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Synthesis, characterization and thermolysis studies on 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT): A key precursor in the synthesis of most powerful benchmark energetic materials (RDX/HMX) of today

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Abstract

This paper reports studies undertaken on 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT). The synthesis of DPT was carried out by the nitration of hexamine based on the lines of reported method with minor modification. DPT was characterized by elemental analysis, scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and ^{1}H nuclear magnetic resonance (NMR) techniques. Thermal stability of DPT was studied using thermogravimetry (TG) and differential scanning calorimetry (DSC). The thermal analysis studies revealed that DPT undergoes decomposition at 211 °C. Decomposition of DPT using TG-FTIR indicated the evolution of carbon dioxide, water and oxides of nitrogen as main gaseous products. The electrochemical behavior of DPT was studied using cyclic voltammetric (CV) studies. The experimentally determined sensitivity parameters indicated the insensitive nature of DPT towards external stimuli. The performance parameters of DPT, RDX and HMX have been computed using Linear Output Thermodynamic User Friendly Software for Energetic Systems (LOTUSES) code. The predicted properties of DPT are interesting and important from the point of process technology and/or safety. The work reported in this paper enriches the existing scanty research and development data on one of the key precursor used for synthesis of important high energy materials (HEMs).
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Keywords: 3,7-Dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT); HMX; Molecular orbital calculations; Thermal analysis; Energetic materials

1. Introduction

3,7-Dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT) is one of the most important key precursors in the production of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)/ hexahydro-1,3,5-trinitro 1,3,5-triazine (RDX). DPT is synthesized by modified Bachmann process and is considered as a limiting intermediate [1–3] in the synthesis of RDX and HMX. Recently, Vagenknecht and Zeman [4] reported the physico-chemical data and basic stability characteristics of the DPT.

The polymorphic forms of HMX are well reported in the literature [5]. The β polymorph of HMX is reported to exist in chair conformation while that of α, γ and δ phases exist in chair—chair conformation [6]. The similar kind of conformational arrangements in DPT has been reported by Oyumi et al. [7]. Differential thermal analysis (DTA) and variable temperature Fourier transform infrared (FTIR) studies were supported the interconvertible solid phase forms between 163 K and the decomposition point (460 K). However, it was noted that preliminary differential scanning calorimetry (DSC) studies showed the absence of solid–solid phase transitions. The understanding of the relation between the structure and decomposition mechanism in energetic materials is complex due to simultaneous formation of several decomposition reactions.

HMX is a powerful military explosive, but its use has been limited by its high cost. Reported manufacturing process for HMX involves the nitration of hexamine. It is known that HMX can be prepared from DPT, and indeed DPT has been identified as a key intermediate in the formation of HMX from the nitration of hexamine, which is also known as the modified Bachmann process [1]. In view of the vital importance of DPT in synthesis of

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HMX, a low cost method for producing this intermediate would certainly add significant contribution toward reducing cost of HMX during its production. It was reported that the nitration of DPT gives 75% of HMX [3,8].

In view of the above observations and our continued interest in the area of high energy materials (HEMs) [9], we report here the studies carried out on DPT in our laboratory. The data generated during this work will enrich the existing scanty scientific data on one of the most sought after HEMs precursor (DPT). The present study was also undertaken to understand the various characteristic properties of DPT such as thermal stability, sensitivity to external stimuli and its electrochemical nature.

2. Experimental

2.1. Materials and methods

The starting materials used in the present study were of analytical grade (AR) grade and used directly as purchased from the trade. Melting point of the synthesized compound was measured using Thomas Hoover capillary melting point apparatus. Elemental analysis was carried out using Perkin-Elmer instrument (model 240C). The purity of DPT was ensured by high performance liquid chromatography (HPLC) (Waters Alliance HPLC system) with reverse phase micro C18 column. The eluent used was the mixture of acetonitrile, methanol and water (5:35:60) with the flow rate 1 ml/min. The IR spectrum was recorded on Perkin-Elmer FTIR-1600 spectrophotometer in KBr matrix and ^{1}H NMR spectrum was scanned on a 300 MHz Varian instrument in deuterated chloroform at 30 °C using trimethyl silane (TMS) as an internal standard. The DSC studies were undertaken on a Perkin-Elmer DSC-7 instrument at the heating rate of 10 °C/min. Differential scanning calorimeter was calibrated using indium and zinc standards and baseline corrections were also performed. Experiments were carried out in nitrogen atmosphere (nitrogen flow rate is 40 ml/min). The thermal decomposition studies were also undertaken on simultaneous thermo gravimetric/differential thermal analyzer of Mettler Toledo (model 8551). Thermo gravimetric Fourier transform infrared (TG-FTIR) studies on DPT was carried out using Bruker (EQUINOX-55) instrument. Mass spectra were obtained with Waters Micromass-Q-Tof micro (YA105) spectrometer using electro spray ionization (ESI) method. Electro spray ionization is the method of choice for analyzing thermo labile compounds using mass spectrometer. This method uses and electrical stress between the ESI probe exit (e.g. capillary) and the counter electrode (located few millimeters from the probe). This process results in the generation of highly charged droplets directly from the infused solution. The formation of positive or negative ions occurs in high yield. In the positive ion mode protonated and/or alkali adduct analyte molecules are generally observed in the mass spectra. Cyclic voltammetric studies were carried in acetonitrile solvent using a CHI-620A electrochemical analyzer. 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 [10]. 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 recorded using Scanning Electron Microscope (SEM) Instrument of Philips (FEI XL-30 model). The performance parameters of the synthesized compounds were predicted using Linear Output Thermodynamic User Friendly Software for Energetic Systems (LOTUSES) code [11]. Geometrical parameters were calculated using Gaussian'03 package [12]. Semi-empirical molecular orbital calculation at parametric model 3 (PM3) level has been performed to optimize the geometry of the molecule.

2.2. Synthesis of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT)

The DPT was synthesized based on the lines of modified Bachmann route [3]. In a five necked round bottomed flask equipped with stirring assembly, 150 ml of glacial acetic acid, 15 ml of acetic anhydride and 2 g of para formaldehyde were taken. The flask with the stirrer assembly was kept in a water bath. The temperature of the bath maintained at 44 ± 1 °C. Solution A consisting of 50 g of hexamine dissolved in 80 ml of glacial acetic acid and solution B consisting of 43.2 g of ammonium nitrate dissolved in 32 ml of 98% nitric acid were prepared. Solution A, B and 150 ml of acetic anhydride were added simultaneously to the reaction flask with the help of pre-calibrated peristaltic pumps over a period of 15 min. After the complete addition of the above reactants, the reaction was quenched by stirring the mixture for 15 min at a temperature of 44 ± 1 °C. The reaction mass was filtered immediately and the solid obtained was washed repeatedly with water and then dried. The yield obtained was 72% (57 g). The synthesized DPT was purified by recrystallising in nitromethane solvent, dried and characterized; melting point (MP): 203–206 °C; HPLC: retention time; 3.29 min (wavelength of 254 nm); IR: 3031, 2974, 2937, 2880, 1602, 1524, 1456, 1289, 1207, 1077, 935, 816 and 780 cm^{-1}; ^{1}H NMR (δ, ppm) = 4.1 (2H, singlet); 5.7, 4.8 (8H, AB quartet).

Table 1
Nitration of hexamine to DPT

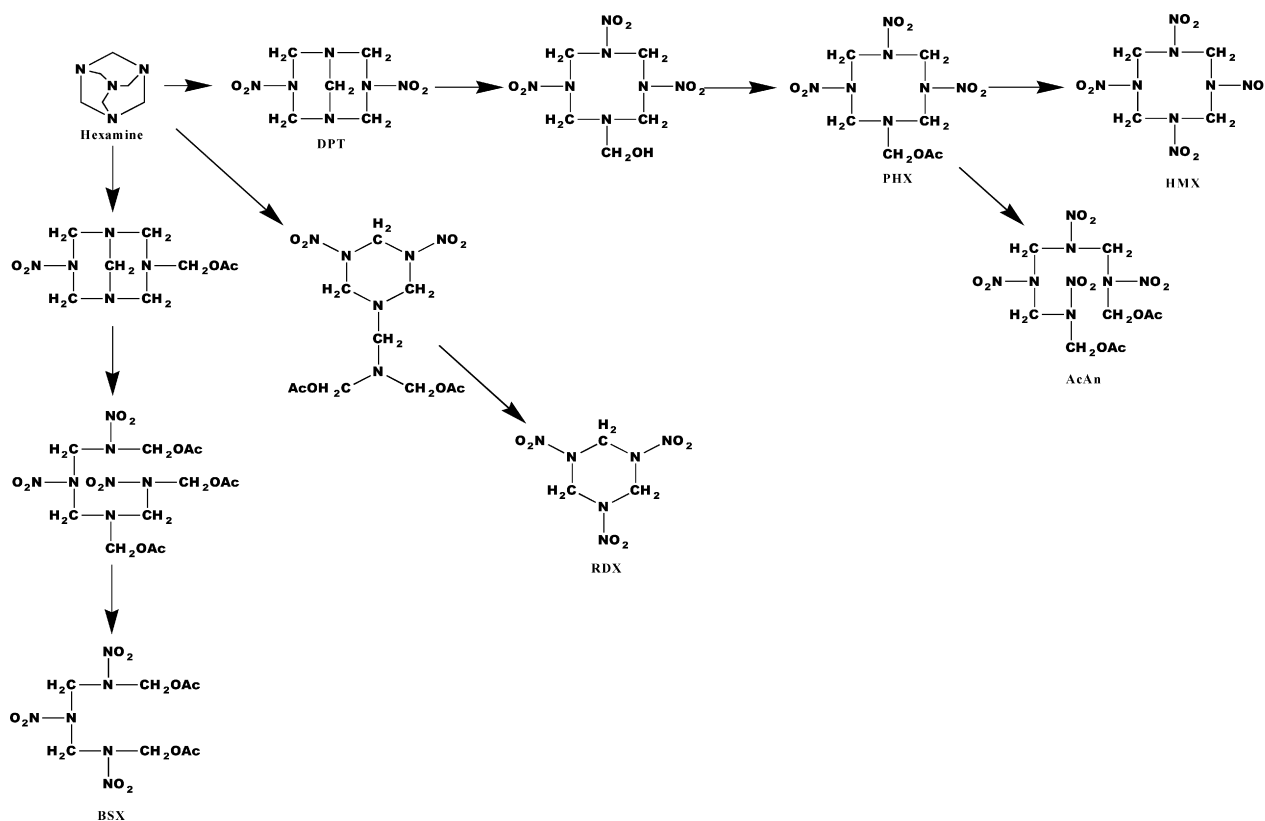| Hexamine (g)	Hex/AcOH solution volume (ml)	Ac$_2$O (ml)	HNO$_3$/NH$_4$NO$_3$ solution (1:0.93 wt ratio) (ml)	DPT (g)	Percent conversion
50.17	485	150	60	55	70.3
50.69	490	150	60	58	73.4
50.59	489	154	60	57	72.3

Fig. 1. Nitration of hexamine.

The nitration experiments data for some of the selective batches is given in the Table 1.

3. Results and discussion

The nitration of hexamethylene tetramine by the modified Bachmann process gives two fundamentally different types of cleavage (Fig. 1), viz. (a) compounds containing three amino nitrogen atoms such as RDX and the linear trinitramine namely, 1,7-diacetoxy-2,4,6-triazaheptane and (b) compounds with four amino nitrogen atoms as DPT, HMX and the linear tetranitramine namely, 1,9-diacetoxy-2,4,6,8-tetrazanonane. The first type of cleavage is favored by high acidity and/or high activity of nitrating agent at higher temperature. The second type of cleavage occurs under conditions of low acidity and/of low activity of the nitrating agent at relatively low temperature, particularly in the initial reaction with the hexamine [3]. The molecular structure of DPT contains an adamantane ring system and is synthesized from hexamethylene tetramine.

The stoichiometric formula of the compound was ascertained by the elemental analysis. The experimentally obtained carbon, hydrogen and nitrogen contents are in close agreement with the theoretically calculated values. The chromatogram of the DPT (Fig. 2) showed the presence of single peak at retention time 3.29 min was found. The DPT showed the IR frequencies (Fig. 3) at 1602 and 1524 cm^{-1} corresponds to asymmetric stretching vibrations of nitro group and symmetric stretching vibrations observed in 1289 cm^{-1}. IR absorptions at 3031, 2974, 2937

and 2880 cm^{-1} assignable to asymmetric and symmetric vibrations of methylene groups of DPT. The ^{1}H NMR (Fig. 4) of DPT showed singlet ($\delta = 4.1$ ppm) for the methylene bridge protons and AB quartets arising from the inequivalence of the axial and equatorial protons for the ring methylene group. The data obtained in the present study is in close agreement with the reported data [13]. The singlet attributed to the bridge protons is usually broadened due to long range coupling with the equatorial protons of the ring methylene groups. The low field portions of the AB quartets are attributed to the equatorial protons.

The mass spectrum of DPT (Fig. 5) exhibited [M+H]$^+$ and [M+Na]$^+$ peaks at 219 and 241, respectively. The [M+H]$^+$ is in high abundance and fragmentation pattern also includes strong
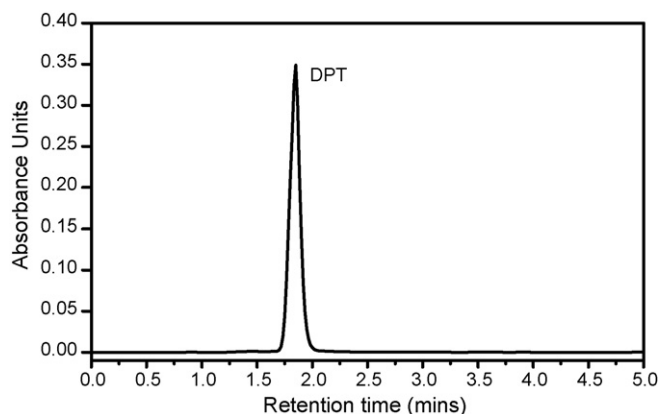

Fig. 2. Chromatogram of DPT.
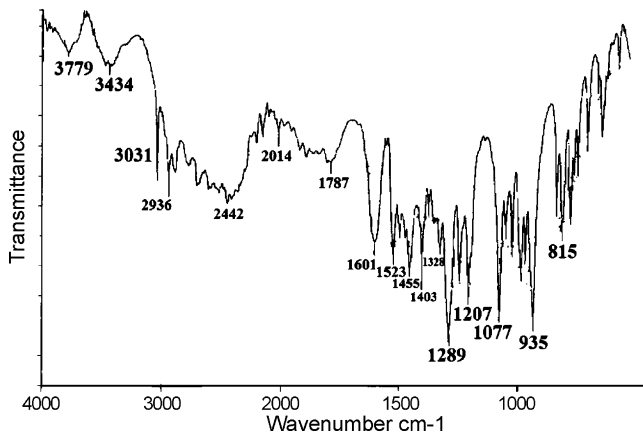
Fig. 3. Fourier transform infrared spectra of DPT.
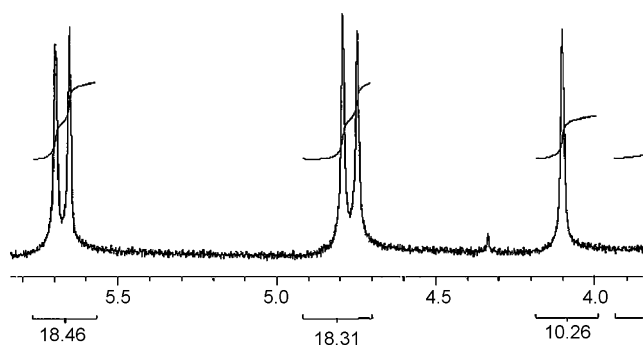
Fig. 4. ^{1}H NMR of DPT.

peaks at 71 and 145. Loss of N–NO$_2$ group results in the formation of mass/charge (m/z) ratio of 158. DPT underwent ionization quite well in electro spray technique and exhibited charge state [M+H]$^+$ making interpretation fairly straightforward. The ESI method of detection in mass spectral studies avoids the small fragments unlike other conventional detection techniques.

The surface morphology studies of DPT showed the presence of hexagonal type (Fig. 6) crystal morphology. The average particle length and width of DPT crystals found was 49 and 6.5 μm, respectively. The structural morphology of the crystals plays an important role in the safety of the chemical process.
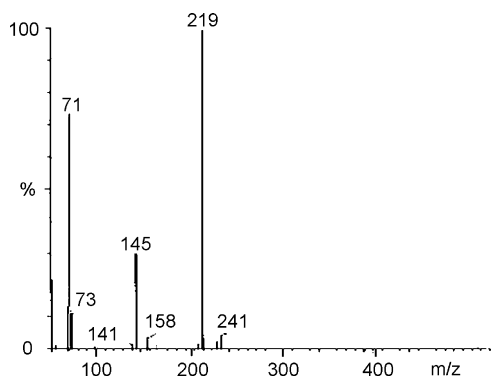
Fig. 5. Mass spectrum of DPT.
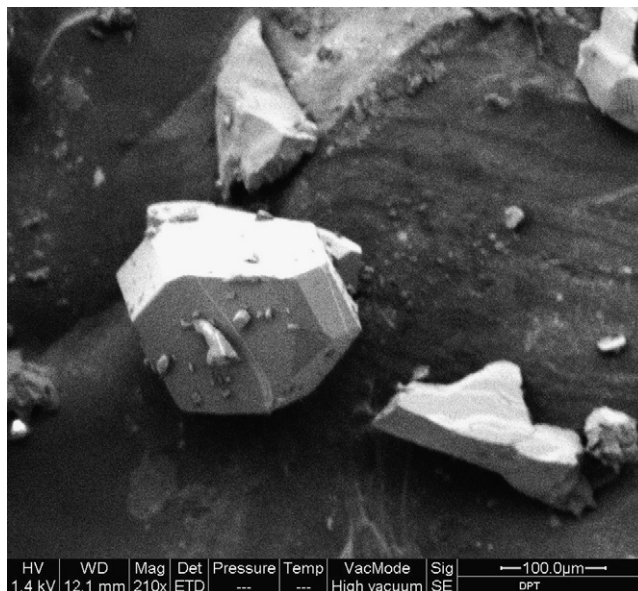
Fig. 6. Scanning electron micrograph of DPT.
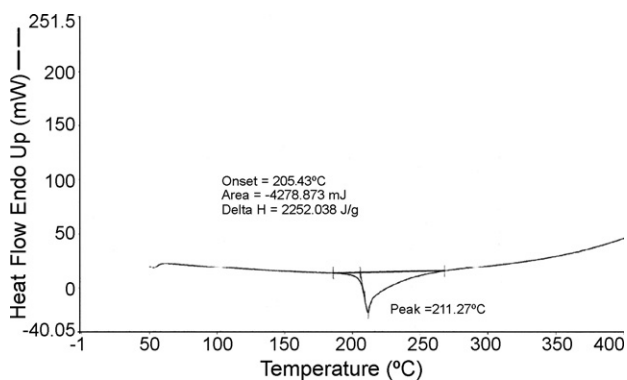
Fig. 7. DSC of DPT.

4. Thermal studies

The DSC of DPT showed exothermic decomposition (Fig. 7) with T_{max} at 211 °C and heat release of the order of 2.84 KJ/g. The TG thermogram for DPT (Fig. 8) revealed the initial decomposition temperature (IDT) temperature at 142 °C and it underwent maximum decomposition at 220 °C.

Fig. 8. Thermogram of DPT.

Table 2
Effect of structure on the level of degradation at different temperatures

Temperature (K)	Weight loss (%)	E_a (KJ mol^{-1})
400–451	12.46	17.33
451–488	37.83	18.77
488–517	40.14	20.15
517–522	8.38	21.71
522–667	1.08	16.16
667–675	0.01	26.15

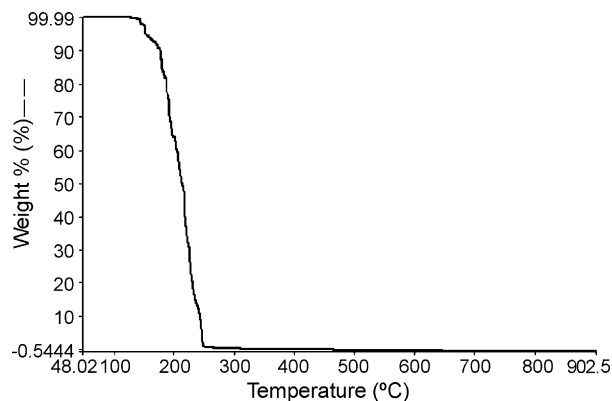Integral procedural decomposition temperature (IPDT) of DPT has been determined based on the concept of Doyle [14,15] to study the thermal stability of DPT. The integral procedural decomposition temperature was derived as a means of summing up the whole shape of the normalized data curve. The calculated value was 184 °C and IPDT is a reproducible datum having practical significance as an integrated half-volatilization temperature. The extracted degradation information of DPT from thermograms is presented in Table 2. The table shows the temperature at which 20, 40, 60, 80 and 100% loss occurs. The 100% decomposition occurs at about 400 °C.

In order to understand, the kinetics of degradation at different stages, a logarithmic relation of concentration was plotted against inverse of temperature (1/T). At every stage of degradation, the percentage weight loss was computed. The activation energy for the different stages of degradation was calculated for DPT using the Doyle equation [16].

$$\ln(1 - C) = -2.315 \left(\frac{A}{B} \right) + 0.4567 \left(\frac{A}{B} \right) \left(\frac{E}{R} \right) \left(\frac{1}{T} \right)$$

where C is concentration of the DPT that remains after degradation at temperature, T, R the universal gas constant, and A and B are constants. Energy of activation was calculated from the slope obtained from the plot of $\ln(1 - C)$ against $(1000/T)$. The calculated energy of activation for different degradation stages is presented in Table 2. DPT undergoes multistage stage degradation and the major loss falls (450–500 K) in the second and third step. The activation energy found to be high (26 KJ/mol) for the final stage. The obtained activation energy was comparable (∼20 KJ/mol) for third and fourth steps and found low (16 KJ/mol) for the fifth step.

Thermal decomposition study on DPT was further investigated by analyzing its decomposed products using TG-FTIR technique. The FTIR profile of decomposition products at different time intervals is shown in Fig. 9. The representative spectrum (a–e) in Fig. 9 corresponds to furnace temperature 80, 130, 180, 230 and 280 °C, respectively. The hyphenated TG-FTIR studies of DPT revealed the evolution of gases containing species such as –CN (2358 cm^{-1}), –NH$_2$ (3743 cm^{-1}), –OH (3258 cm^{-1}) species and the oxides of nitrogen.

The experimentally determined sensitivity test results of DPT indicated its impact insensitive [$h_{50\%}$ explosion, 43 cm] and friction insensitive [up to load of >36 kg] nature. These trends suggest its overall low vulnerability to mechanical stimuli compared to that of other nitramine explosives such as RDX and HMX (friction insensitive up to 16 and 19 kg, respectively).

Time intervals : (a) 5 min   (b) 10 min   (c) 15 min   (d) 20 min   (e) 25 min
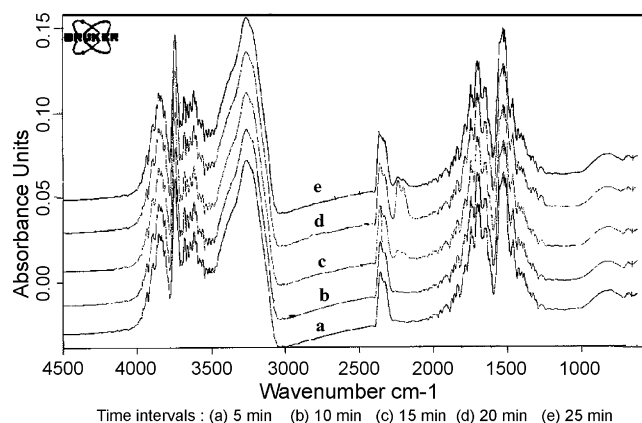
Fig. 9. TG-FTIR spectrums of DPT at various time intervals.

Therefore, appropriate safety measures must be observed during DPT utilization for the synthesis of powerful energetic materials such as RDX and HMX.

Cyclic voltammetric study on DPT was performed at the scan rate of 0.1 V/s in neutral medium (Fig. 10). The CV studies on DPT at pH 7 showed a reduction peak at a potential of −0.8 V. In addition, a weak reduction peak also appeared at 0.3 V. The reduction peaks may be due to the formation of intermediates during the course of reduction of DPT [–NO$_2$ to –NH$_2$]. This observation suggests that DPT undergoes electrochemical redox reaction at pH 7. The results indicate the electro active nature of DPT. Thus, CV technique may be used to develop detection method for monitoring environment pollution as well as waste disposal.

5. Molecular orbital calculations

The present study also involves molecular orbital calculation of DPT in order to optimize the geometry using semi-empirical PM3 method. Optimized geometry was confirmed by the frequency calculations, which exhibited zero imaginary frequency. The optimized geometry of DPT (with general numbering of the different atoms in the molecule) is shown in Fig. 11. The calculated gas phase heat of formation of DPT was +159.1 KJ/mol. The molecular structure of DPT optimized by the PM3 method has been compared with the crystal structure elucidated from X-ray diffraction data [17]. In general, the computed geometri-

Fig. 10. Cyclic voltammogram of DPT.

Fig. 11. PM3 optimized geometry of DPT.

Fig. 12. Bond length and bond angle data of DPT.

Table 3
Bond length obtained from PM3 calculations

Atoms	Bond length (A°)	Atoms	Bond length (A°)	Atoms	Bond length (A°)
R(1,2)	1.514	R(4,6)	1.484	R(7,23)	1.111
R(1,3)	1.514	R(4,15)	1.492	R(8,9)	1.470
R(1,12)	1.470	R(5,7)	1.484	R(9,10)	1.206
R(2,5)	1.484	R(5,15)	1.492	R(9,11)	1.207
R(2,16)	1.110	R(6,8)	1.514	R(12,13)	1.206
R(2,17)	1.111	R(6,20)	1.111	R(12,14)	1.207
R(3,4)	1.484	R(6,21)	1.110	R(15,24)	1.109
R(3,18)	1.111	R(7,8)	1.514	R(15,25)	1.109
R(3,19)	1.110	R(7,22)	1.110		

Table 4
Bond angle obtained from PM3 calculations

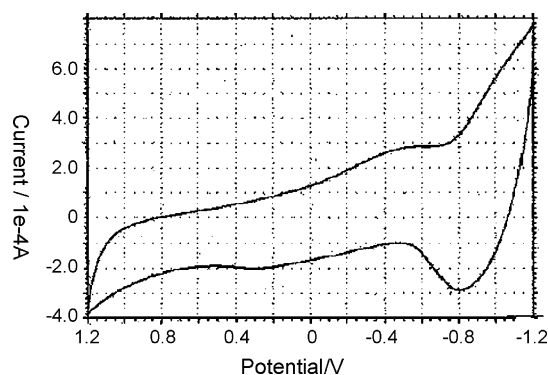| Atoms	Angle	Atoms	Angle	Atoms	Angle
A(2,1,3)	115.7	A(3,4,15)	110.8	A(22,7,23)	108.3
A(2,1,12)	118.1	A(6,4,15)	110.8	A(6,8,7)	115.7
A(3,1,12)	118.1	A(2,5,7)	116.0	A(6,8,9)	118.1
A(1,2,5)	111.4	A(2,5,15)	110.8	A(7,8,9)	118.1
A(1,2,16)	109.5	A(7,5,15)	110.8	A(8,9,10)	116.8
A(1,2,17)	110.9	A(4,6,8)	111.4	A(8,9,11)	116.8
A(5,2,16)	109.1	A(4,6,20)	107.6	A(10,9,11)	126.5
A(5,2,17)	107.6	A(4,6,21)	109.1	A(1,12,13)	116.8
A(16,2,17)	108.3	A(8,6,20)	110.9	A(1,12,14)	116.8
A(1,3,4)	111.4	A(8,6,21)	109.5	A(13,12,14)	126.5
A(1,3,18)	110.9	A(20,6,21)	108.3	A(4,15,5)	107.4
A(1,3,19)	109.5	A(5,7,8)	111.4	A(4,15,24)	110.6
A(4,3,18)	107.6	A(5,7,22)	109.2	A(4,15,25)	110.6
A(4,3,19)	109.2	A(5,7,23)	107.6	A(5,15,24)	110.6
A(18,3,19)	108.3	A(8,7,22)	109.5	A(5,15,25)	110.6
A(3,4,6)	116.0	A(8,7,23)	110.9	A(24,15,25)	107.1

cal parameters overlap with experimental X-ray diffraction data. The optimized geometry of DPT and the computed bond length and bond angle observed from PM3 calculation are shown in Fig. 12. Analysis of the bond length shows that PM3 over estimates bond lengths in general except N–O bond lengths. In the case of bond angle, O–N–O bond angle is overestimated by about 2° while bridged N–C–N angle is underestimated by 3°. The computed values from theoretical method are in gaseous phase,

while the experimental X-ray diffraction values were obtained in solid phase. Hence the deviations in the computed values from experimental data may be attributed to packing effects in solid phase. In addition, electron correlation and basis set employed in the calculations would also influence structural parameters. The complete bond length, bond angle and dihedral angle are given in Tables 3–5. Dipole moment of DPT was estimated to be 5.46 Debye using PM3 calculations.

Table 5
Dihedral angle obtained from PM3 calculations

Atoms	Dihedral angle	Atoms	Dihedral angle	Atoms	Dihedral angle
D(3,1,2,5)	43.1	D(1,3,4,6)	−73.6	D(2,5,15,4)	65.1
D(3,1,2,16)	163.9	D(1,3,4,15)	53.9	D(2,5,15,24)	−55.6
D(12,1,2,5)	−168.7	D(18,3,4,6)	164.7	D(7,5,15,4)	−65.1
D(2,1,3,4)	−43.1	D(3,4,6,8)	73.6	D(4,6,8,7)	43.1
D(2,1,3,18)	76.7	D(3,4,6,20)	−164.7	D(4,6,8,9)	−168.7
D(12,1,3,4)	168.7	D(15,4,6,8)	−53.9	D(20,6,8,7)	−76.7
D(2,1,12,13)	16.9	D(3,4,15,5)	−65.1	D(5,7,8,6)	−43.1
D(2,1,12,14)	−164.2	D(3,4,15,24)	55.6	D(5,7,8,9)	168.7
D(3,1,12,13)	164.3	D(6,4,15,5)	65.1	D(22,7,8,6)	−163.9
D(1,2,5,7)	73.6	D(2,5,7,8)	−73.6	D(6,8,9,10)	16.9
D(1,2,5,15)	−53.9	D(2,5,7,22)	47.5	D(6,8,9,11)	−164.2
D(16,2,5,7)	−47.5	D(15,5,7,8)	53.9	D(7,8,9,10)	164.3

Table 6
Theoretically predicted performance properties of DPT using LOTUSES code.

HEM	MW	Elemental composition (%)				OB (%)	ρ g cm^{-3}	ΔH_f kcal/mol	DF	VOD km/s	CJ P (GPa)	RS (%)	SI (db)	HOE kJ/kg	PI (%)	ET (K)	VDP (J/kg)
		C	H	N	O												
DPT $C_5H_{10}N_6O_4$	218	27.53	4.62	38.52	29.33	−80.66	1.68	−18.14	4.0	6.81	20.35	85	282	1702	89	2000	1408
Nitroso DPT $C_5H_{10}N_6O_2$	186	32.26	5.41	45.14	17.19	−111.7	1.52	53.60	2.9	4.89	9.70	141	192	2405	147	2200	1649
RDX $C_3H_6N_6O_6$	222	16.22	2.72	37.84	43.21	−21.61	1.81	+71	5.17	8.93	36.48	174	353	5098	181	4400	957
HMX $C_4H_8N_8O_8$	296	16.22	2.72	37.84	43.21	−21.61	1.91	+87	5.23	9.04	39.49	173	355	5073	180	4400	957

OB: oxygen balance; ρ: density; ΔH_f: enthalpy of formation; DF: detonation factor; VOD: velocity of detonation; CJ P: C-J pressure; RS: relative strength; SI: sound intensity; HOE: heat of explosion; PI: power index; ET: explosion temperature; VDP: volume of detonated products.

6. Theoretical performance

The performance parameters of DPT theoretically predicted by applying Linear Output Thermodynamic User Friendly Software for Energetic Systems code are given in Table 6. The theoretically predicted velocity of detonation (VOD), relative strength (RS) and sound intensity (SI) of DPT was found superior in comparison to its nitroso derivative. This study warrants the further in depth studies on the experimental determination of velocity of detonation and other parameters to confirm the performance of the material synthesized in the present study.

7. Conclusions

The work reports the synthesis, characterization, thermolysis and theoretical performance evaluation of one of the most sought after key precursor (DPT) in the area of high energy materials synthesis. The DPT is an important and key synthon for the synthesis of two most widely used benchmark military explosives namely RDX and HMX. The data presented in the present work not only enriches the existing scanty data on DPT but also gives an insight into its possible thermal decomposition mechanism. The work reported in this paper warrants further in depth studies on DPT in terms of its performance parameters, which is interesting and important from the point of safety during its use as an intermediate for the synthesis of RDX and HMX.

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