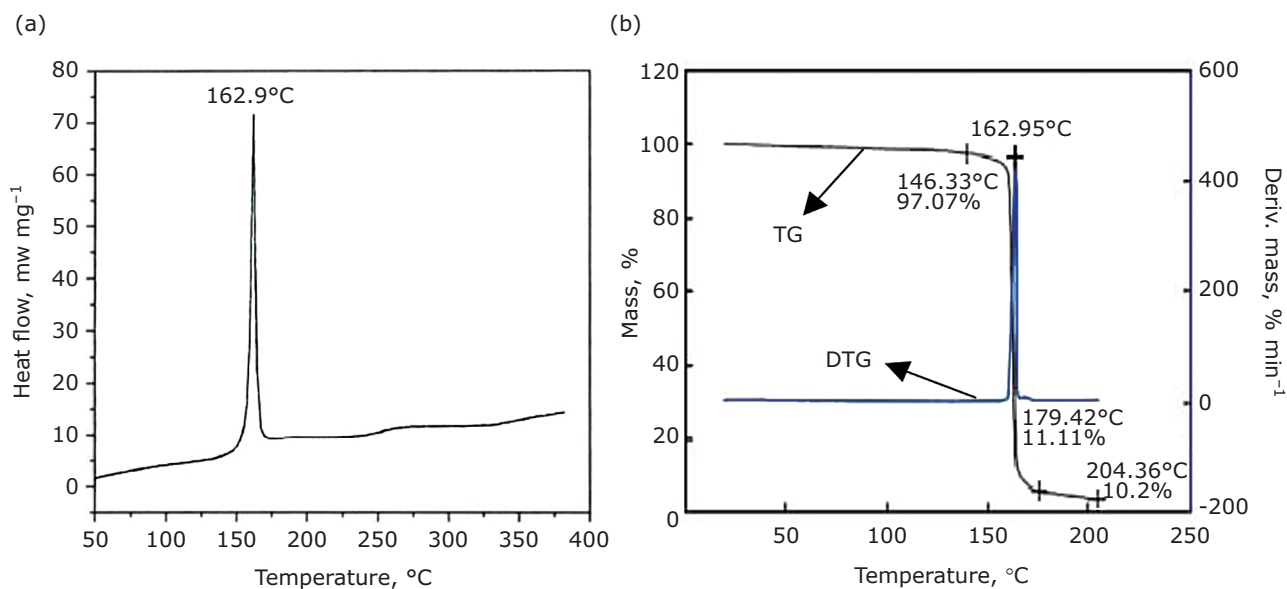
Fig. 6. DSC and TG-DTG curves of 3,6-dihydrazino-1,2,4,5-tetrazine (DHT): (a) DSC curves for DHT at a heating rate of 10°C min^{-1}; (b) TG-DTG curves for DHT at a heating rate of 10°C min^{-1}. Reprinted from (76). Copyright (2014), with permission from *Chinese Journal of Explosives & Propellants*

sensitivity ignition agent. The ignition performance was improved, the gas consumption was high and there were few solid residues. The gas conversion rate of BHT ammonium salt system reached 97%, the burning rate was 11.43 mm s^{-1} (under 7 MPa) and the combustion was stable without flameout. In a US study of solid propellant gas generator (SPGG) technology used in aero-engine fire extinguishing equipment, it was indicated that for the propellant containing BHT, the combustion speed was greater than 63.5 mm s^{-1} (under 7 MPa) (79). Chavez *et al*. (80) carried out research on the technology of high-nitrogen substances in low (no) smoke pyrotechnics. DHT was used as a fuel, together with the oxidant ammonium perchlorate, a small amount of metal salt, or a high-nitrogen compound metal salt colourant, resulting in a variety of pure colours and high ornamental value for low smoke fireworks. Improvement of the DHT production process is expected to widen its potential application in pyrotechnics and other products.
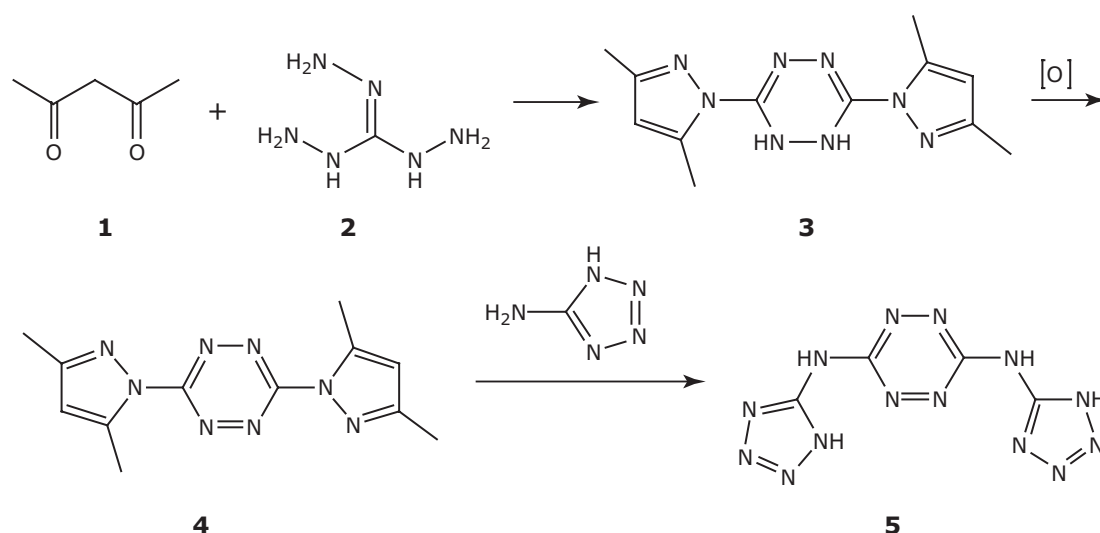
5. 3,6-Bis(1H-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine (BTATz)

The chemical name of BTATz is 3,6-bis(1H-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine. The molecular structure includes two high-nitrogen heterocyclic systems: tetrazine and tetrazole.

Nitrogen content is as high as 80%, so it is one of the compounds with the highest nitrogen content among high-nitrogen energy compounds.

5.1 Synthesis of BTATz

The general synthesis method of BTATz is by the reaction of BT, BDT or 3,6-dichloro-1,2,4,5-tetrazine with 5–aminotetrazole (5–AT). BTATz was first synthesised in acetonitrile from the sodium salt of 3,6-dichloro-1,2,4,5-tetrazine and 5–AT by Hiskey *et al*., LANL, USA (81, 82). Wang *et al*. (83) conducted a detailed study of its synthesis by means of purification and quantum chemistry. Yue *et al*. (84) used hydrazine hydrate and guanidine nitrate as starting materials to synthesise triaminoguanidine nitrate (TAGN). After recyclisation and oxidative dehydrogenation, BDT was obtained. Further nucleophilic substitution with 5–AT resulted in the target compound BTATz being obtained. Wang *et al*. (83) improved the oxidation step of the BTATz synthesis process. BTATz was synthesised from triaminosulfonium nitrate and pentadione as starting materials by condensation, oxidation and substitution. By using sodium nitrite/acetic acid instead of nitrogen dioxide/*N*-methylpyrrolidone, the oxidation step is improved, the cost is reduced and the synthetic process is simplified. The synthetic path is shown in **Scheme III**.

Scheme III. Synthetic process of 3,6-bis(1H-1,2,3,4-tetrazol-5-amino)-1,2,4,5-tetrazine (BTATz)

5.2 Structure and Theoretical Analysis of BTATz

Xiong (85) used the Gaussian 03 program to optimise the geometrical structure of BTATz at the B3LYP/6-311G(d,p) level (shown in **Figure 7(a)**). Except for the strong delocalisation of the tetrazine ring and the tetrazole ring, the solitary pair electrons of the N atom connecting the two rings have a strong electronic effect on the antibonded π orbitals of the C–N bonds between the two rings. The geometric optimisation of BTATz was calculated by Gaussian 09 program at DFT-B3LYP/6-31G(d,p) level. The vibration analysis has no virtual frequency and it is a relatively stable structure. The configuration of BTATz after geometry optimisation and atom numbering is shown in **Figure 7(b)**. As can be seen from **Figure 7(b)**, all the atoms in the molecule are basically in one plane: one six-membered ring and two five-membered rings. Each forms a conjugated system. Due to the formation of the conjugated system, the N–N and C–N bonds in the ring are longer (1.289 Å ~ 1.378 Å) than standard double bonds (1.22 Å), shorter than a standard single bond (1.46 Å) and tend towards the average, making the whole molecule good in aromaticity and stability. The geometry of BTATz in **Figure 7(b)** is similar to that obtained by Wang (83). Wang proposed that the N atom with H in the five-membered ring provides a pair of electrons and the other four atoms each provide one electron; the six atoms in the six-membered ring each provide one electron; and two five-membered rings and one six-membered ring respectively provide six electrons, thus satisfying the $4n + 2$

aromaticity rule so that the whole molecule forms a large π bond. It can be seen that the structures of BTATz are similar in **Figure 7(a)** and **Figure 7(b)**; therefore, BTATz may be considered to exist in a conjugated system.

5.3 The Performance of BTATz

5.3.1 Physical Properties of BTATz

BTATz is a red-brown solid and its molecular formula is $C_4N_{14}H_4$. It has a relative molecular weight of $M_r = 220$, a nitrogen content of 79.0%, a density $\rho = 1.76$ g cm^{-3} and a melting point of 264°C ~ 285°C. BTATz is insoluble in water, acetone, acetonitrile, DMF and other solvents. It is soluble in DMSO, hot benzene and other solvents and has good compatibility with nitrocellulose, nitroglycerine and commonly used catalysts (84).

5.3.2 Sensitivity of BTATz

Friction sensitivity >36 N, impact sensitivity $H_{50} = 160$ cm ~ 200 cm. As a whole, BTATz sensitivity is low (84).

5.3.3 Energy and Detonating Performance of BTATz

HOF = 883 kJ mol^{-1} and detonation velocity $D = 7520$ km s^{-1} when the density is 1.75 g cm^{-3}. The burning speed was tested between 5.6 mm s^{-1} (0.1 MPa) and 75 mm s^{-1} (19 MPa). The corresponding pressure index was calculated as 0.49 (84).
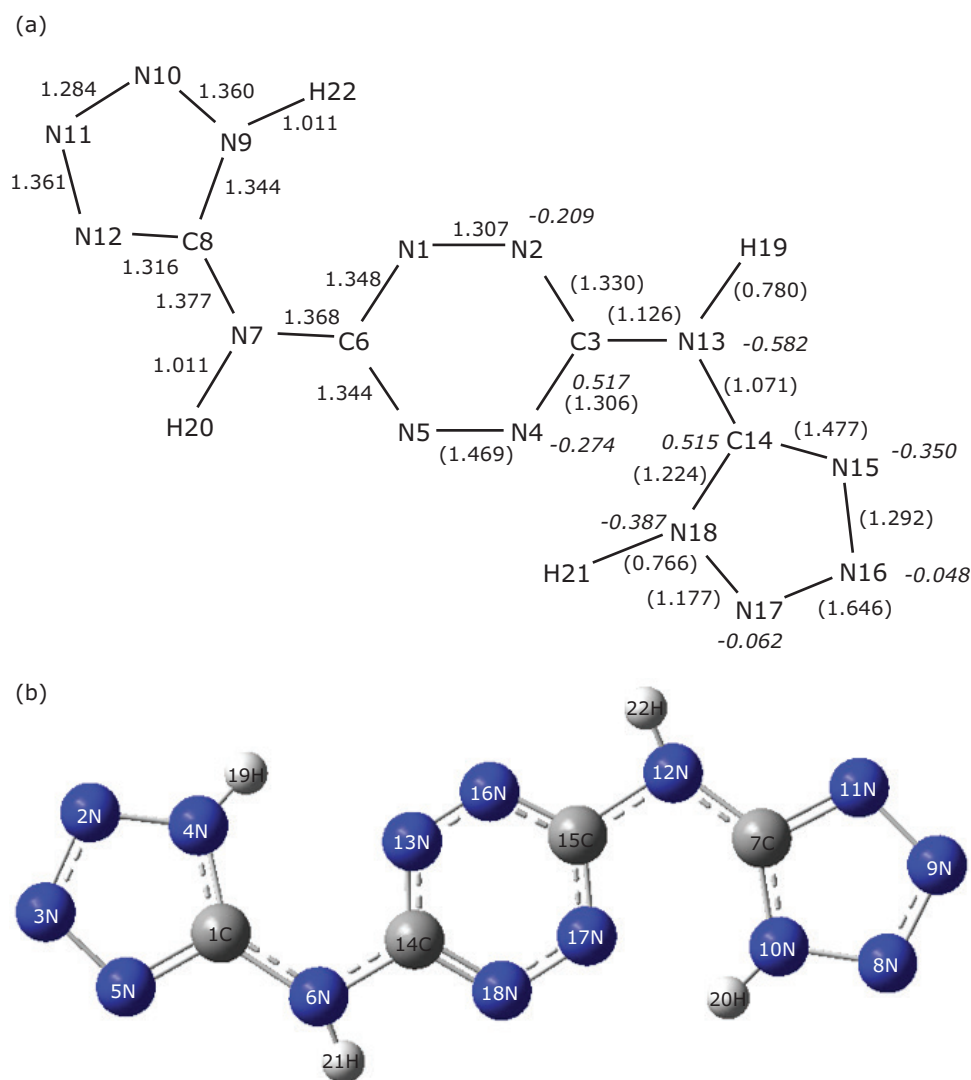
(a)

(b)

Fig. 7. Optimised structure of 3,6-bis(1H-1,2,3,4-tetrazol-5-amino)-1,2,4,5-tetrazine (BTATz): (a) the structure optimised after B3LYP/6-311G(d,p) level of BTATz (BTATz geometry and related parameters (bond length (Å), data in parentheses indicate the Wiberg bond order and italic data represents the NBO charge)). Reprinted from (85). Copyright (2008), with permission from *Journal of Explosives & Propellants*; (b) the structure optimised after B3LYP/6-31G(d,p) level of BTATz

5.3.4 Thermal Stability of BTATz

Saikia *et al*. (86) reported characterisation and thermolysis studies of BTATz. TGA and DSC results suggested that BTATz decomposes in the range 265°C ~ 350°C and the calculated energy of activation of BTATz is 212.69 kJ mol⁻¹. The initial decomposition temperature of BTATz is about 260°C and the decomposition peak temperature on the DSC curve is about 320°C. The standard formation enthalpy of BTATz is 883 kJ mol⁻¹ and the combustion heat is 12,204.13 kJ kg⁻¹ (84). The results of *ab initio* molecular dynamics simulation showed that the initial pyrolysis of BTATz occurs on the tetrazole ring. One route is the four-azole ring to eliminate ammonia (NH_3)

directly and the other is the breaking of the NH–N bond on the tetrazole ring. The latter is the main decomposition approach. When the NH–N bonding on the tetrazole ring is broken, the secondary reaction involves three conditions that a further bond breaking on the tetrazole ring and the removal of one N_2, a tetrazole ring undergoes a ring-opening reaction and another tetrazole ring undergoes a ring-opening reaction (85). Zhang (87) measured the TGA-DTG curve of BTATz under normal pressure as shown in **Figure 8**. There are two weight loss steps plus DTG peak temperatures at 322.41°C and 493.36°C. The weight loss in the first stage is caused by the gas released from the ring opening of the tetrazine and tetrazole rings. This stage reaches 342.93°C and the remaining
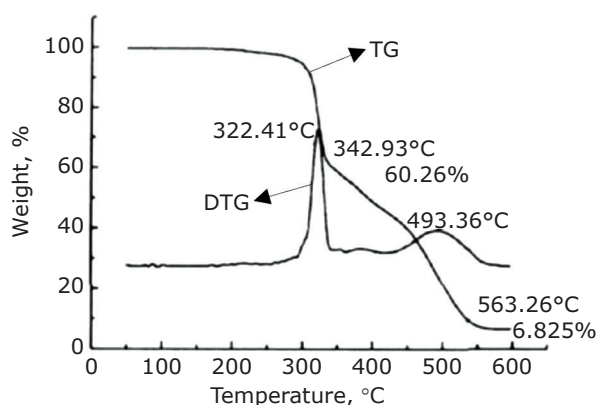
Fig. 8. TGA-DTG curves of 3,6-bis(1H-1,2,3,4-tetrazol-5-amino)-1,2,4,5-tetrazine (BTATz). Reprinted from (87). Copyright (2007), with permission from *Journal of Propulsion Technology*

mass percentage is 60.26%. The weight loss in the second stage is further degraded by the first stage of condensed phase products such as ammonium azide (NH_4N_3) and melamine. The two weight loss processes are closely linked. The decomposition heat release mainly comes from the first weight loss stage, which is reflected in the DSC diagram with only one exothermic decomposition peak.

From the performance data of BTATz, it can be seen that BTATz has low sensitivity, high detonation velocity, good thermal and chemical stability and has the characteristics of high burning speed and low pressure index (77).

5.4 The Use and Potential Value of BTATz

Because of its high nitrogen content, high energy and low sensitivity, BTATz has been widely studied in the areas of solid propellants, gas generators and explosives. Hiskey *et al*. (81) studied the specific impulse of aluminium powder when it was completely replaced by BTATz in the formula AP/THPB/Al(70/14/16) and found that the specific impulse decreased from 2587 N s kg^{-1} to 2274 N s kg^{-1}. Although there is a loss, the characteristic signal of the propellant is obviously reduced. Li (88) *et al*. prepared and characterised double base (DB) propellants containing lead complex based BTATz (LCBTATz) and composite modified double base (CMDB) propellant. The results showed that LCBTATz is a highly efficient dual-base combustion catalyst, which can significantly increase the combustion rate and significantly reduce the pressure index over a wide range of pressures.

In China, the National University of Defence Technology and the Xi'an Modern Chemistry Research Institute (87, 89–93) have taken the lead in studying the synthesis and properties of the high-nitrogen compound BTATz. It was found that the oxygen balance of BTATz was low and the characteristic energy parameters of the propellant decrease with increasing content of the propellant. In order to retain the propellant energy level, BTATz should be used in combination with high-energy additive components. BTATz has outstanding potential to improve burning rate, especially under a catalytic system where the effect of increasing the burning rate is more obvious. Since BTATz does not have a melting process similar to RDX, this type of propellant produces a divergent flame, the combustion surface changes from a melt to a loose coral-like shape and the flame intensity increases. Some workers (94–96) have combined BTATz with metals to synthesise high-energy metal salts to use as propellants. High-energy metal salts can play a catalytic role in combustion and provide an effective way to regulate combustion performance.

6. 3,3'-Azobis(6-amino-1,2,4,5-tetrazine) (DAAT)

3,3'-Azobis(6-amino-1,2,4,5-tetrazine) (DAAT) is a typical representative of an azotetrazine high-nitrogen energetic compound with a nitrogen content of up to 76.36%, good thermal stability and low sensitivity. Chavez *et al*., LANL, USA (63) reported the first correlation study of DAAT.

6.1 Synthesis of DAAT

In 2000, DAAT was synthesised by Chavez *et al*. (63) and its physicochemical properties and sensitivities were studied. The results concluded that the energy of DAAT obviously increased after the azo bridge was introduced between the two tetrazine rings. DAAT is a typical high-nitrogen energetic compound with excellent properties. In 2002, Hiskey *et al*. (97) further optimised the synthesis of DAAT, using peroxytrifluoroacetic acid as an oxidant to synthesise DAAT and its coordination oxide DAATO$_n$. Later, Germany's Kerth *et al*. (75) and India's Talawar *et al*. (66) further studied the synthesis and properties of DAAT and characterised its structure. In China, a synthetic route to DAAT was optimised and scaled up by Yue and Xu *et al*. (98, 99) of the National University of Defence Technology. In 2005, Xu *et al*. (100) synthesised DAAT in seven steps

using guanidine nitrate and hydrazine hydrate as starting materials. In 2006, Wang *et al*. (101) used triaminoguanidine nitrate and pentanedione as starting materials to synthesise DAAT in six steps, including condensation, oxidation, hydrazinolysis, bromination, ammonolysis and hydrolysis. The total yield was 19%. On the basis of the literature (63, 98–101), Xu *et al*. (102) further optimised the synthesis of DAAT using BT as the starting material. DAAT was synthesised in four steps, including nucleophilic substitution, oxidative dehydrogenation, ammonolysis and hydrolysis. The synthetic route is shown in **Scheme IV(a)**. According to **Scheme IV(a)**, HDPT is obtained by nucleophilic substitution of BT with hydrazine in isopropanol; ABDPT is obtained by NBS oxidative dehydrogenation in acetonitrile; DAAT·2DMSO is obtained by ammonolysis of ABDPT in DMSO and

DAAT is obtained by further hydrolysis in DMSO. There are many deficiencies in the synthesis of DAAT from the literature (63, 66, 75, 97–102), including: too many reaction steps; operation conditions that are difficult to control; low total yield; expensive reagents; and lack of industrial application prospects. In 2009, Wang *et al*. (103) devised a novel synthetic approach to DAAT. They used BDT as a starting material to synthesise DAAT by high pressure ammonolysis and potassium permanganate oxidation. Compared with the four-step reaction in the literature (102), this new approach is reduced to two steps. The reaction steps were shortened and the total yield increased significantly, reaching 58.1%. The structure of DAAT was characterised by quantum chemical methods. The synthetic route to DAAT is shown in **Scheme IV(b)**.

(a)

(b)

Scheme IV. Synthetic process of 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (DAAT)

6.2 Structure and Theoretical Analysis of DAAT

DAAT is a typical representative of ditetrazine compounds and the two tetrazine rings are connected by an azo bridge. It is a high-nitrogen energetic compound with excellent properties. The structure of DAAT is shown in **Figure 9**.

Fig. 9. The structural formula of 3,3'-amino-1,2,4,5-tetrazine) (DAAT)

In 2007, Xiong (104) studied the molecular configuration and electronic structure of DAAT at B3LYP/6-311G(d,p) level (in **Figure 10(a)**). It was found that DAAT contains a large delocalised π orbital. The bond length and bond order of each bond and the NBO charge on each atom are shown in **Figure 10(a)**. In 2009, Wang *et al*. (103) used the Gaussian 98 application program to calculate DAAT geometrically at the level of DFT-B3LYP/6-31G(d,p). The vibration analysis had no virtual frequency and it was a relatively stable structure. The configuration and atomic number of DAAT after geometric optimisation are shown in **Figure 10(b)**. It can be seen from **Figure 10(b)** that the DAAT structure is highly axisymmetric, with the tetrazine ring and the amino group substantially on the same plane and a large conjugated π bond is formed. After the formation of the conjugated system, the

Fig. 10. Optimised structure of 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (DAAT): (a) the structure optimised after B3LYP/6-311G(d,p) level of DAAT (DAAT geometry and related parameters (bond length (Å), data in parentheses indicate the Wiberg bond order and italic data represents the NBO charge)). Reprinted from (104). Copyright (2007), with permission from Chinese Academy of Engineering Physics; (b) the structure optimised after B3LYP/6-31G(d,p) level of DAAT. Reprinted from (103). Copyright (2009), with permission from *Chinese Journal of Organic Chemistry*

N–N and C–N bonds on the ring (in the range of 1.311 Å to 1.358 Å) are longer than the standard double bond (1.22 Å) and shorter than the standard single bond (1.46 Å) and tend towards the average. Since the C(2)–N(10) bond is long, it is prone to breakage. As shown in **Figures 10(a)** and **10(b)**, the structures of the two compounds are similar. The results show that the tetrazine rings and amino groups on both sides of DAAT azo are basically in the same plane and form a large conjugated π bond. The structure is relatively stable.

6.3 The Performance of DAAT

6.3.1 Physical Properties of DAAT

The molecular formula of DAAT is $C_4N_{12}H_4$, the relative molecular mass $M_r = 220$ and the nitrogen content is 76.36%. DAAT is a crimson powder, soluble in DMSO, NMP, DMF and sulfoxide. It is insoluble in water. Chavez and Kerth *et al*. (63, 75) measured the density $\rho = 1.84$ g cm^{-3} by experiment. The K-J equation is used when the density is 1.84 g cm^{-3}. It is estimated that the detonation velocity and detonation pressure of DAAT are 8591.82 m s^{-1} and 28.48 GPa respectively.

6.3.2 Sensitivity of DAAT

The impact sensitivity H_{50} of DAAT is 70 cm (HMX 25 cm) and it is insensitive to electrostatic cremation (>0.36 J) and friction (BAM friction test >36 kg).

The vacuum stability test results are 0.29 ml g^{-1} and the explosion point is 288°C (63, 75).

6.3.3 Energy and Detonating Performance of DAAT

The HOF of DAAT is 862 kJ mol^{-1} (63, 75). Xu (102) calculated the detonation performance of DAAT using VLW equation of state (EOS), the results showed that the theoretical detonation velocity $D = 9.025$ km s^{-1}, HOF = 3911.6 kJ g^{-1}, detonation pressure was 27.2 GPa, detonation temperature was 3523 K and detonation capacity was 0.456 ml g^{-1}.

6.3.4 Thermal Stability of DAAT

The thermal decomposition properties of DAAT were studied by DSC, pressure differential scanning calorimetry (PDSC) and TGA-DTG techniques by Xu (102). The DSC, PDSC and TGA-DTG curves under different conditions were obtained. DSC experiments were carried out at constant pressure and three different heating rates: 2°C min^{-1}, 5°C min^{-1} and 10°C min^{-1}. The results are shown in **Figure 11(a)**. The DSC curve of DAAT at heating rate 5°C min^{-1} is shown in **Figure 11(b)**. At this heating rate, DAAT began to decompose at around 283°C and there was a strong liberation heat peak at 320.23°C. The decomposition enthalpy of the exothermic peak was 1974.33 J g^{-1}, which was similar to the research result of Kerth *et al*. (75).
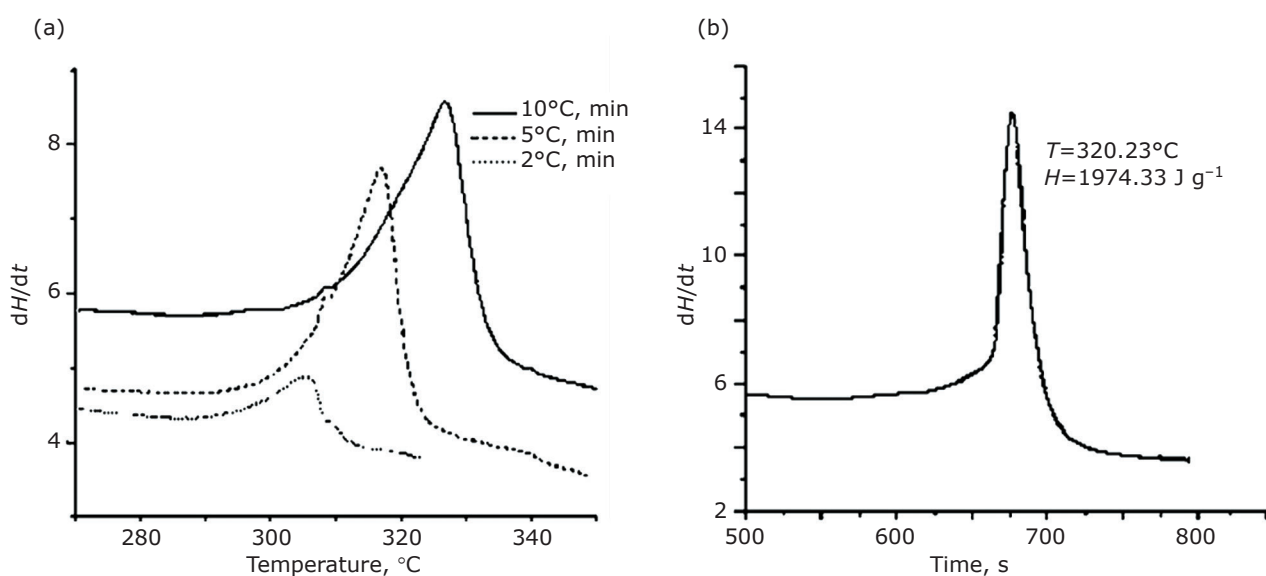

Fig. 11. DSC curves of 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (DAAT): (a) DSC curves of DAAT at different heating rates; (b) DSC curves for 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (DAAT) at a heating rate of 5°C min^{-1}. Reprinted from (102). Copyright (2006), with permission from *Chemistry Bulletin*
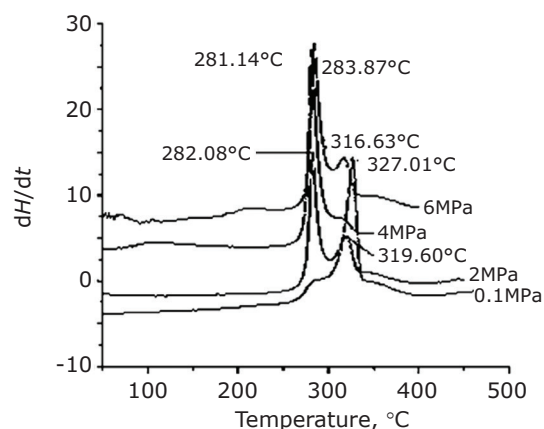
Fig. 12. DSC of 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (DAAT) under various pressures (the temperature and percentage indicated in the figure are the temperature and residual percentage corresponding to the weight loss step). Reprinted from (102). Copyright (2006), with permission from *Chemistry Bulletin*
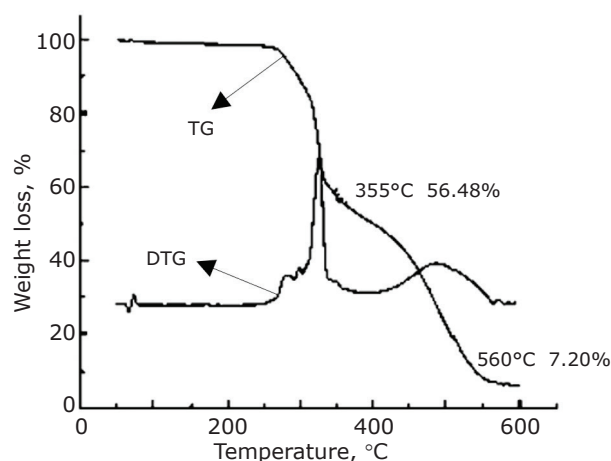

Fig. 13. TG-DTG curves of 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (DAAT) (the temperature and percentage indicated in the figure are the temperature and residual percentage corresponding to the weight loss step). Reprinted from (102). Copyright (2006), with permission from *Chemistry Bulletin*

Figure 12 is the PDSC curve of DAAT under 0.1 MPa, 2 MPa, 4 MPa and 6 MPa ambient pressure. Under different pressures, DAAT showed two closely related exothermic peaks at around 300°C, namely pyrolysis and low temperature decomposition of DAAT. At normal pressure, it mainly showed pyrolysis and under high pressure, it mainly showed low temperature decomposition. The thermal decomposition of DAAT is sensitive to pressure and the rate of decomposition is proportional to the ambient pressure. At normal pressure, the TGA-DTG curves of DAAT are shown in **Figure 13**. There are two weight loss steps in DAAT and DTG peak temperatures are found at 326°C and 490°C. The initial peak temperature of the first stage weight loss is about 280°C, which is consistent with the initial decomposition peak temperature of DSC in **Figure 11(b)**. There is nearly 50% weight loss at 355°C, then the second stage of weight loss occurs at 370°C ~ 560°C and the DAAT basically decomposes completely.

6.4 The Use and Potential Value of DAAT

DAAT has the advantage of high nitrogen content, good detonation performance, good thermal stability and high energy. It is suitable for gas-producing fuels with gas-generating agents. Its thermal decomposition rate is sensitive to pressure and proportional to ambient pressure. It is expected to have wide application prospects in the field of energetic materials including high

energy insensitive explosives (102). The molecular structure of DAAT contains a large number of N–N and C–N bonds and the chemical potential is mainly derived from its positive enthalpy. The high nitrogen content and low carbon and hydrogen contents in the molecular structure mean it produces a large amount of gas and lower smoke or smokeless combustion products, but also makes it easier to achieve oxygen balance (63, 66, 105, 106). These types of high-nitrogen compounds not only have high energy content, but also have low electrostatic sensitivity, impact sensitivity and friction sensitivity (63, 107). Therefore, they can be widely used in low characteristic signal propellants, gas generators, flameless low-temperature fire extinguishing agents and smokeless pyrotechnic technology (108, 109).

7. Conclusions

Azine energetic compounds have a relatively stable structure, low sensitivity, high enthalpy of formation, generate high heat during combustion, emit huge energy by explosion and produce large amounts of N_2 by combustion, which is more friendly to the environment compared to alternatives. Therefore, as a HEDC, this class of compounds have good application prospects in the fields of national defence and spaceflight.

Due to the strong delocalisation and strong hydrogen bonding of the LLM-105 molecule, the stability of the entire molecule is enhanced,

the formation of crystals with higher density is facilitated and the crystal structure is slippery to make it more sensitive. It has good compatibility with other explosive components and has great potential as an explosive with good heat stability. It can be potentially applied to booster explosives, detonator charges, main charges and other explosives to make eutectic explosives to improve the performance of other explosives. However, at present, the cost of its synthesis is high and it needs further research.

Due to the formation of a large conjugated system in the TAAT molecule, the stability of the whole molecule is enhanced, with high stability and decomposition temperature, low friction sensitivity, nitrogen content of 79.55% and extremely high heat of formation of 2171 kJ mol^{-1}. Besides being used as an energetic material, TAAT can be pyrolysed to prepare nitrogen-rich C/N nanotubes and nanospheres, which are expected to be used in biocompatible materials, battery electrodes, corrosion protection, sensors, propellants and fuels.

Because DHT is both a high-nitrogen compound and a high-hydrogen compound, it burns violently in the air, generating nitrogen and water and releasing enormous energy. These characteristics can be used in such fields as explosives, gas generators, solid propellants, pyrotechnic technology and more. DHT has high enthalpy of formation and thermal stability and its thermodynamic properties indicate that it can be used as an energy-enhancing component added to propellants or explosives to improve their performance.

BTATz has low sensitivity, high detonation velocity, excellent thermal stability and chemical stability and has the characteristics of high burning speed and low pressure index. It can be applied to solid propellants, gas generating agents and explosives. It combines with metals to synthesise energetic metal salts, which can be applied in the field of propellants. High-energy metal salts can play a catalytic role in combustion and provide an effective way to regulate combustion performance.

DAAT has the advantages of high nitrogen content, good thermal stability, high energy, low sensitivity, positive enthalpy of formation and easy achievement of oxygen balance. Its thermal decomposition rate is sensitive to pressure and is proportional to ambient pressure, so it can be widely used in low characteristic signal propellants, gas generators, flameless low-temperature fire extinguishing agents, smokeless pyrotechnics and energetic materials such as high-energy insensitive explosives.

Above all, the application of azine energetic compounds in propellants can effectively improve the burning rate and reduce the characteristic signal; the application of azine energetic compounds in mixed explosives can reduce the sensitivity and improve the detonation performance; and the application of azine energetic compounds in gas generators can reduce the combustion temperature and increase the gas content. Therefore, this class of compounds have broad application prospects in energetic materials.

Acknowledgment

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