# Synthesis, characterization and thermal studies on furazan- and tetrazine-based high energy materials

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## Abstract

This paper reports the synthesis of high energy materials (HEMs) viz. 3,3′-diamino-4,4′-azoxyfurazan (DAAF), 3,3$^{s'}$-azobis(6-amino–1,2,4,5-tetrazine) [DAAT] and 1,4-dihydrazino tetrazine (DHTz). The products obtained were characterized by IR, $^{1}$H NMR, $^{13}$C NMR and mass spectra. Thermolysis of these compounds carried out by applying TG-DTA and DSC techniques indicated that the thermal stability of DAAF and DAAT was in the temperature range of 230–250 °C, whereas that of DHTz was up to ~140 °C. TG-FTIR of gaseous products of these compounds suggests the evolution of $NH_2CN/NH_3$ and HCN as major decomposition products. The impact and friction sensitivity data revealed that DAAF is insensitive to mechanical stimuli whereas DAAT and DHTz are vulnerable to impact stimuli. The cyclic voltammetric studies brought out that, DAAF, DAAT and DHTz are electroactive compounds and thereby can be detected at even low concentration at pH 7 and 13. The theoretical predictions of explosive power of DAAF, DAAT and DHTz alone and their combinations with well-known insensitive high explosives using Becker–Kistiakowsky Wilson (BKW) code as well as that of propellants based on them by NASA-CEC-71 suggest their potential in specific systems.
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*Keywords:* Insensitive high energy materials; Diaminofurazan (DAF); 3,3′-Diamino-4,4′-azoxyfurazan (DAAF); 3,3′-Azobis(6-amino-1,2,4,5-tetrazine) (DAAT); 1,4-Dihydrazino tetrazine (DHTz); Thermolysis; Cyclic voltammetry

## 1. Introduction

The explosives belong to the category of the most hazardous high energy materials (HEMs). Owing to increased threat perceptions with the introduction of long-range projectiles and missiles including intercontinental ballistic missiles (ICBM), the risk management of hazardous materials like explosives has acquired great importance. The unprecedented quest for HEMs with low vulnerability and highest possible performance led to the discovery [1–3] of compounds like 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), 3-nitro-1,2,4-triazole-5-one (NTO), 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclododecane (TEX), 1,1-diamino-2,2-dinitroethylene (FOX-7) and 2,6-diamino-3,4-dinitro-

pyrazine oxide (LLM-105). Despite being inherently hazardous, these molecules are often referred as insensitive high explosive (IHE) due to their low vulnerability to unplanned stimuli. Many of these IHEs are at various stages of their pilot plant scale productions in different countries.

Theoretical modelling studies reported by Russian workers [4] bring out the potential of furazan and furoxans as advanced HEMs. Furazan-based HEMs are interesting class of compounds due to their low vulnerability and high density emanating from planarity of the ring, positive heat of formation, and high percentage of nitrogen content [5]. In the initial phase of research and development (R&D) work on furazans way back during 1970–1980, non-realization of 3,4-diaminofurazan (DAF) in bulk quantity posed severe limitations on their introduction for practical applications. However, R&D efforts in this field led to a major technological breakthrough in 1990 and resulted in the establishment of an inexpensive method [6] for the synthesis of

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DAF based on a vicarious nucleophilic substitution (VNS) reaction.

3,3′-Diamino-4,4′-azoxyfurazan (DAAF) has received major attention as an insensitive HEM of this class due to its positive heat of formation (+106 kcal/mol). The first synthesis of DAAF was reported by Russian workers [7] in 1981. They used a variety of peroxides for the oxidation of DAF to DAAF. Chavez et al. [8] from Los Alamos National Laboratory, USA reported the synthesis and characterization of DAAF by the oxidation of DAF using $H_2O_2$ and $H_2SO_4$ at 18 °C. These workers demonstrated the potential of DAAF as an explosive by applying poly-ρ-test. More recently, a United States patent [9] claimed the improved process for the preparation of DAAF and diaminoazofurazan (DAAzF) as well as their use as insensitive HEMs. The precursors of DAAF, viz. diaminoglyoxime (DAG) and DAF are reported [10] as potential burn rate suppressants for composite propellants. In addition to DAAF, a wide spectrum of versatile advanced HEMs can be obtained from DAF [11].

Recently, Los Alamos National Laboratory (LANL), USA reported that the potential of high nitrogen content high energy materials [HNC–HEMs] has remained an unexplored field. Unlike conventional HEMs, HNCs derive their energy from a combination of positive heat of formation and generation of large volume of $N_2$ with high order of energy release. A large number of C–N and N–N bonds and low percentage of carbon and hydrogen in these compounds also entails higher density and need of lesser amount of oxygen for combustion in comparison to conventional HEMs [12,13].

The tetrazine class of HNC HEMs, viz. 3,3′-azobis(6-amino-1,2,4,5-tetrazine) (DAAT) and 1,4-dihydrazino tetrazine (DHTz) have received major attention due to their high positive heat of formation (+1032 and +530 kJ/mol, respectively). The DAAT may find wide spectrum applications as an energetic component of rocket propellants and low vulnerable explosive formulations. The DHTz has been reported as an energetic eco-friendly smoke ingredient of pyrotechnic composition for special applications. Hiskey and co-workers [14–17] and Kerth et al. [18] have reported synthesis of DAAT and DHTz at LANL, USA and Institute of Chemical Technology (ICT), Germany, respectively.

In view of the continued interest [19] in the area of low vulnerable high explosives, we report the improved synthesis of DAF, DAAF, DHTz and DAAT in multigramme quantities in our laboratory on the lines of reported method [6,8,17,18] in an attempt towards risk mitigation without much penalty on performance potential. The synthesized compounds were characterized by spectral techniques and results obtained were compared with the reported data to ascertain their structural features. Thermal studies on DAAF and DHTz was undertaken in view of scanty information available on these compounds. DAAT was also subjected to thermal analysis and results obtained were compared with the reported data. In addition, authors have scanned FTIR spectra of decomposition products to obtain during thermo gravimetry experiments to understand energy release process. The

cyclic voltammetric studies on these compounds were also undertaken to develop a possible detection method, which may be useful from the point of waste management as well as environment control. The theoretical performance of the compounds was determined with respect to well-established insensitive HEMs to assess their energy potential.

## 2. Experimental

### 2.1. Materials and methods

All the reagents and chemicals of AR grade were used as such in the present study. The IR spectra were recorded on Perkin Elmer FTIR-1600 spectrophotometer in KBr matrix and $^1H$ NMR spectra scanned on a 300 MHz Varian instrument in deuterated chloroform at 30 °C with TMS as an internal standard. Mass spectra of the samples were recorded by electron impact method (70 eV) using a Finnigan Mat instrument (Model 1020). The sample was vaporized by external heating. The DSC studies were undertaken on a Perkin Elmer DSC-7 instrument at the heating rate of 10 °C/min in a nitrogen atmosphere with 1 mg of sample. The thermal decomposition studies were also undertaken on simultaneous thermogravimetric/differential thermal analyzer (TG/SDTA) of Mettler Toledo make (8551). FTIR spectra of decomposition products were recorded on Bruker (EQUINOX-55) instrument coupled with TG. The sensitivity to impact stimuli was determined by applying standard staircase method using a 2 kg drop weight and the results are reported in terms of height for 50% probability of explosion ($h_{50\%}$) of the sample [20]. Figure of insensitivity (F of I) was computed by using tetryl (composition exploding; CE), as reference. The friction sensitivity of the compound was determined on a Julius Peter's apparatus until 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. The crystal morphology was studied on a scanning electron microscope (SEM) of Philips Icon make and the cyclic voltammetric studies were carried out using a (CHI-620A) electrochemical analyzer. The theoretical performance of selected insensitive high explosive combinations was computed using the well-known BKW code [21]. The ballistic performance of these materials as an energetic additive for solid propellants was also predicted using NASA-CEC-71 code [22].

### 2.1.1. Methodology

DAAF [8], DAAT and DHTz [14,17] were synthesized on the lines of the reported method. The synthesis of DAAF involved the preparation of diaminoglyoxime (**1**) and 3,4-diaminofurazan (DAF) (**2**) as intermediates.

*2.1.1.1. Synthesis of DAF (**2**).* An aqueous solution containing potassium hydroxide (160 cm³, 2 M) and DAG (47.2 g, 0.4 mol) synthesized by reported method [6] was

charged into a stainless steel (Parr) reactor. The reactor was closed and the solution was kept under stirring. The temperature was gradually raised to 180 °C. The pressure developed inside the reactor during the course of the reaction was of the order of 28–30 bar. After 2 h, the chilled water was passed through the jacket of the reactor and contents were allowed to cool down to room temperature under constant stirring of the contents. The reactor was opened after 3 h of completion of reaction in exhaust chamber (to avoid the contact with ammonia escaping from reactor). The rod shaped white crystals of DAF obtained were washed with cold methanol (10–15 cm$^3$) in a beaker and filtered. The isolated product was washed with cold methyl alcohol/ether and dried to obtain 50 g of the compound (yield 70%).

*2.1.1.2. Conversion of DAF to DAAF.* A 50% hydrogen peroxide (100 g, 0.8 M) solution was cooled down to 20 °C while stirring and 98% sulphuric acid (55 g, 0.56 mol) was added over a period of 5–7 min. The temperature of the contents was allowed to increase to 25–27 °C. Subsequently, the reaction mixture was cooled down to 20 °C. The DAF (10 g, 0.10 mol) was added in small instalments and the reaction mixture was kept stirring for 18 h at 25 °C. The colourless reaction mixture acquired intense orange yellow colour and fine precipitate of DAAF (**3**) formed was filtered through a sintered glass crucible. The precipitate was washed with ice-cold water and air-dried to obtain 9.31 g of crude material (yield 89%). The crude DAAF was reprecipitated by dissolving it in a minimum amount of dimethyl sulphoxide solvent, and then adding water over a period of 5 min while stirring the contents. The recrystallized DAAF was filtered and washed with water. The product obtained was air-dried.

*2.1.1.3. Synthesis of DAAT (8).* The synthesis of DAAT [14,18] involved preparation of 3,6-bis(3,5-dimethyl pyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine (**4**), 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (**5**), *N,N′*-bis-(1,2,4,5-tetrazine-3-yl-3,5-dimethylpyrazol)-hydrazine (**6**) and 3,3′-azobis(bis[6,6′-(4-bromo-3,5-dimethylpyrazol-l-yl)])-1,2,4,5-tetrazine (**7**) as intermediates. All the synthesized precursors were characterized by spectral techniques.

Ammonia gas (7.0 g, 0.41 mol) was rapidly bubbled through one litre of dimethyl sulfoxide (DMSO). Its solution in DMSO (100 cm$^3$) was taken in reaction flask and compound **7** (11.04 g, 0.021 mol) was added. The solution was stirred for 15 min and diluted with 100 cm$^3$ of

2-propanol. The red solid precipitate was filtered, washed with 2-propanol and air-dried to yield 1.7 g of DAAT solvate (yield 22%). The material was added to the minimum amount of distilled water and boiled for a few minutes to separate the solvate envelope and filtered. The product was washed with water and air-dried to get pure DAAT (**8**). DAAT is insoluble in most of the common organic solvents and sparingly soluble in dimethyl formamide (DMF) and DMSO.

*2.1.1.4. Synthesis of DHTz (9).* The title compound (**4**) was also used as a precursor for the synthesis [17] of DHTz (**9**). 3,6-Bis(3,5-dimethyl pyrazolyl-1-yl)-1,2-dihydro-1,2,4,5-tetrazine (**4**) (27.3 g, 0.1 mol) was taken in a reaction flask and 150 cm$^3$ of acetonitrile was added. The contents were mixed well and the temperature of the reaction mixture was maintained between 10 and 15 °C. Hydrazine monohydrate (99%) (11.5 g, 0.21 mol) was added drop wise to the contents under continuous stirring. Subsequently, the reaction mixture was kept at 30 °C for 30 h. A maroon red solid was obtained after filtration. The product was washed with acetonitrile and dried to get 13.05 g (92%) of (**9**).

## 3. Results and discussion

### 3.1. Synthesis and characterization

Vicarious nucleophilic substitution reaction [6] of glyoxime with hydroxylamine hydrochloride offers a cleaner and high yielding method of preparation of DAG in comparison to conventional method involving its preparation from dithioxamide as reactant. A well-defined method of synthesis for DAF, DAAF, DAAT and DHTz established during this work is presented in Figs. 1 and 2. The precursors and final products were characterized by spectroscopic techniques.

### 3.1.1. DAG (1)
Melting point 201–202 °C, IR (KBr): 3470 (–OH), 3368, 3104 (–NH$_2$), 1654 (NH), 1604, 1572 (C=N), 1446 (C–N), 1400, 1114, 939 cm$^{-1}$. $^1$H NMR (dimethyl sulfoxide-d$_6$) δ 5.2 (s, 4H, NH$_2$), 9.8 (s, 2H, OH). MS: 118 (*m/z* and base peak).

### 3.1.2. DAF (2)
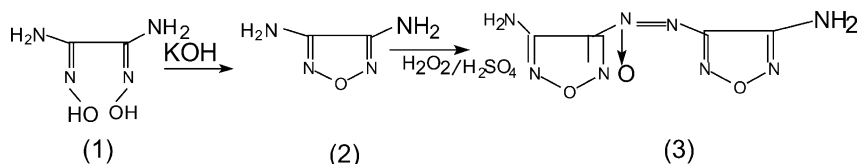Melting point 180–181 °C, IR (KBr): 3423, 3318 (NH$_2$), 1647, 1591 (C=N), 1354 (C–N) cm$^{-1}$. $^1$H NMR (dimethyl
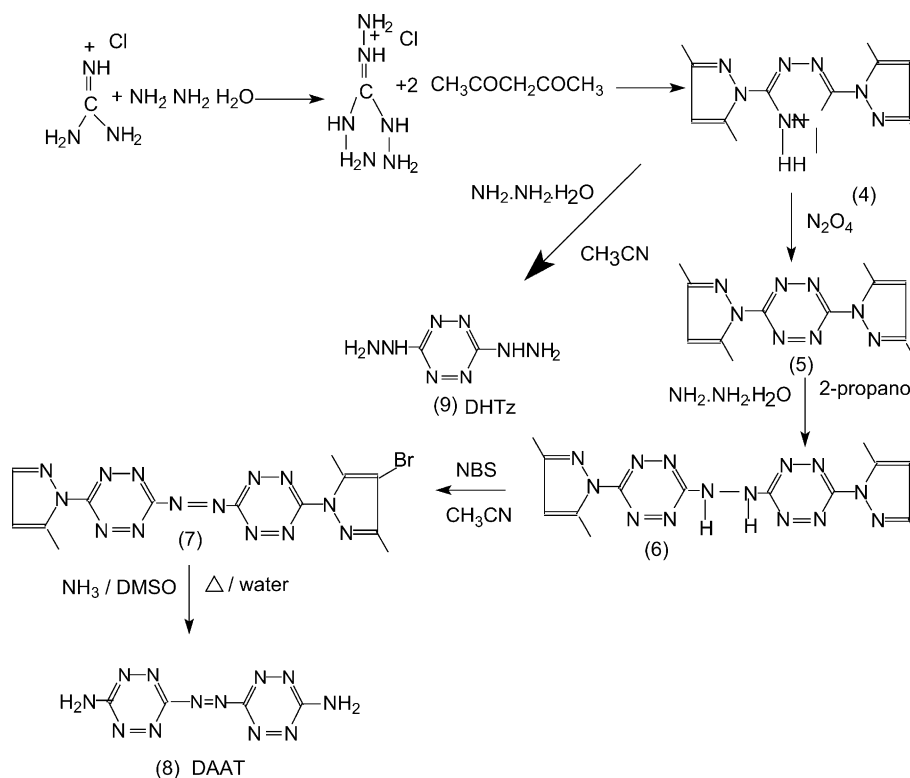


Fig. 1. Synthesis scheme of DAAF.

Fig. 2. Synthesis scheme of DAAT and DHTz.

sulphoxide-$d_6$) $\delta$ 5.81 (bs, 4H, NH$_2$), MS: *m/z*: 100 (base peak).

### 3.1.3. DAAF (3)

IR (KBr): 3328, 3204 (NH$_2$), 1636 (NH), 1510 (C=N), 1462 (C–N), 1296 and 1178 (N–O–N), 1122, 1022, 914, 874, 776 cm$^{-1}$. $^1$H NMR ($d_6$-DMSO) $\delta$ 6.65 (s, 2H, NH$_2$), 6.93 (s, 2H, NH$_2$) and $^{13}$C NMR ($d_6$-DMSO) $\delta$ 147.2, 149.9, 151.2, 153.2. MS: 212 (*m/z*) and 94 (base peak).

### 3.1.4. 6-Bis(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine (4)

Melting point 148–150 °C, IR (KBr): 3286 (NH), 2918 (CH), 1680 (NH), 1062 cm$^{-1}$. $^1$H NMR (deuterio chloroform): $\delta$ 2.22 (s, 6H, 2× CH$_3$), 2.47 (s, 6H, 2× CH$_3$), 5.94 (s, 2H, CH), 8.09 (bs, 2H, NH).

### 3.1.5. 6-Bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (5)

Melting point 226 °C, IR (KBr): 3028 (CH), 1460 (C=N), 1355 (C–N), 1269, 1076 cm$^{-1}$.

### 3.1.6. N,N′-Bis-(1,2,4,5-tetrazine-3-yl-3,5-dimethylpyrazol)-hydrazine (6)

Melting point 215–217 °C, IR (KBr): 3196 (NH), 1570, 1484 (C=N), 1414 (C–N) cm$^{-1}$. $^1$H NMR (deuterated DMSO): $\delta$ 2.21 (s, 6H, 2× CH$_3$), 2.49 (s, 6H, 2× CH$_3$), 6.22 (s, 2H, CH), 11.2 (bs, 2H, NH).

### 3.1.7. 3′-Azobis(bis[6,6′-(4-bromo-3,5-dimethyl pyrazol-1-yl)])-1,2,4,5-tetrazine (7)

Melting point 195–197 °C, IR (KBr): 3010 (CH), 1500, 1452 (C=N), 1346 (C–N), 900, 850 (C-Br) cm$^{-1}$. $^1$H NMR (deuterated chloroform): $\delta$ 2.44 (s, 6H, 2× CH$_3$), 2.84 (s, 6H, 2× CH$_3$).

### 3.1.8. DAAT (8)

Melting point 250–252 °C (d) IR (KBr): 3370, 3290 and 1630 (NH$_2$), 1506, 1456 (C=N), 1340 (C–N), 1062 and 982 cm$^{-1}$. $^1$H NMR (deuterated chloroform): $\delta$ 8.93 (s, 4H, NH$_2$).

### 3.1.9. DHTz (9)

Melting point 158–160 °C, IR (KBr): 3350, 3294, 3220, 1638 (NH$_2$), 1538, 1452 (C=N). $^1$H NMR (deuterio chloroform): $\delta$ 4.32 (bs, 4H, 2× NH$_2$), 8.44 (s, 2H, 2× NH). $^{13}$C NMR (deuterated chloroform) $\delta$ 163.1.

The absence of –OH stretching frequency (3470 cm$^{-1}$) and presence of N–O–N stretching frequency (1050–1150 cm$^{-1}$) in the IR spectrum of DAF clearly confirms the conversion of DAG to DAF. The reaction was carried out under the pressure of the order of 28–30 bar. To the best of our knowledge none of the reported papers [6] on the synthesis of DAF mentions the pressure of the reaction during the synthesis of DAF. The $^1$H NMR and mass spectra also provide evidence of the formation of DAF. The possible contaminants such as nitraminofurazan, nitrosofurazan, and

hydroxyl aminofurazan formed during oxidation of DAF to DAAF were removed by recrystallisation of DAAF using DMSO/$H_2O$ solvent. The temperature of the reaction for the conversion of DAF to DAAF employed in the present work is of the order of 25–27 °C and the reaction time was 18 h in comparison to reported [8] reaction time (24 h) and the reaction temperature (18 °C). The N–O–N linkage of furazan ring in DAAF appeared in IR spectrum at 1020–1122 cm$^{-1}$. In NMR, the $NH_2$ protons of DAAF resonated at $\delta$ 6.65. The $^{13}$C NMR clearly showed the presence of two types of carbon, i.e. C–$NH_2$ and C–N $\rightarrow$ O. The former resonated at $\delta$ 147.2 and 149.9 while latter at $\delta$ 151.2 and 153.2. The mass spectrum of DAAF exhibited $m/z$ peak at 212.

During the synthesis of DAAT, the reaction time for the key precursor, viz. 3,6-bis(3,5-dimethyl pyrazolyl-1-yl)-1,2-dihydro-1,2,4,5-tetrazine, was brought down to 3 h as against reported [23] 4 h. $N,N'$-bis-(1,2,4,5-tetrazine-3-yl-3,5-dimethylpyrazol)-hydrazine (**6**) was prepared using quantitative amount of 99% hydrazine hydrate in place of reported [14] anhydrous hydrazine. The IR spectrum of DAAT displayed N–H stretching and deformation vibrations of the amine groups at 3370, 3290 and 1630 cm$^{-1}$, respectively. The $^1$H NMR spectrum of DAAT exhibited a broad resonating signal for amine protons ($2\times$ $NH_2$) at $\delta$ 8.93.

The reaction time during the synthesis of DHTz was brought down to 30 h in place of reported [17] 48 h. Alternatively DHTz was also synthesized by reacting hydrazine hydrate with 3,6-bis(3,5-dimethyl pyrazol-1-yl)-1,2,4,5-tetrazine (**5**). The DHTz displayed N–H stretching and deformation vibrations of the amine groups at 3350, 3294 ($NH_2$), 3220 (NH) and 1638 ($NH_2$) in IR spectrum, while $^1$H NMR exhibited broad resonating signal for primary and secondary amino group at $\delta$ 4.32 ($2\times$ $NH_2$) and $\delta$ 8.44 ($2\times$ NH), respectively. The spectral features of the compounds are in close agreement with the reported values and confirm the formation of the product by the method adopted during the work.

The SEM of DAAF (Fig. 3) revealed cube shaped morphology whereas that of DAAT (Fig. 4) and DHTz (Fig. 5) showed spherical shaped morphology. The cube shaped morphology is hazardous due to sharp edges during processing of propellant/explosive formulations. However spherical shaped morphology minimises the risk management during their handling. Therefore, process for the synthesis of DAAF of spherical shape need to be optimised prior to its evaluation.

The impact ($h_{50\%} > 170$ cm) and friction sensitivity (insensitive up to >36 kg) results established insensitive nature of DAAF. However, DHTz and DAAT gave $h_{50\%}$ of 70 and 37 cm, respectively, indicating their susceptibility to impact stimuli. As regards friction sensitivity, both were found insensitive (up to 36 kg). The sensitivity results are also in agreement with the reported data [17,18].

Although, the compounds synthesized are insensitive towards friction stimuli, they fall under the hazard category
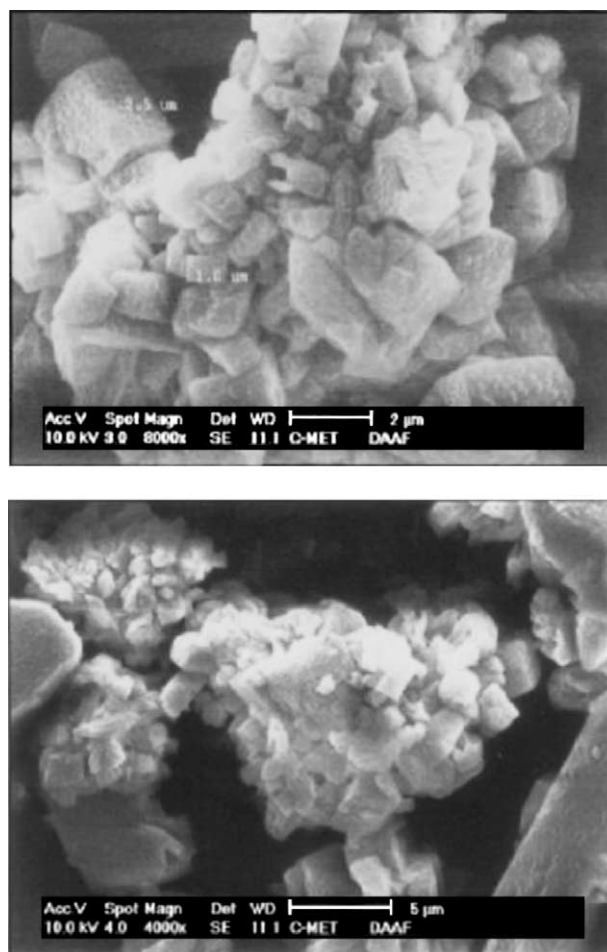


Fig. 3. SEM of DAAF.

of 1.1 as per the United Nations classification of explosives. Therefore, these materials need to be handled by the highly skilled HEMs chemists/scientists during their synthesis, characterization, scale up, storage, transport and evaluation. The unplanned/accidental imitation of these materials can cause mass explosion, blast, severe injury to the personnel and to the surrounding.

### 3.2. Thermal studies

The DSC and TG revealed that DAAF is thermally stable up to 230 °C. The DAAF exhibited an exotherm in DSC (Fig. 6) with $T_{max}$ at 252 °C and heat release ($\Delta H$) of the order of 2235 J/g. In TG, DAAF showed the percentage weight loss of 76% (Fig. 7) in the temperature range of 230–260 °C. The energy of activation obtained for this step was of the order of 168.5 kJ/mol. The FTIR profile (Fig. 8) of decomposition products revealed absorption bands at 3600, 3250, 2358 cm$^{-1}$ suggesting the presence of $NH_2OH/NH_2CN/NH_3$ and HCN. There is also a possibility of simultaneous cleavage of furazan rings and azoxy group (N=N $\rightarrow$ O) during the thermal decomposition of DAAF.
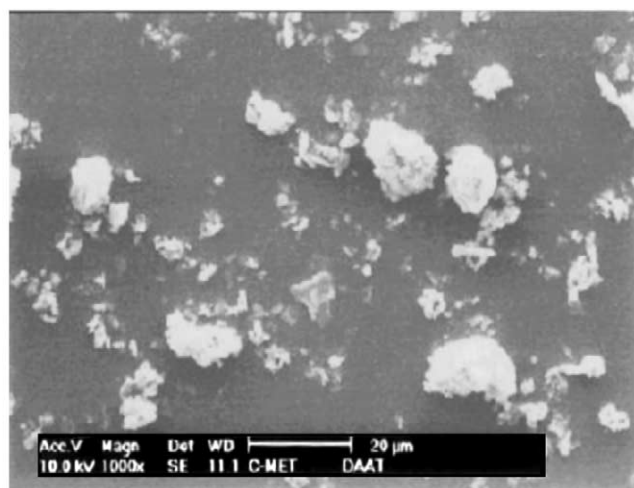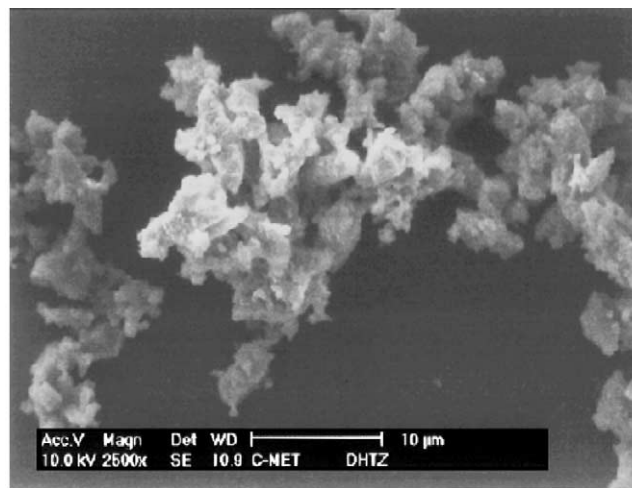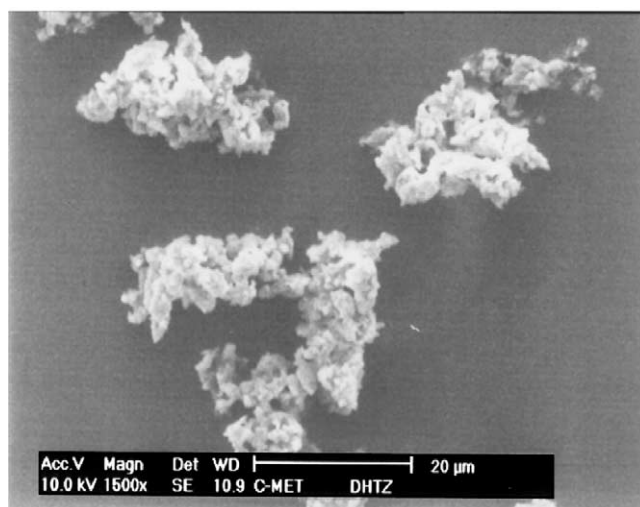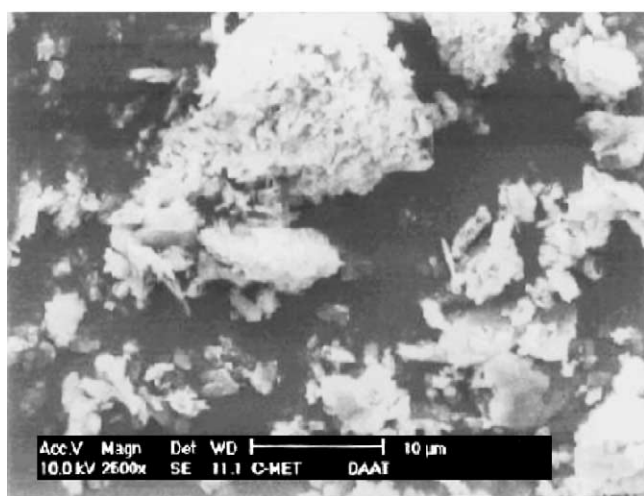
Fig. 4. SEM of DAAT.



Fig. 5. SEM of DHTz.

The DSC and TG revealed that DAAT is thermally stable up to 251 °C. In DSC, DAAT gave an exotherm with maxima at 320 °C and $\Delta H$ of 2827 J/g (Fig. 9). This trend is in line with the [14] highest heat evolution reported for DAAT among C, H and N organic compounds. The TG analysis revealed that DAAT decomposed in two steps (Fig. 10). The first decomposition step was accompanied with the weight loss of 64% commenced at 251 °C and completed at 323 °C. The second decomposition step ended at 402 °C with a weight loss of 26%. The energy of activation obtained for first and second decomposition steps was 57 and 121 kJ/mol, respectively. The DHTz also revealed its thermal stability up to 140 °C in DSC and TG. The DSC (Fig. 11) of DHTz exhibited single exotherm with maxima at 161 °C and $\Delta H$ of 1660 J/g. The TG of DHTz (Fig. 12) also showed single step decomposition in the temperature range of 140–160 °C with a weight loss of 64.9%. The FTIR of the gases evolved during TG of DAAT and DHTz revealed formation of those for DAAF ($NH_2CN/NH_3$ and HCN) (Figs. 13 and 14). In addition, $H_2O$, $CO_2$ and HNCO were also detected in the decomposition products of DAAT and DHTz.

The thermal analysis studies indicate the thermal hazards associated with the HNC–HEMs for their possible use as an energetic additive for propellant and explosive formulations.

### 3.3. Cyclic voltammetric (CV) studies

The CV studies on DAAF at pH 1 showed a reduction peak at a potential of 0.25 V in cathodic scan. The oxidation peaks were observed at pH 7 and 13 (Fig. 15).

DAAT at pH 7 showed (Fig. 16a) predominant reduction peak ($-0.23$ V) whereas four reductions and three oxidation peaks were observed at pH 13 (Fig. 16b). The reduction peaks may be due to the formation of intermediates during the course of reduction of DAAT [N $\rightarrow$ O–N, –NO $\rightarrow$ –NHOH, –NHOH $\rightarrow$ NH_2 group]. The appearance of three oxidation peaks may be [NH_2 $\rightarrow$ –NHOH, –NHOH $\rightarrow$ –NO, –NO $\rightarrow$ –NO_2] resulting from oxidation of NH_2. It can be inferred that DAAT undergoes complex electrochemical reaction at pH 13, while it undergoes simple electrochemical redox reaction at pH 7. Hence, detailed studies were carried out at pH 7 and the effect of scan rate was determined in the
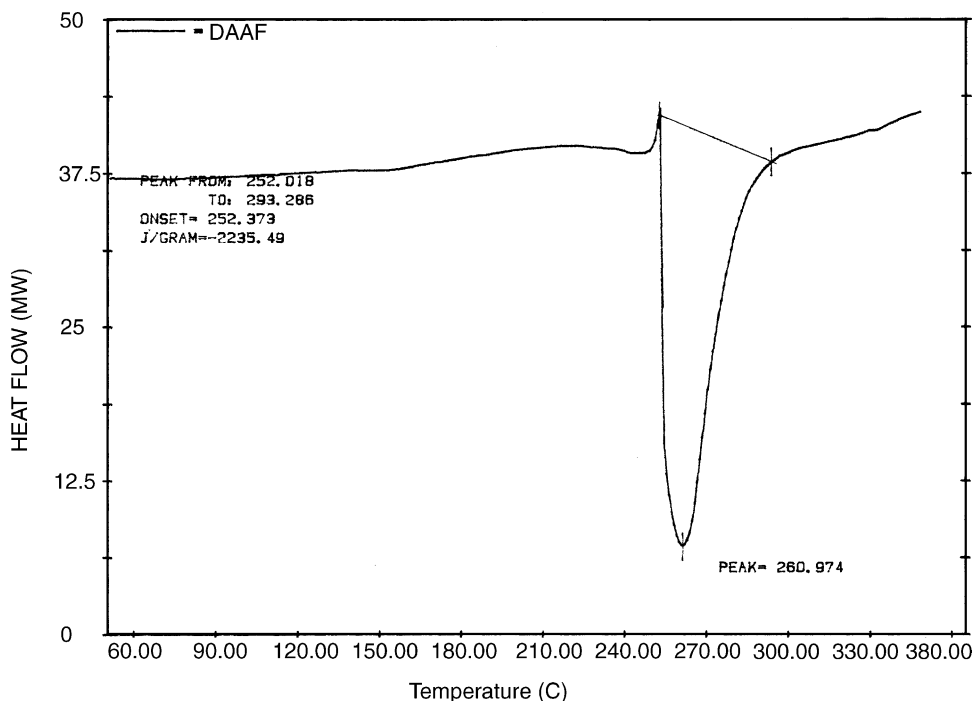
Fig. 6. DSC of DAAF.

range of 50–500 mV/s. Peak potential values remained constant during various sets of experiments. However, splitting of the peak was observed at higher scan rate probably due to fast electron transfer reaction at 0.4 V potential.

The CV studies on DHTz at pH 1 showed a broad reduction peak (+0.07 V). Additional peaks appeared at pH 7 and 13 suggesting that it undergoes complex electrochemical reaction (Fig. 17a and b) under these conditions. It may be
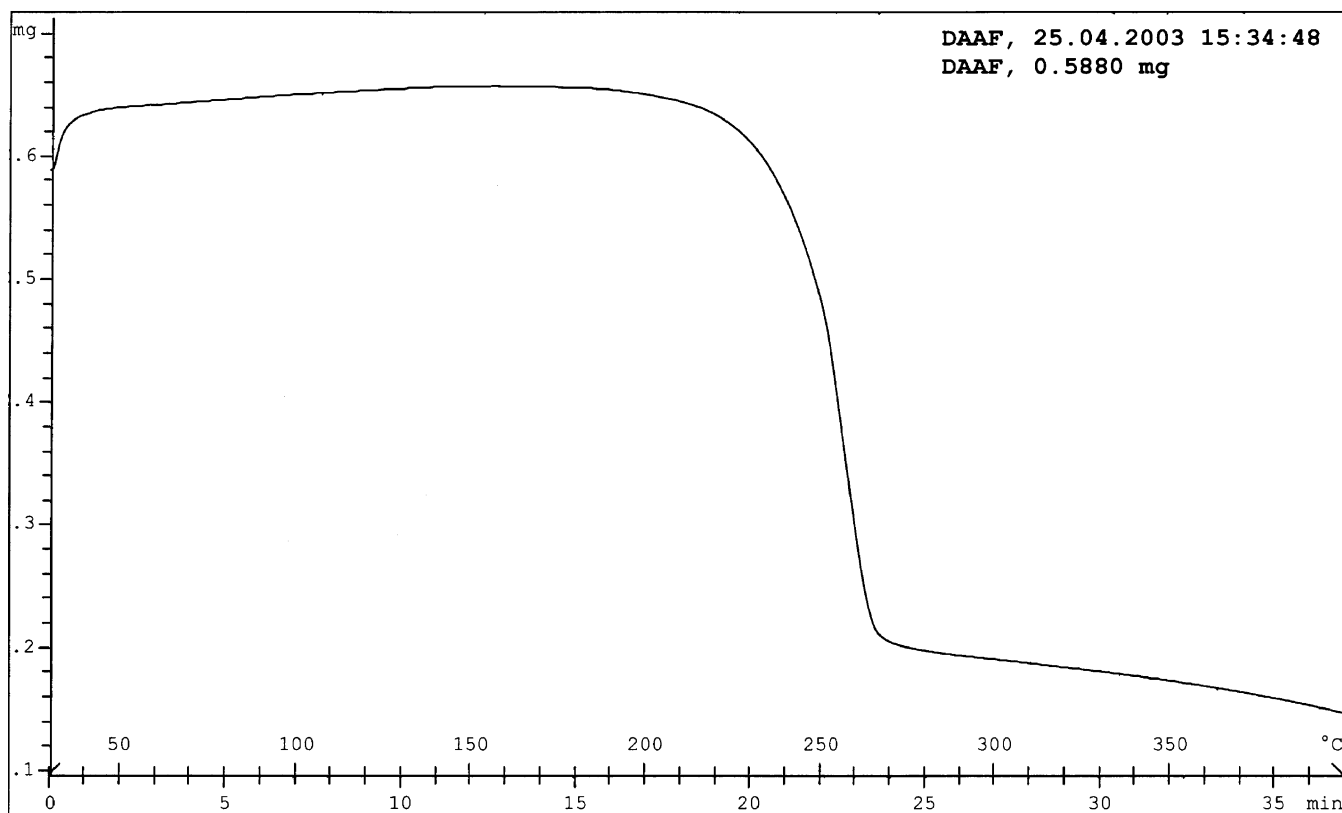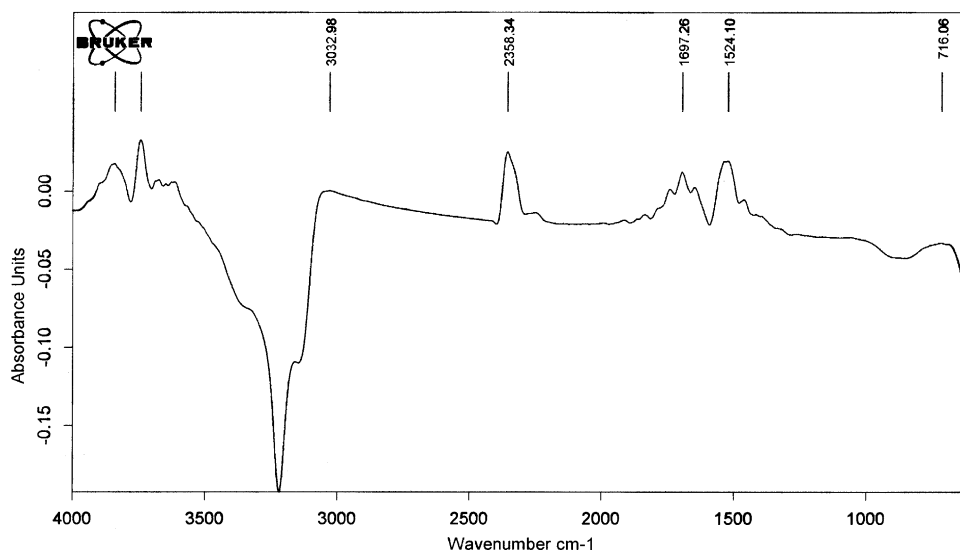


Fig. 7. TG of DAAF.

Fig. 8. TG-FTIR of DAAF.

outcome of the fact that DHTz is highly electroactive probably because of presence of two hydrazino groups present at 1,4-position of DHTz, which are susceptible to electrochemical oxidation.

The results obtained in CV studies clearly indicate the electroactive nature of DAAF, DAAT and DHTz. The CV technique may open up new vistas in the development of possible detection method for the hazardous high nitrogen content HEMs and also for monitoring environment pollution as well as waste disposal.

## 4. Performance evaluation

The performance of DAAF, DAAT and DHTz was predicted by applying BKW code (Table 1). The RDX equation state of parameters were used (alpha = 5.00000E−01, beta = 1.60000E−01, theta = 4.00000E + 02, kappa = 1.090978−E + 01) for these calculations. The theoretically obtained results are compared with the benchmark low vulnerable high explosives, viz. nitrotriazolone (NTO) and triaminotrinitrobenzene (TATB) whereas DAAT and DHTz
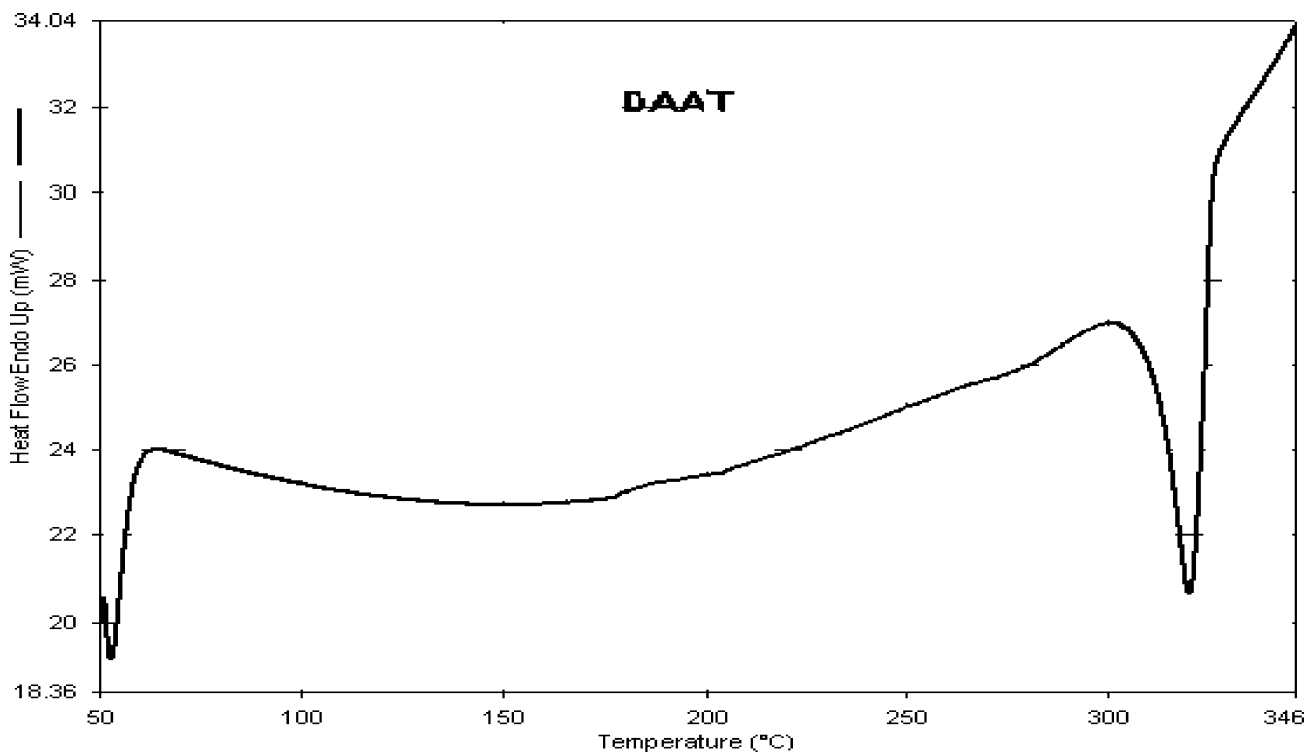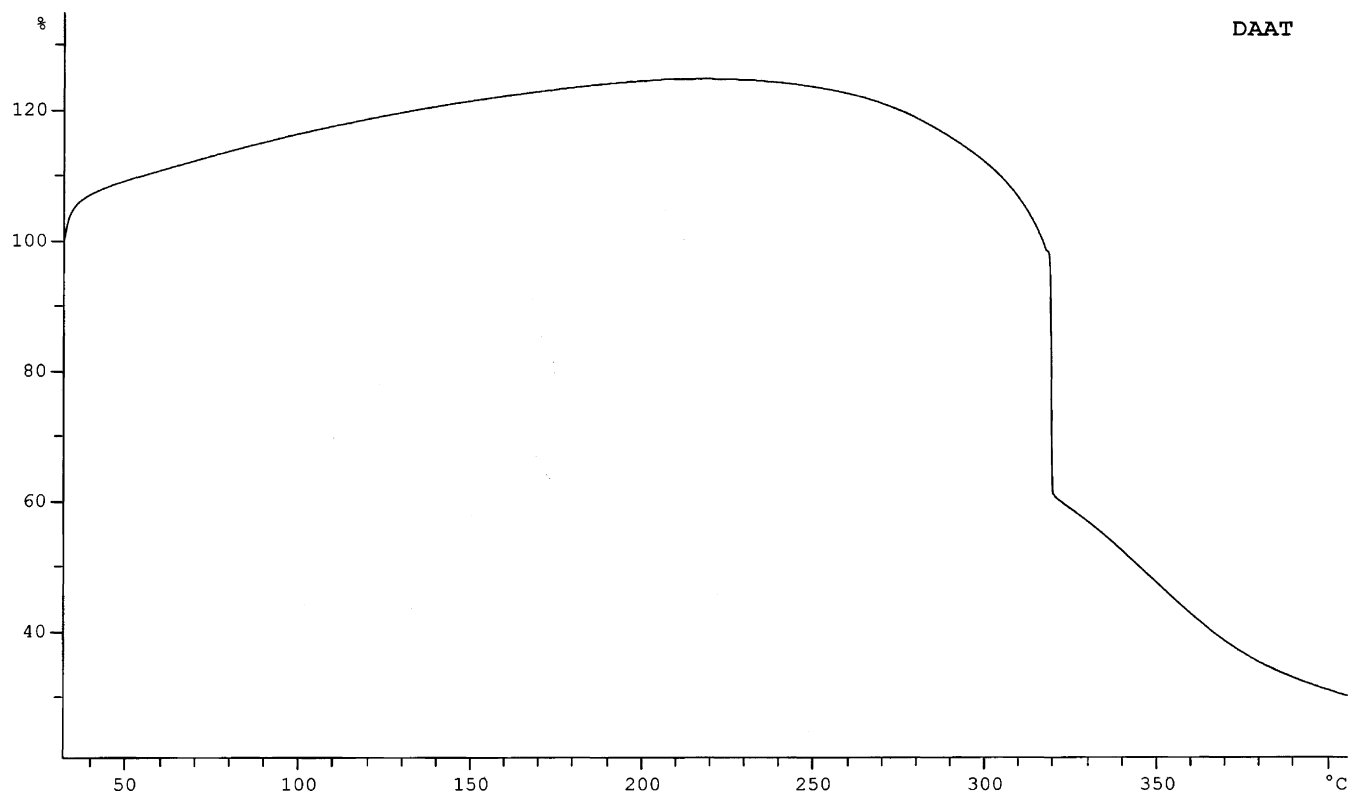


Fig. 9. DSC curve of DAAT.
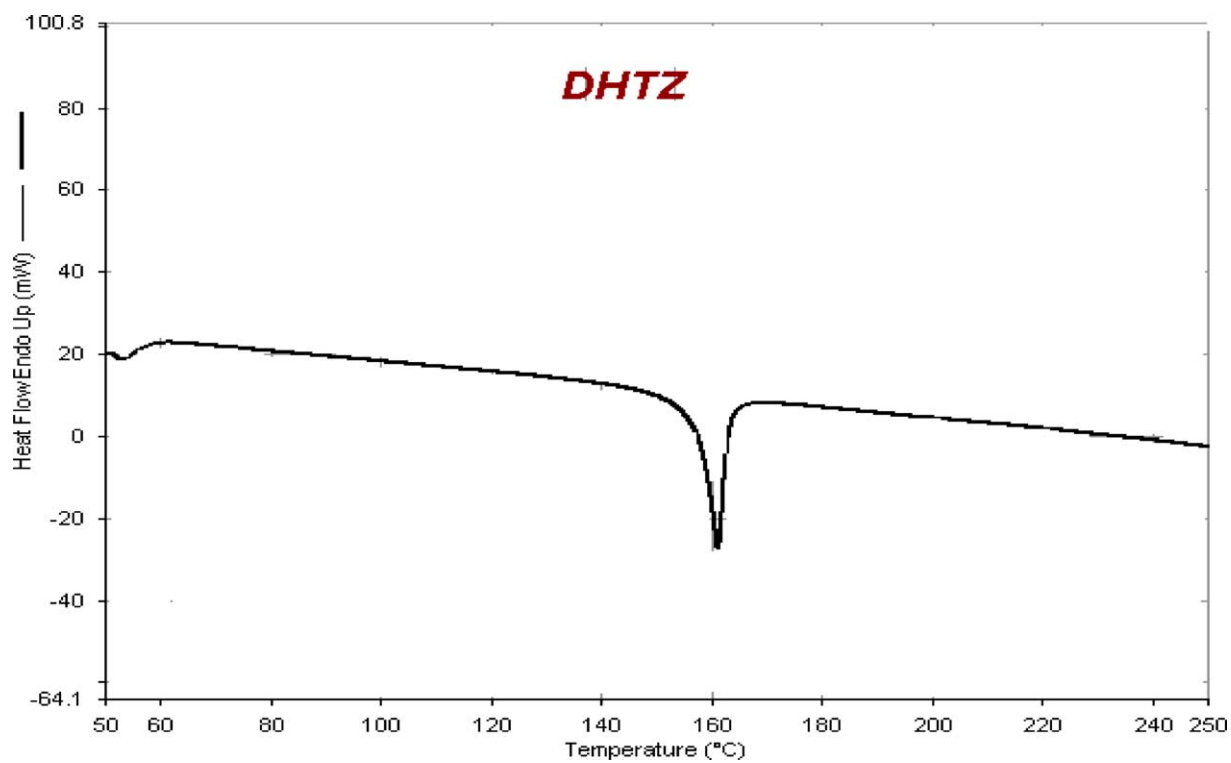
Fig. 10. TG curve of DAAT.
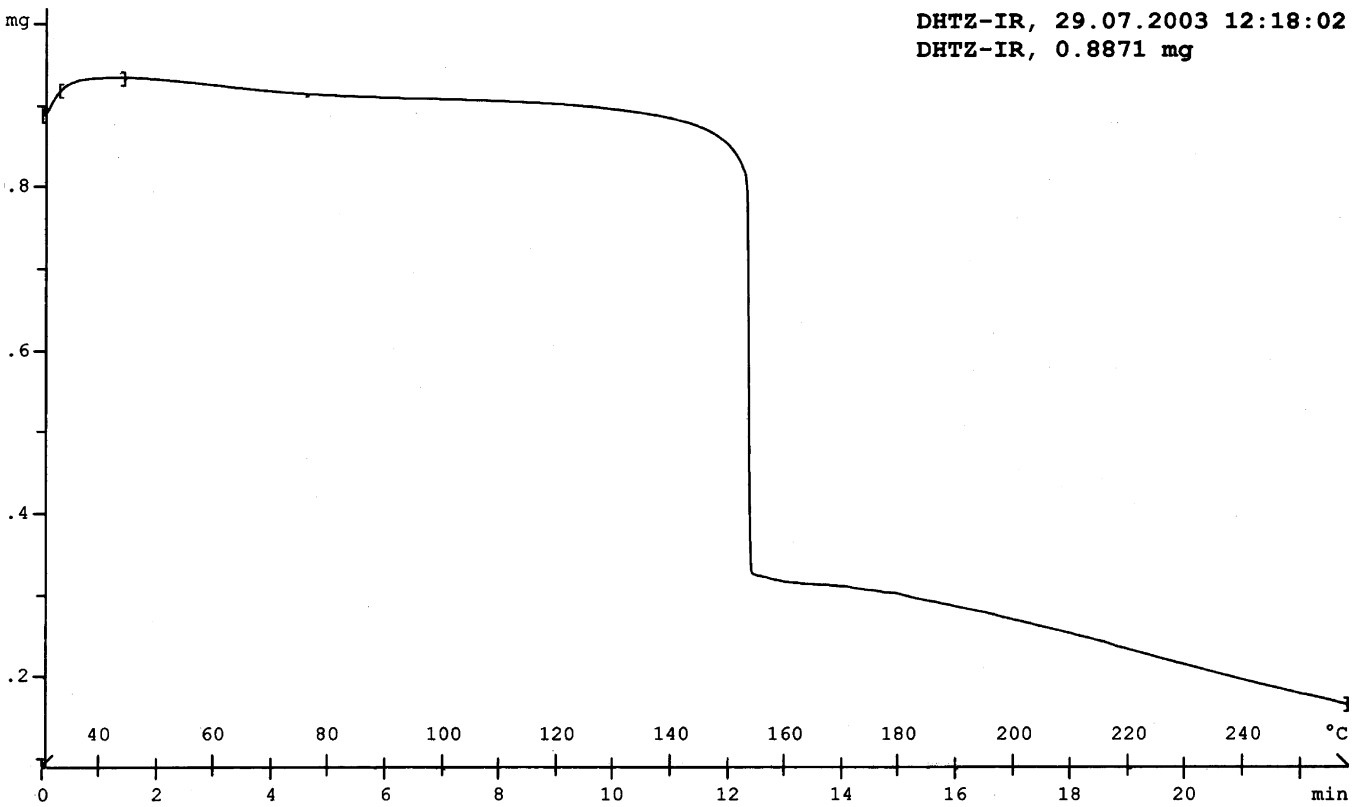


Fig. 11. DSC of DHTz.

Fig. 12. TG of DHTz.

gave relatively higher performance which may be due to non availability of equation of state coefficients for C,H,N class of explosives in literature. The theoretically predicted performance parameters may show variation if trinitrotoluene (TNT)/general/Sandia National Laboratory (SNL) equation state of parameters are used (in place of RDX equation state of parameters) during BKW calculation. Predicted performance parameters need to be confirmed by generating exhaustive theoretical and experimental data. The theoretical performance evaluation of DAAF (75%) or DAAT (75%) in
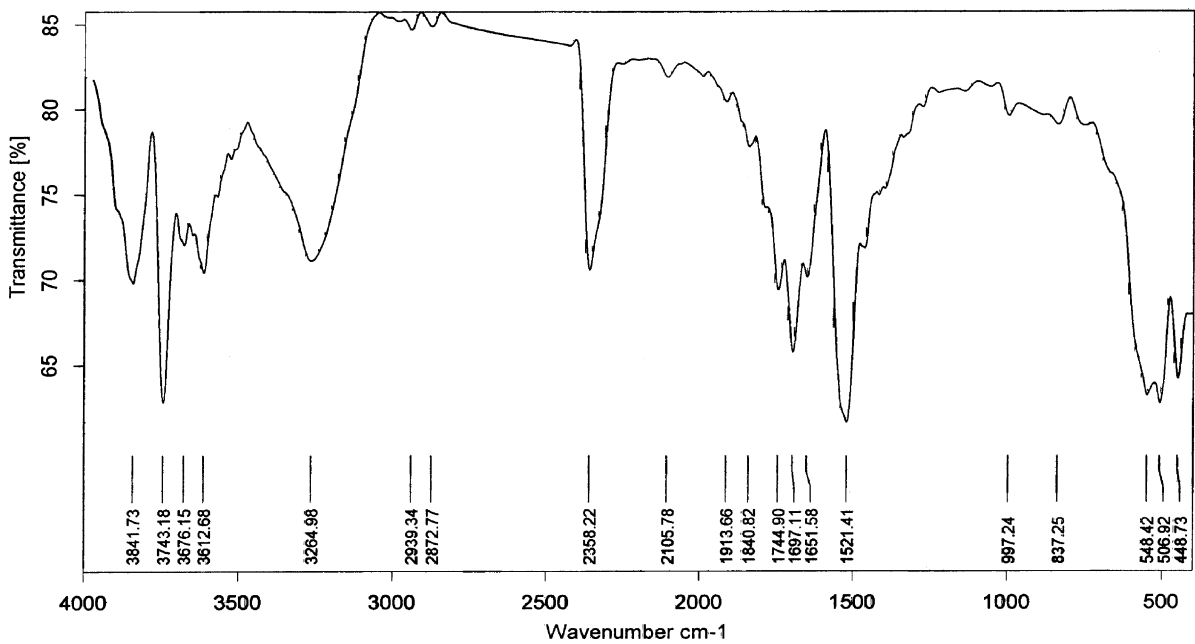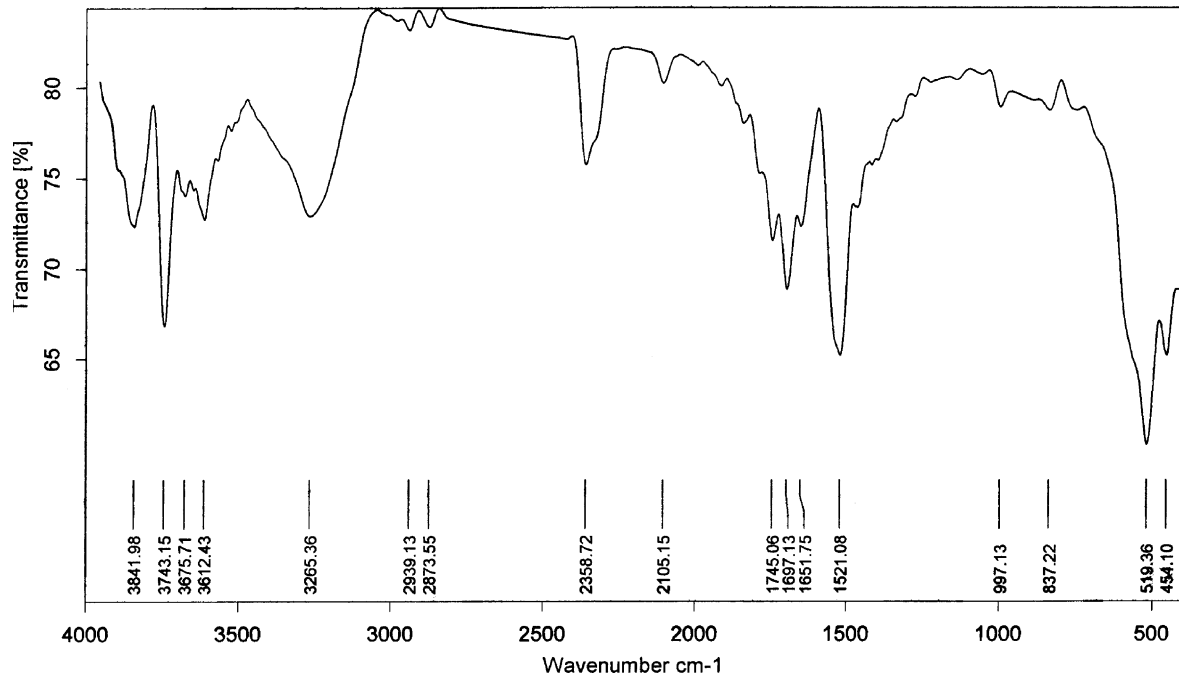


Fig. 13. TG-FTIR of DAAT.
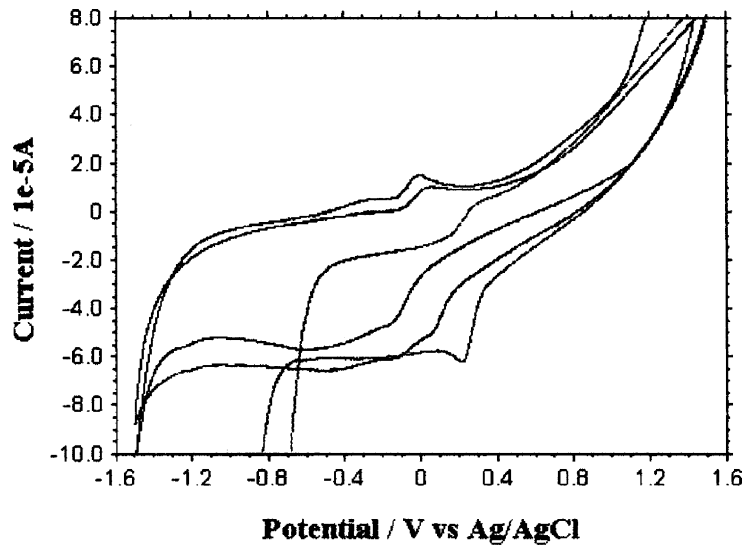
Fig. 14. TG-FTIR of DHTz.



Fig. 15. Cyclic voltammetric curve of DAAF.

Table 1
Theoretically predicted performance parameters of DAAF, DAAT and DHTz

| Property | DAAF | DAAT | DHTZ | NTO | TATB |
|---|---|---|---|---|---|
| Density (g/cm$^3$) | 1.74 | 1.84 | 1.69 | 1.93 | 1.93 |
| VOD (km/s) | 8.06 | 9.115 | 10.152 | 8.392 | 8.004 |
| CJ pressure (GPa) | 28.1 | 35.98 | 39.24 | 31.4 | 28 |
| CJ temperature (°K) | 2362 | 1322 | 974 | 1865 | 2108 |
| CJ volume (cc/g) | 0.43 | 0.415 | 0.458 | 0.409 | 0.421 |
| Heat of formation (kJ/mol) | +443.5 | +862 | +536 | −130 | −154 |

Table 2
Theoretically predicted performance parameters of DAAF in combination with other IHEs

| Explosive formulation | Density ($g/cm^3$) | Heat of formation (kcal/mol) | CJ pressure (kbar) | CJ VOD (km/s) | CJ temperature (°C) | CJ volume (cc/g) |
|---|---|---|---|---|---|---|
| DAAF/TATB (50:50) | 1.80 | 42.882 | 302 | 8.26 | 1816 | 0.418 |
| DAAF/TATB (25:75) | 1.86 | 6.452 | 322 | 8.42 | 1622 | 0.4049 |
| DAAF/TATB (75:25) | 1.80 | 75.913 | 307 | 8.3 | 1903 | 0.4173 |
| DAAF/DAAT (50:50) | 1.75 | 175.19 | 299 | 8.3 | 1910 | 0.4287 |
| DAAF/DAAT (25:75) | 1.79 | 210.76 | 332 | 8.71 | 1660 | 0.42157 |
| DAAF/DAAT (75:25) | 1.72 | 140.28 | 274 | 7.99 | 2106 | 0.4359 |
| DAAF/NTO (50:50) | 1.79 | 22.932 | 334 | 8.83 | 1354 | 0.4235 |
| DAAF/NTO (25:75) | 1.85 | −5.26 | 343 | 8.88 | 1159 | 0.4122 |
| DAAF/NTO (75:25) | 1.74 | 58.807 | 303 | 8.46 | 1691 | 0.4342 |
| DAAF/TEX (50:50) | 1.82 | 10.954 | 314 | 8.37 | 1870 | 0.4126 |
| DAAF/TEX (25:75) | 1.90 | −44.505 | 341 | 8.57 | 1665 | 0.3972 |
| DAAF/TEX (75:25) | 1.75 | 60.857 | 287 | 8.12 | 2045 | 0.4283 |
| DAAF/LAX-112 (50:50) | 1.77 | 66.221 | 326 | 8.69 | 1587 | 0.4259 |
| DAAF/LAX-112 (25:75) | 1.82 | 51.533 | 345 | 8.86 | 1391 | 0.4162 |
| DAAF/LAX-112 (75:25) | 1.73 | 84.011 | 296 | 8.34 | 1851 | 0.4354 |
| DAAF/LLM-105 (50:50) | 1.79 | 55.029 | 297 | 8.19 | 1929 | 0.4198 |
| DAAF/LLM-105 (25:75) | 1.85 | 29.186 | 319 | 8.39 | 1787 | 0.4079 |
| DAAF/LLM-105 (75:25) | 1.74 | 80.632 | 277 | 8.01 | 2062 | 0.4316 |

Table 3
Theoretically predicted performance parameters of DAAT in combination with other IHEs

| Explosive formulation | Density ($g/cm^3$) | Heat of formation (kcal/mol) | CJ pressure (kbar) | CJ VOD (km/s) | CJ temperature (°C) | CJ volume (cc/g) |
|---|---|---|---|---|---|---|
| DAAT/TATB (50:50) | 1.81 | 116.35 | 307 | 8.305 | 2090 | 0.416 |
| DAAT/TATB (25:75) | 1.87 | 42.9 | 324 | 8.434 | 1894 | 0.403 |
| DAAT/TATB (75:25) | 1.75 | 184.17 | 280 | 8.047 | 2261 | 0.430 |
| DAAT/NTO (50:50) | 1.81 | 72.242 | 343 | 8.970 | 1325 | 0.422 |
| DAAT/NTO (25:75) | 1.87 | 14.7 | 349 | 8.999 | 1194 | 0.412 |
| DAAT/NTO (75:25) | 1.75 | 146.72 | 337 | 9.009 | 1463 | 0.435 |
| DAAT/TEX (50:50) | 1.83 | 75.24 | 316 | 8.383 | 2068 | 0.412 |
| DAAT/TEX (25:75) | 1.91 | 22.36 | 337 | 8.543 | 1833 | 0.397 |
| DAAT/TEX (75:25) | 1.76 | 164.7 | 297 | 8.269 | 2200 | 0.427 |
| DAAT/LAX-112 (50:50) | 1.78 | 121.4 | 358 | 9.231 | 1388 | 0.430 |
| DAAT/LAX-112 (25:75) | 1.82 | 76.42 | 361 | 9.155 | 1380 | 0.420 |
| DAAT/LAX-112 (75:25) | 1.74 | 176.88 | 338 | 9.021 | 1570 | 0.438 |
| DAAT/LLM-105 (50:50) | 1.80 | 123.92 | 303 | 8.268 | 2147 | 0.419 |
| DAAT/LLM-105 (25:75) | 1.85 | 63.231 | 323 | 8.433 | 2028 | 0.407 |
| DAAT/LLM-105 (75:25) | 1.75 | 185.17 | 299 | 8.342 | 2095 | 0.432 |

Table 4
Theoretical performance prediction of DAAF, DAAT and DHTz as an energetic ingredient in rocket formulations

| Properties | DAAF | DAAT | DHTZ | Compound A | Compound B | Compound C |
|---|---|---|---|---|---|---|
| Flame temperature (chamber) (K) | 2569 | 2894 | 2222 | 2404 | 2180 | 1972 |
| Mean molecular weight | 23.56 | 27.43 | 20.36 | 22.6 | 21.21 | 19.73 |
| Characteristic velocity (m/s) | 1464 | 1474 | 1467 | 1423 | 1387 | 1367 |
| Specific impulse ($I_{sp}$) (s) | 232.9 | 241.8 | 234.7 | 225.9 | 221.1 | 219.4 |
| $I_{sp}$ in vacuum (s) | 250.2 | 261.9 | 252.4 | 242.6 | 238.8 | 237.5 |

Composition: nitrocellulose (nitrogen 12.2%): 20%; nitroglycerin: 31.2%; diethylphthalate: 8%; 2,4-dinitrophenyl amine: 0.8%; diaminoazoxy furazan: 40% (composition A)/diaminoazobistetrazine: 40% (composition B)/dihydrazinotetrazine: 40% (composition C).
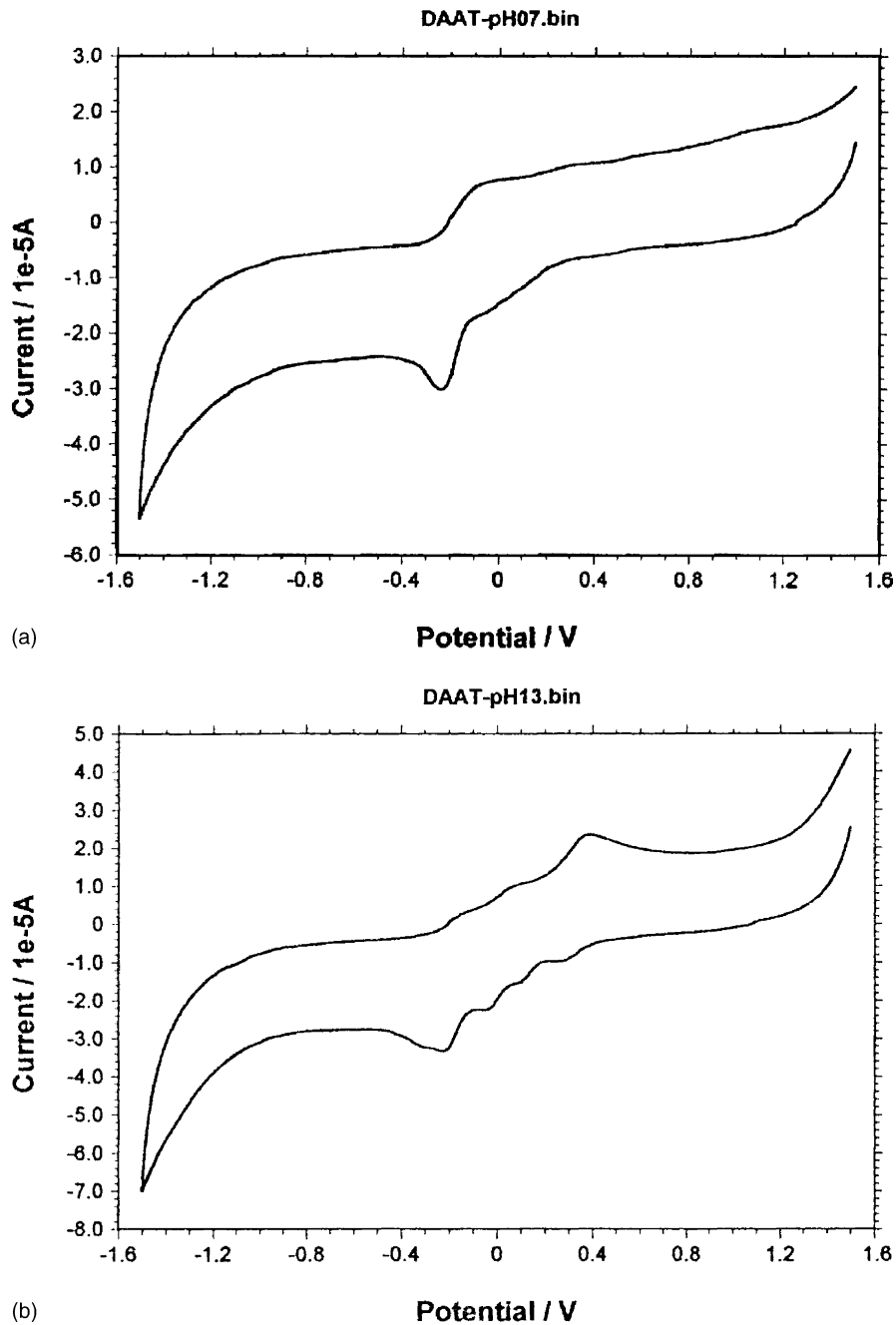
Fig. 16. (a) Cyclic voltammetric curve of DAAT at pH 7 and (b) cyclic voltammetric curve of DAAT at pH 13.

combinations with other IHEs (25%) reveals the following order of CJ temperature (Tables 2 and 3).

DAAF : LLM-105 > DAAF : TEX > DAAF : TATB

  > DAAF : LAX-12 > DAAF : NTO > DAAT : TATB

  > DAAT : TEX > DAAT : LLM-105.

    DAAT : LAX-112 > DAAT : NTO.

The theoretical performance evaluation of combination of DAAF (75%) and DAAT (25%) gave highest CJ temperature (2106 °C). The predicted data obtained in this work further supports the claims made by the US patent [9] about the potential of DAAF as an attractive additive for TATB based explosive formulations for obtaining high CJ temperature.

The theoretically predicted explosive performance parameters of DAAF and DAAT as well as their combination with modern insensitive high explosives showed velocity of detonation >8 km/s. Therefore these materials and their formulations falls under the category of high explosives.

The theoretical performance prediction of DAAF, DAAT and DHTz as an energetic ingredient in double base matrix was carried out using NASA-CEC-71 programme. The results obtained showed that these HEMs can find application

DHTZ-pH07.bin
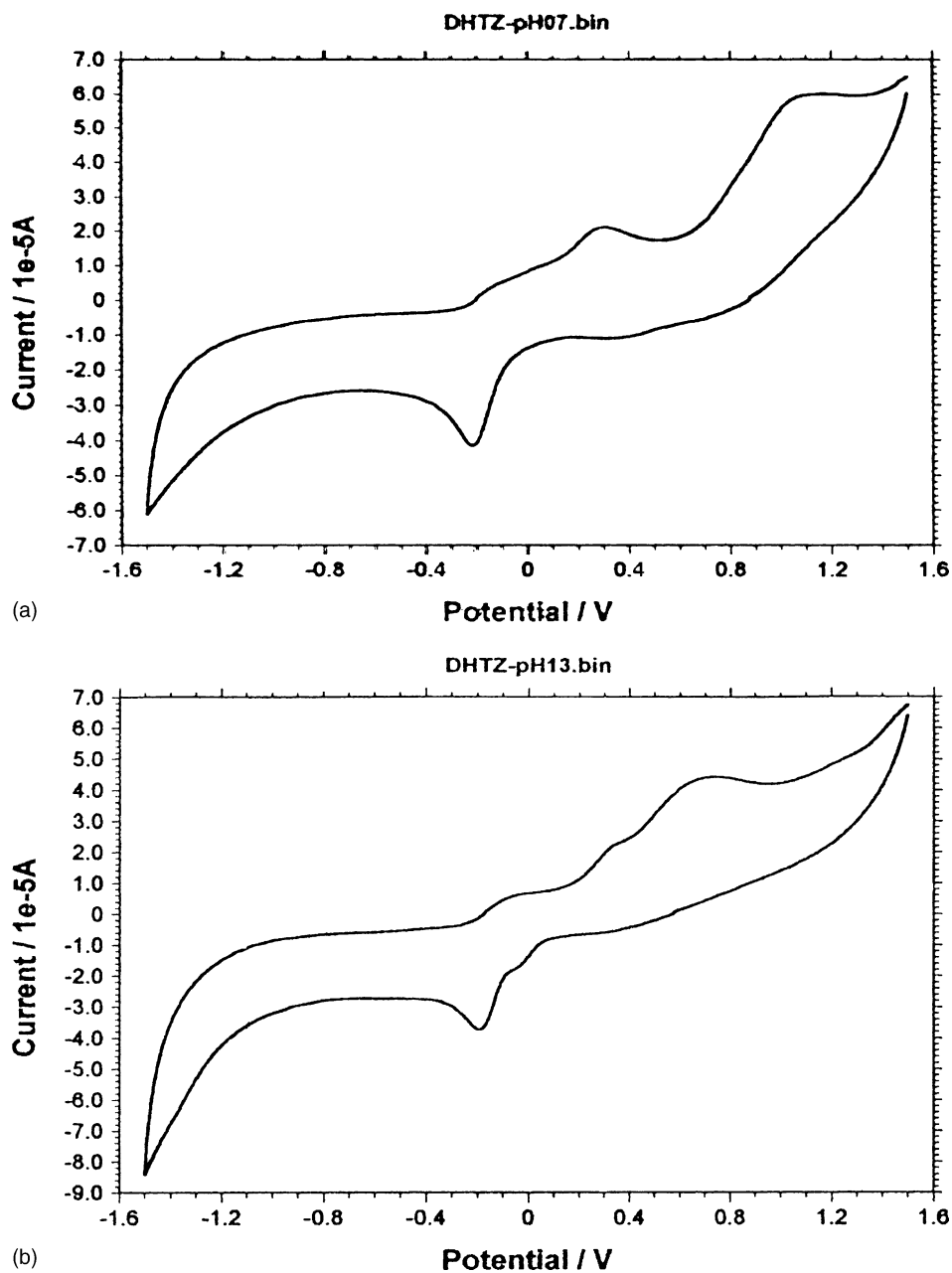


(a)

DHTZ-pH13.bin



(b)

Fig. 17. (a) Cyclic voltammetric curve of DHTz at pH 7 and (b) cyclic voltammetric curve of DHTz at pH 13.

as energetic additives for rocket propellants. DAAT gave higher specific impulse ($I_{sp}$, 261.9 s) and flame temperature (2894 K) in comparison to DAAF and DHTz (Table 4).

## 5. Conclusion

The synthesis of advanced HEMs—DAAF, DAAT and DHTz is established during this work. The compounds were characterized and results obtained were in agreement with the reported data establishing the formation of product by adopting the method described in this paper. The DSC and TG showed that DAAF and DAAT are thermally stable up to 230 and 250 °C, respectively, whereas DHTz showed thermal stability up to 140 °C. The gaseous products characterized during TG-FTIR studies indicate the presence of $NH_2CN/NH_3$ and HCN as major decomposition products in all the cases. The synthesized DAAF, DAAT and DHTz were found responsive to CV potential suggesting the possibility of application of this technique for monitoring environmental pollution and waste disposal. The preliminary theoretical performance computation of DAAF, DAAT and DHTz brings out their potential as an energetic additive for high explosive/rocket propellant formulations. The present work aims at the development of safer and cleaner HEMs for futuristic applications. The predicted performance data

indicates that these compounds fall under the category of UN hazard classification category 1.1.

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