



Synthesis and characterization of 3,6-bis(1H-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine (BTATz): Novel high-nitrogen content insensitive high energy material

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ABSTRACT

This paper reports the synthesis, characterization and thermolysis studies of 3,6-bis(1H-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine (BTATz) and 3-(1H-1,2,3,4-tetrazol-5-ylamino)-6-(3,5-dimethyl-pyrazol-1-yl)-s-tetrazine monohydrate (TADPTz). The synthesized BTATz and TADPTz have been characterized by spectroscopic techniques and the data obtained confirm their structure. TGA and DSC results suggested that BTATz decomposes in the range 265–350 °C and TADPTz in the range 245–275 °C respectively. The calculated energy of activation of BTATz and TADPTz is 212.69 and 257.29 kJ/mol respectively. The experimentally determined ΔH_f value matches with theoretically computed heat of explosion. The computed volume of gases indicates that they can find application in gas generating compositions.

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1. Introduction

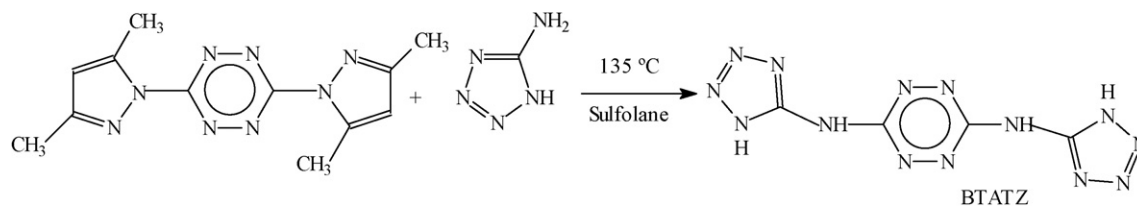
Development of energetic materials with improved performance and reduced sensitivity characteristics is a major goal in the area of high energy materials (HEMs). Desirable properties of a candidate for energetic material application as propellant/gas generant include high thermal stability, clean low molecular weight gases as the combustion products, low detonability, insensitivity to spark and mechanical stimuli. The high carbon content of traditional energetic materials leads to the formation of carbon dioxide, carbon monoxide, and unburned carbon particulates (soot) [1,2] during decomposition. The above problems are not encountered in the case of high-nitrogen content energetic materials, which contain a high percentage of nitrogen by weight. In addition to application in energetic material applications, high-nitrogen materials find utility as precursors in the fabrication of materials such as nitrogen-rich carbon nitrides, carbon nanoparticles, and nanostructured metal foams. Further, the main combustion product of this material is typically nitrogen gas (N_2), the most abundant gas in the earth's atmosphere.

High-nitrogen heterocycles have high percentage of nitrogen, low carbon and zero percent of halogens and possess desirable sta-

bility. Recently, considerable attention has been paid in the study of tetrazole and 1,2,4,5-tetrazine heterocycles [3–14]. Tetrazine moiety displayed unique and interesting characteristic properties. Tetrazines have demonstrated powerful synthetic utility through their ability to participate in inverse electron demand Diels–Alder reactions [3] providing access to a wide range of heterocycles based high energy materials. Furthermore, tetrazines also possess high positive heats of formation and crystal densities, properties important for energetic materials applications [8–11].

Recently, bis tetrazolylaminotetrazine (BTATz) has been synthesized and characterized by Los Alamos National Laboratory, USA [15,16]. The salient features of BTATz are low impact sensitivity, non-explosive, non-pyrotechnique, and an inflammable solid that decomposes rapidly without flame and produces nitrogen as the main combustion product. BTATz is a solid compound that decomposes primarily to nitrogen gas once initiated by heat and the decomposition is rapid, self-sustained, flameless, and occurs readily at most pressures. The nitrogen gas produced from BTATz at a high degree serves to displace oxygen, thus extinguishing a fire. Because of these qualities, BTATz has been identified as a composition highly suitable for fire suppression applications. BTATz can also be used as a gas generating ingredient in automobile airbags. BTATz burns very rapidly generating 0.71 of nitrogen gas per gram of solid. Because of its low carbon content, it burns cleanly, without smoke, leaving a minimal residue. It burns at a temperature hundreds of degrees lower than those for carbon-rich compounds of similar

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Scheme 1. Synthesis of BTATz.

molecular weight. BTATz is structurally similar to 5-aminotetrazole (5-AT) which appears to provide increased means for reducing propellant combustion temperature.

This paper reports the synthesis and characterization of BTATz with improved yield and simple work-up details. It also describes the purification of BTATz with the objective of generating additional data on this class of compounds in view of their increasing importance in the field of HEMs. Further, one of the byproduct (3-(1H-1,2,3,4-tetrazol-5-ylamino)-6-(3,5-dimethyl-pyrazol-1-yl)-s-tetrazine monohydrate, TADPTz) formed during the synthesis of BTATz was also synthesized and characterized completely during this study. The products were characterized by spectroscopic methods. Thermal studies were carried out to understand decomposition pattern. Hyphenated TG–FTIR studies were conducted to identify the gaseous products of decomposition of BTATz and TADPTz. The trends obtained were discussed on the lines of the reported literature [17,18]. The theoretical performance data of these compounds were also generated.

2. Experimental

2.1. Materials

All the reagents and chemicals used in the present study were of AR grade and used as such. The IR spectra were recorded on Perkin Elmer FTIR-1600 spectrophotometer in KBr matrix. ^1H NMR spectra were recorded on 300 MHz Varian instrument at 30 °C with TMS as an internal standard. Elemental analysis of the sample was carried out on elemental analyzer of CE Instruments make (Model CHNO-1110). DSC studies were undertaken on a Perkin Elmer DSC-7 instrument operating at different heating rate (5, 10, 15 and 20 °C/min) in nitrogen atmosphere with 1 mg of sample. The thermal decomposition studies were also carried out on Thermo Gravimetric/Simultaneous Differential Thermal Analyzer (TG/SDTA) of Mettler Toledo makes (8551). FTIR of decomposition

products was recorded on Bruker (EQUINOX-55) make instrument coupled with TG. The crystal morphology has been studied by Scanning Electron Microscope (SEM) instrument of Philips Icon make.

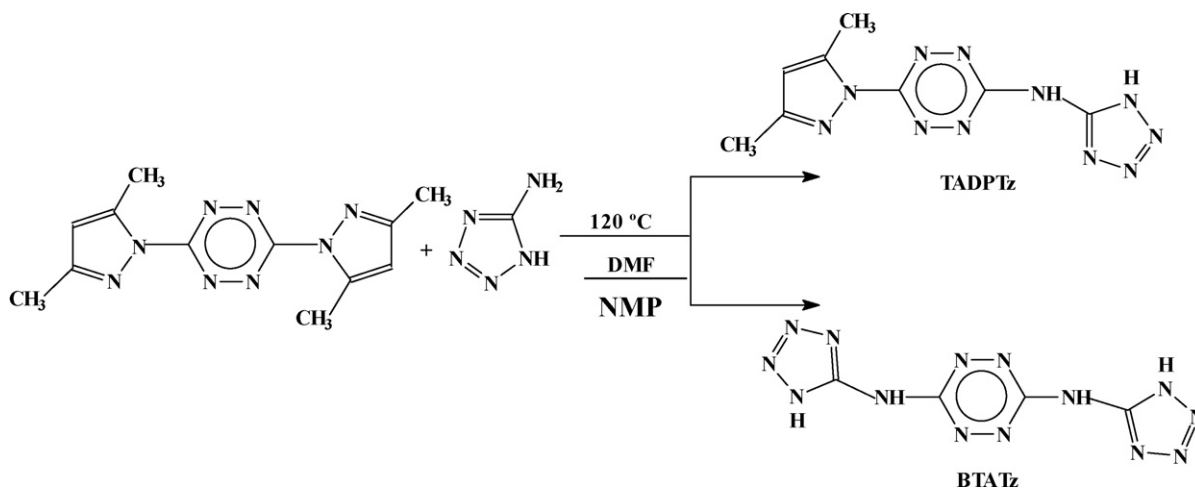
The sensitivity to impact stimuli was determined by fall hammer apparatus applying standard staircase method using a 2 kg drop weight and the results were reported in terms of height for 50% probability of explosion ($h_{50\%}$) of the sample. Figure of Insensitivity (F of I) was computed by using *N*-methyl-*N*,2,4,6-tetranitroaniline (tetryl, composition exploding, CE), as reference. The friction sensitivity of the compound was determined on Julius Peter's apparatus till there was no explosion/ignition in five consecutive test samples at that weight. The results obtained for impact and friction sensitivity were within the uncertainty limits of ± 5 cm and ± 0.2 kg respectively.

2.2. Synthesis

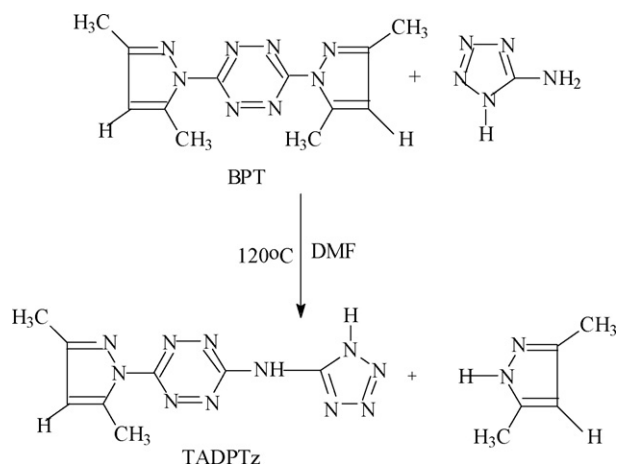
The synthesis of precursors such as triaminoguanidine hydrochloride (TAG-HCl), 3,6-bis(3,5-dimethyl-pyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine (DHBPT) were as per the reported procedures [8–11].

2.2.1. 3,6-Bis(3,5-dimethyl pyrazol-1-yl)-1,2,4,5-tetrazine (BPT)

About 5 g (0.0184 mol) of 3,6-bis(3,5-dimethyl-pyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine (DHBPT) was taken in a 100 ml beaker. About 25 ml acetic acid was added to this and stirred for half an hour at ambient temperature. To the reaction mixture, 1 g (0.0126 mol) of sodium nitrite was added in installments in a period of 1/2 h time. Stirring continued for another 2 h. The reaction mixture was quenched in a crushed ice and the product was filtered. The product was washed with water to remove the occluded acidity (checked by pH paper), dried in oven at 50 °C (4.73 g; yield, 92%). The product was recrystallized from acetone.



Scheme 2. Synthesis of mixture of BTATz and TADPTz.



Scheme 3. Synthesis of TADPTz alone.

2.2.2. 3,6-Bis(1H-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine (BTATz) (Scheme 1)

Anhydrous 5-aminotetrazole (39.4 g, 0.458 mol) and sulfolane solvent (380 ml) were taken in a 1000 ml three necked round bottom flask equipped with mechanical stirrer under stirring. 3,6-Bis(3,5-dimethyl pyrazol-1-yl)-1,2,4,5-tetrazine (50.0 g, 0.185 mol) was charged into the flask in small portions and the contents were stirred vigorously. The reaction mixture was slowly heated to 135 °C and maintained for 16 h. The reaction mixture was initially orange in colour and slowly changed into a dark solution. Dark brown

coloured solid product, BTATz begins to precipitate after 1 h. After 16 h, the slurry was slowly cooled to 35 °C and 300 ml of ethyl acetate was added to sulfolane to prevent it from freezing. The solid product was filtered, washed with ethyl acetate and oven dried. BTATz was then stirred with 150 ml of DMF for 4 h at 90 °C. Finally, the solid was refluxed two times with 150 ml of ethyl alcohol for 2 h each. The final product (32.15 g; yield, 70%) was dried and taken up for further purification by re-precipitation. Following two different re-precipitation methods were followed.

BTATz was dissolved in 120 ml of dimethylsulfoxide (DMSO) at 70 °C under stirring. To this solution three times equivalent (360 ml) of methanol was added slowly in a period of 1 h time under continuous stirring. During addition of methanol crystalline BTATz started precipitating from the solution. The crystalline material (25.72 g; yield, 56%) was filtered and dried at 50 °C for 4 h. The BTATz obtained by this method is called as re-precipitated BTATz.

Further, about 2 g of crude BTATz was dissolved in 10 ml of DMSO at 90 °C under stirring. After complete dissolution of BTATz, the temperature of the DMSO solution was brought to 60 °C and methanol was added from a burette till there was a precipitate formation on the DMSO solution. Methanol addition was stopped. The DMSO–methanol solution was heated for the dissolution of the solid. The hot clear solution was allowed to cool to get crystalline BTATz (1.5 g; yield, 75%). The obtained BTATz crystals will be termed as crystalline BTATz.

Apart from the modified reported methods, synthesis of BTATz has been attempted by changing the solvent and temperature of the reaction. In the synthesis of BTATz, attempts were made to use dimethylformamide and N-methyl pyrrolidinone as reaction medium, in place of sulfolane.

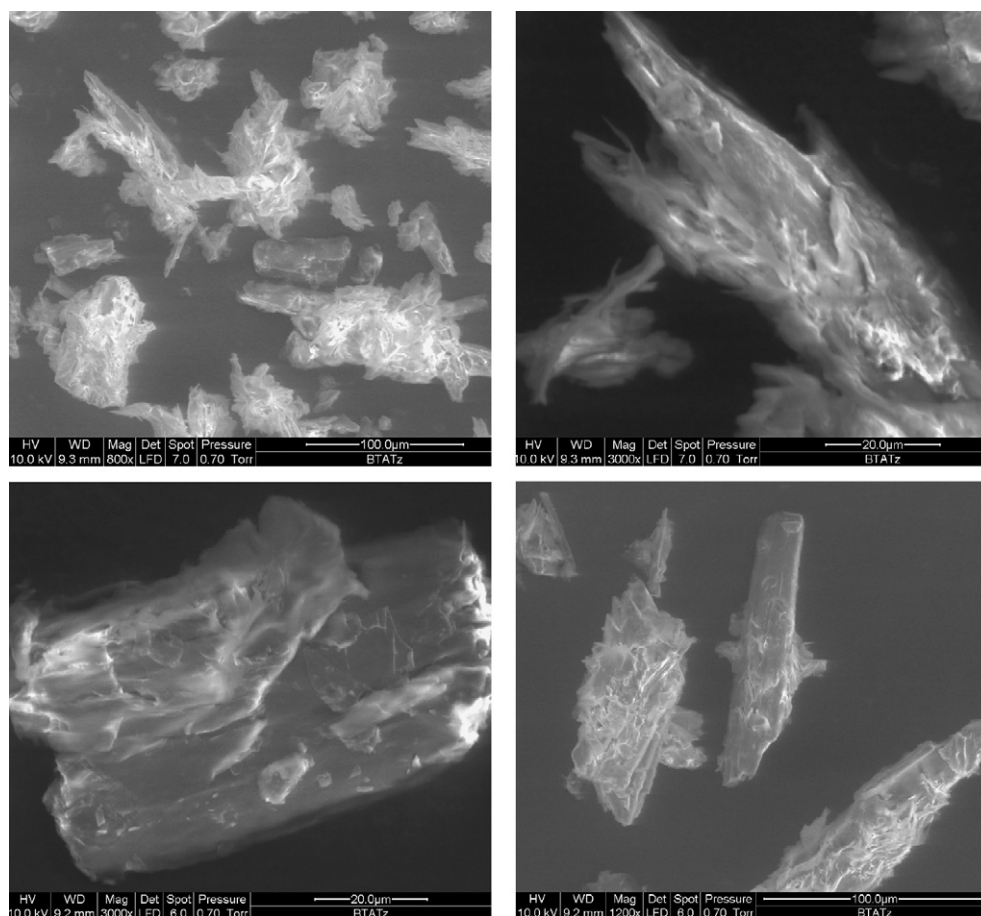


Fig. 1. SEM image of crude BTATz.

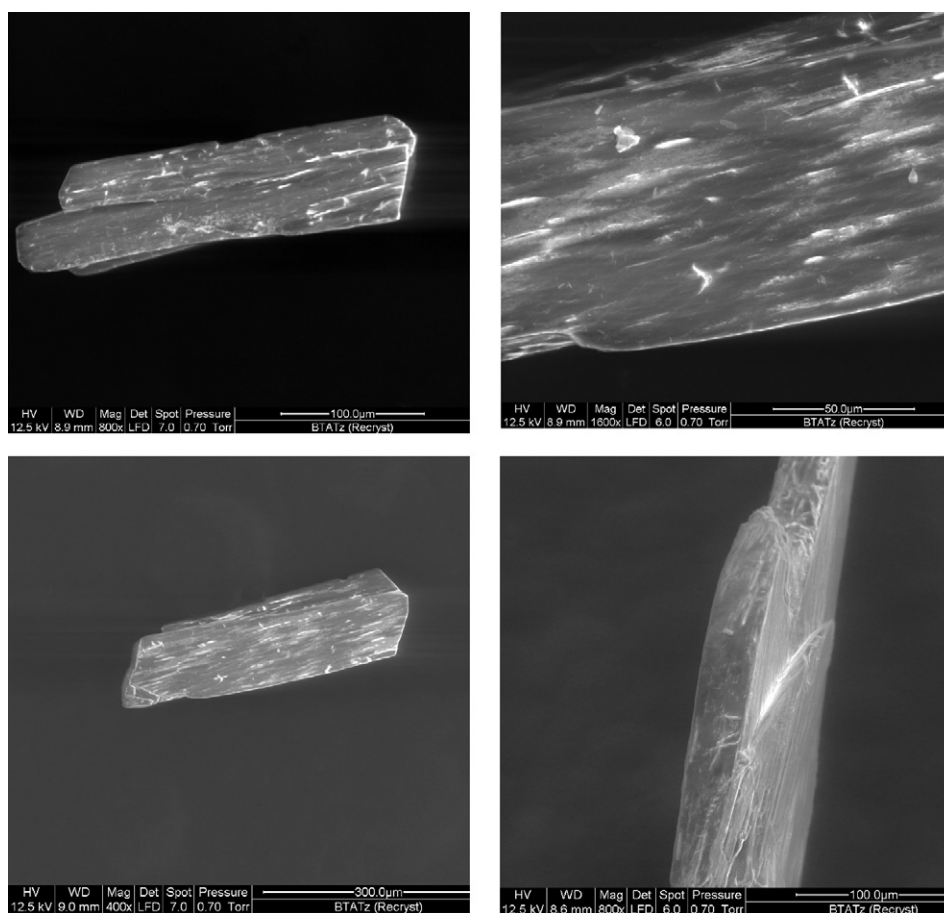


Fig. 2. SEM image of crystallized BTATz.

2.3. Dimethylformamide (DMF) as solvent (Scheme 2)

Anhydrous 5-aminotetrazole (3.9 g, 0.0453 mol) and 3,6-bis(3,5-dimethyl pyrazol-1-yl)-1,2,4,5-tetrazine (5.0 g, 0.0185 mol) were added to dry dimethylformamide solvent (100 ml) under stirring. The reaction mixture was slowly heated to 120 °C and maintained for 24 h. The reaction mixture was initially orange in colour and slowly changed into a dark solution. The reaction mixture was cooled and concentrated and poured into 200 ml of dichloromethane. The dark brown solid product was filtered, washed with dichloromethane and dried. The dried product was mixed and refluxed with 50 ml portions of ethyl alcohol repeatedly (thrice) and the washings were concentrated to obtain 3-(1H-1,2,3,4-tetrazol-5-ylamino)-6-(3,5-dimethyl-pyrazol-1-yl)-s-tetrazine monohydrate (TADPTz) as the partially substituted intermediate. TADPTz obtained from ethanol solution was recrystallized from methanol to get pure rod shape crystals. The orange colour BTATz solid was dissolved in DMSO and re-precipitated with methanol. The obtained solid was filtered, washed with methanol and dried at 50 °C for 4–6 h. The final product of BTATz (2.15 g; yield, 47%) and TADPTz (2.17 g; yield, 42.3%) were characterized and found identical in all respects with their corresponding standards.

2.4. N-methyl pyrrolidinone (NMP) as solvent (Scheme 2)

Anhydrous 5-aminotetrazole (3.9 g, 0.0453 mol) and 3,6-bis(3,5-dimethyl pyrazol-1-yl)-1,2,4,5-tetrazine (5.0 g, 0.0185 mol) were heated at 135 °C for 24 h in N-methyl pyrrolidinone solvent. The

reaction mixture was poured over 2 l of ice cooled water to obtain an orange precipitate. The precipitate filtered and mixed with ethanol and refluxed. The resultant solid was again purified as mentioned in the above procedures. The isolated BTATz was re-precipitated with DMSO and methanol. The quantity obtained was of 0.918 g (yield 20%).

Table 1
Characterization of BTATz and TADPTz.

| Parameters | BTATz | TADPTz |
|-------------------------|---------------------------------|---|
| M.P. (°C) | 270 (decomposition) | 250 (decomposition) |
| SEM | Rod type crystal | Rod type crystal |
| UV (nm) | 219, 264, 419 and 511 | 244, 263, 301, 392 and 517 |
| IR (cm ⁻¹) | 1386, 3318, 3210, 1684 and 1614 | 3136, 2910, 3310 and 3205 |
| ¹ H NMR (δ) | 12.37 | 2.24, 2.50, 6.27, 6.45, 14.5 |
| ¹³ C NMR (δ) | 157.93 and 150.75 | 13.03, 13.46, 109.76, 142.06, 150.38, 151.26, 157.85 and 158.69 |
| DSC (°C) | | |
| <i>T_i</i> | 265 | 250 |
| <i>T_m</i> | 320 | 275 |
| <i>T_f</i> | 350 | 285 |
| Δ <i>H</i> (J/g) | 1562 | 966 |
| TG (°C, % mass loss) | 93% wt loss in 271–338 °C | 6% wt loss in 83–125 °C 68% wt loss in 256–314 °C |

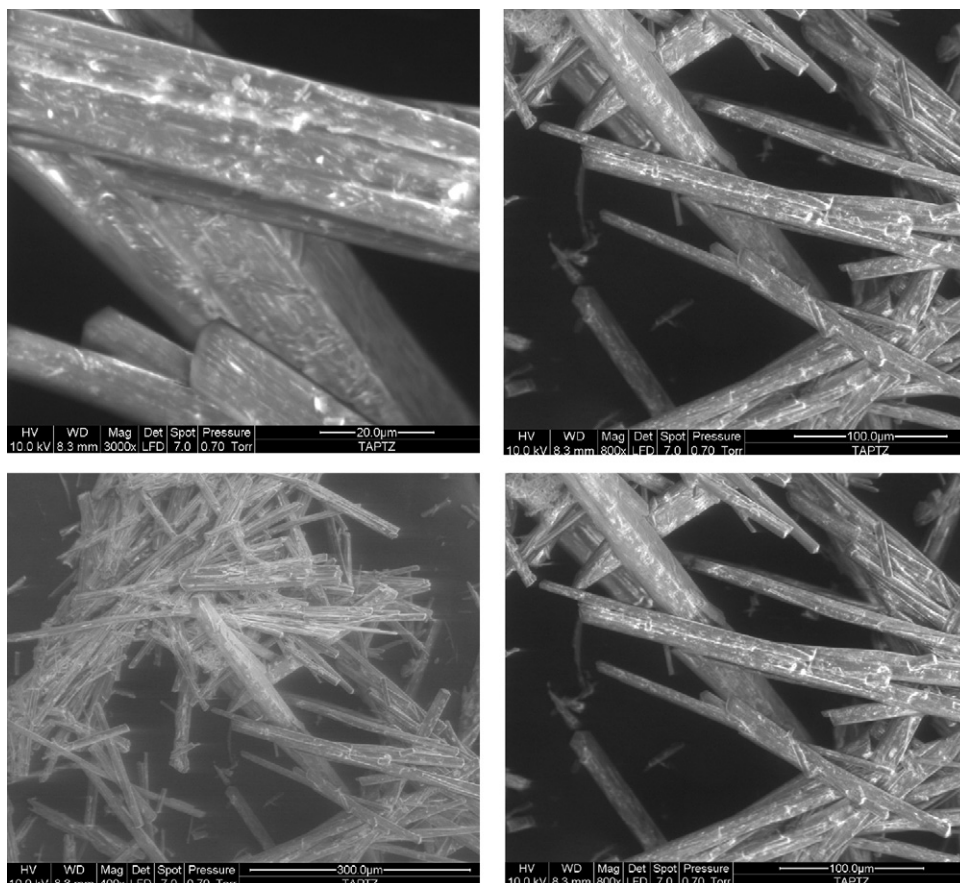


Fig. 3. SEM image of crystallized TADPTz.

2.4.1. 3-(1H-1,2,3,4-tetrazol-5-ylamino)-6-(3,5-dimethylpyrazol-1-yl)-s-tetrazine monohydrate (TADPTz) (Scheme 3)

Anhydrous 5-amino-1H-tetrazole (3.14 g, 0.0365 mol) and 3,6-bis(3,5-dimethyl pyrazol-1-yl)-1,2,4,5-tetrazine (5.0 g, 0.0185 mol) were taken in a RB flask. About 50 ml of dry dimethylformamide was added to the above flask. The reaction mixture was heated slowly to 120 °C and maintained for 4 h. The progress of the reaction was monitored by TLC. When the reactant BPT was consumed completely in the reaction (from the absence of BPT in TLC), the hot solution was poured over crushed ice, stirred, filtered to get rosy red precipitate. The precipitate was washed thoroughly with water and dried. The filtered cake was then refluxed with acetone and dissolved in hot methanol. The methanol solution was allowed cool to get crystals of the product (3.33 g; yield, 65%).

The synthesized products were characterized by spectroscopic and thermal methods (Table 1).

3. Results and discussions

3.1. Spectral studies

The UV spectrum of BTATz showed absorption bands in ultraviolet and visible region at 219 and 264 and 419 and 511 nm due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions and TADPTz showed at 244, 263 and 301 and 392 and 517 due to the same transitions.

The IR spectrum of BTATz showed an asymmetric ring stretching ($-\text{CN}$) vibration at 1386 cm^{-1} in addition to peaks attributable to secondary amino group ($-\text{NH}$) at 3318 and 3210 and 1684 and 1614 cm^{-1} corresponding to stretching and bending frequen-

cies respectively. TADPTz showed absorption in IR spectrum at 3136 and 2910 cm^{-1} stretching due to methyl, methine protons of dimethylpyrazole and the two amino groups ($-\text{NH}$) of tetrazole at 3310 and 3205 cm^{-1} attributable to asymmetric and symmetric stretching vibrations.

In proton NMR spectrum of BTATz, the protons of amino group resonated at δ 12.4 (bs, 4H, $-\text{NH}$). In the case of TADPTz, the dimethylpyrazolyl moiety, the two methyl ($-\text{CH}_3$) groups resonated at δ 2.24 and 2.49 and the methine proton ($-\text{CH}-$) resonated at δ 6.26 whereas the protons of amino groups resonated at δ 12.4 (s, 2H, N-H).

In ^{13}C NMR spectrum, the carbon atoms present in the tetrazine ring appeared at δ 157.9 and the carbon atoms of tetrazole ring resonated at δ 150.75. In the case TADPTz, the carbon atoms of the dimethylpyrazolyl, tetrazine and tetrazole rings appear at δ values of 13.03, 13.46, 109.76, 142.06, 150.38, 151.26, 157.85 and 158.69.

The elemental analysis (%) results for BTATz (C, 19.19; H, 1.72; and N, 79.16) were close to the theoretical values (C, 19.35; H, 1.61; and N, 79.03).

3.2. SEM studies

The SEM images of re-precipitated sample of BTATz showed agglomerated glittering crystals (Fig. 1) with uneven crystal morphology whereas the crystalline sample (Fig. 2) has small plate type crystal morphology with sharp edges. The images reveal that crystals of the latter one were more uniform and regular in shape. The surface morphology study on of TADPTz (Fig. 3) crystals showed rod type crystal morphology. The crystals were long, uniform rods with shining appearance to SEM.

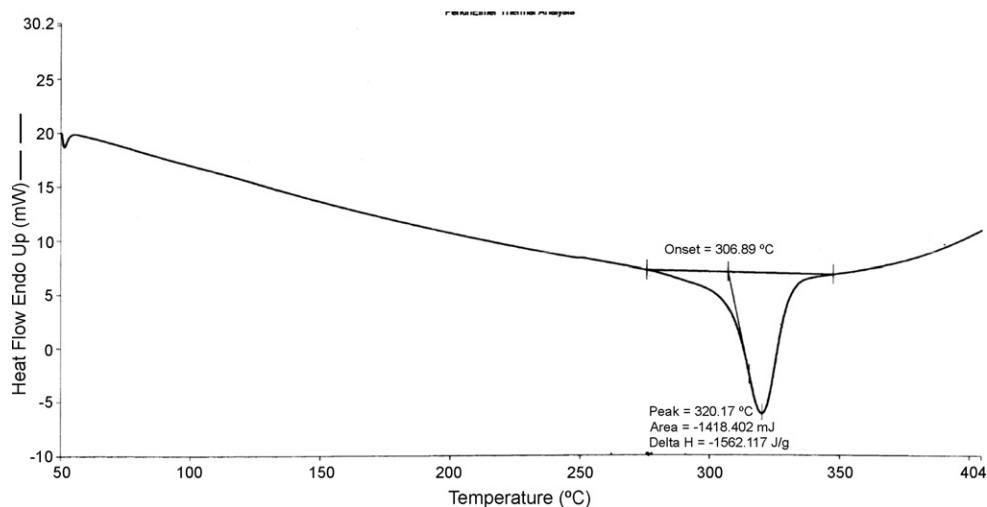


Fig. 4. DSC of BTATz.

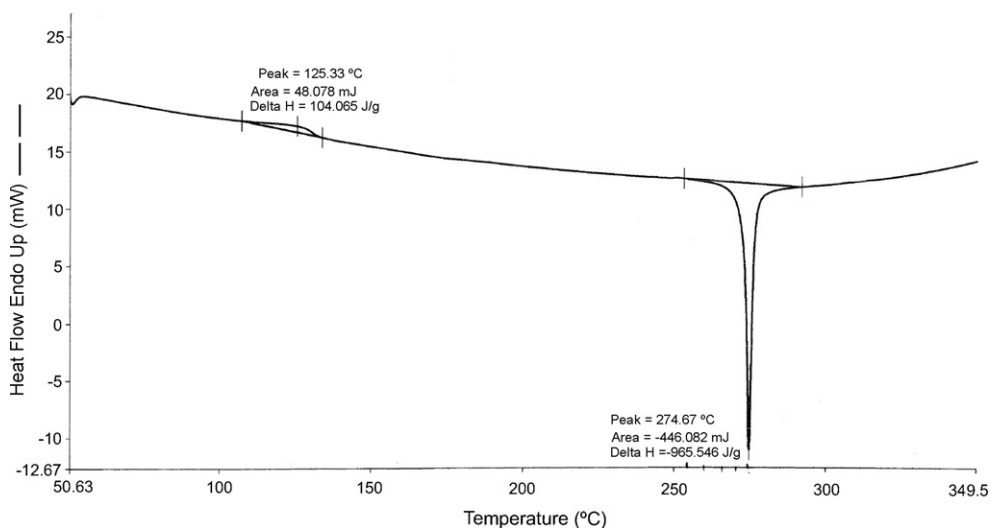


Fig. 5. DSC of TADPTz.

3.3. Thermal studies

DSC results revealed that BTATz (Fig. 4) showed an exothermic decomposition at 265–350 °C ($T_m = 320$ °C) with the heat evolution of 1562 J/g at the heating rate of 10 °C/min. The activation energy for exothermic decomposition of BTATz computed by using ASTM stan-

dard method [19] (based on Kissinger correlation) was found to be 212.69 kJ/mol (Table 2 and Fig. 8). TADPTz showed an endothermic peak (Fig. 5) at the temperature range of 110–125 °C corresponding to loss of water molecule and exothermic decomposition peak in the temperature range of 245–275 °C ($T_m = 274$ °C) with the heat evolution of 965 J/g at heating rate of 10 °C min⁻¹. The endothermic

Table 2
DSC data on BTATz at various heating rates (Kissinger method).

| β (°C) | T_m (K) | T_m^2 | $1/T_m$ | β/T_m^2 | $-\ln(\beta/T_m^2)$ | Activation Energy (kJ/mol) |
|--------------|-----------|---------|----------|-------------------------|---------------------|----------------------------|
| 5 | 579 | 335,241 | 0.001727 | 1.4915×10^{-5} | 11.1132 | 212.69 |
| 10 | 588 | 345,744 | 0.001701 | 2.8923×10^{-5} | 10.4509 | |
| 15 | 593 | 351,649 | 0.001686 | 4.2656×10^{-5} | 10.0623 | |
| 20 | 597 | 356,409 | 0.001675 | 5.6115×10^{-5} | 9.7881 | |

Table 3
DSC data on TADPTz at various heating rates (Kissinger method).

| β (°C) | T_m (K) | T_m^2 | $1/T_m$ | β/T_m^2 | $-\ln(\beta/T_m^2)$ | Activation energy (kJ/mol) |
|--------------|-----------|---------|----------|-------------------------|---------------------|----------------------------|
| 5 | 541 | 292,681 | 0.001848 | 1.7083×10^{-5} | 10.9774 | 257.29 |
| 10 | 547 | 299,209 | 0.001828 | 3.3421×10^{-5} | 10.3063 | |
| 15 | 551 | 303,601 | 0.001815 | 4.9407×10^{-5} | 9.9154 | |
| 20 | 554 | 306,916 | 0.001805 | 6.5164×10^{-5} | 9.6386 | |

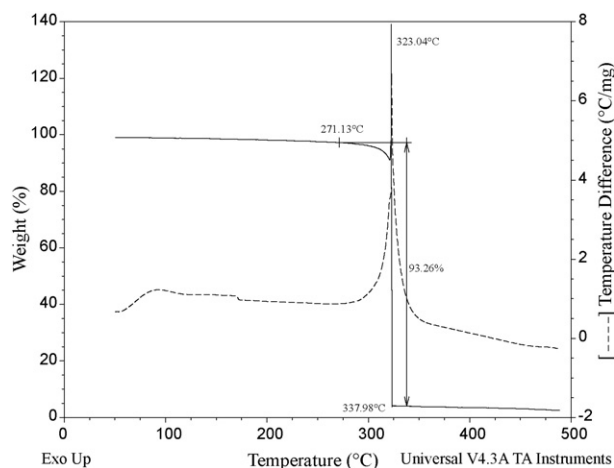


Fig. 6. TGA of BTATz.

peak can be avoided by drying TADPTz at 110 °C for 2 h. The computed activation energy of decomposition is 257.29 kJ/mol (Table 3 and Fig. 9).

The TG of BTATz showed 93.26% weight loss corresponding to decomposition of the compound in the temperature range of 271–338 °C (Fig. 6). The TG of TADPTz showed 6% weight loss due to water loss at the temperature range 83–125 °C and major weight loss (67.5%) was observed due to decomposition of the compound in a single step in the temperature range of 256–314 °C (Fig. 7). The FTIR of decomposition products evolved during TG of BTATz showed peaks at 3255–3261 cm^{-1} for $-\text{NH}$ and 2356–2358 cm^{-1} for $-\text{C}\equiv\text{N}$ whereas TADPTz showed peaks attributable to $-\text{C}\equiv\text{N}$, $>\text{C}=\text{O}$ and $-\text{NH}$.

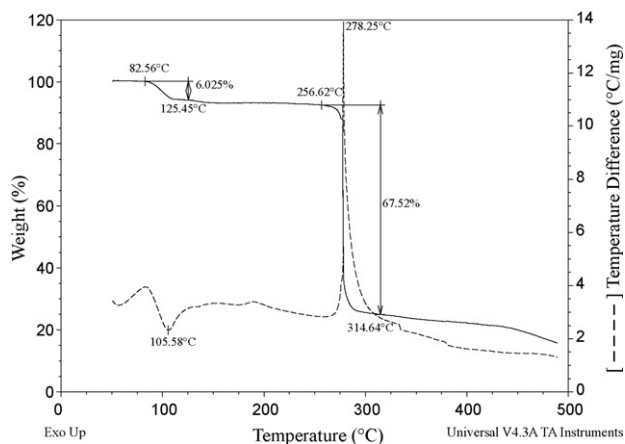


Fig. 7. TGA of TADPTz.

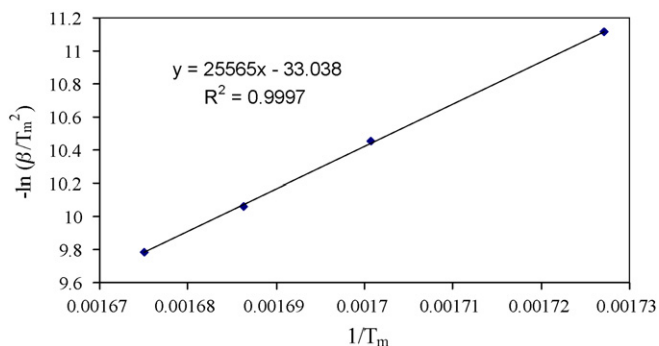


Fig. 8. Plot for BTATz.

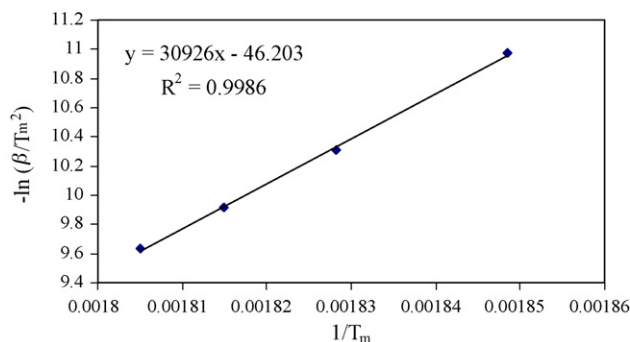


Fig. 9. Plot for TADPTz.

3.4. Sensitivity studies

The experimentally obtained impact and friction sensitivity of BTATz are 116 cm ($H_{50\%}$ explosion, 2 kg weight) and 36 kg respectively indicating that BTATz is insensitive to friction and little sensitive to impact stimuli. But TADPTz is insensitive to impact (>170 cm) as well as friction (up to 36 kg) stimuli. The spark sensitivity value of BTATz is 190 mJ and suggests its sensitive nature to spark initiation. Hence, BTATz has to be coated with some spark insensitive material before its application in any of the devices.

3.5. Performance evaluation

The theoretical performance data of the BTATz and TADPTz were generated using the Linear Output Thermodynamic User-friendly Software for Energetic Systems (LOTUSES) [20,21]. The predicted volume of gaseous products for BTATz is 1237 l/kg of explosive compared to 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX, 957 l/kg), which can be used as potential gas generator. The heat of explosion of BTATz was 3557 kJ/kg lesser than that of RDX (5041 kJ/kg), which can find application as a coolant or flame suppressant in propellant formulations. The above results are to be confirmed by generating experimental data by incorporating these ingredients in various formulations. Theoretically computed data revealed that BTATz and TADPTz can find application in propellant and in gas generator formulations as an energetic ingredient.

4. Conclusion

The synthesis and characterization of BTATz and TADPTz were established during this study. The DSC results showed that BTATz synthesized in the present work was decomposed at 265–350 °C whereas TADPTz is stable upto 245 °C. TG–FTIR studies of these compounds suggest that the presence of NH_3 and HCN in the decomposition products. Impact and friction test results indicated the insensitive nature of BTATz and TADPTz to impact and friction stimuli. But BTATz is sensitive to spark initiation. Theoretically predicted detonation performance parameters of these materials also discussed.

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