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SYNTHESIS AND CHARACTERIZATION OF DINITRO PENTAMETHYLENE TETRAMINE (DPT)

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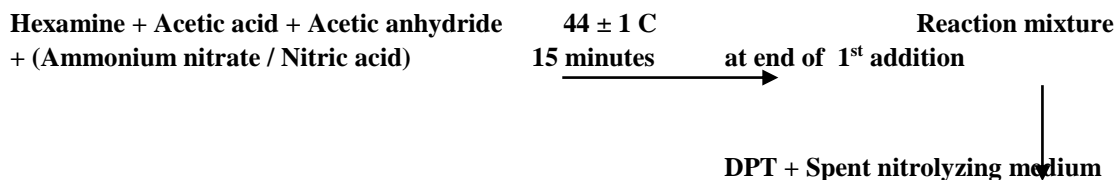
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Abstract--- Preparation of dinitro pentamethylene tetramine (DPT) through the action of nitrating mixture formed of ammonium nitrate and fuming nitric acid on hexamine in presence of acetic acid, acetic anhydride and p-formaldehyde has been carried out. DPT was also prepared from hexamine dinitrate which is an important intermediate appears through preparation of DPT from hexamine directly. Prepared DPT was purified and then characterized through the determination of melting point, element test, FTIR spectrometry, UV spectrometry, and high performance liquid chromatography "HPLC". The obtained results were reliable and consistent with the literature.

Key Words--- Energetic Materials, Hexamine, DPT, Hexamine dinitrate, Preparation, Characterization, Analysis techniques

1. INTRODUCTION

Design of future defense systems requires the use of energetic material formulations having enhanced performance (energy output) and reduced vulnerability during manufacturing, handling, storage and transportation. Several important design considerations for such formulations include improved mechanical properties, extended service life and reduced environmental impact in manufacture, use and disposal [1]. Energetic materials are substances or mixtures that react chemically to release energy required for their intended application. Bachmann and Sheehan [2] developed a method of preparing DPT. This method involved nitrolysis of hexamine with ammonium nitrate – nitric acid solution and acetic anhydride. The steps of the formation of DPT can be presented according to the following scheme:-[3,4,5]



II. EXPERIMENTAL WORK

Samples were prepared and filtered in a fuming cupboard provided with glass shelter and air suction system for ventilation. Safety regulations have been strictly applied. The preparation setup consisted of a flat-bottom 0.5L flask equipped with a mechanical stirrer, three dropping funnels, and a thermometer. Filtration of the prepared samples was done using Buchner funnel - pump system.

Preparation of hexamine dinitrate

Hexamethylene dinitrate ("hexamine" dinitrate) is an important intermediate in the pathway of preparation of DPT (Dinitro–Pentamethylene–Tetramine). Its preparation [6,7] involved the addition of a solution of hexamine (10g, 0.07mol) in distilled water (17.5ml, 0.972mol) drop by drop to nitric acid (specific gravity =1.4, 11.75ml, 0.261mol) already present in the above-mentioned setup. The reaction temperature was fixed at 15 °C; and the rate of hexamine solution addition was controlled to meet this condition. Finally, the mixture was cooled to 5 °C and Hexamine dinitrate was separated from the reaction mixture using a vacuum pump and dried in a vacuum oven.

Preparation of DPT

Preparation of DPT from hexamine

DPT is an important energetic material [8,9,10]. This preparation was effected by the introduction of a mixture of p- formaldehyde (0.566g, 0.0188mol), glacial acetic acid (25ml, 0.437 mol) and acetic anhydride (0.4ml, 0.0042 mol) into the reaction flask.

The following reagents were added simultaneously at controlled rates over a fifteen minutes period, a solution of hexamine (3.366g, 0.024 mol) in glacial acetic acid (5.248 ml, 0.0917 mol), acetic anhydride (10 ml, 0.106 ml), and a solution of ammonium nitrate (2.9g, 0.036 mol) in nitric acid (2ml, 0.0476 mol conc. 99% or more). The reaction temperature was maintained at 44 ± 1 °C throughout this procedure. The mixture was left for an additional 15 minutes. The reaction mixture was then quenched by chilling it to 12 °C. Rapid separation of the solid phase by filtration was then carried out.

Preparation of DPT from hexamine dinitrate

DPT was also prepared starting from the hexamine dinitrate. To a mixture formed of glacial acetic acid (5ml, 0.0874mol) and acetic anhydride (2ml, 0.0212mol), hexamine dinitrate (1g, 0.00375mol) was added as one portion. Then the reaction mixture was left, for a fifteen minute period, at a temperature of (44 ± 1) °C which was also maintained throughout this procedure. The reaction mixture was then quenched by chilling it to 12 °C. Rapid separation of the solid phase was then carried out.

Characterization of prepared samples

Melting point determination

An "IA – 9100 series" Digital melting point apparatus was used to measure the melting point of both the standard and the prepared samples. Small amount of the perfectly dried material was inserted in a capillary tube and placed into the metallic block which is equipped with a glass window and a digital monitor for displaying the temperature. For each substance, three consecutive trials were performed and the average value was calculated [40].

III. ELEMENTAL ANALYSIS

Carbon, hydrogen and nitrogen were determined using a Perkin-Elmer 2400, CHN elemental analyzer equipped with AD-4 auto balance. Aluminum capsules of special design were used. In these capsules, the samples were decomposed in presence of oxygen at a temperature of 950 °C. The mentioned elements were converted into their stable oxides. The combustion tubes contained chemicals which can absorb the interfering products; while the remaining products like carbon dioxide, water, nitrogen oxides and residual oxygen were transferred by means of a stream of helium to the reduction stage. The reduction tube was packed with copper and it was maintained at a temperature of 670 °C, in which nitrogen oxides were reduced [41]. The remaining gaseous products (water and carbon dioxide) were not reduced but transferred to the stage of absorption. The percentage of carbon, hydrogen, and nitrogen could therefore be recorded precisely.

FTIR spectrometry

FTIR is one of the most powerful identification spectroscopic techniques. The IR spectrum acts as a fingerprint for each structure. No two compounds have the same IR spectrum. This technique is used in qualitative analysis and identification of most commonly used explosives. A Shimadzu 8100 series FTIR spectrophotometer was used to obtain the FTIR spectrum for the prepared samples. The solid sample (2 mg) and the dry KBr (350 mg) were ground, mixed and pressed in the form of a standard disc using an E-Z press (12 ton).

The selected wave number range used was 400– 4000 cm^{-1} (appropriate range for most organic compounds). The IR-spectrum was also obtained for pure KBr for calibration of the instrument. The selected FTIR operating conditions were as follows:-

Measuring mode: Transmission T %, Resolution: 4.0 cm^{-1} , Detector: standard, Range: 4000:400 cm^{-1} , Number of scans: 40, and Aperture: auto.

UV spectrometry

UV spectroscopy is one of the most suitable methods in quantitative analysis especially for dilute solutions. UV detectors are commonly employed in most chromatographic systems. A Shimadzu UV-vis spectrometer double beam, UV-1700 has been used to run spectroscopic analysis of the prepared hexamine dinitrate and DPT by measuring its wave length at maximum absorption. The selected operating conditions were: Wavelength range: from 600 to 190 nm, Scan speed: medium, Sampling interval: 1 nm, and Measuring mode: absorbance.

High performance liquid chromatography

High performance liquid chromatography (HPLC) technique can be used as a qualitative and quantitative method of identification of explosives and other organic substances through the retention time and the peak area. HPLC can also be employed not only for separation but also for identification, by comparing the retention time of the unknown compound to that of a known one (standard) under the same operating conditions. The instrument in this work was Agilent 1100 series HPLC instrument. The column was Zorbax elipse (XDB-C8, analytical 4.6x150mm, 5-micron) the working temperature was 28 °C. The mobile phase was 30 % ACN – 70 % water (HPLC grade). The UV detector was tuned at 220 nm. The flow rate was 0.5 ml/min., cover a period of 25 minutes, and the injection volume was 3 ml. Many trials have been done to obtain chromatograms separated with high resolution. The mentioned operating conditions were used and separation was done perfectly except that of hexamine and hexamine dinitrate. It was difficult to separate them with high resolution since interference took place nearly at the same retention time.

IV. RESULTS

Yield of prepared compounds

Yield of the hexamine dinitrate

Characteristics of the maximum obtainable hexamine dinitrate were found and given in Tables shown below. Starting by 10g of hexamine; about 17g of dry hexamine dinitrate was obtained. The average yield was therefore about 89% .The yield; according to the published data is about 95 % [11]. Solubility of a small fraction of the product in the spent acid may be the main reason of the disagreement.

Yield of the DPT

Characteristics of the prepared DPT were determined and are presented in Tables (1 - 4). Yield of the prepared DPT was about 65% but in the absence of para-formaldehyde it was only about 30%. These results are in good agreement with those found in the literature [2][42]. The prepared hexamine dinitrate was also converted into DPT under the action of acetic anhydride- acetic acid mixture at about 45 °C according to the published procedures [2], [10]. After aging the mixture for 15 minutes, it was cooled down to about 12 °C by adding a suitable quantity of ice. The product was then filtered and dried under vacuum. Again, the yield was about 65%.

Characterization of prepared compounds

Melting point values

Referring to characteristics of the pure compounds, it is clear that the prepared compounds are of high purity as in table (1).

Table (1) Melting points of the prepared compounds.

Compound		Measured melting point (°C)	Melting point (from literature) (°C)	Remarks
DPT	prepared	213	--	Nearly pure DPT crystals
	pure	--	213 [12], [13]	
Hexamine dinitrate	prepared	160	160	Nearly pure Hexamine dinitrate crystals

Elemental microanalysis results

Comparing with the characteristics of the pure compounds, it is clear from table (2) that the prepared compounds are of good quality.

Table (2) Elemental analysis of the prepared compounds.

Compound		C (%)	H (%)	N(%)
Hexamine dinitrate	Pure	27.06	5.26	31.57
	Prepared	26.91	5.29	31.745
DPT	Pure	27.52	4.58	38.53
	Prepared	27.21	4.536	38.094

FTIR results

Vibrations of organic molecules can be divided into two types; vibrations associated with the molecule as a whole and vibrations associated with the present functional groups. Employing one of the modern FTIR

spectrometer, the obtained IR spectrum is usually in the range of 4000 cm^{-1} to 250 cm^{-1} . The vibrations characterizing the molecule as a whole usually give rise to absorption bands below 1300 cm^{-1} . These bands are useful for identification of the unknown molecules by comparing their spectrum to that of authentic known standard molecules. This region is oftenly called the "fingerprint region". The vibrations associated with the functional groups give usually absorption bands above 1500 cm^{-1} . These bands are useful in qualitative analysis of the unknown organic matter [43]. Two characteristic intense bands are always associated with the NO_2 group. These bands can be attributed to the symmetric (ν_s) and asymmetric (ν_{as}) vibrations of the mentioned group. For the prepared DPT, the IR absorption bands found using the 8100 series FTIR spectrophotometer are presented in Table (3). Fingerprints for the prepared DPT samples are presented in Figure (1). Analyzing the above mentioned spectra and referring to the reproducibility of the results, the prepared compounds could be identified with acceptable precision.

Table (3) IR absorption bands for prepared DPT and HMX.

Compound		The Intense NO_2 stretching bands (cm^{-1})	The CH stretching mode (cm^{-1})	The stretching vibrations of the ($\text{N}-\text{NO}_2$) bond in nitramines (cm^{-1})
Prepared DPT	ν_s	1334.6	Band at 2923.9	1272.9
	ν_{as}	1525.6		1525.6

UV results

The obtained UV absorption spectra of hexamine dinitrate and DPT in ethanol are presented in figures (2) and (3) respectively. In the ultraviolet region, the absorption bands depend on the electronic transitions occurring and also on the effect of the atomic environment on these transitions. The obtained absorbance regions and also the values of the maximum absorbance wave length are given in Table (4). Since λ_{max} of Hexamine dinitrate is very close to that of the DPT when ethanol is employed as a solvent, from these results, it is clear that identification of the prepared compounds via their UV spectra is somewhat difficult.

Table (4) UV Absorbance regions and maximum absorbance for the prepared compounds

No.	Compounds	Maximum absorbance " λ_{max} "(nm) in methanol	Maximum absorbance " λ_{max} "(nm) in ethanol	Absorbance region (nm) (from literature)
1	Prepared Hexamine dinitrate	222	204	200 to 240 [15]
2	Prepared DPT	248	203	200 to 250[15]

Results of HPLC analysis

Figures (4 - 7) represent the results obtained by HPLC analysis. These figures show the chromatograms obtained at the end of the investigated reaction time. By examining the obtained chromatograms, the prepared compounds were identified qualitatively.

V. CONCLUSION

The yield of the DPT prepared was about 65%; while the yield of the hexamine dinitrate prepared was about 89%. The analysis of the prepared samples using an efficient HPLC was a very reliable procedure. Recently, It was established that using nanocomposites and nanoparticles has a great influence not only on the field of energetic materials but also in other applications including medical, environmental, and industrial applications. [16-40]

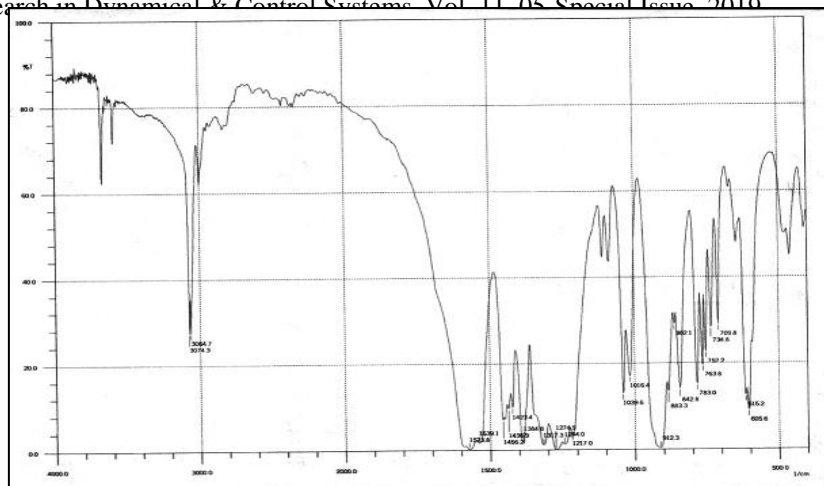


Fig. (1) IR spectrum of the prepared DPT

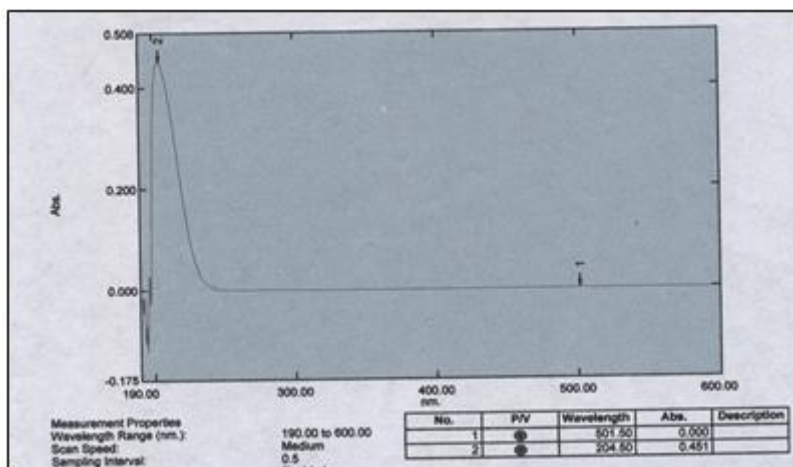


Fig. (2) UV spectrum of hexamine dinitrate in ethanol

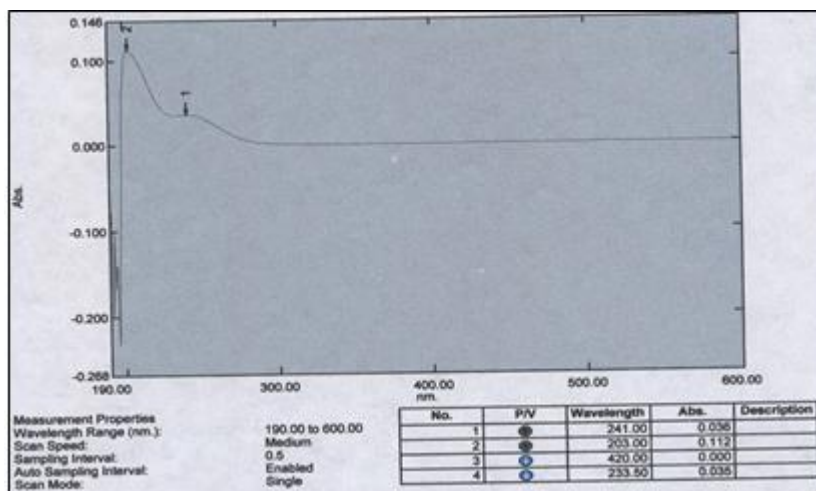


Fig. (3) UV spectrum of DPT in ethanol

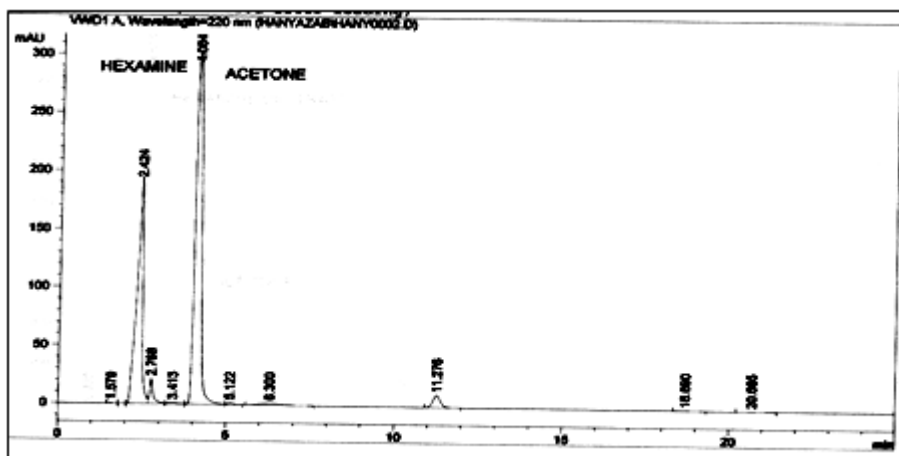


Fig. (4) HPLC Chromatogram of standard hexamine

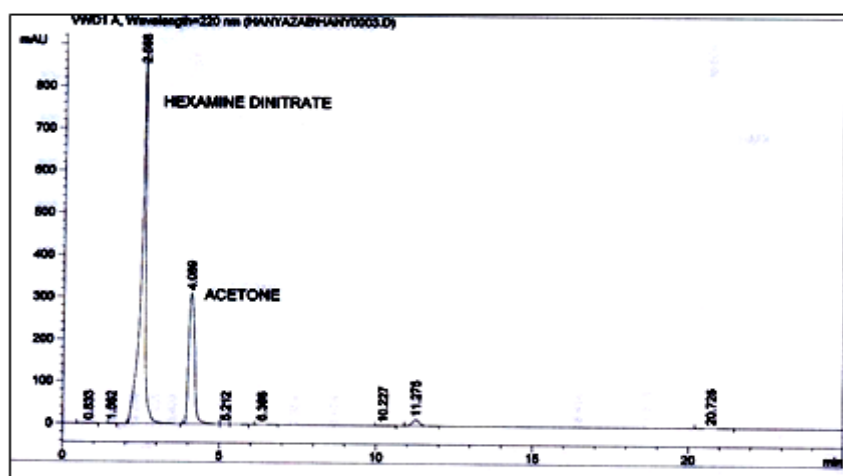


Fig. (5) HPLC Chromatogram of prepared hexamine dinitrate

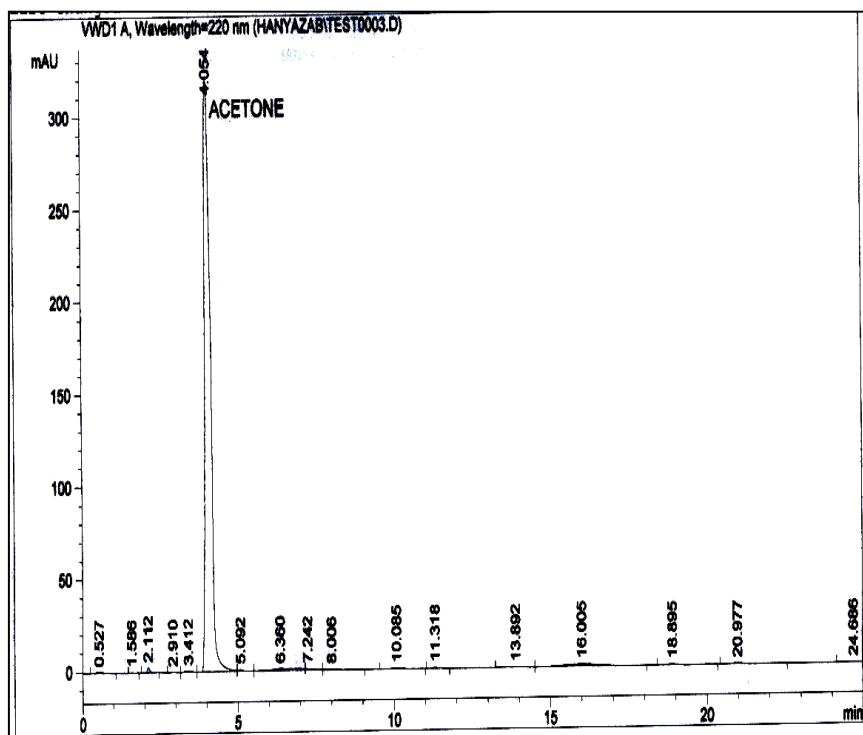
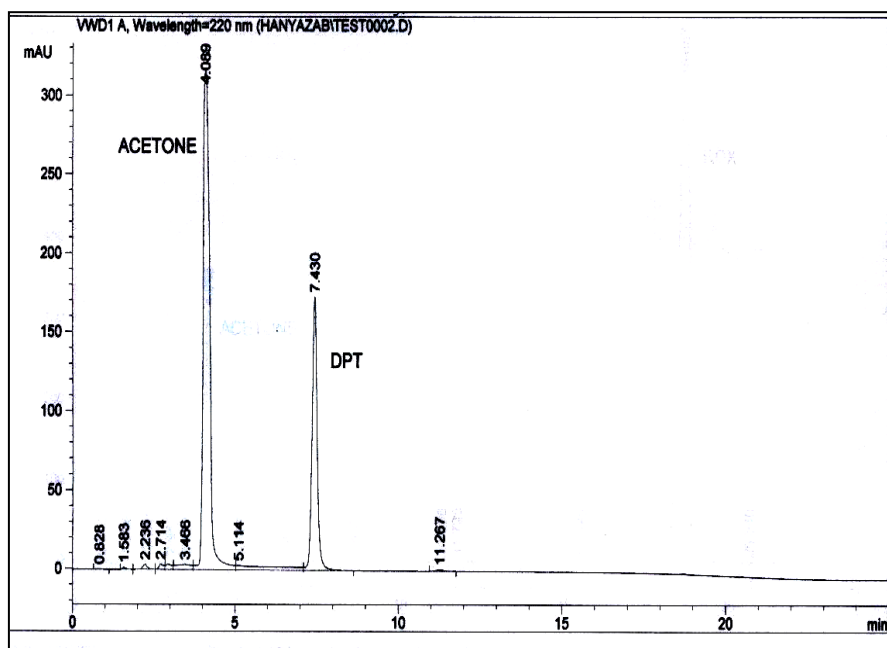


Fig. (6) Chromatogram of standard acetone

HPLC



HPLC

Fig. (7) Chromatogram of prepared DPT

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