

# Some aromatic nitrate esters: synthesis, structural aspects, thermal and explosive properties

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## Abstract

1-(2-Nitroxyethylnitramino)-2,4,6-trinitrobenzene (I-A), 1,3-bis(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (II-A) and 1,3,5-tris(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (III-A) have been prepared by condensing picryl chloride, styphnyl chloride and 1,3,5-trichloro-2,4,6-trinitrobenzene with ethanol amine, respectively, followed by nitration. These compounds have been characterized by infrared spectrum (IR), the elemental analysis and <sup>1</sup>H NMR. Further, these compounds have been studied for their thermal and explosive properties. The activation energy of thermal decomposition of these compounds has also been determined using the Ozawa and the Kissinger methods. The data on explosive properties indicate that the impact, friction and velocity of detonation (VOD) increase with an increase in the number of nitrate ester groups. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Aromatic nitrate esters; Structural aspects; Explosive and thermal properties; Synthesis; Base/booster charge for detonators and substitute for PETN

## 1. Introduction

Nitrate esters impart high energy to explosive/propellant formulations because of their better oxygen balance as compared to aromatic nitro compounds. At the same time, these compounds possess high sensitivity due to the presence of –O–NO<sub>2</sub> bond [1],

*Abbreviations:* VOD, Velocity of detonation; DP, Detonation pressure; *E<sub>a</sub>*, Activation energy; PETN, Pentaerythritol tetranitrate; NC, Nitrocellulose; NG, Nitroglycerine; TCB, 1,3,5-trichlorobenzene; TCTNB, 1,3,5-trichloro-2,4,6-trinitrobenzene; *T<sub>i</sub>*, Temperature of initiation; *T<sub>m</sub>*, Peak maximum temperature; IR, Infrared spectrum; <sup>1</sup>H NMR, Proton nuclear magnetic resonance

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which is a weak bond as compared to  $\text{N-NO}_2$  and  $\text{C-NO}_2$  bonds. This class of energetic materials consists of a wide variety of materials such as pentaerythritol tetranitrate (PETN), nitrocellulose (NC) and nitroglycerine (NG). PETN is a well-known high explosive and is used as a booster/base charge in detonators. NC and NG are other well-known nitrate esters, which are used extensively for gun and rocket propellants [2].

Literature survey indicates that active amino groups of amino acids condense with polyhalonitrobenzenes and yield a new series of compounds. In this series, condensation products of picryl chloride/styphnyl chloride with glycine/alanine have been reported [3]. Similarly, the ethanol amine has been reported to condense with 2,4-dinitrochlorobenzene followed by nitration, resulting in 2,4,6-trinitrophenyl-*N*-ethyl nitramine [4]. In the same way, condensation products of hydroxyl ethylamine and mobile halogen of 2,4-dinitrochlorobenzene/2,4,6-trinitrochlorobenzene have been reported, resulting in compounds 2,4-dinitrohydroxy ethyl aniline/2,4,6-trinitrohydroxy ethyl aniline [5]. To extend this work further, condensation product of 1,3,5-trichloro-2,4,6-trinitro benzene (TCTNB) with ethanol amine has been reported by Giua and Pansini [6]. A detailed study on high melting aromatic nitrate esters by condensing ethanol amine with polynitrohalobenzenes followed by nitration to yield compounds with  $\text{-O-NO}_2$  group has recently been reported by Sitzmann [7]. Such compounds have potential as substitutes for PETN, which is used as a booster/base charge for detonators.

The literature survey reveals that thermal and explosive properties of condensation products of ethanol amine and mono-, di-, tri-chloropolynitrobenzenes with both  $\text{-N-NO}_2$  (nitramino) and  $\text{-O-NO}_2$  (nitrate ester) groups, which may be of interest as booster/base charge, have not been studied. Therefore, the present work was undertaken to carry out a systematic study on ethanol amine derivatives of polynitrochlorobenzenes and their nitrated products with both  $\text{-N-NO}_2$  and  $\text{-O-NO}_2$  linkages. This investigation consists of methods of synthesis and characterization of 1-(2-nitroxyethyl-nitramino)-2,4,6-trinitrobenzene (**I-A**), 1,3-bis(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (**II-A**) and 1,3,5-tris(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (**III-A**) followed by study of their physical, structural aspects, thermal and explosive properties.

## 2. Experimental

### 2.1. Materials

The chemicals, used for this work — methanol, ethanol amine, nitric acid, sulfuric acid, ethyl acetate, pyridine and phosphorus oxychloride, were of LR grade. Picric acid and styphnic acid were procured from trade while 1,3,5-trichlorobenzene (TCB) with 99.5% purity was from Fluka (Switzerland) and fuming sulfuric acid (oleum) 25% was procured from the High Explosives(H.E.) factory, Pune.

## 3. Methods

### 3.1. Synthesis of 1-(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene

Synthesis of 1-(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene involves two steps.

### 3.1.1. Synthesis of 1-(2-hydroxyethylamino)-2,4,6-trinitrobenzene (**I**)

12.37 g of picryl chloride, a starting compound obtained on treatment of picric acid with pyridine followed by phosphorus oxychloride, were dissolved in 100 ml of methanol and transferred to a three-necked round-bottomed flask. To this, 3.05 g of ethanol amine, dissolved in 30 ml of methanol, was added dropwise over a period of 40 min with continuous stirring at ambient temperature ( $\approx 30^\circ\text{C}$ ). The stirring continued for another 3 h to complete reaction. The reaction mixture was poured into ice-cold water. A yellow precipitate obtained was filtered and recrystallised from hot water, dried and weighed. The yield was 95% ( $\approx 13.0$  g) and the melting point was  $108.9\text{--}110^\circ\text{C}$ .

### 3.1.2. Synthesis of 1-(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (**I-A**)

To a 250-ml round-bottomed flask, 10 ml of concentrated  $\text{H}_2\text{SO}_4$  were transferred and 10 ml of fuming nitric acid were added dropwise at room temperature ( $\approx 30^\circ\text{C}$ ) with stirring. To this nitrating mixture, 8.1 g of 1-(2-hydroxyethylamino)-2,4,6-trinitrobenzene (**I**) was added slowly over a period of 20 min. The whole mixture was stirred at  $40^\circ\text{C}$  for 1 h. The reaction mixture was cooled and poured into ice-cold water resulting in a precipitation of creamy solid compound, which was filtered and thoroughly washed with water until it was acid free. It was recrystallised from benzene, dried and weighed. The yield was 81% ( $\approx 8.8$  g) and the melting point was  $127.4\text{--}129^\circ\text{C}$ .

## 3.2. Synthesis of 1,3-bis(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene

Its synthesis also involves two steps.

### 3.2.1. Synthesis of 1,3-bis(2-hydroxyethylamino)-2,4,6-trinitrobenzene (**II**)

14.1 g of styphnyl chloride, obtained from styphnic acid on treatment with pyridine followed by phosphorus oxychloride ( $\text{POCl}_3$ ), was dissolved in 150 ml of methanol. To this, 6.1 g of ethanol amine, dissolved in 60 ml methanol was added dropwise over a period of 30 min with stirring at ambient temperature ( $\approx 30^\circ\text{C}$ ), which was maintained for 2 h. The reaction mixture was filtered. On filtration, a yellow solid precipitate was obtained, dried and weighed. The yield was 84% ( $\approx 14$  g) and the melting point was  $199.6\text{--}201^\circ\text{C}$ .

### 3.2.2. Synthesis of 1,3-bis(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (**II-A**)

To a 10 ml of concentrated  $\text{H}_2\text{SO}_4$ , 20 ml of fuming  $\text{HNO}_3$  was added dropwise over a period of 30 min with stirring at ambient temperature ( $\approx 30^\circ\text{C}$ ). To this nitrating mixture, 5 g of 1,3-bis(2-hydroxyethylamino)-2,4,6-trinitrobenzene was added slowly. The reaction temperature was raised to  $\approx 50^\circ\text{C}$  and maintained for 2 h. The reaction mixture was cooled to ambient temperature and poured into ice-cold water. A pale yellow precipitate obtained was filtered and washed with water until acid free. It was recrystallised from ethyl alcohol, dried and weighed. The yield was 90% ( $\approx 6.2$  g) and the melting point was  $121.1\text{--}123^\circ\text{C}$ .

## 3.3. Synthesis of 1,3,5-tris(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene

Contrary to the synthesis of **I-A** and **II-A**, synthesis of this compound involves three steps which are as follows:

(a) Synthesis of 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB)

(b) Synthesis of 1,3,5-tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene (**III**)

(c) Synthesis of 1,3,5-tris(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (**III-A**)

### 3.3.1. Synthesis of 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB)

To a 250-ml round-bottomed flask, placed in an oil bath, 60 ml of 25% oleum was transferred and 12 ml of fuming  $\text{HNO}_3$  was added to it dropwise. After this, heating of the oil bath was started and when the temperature of the acid mixture reached  $105^\circ\text{C}$ , heating of the oil bath was stopped and 10 g of 1,3,5-trichlorobenzene (TCB) was added slowly with stirring. Heating of the oil bath was again started and the temperature of the reaction mixture was raised slowly and maintained at  $150^\circ\text{C}$  for 3.5 h [8]. The reaction mixture was cooled to ambient temperature ( $\approx 30^\circ\text{C}$ ) and then poured over crushed ice. The white granular precipitate obtained was filtered, washed thoroughly with water and recrystallised from trichloroethylene thrice to get pure TCTNB. The yield was 92% ( $\approx 16.5$  g) and the melting point was  $189\text{--}190^\circ\text{C}$ .

### 3.3.2. Synthesis of 1,3,5-tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene (**III**)

Methanol solution of ethanol amine (6 g ethanol amine dissolved in 60 ml methanol), was added slowly to a solution of 9.5 g of TCTNB dissolved in 150 ml methanol at room temperature and stirred for a further 3 h. At the end of this period, a pale yellow precipitate was obtained, which was filtered, dried and weighed. The yield was 80% ( $\approx 9.4$  g) and the melting point was  $200\text{--}202^\circ\text{C}$  (with decomposition).

### 3.3.3. Synthesis of 1,3,5-tris(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (**III-A**)

To 50 ml of concentrated  $\text{H}_2\text{SO}_4$  in a round-bottomed flask, 30 ml of fuming  $\text{HNO}_3$  was added dropwise with continuous stirring. To this nitrating mixture, 5 g of 1,3,5-tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene was added in small portions at ambient temperature ( $\approx 30^\circ\text{C}$ ). The temperature of the reaction mixture was raised to  $50^\circ\text{C}$  and maintained for 2 h. A pale yellow precipitate was obtained by pouring the reaction mixture into ice-cold water. It was filtered and washed thoroughly with water until acid free. It was recrystallised from ethanol and ethyl acetate (50:50), dried and weighed. The yield was 70% ( $\approx 6$  g) and the melting point was  $149.3\text{--}151^\circ\text{C}$ .

## 4. Characterization

### 4.1. Physical properties

- The melting points were determined by using Automatic melting point apparatus (Veego).
- The density was determined by experimentally using Archimedes principle.

### 4.2. Structural aspects

- The IR spectra were recorded by KBr disc method using Perkin-Elmer FTIR Spectrophotometer, Model 1600.

- The elemental analyses were performed on Elemental Analyser, Model EA-1108, Carlo Erba instruments.
- The  $^1\text{H}$  NMR spectra were recorded on Bruker 90 MHz instrument, Model WH-90 using  $\text{DMSO-d}_6$  as a solvent with TMS as an internal standard.
- Differential thermal analysis (DTA) was recorded on a locally fabricated DTA apparatus [9], by taking a 10 mg sample, at a rate of  $10^\circ\text{C}/\text{min}$  in the presence of static air. The activation energies of these compounds were determined by using the Ozawa and the Kissinger methods [10,11].

### 4.3. Explosive properties

The impact sensitivity of nitrate esters and their precursors was determined by Fall Hammer method [12] using 2 kg drop weight, and friction sensitivity was determined by Julius Peter's apparatus [13].

VOD was calculated theoretically with the help of the following expressions [14]. A simple, empirical relationship between the detonation velocity at theoretical maximum density and a factor  $F$  that is dependent solely upon chemical composition and structure is postulated for a gamut of ideal explosives. The relation between the velocity of detonation ( $D$ ) and  $F$  is expressed by the following linear equation:

$$D = \frac{F - 0.26}{0.55},$$

where  $D$  = velocity of detonation;  $F$  = factor, which may be calculated as follows:

$$F = 100 \times \left( \frac{n(\text{O}) + n(\text{N}) - \frac{n(\text{H})}{2n(\text{O})} + \frac{A}{3} - \frac{n(\text{B})}{1.75} - \frac{n(\text{C})}{2.5} - \frac{n(\text{D})}{4} - \frac{n(\text{E})}{5}}{\text{MW}} \right) - G,$$

where  $G = 0.4$  for liquid and  $G = 0$  for solid explosives;  $A = 1.0$  if the compound is aromatic, otherwise  $A = 0$ ; MW = molecular weight;  $n(\text{O})$  = number of oxygen atoms;  $n(\text{N})$  = number of nitrogen atoms;  $n(\text{H})$  = number of hydrogen atoms;  $n(\text{B})$  = number of oxygen atoms in excess of those already available to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ;  $n(\text{C})$  = number of oxygen atoms double bonded to carbon as in  $\text{C}=\text{O}$ ;  $n(\text{D})$  = number of oxygen atoms singly bonded directly to carbon in  $\text{C}-\text{O}-\text{R}$  linkage where  $\text{R} = -\text{H}$ ,  $-\text{NH}_4$  or  $-\text{C}$ ;  $n(\text{E})$  = number of nitrate groups either as nitrate esters or nitrate salts.

Detonation pressure (DP): The peak dynamic pressure in the shock front is called the DP of the explosive. The empirical method for calculation of DP is given below [15]:

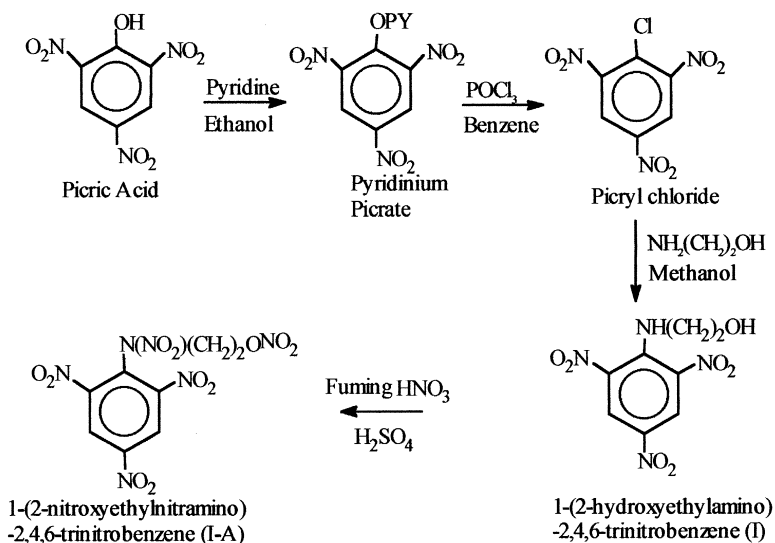
$$\text{DP (GPa)} = \frac{\partial D^2}{4},$$

where  $\partial$  = the density of compound,  $\text{g}/\text{cm}^3$ ;  $D$  = velocity of detonation,  $\text{km}/\text{s}$ .

## 5. Results and discussion

### 5.1. Structural aspects

(I) The reaction scheme for synthesis of 1-(2-nitrosoxyethylnitramino)-2,4,6-trinitrobenzene is as follows:



The FTIR spectra of compounds **I** and **I-A** are given in Fig. 1A and B, respectively, and their major absorption bands are summarized in Table 1. The presence of an additional band at 1640 cm<sup>-1</sup> and the absence of bands at 3576 and 3296 cm<sup>-1</sup>, which correspond to –OH and –NH groups, in compound **I-A** indicate conversion of –OH and –NH groups into corresponding –O–NO<sub>2</sub> and –N–NO<sub>2</sub> groups, respectively.

The experimental and calculated (based on assigned structures) values of the elemental analysis of compounds **I** and **I-A** are given in Table 2. It is evident from the data that the experimental values of C, H and N closely match with the calculated values in both the compounds.

The <sup>1</sup>H NMR spectra of compounds **I** and **I-A** are given in Fig. 2A and B and the values of chemical shifts (ppm) are summarized in Table 3. In the case of compound **I**, the protons of –CH<sub>2</sub> groups attached to –OH group appear at 3.5 ppm, while protons of –CH<sub>2</sub> groups attached to –NH group appear at 3.0 ppm [7]. The aromatic protons appear at 8.7 ppm and –NH protons appear at 9.0 ppm. The hydroxyl protons of –CH<sub>2</sub>OH appear at 5.0 ppm. Further, in the case of compound **I-A**, protons of –CH<sub>2</sub> groups attached to –O–NO<sub>2</sub> group appear at 4.6 ppm, while the protons of –CH<sub>2</sub> groups attached to –N–NO<sub>2</sub> group appear at 4.4 ppm. The aromatic protons appear at

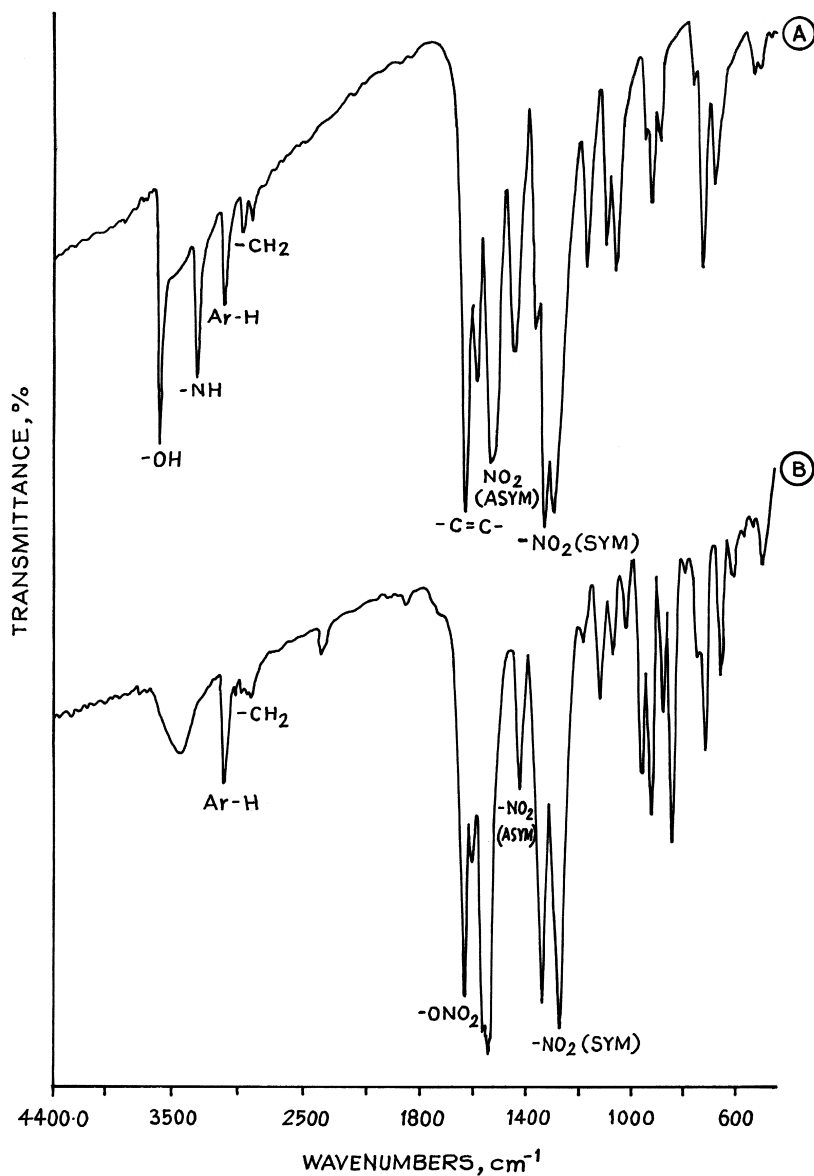
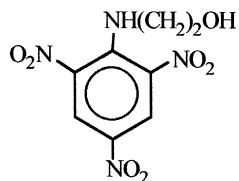
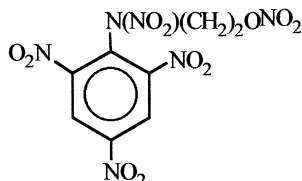


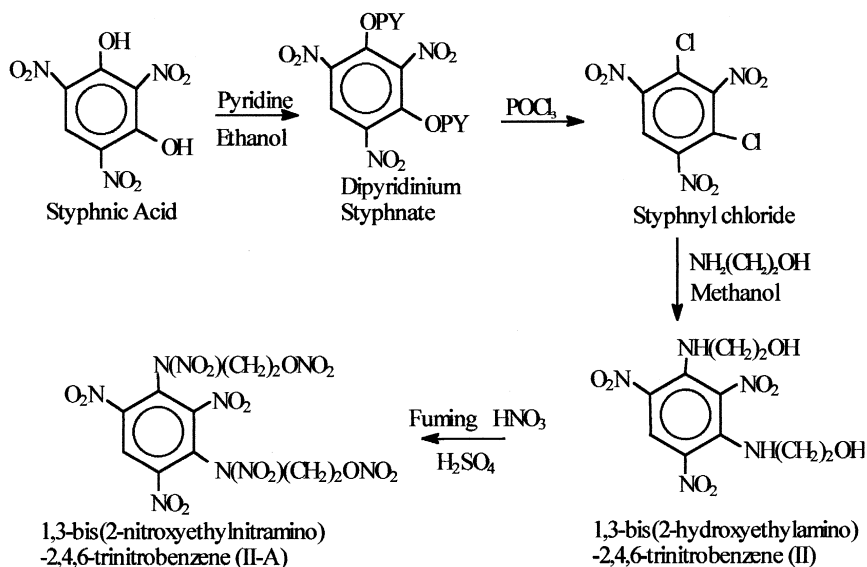
Fig. 1. FTIR spectra of: (A) 1-(2-hydroxyethylamino)-2,4,6-trinitrobenzene (I); (B) 1-(2-nitroxyethyl-nitramino)-2,4,6-trinitrobenzene (I-A).

9.1 ppm. The absence of protons of  $-\text{OH}$  and  $-\text{NH}$  groups indicate full conversion of these protons to corresponding  $-\text{NO}_2$  groups.

Based on FTIR, the elemental analysis and  $^1\text{H}$  NMR, structures of compounds **I** and **I-A** may be assigned as:

**I****I-A**

(II) The reaction scheme for synthesis of 1,3-bis(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene is as follows:



The FTIR spectra of compounds **II** and **II-A** are given in Fig. 3A and B and major absorption bands are assigned in Table 1. It shows the presence of an additional band at  $1644\text{ cm}^{-1}$ . The absence of bands at  $3534$  and  $3244\text{ cm}^{-1}$ , corresponding to  $-\text{OH}$  and  $-\text{NH}$  groups, respectively, in the case of compound **II-A** indicate complete conversion of  $-\text{OH}$  and  $-\text{NH}$  groups to corresponding  $-\text{O}-\text{NO}_2$  and  $-\text{N}-\text{NO}_2$  groups.

The experimental and calculated (based on assigned structures) values of the elemental analysis of the compounds **II** and **II-A** are given in Table 2 and it is evident that the



Table 1

Assignment of major IR bands in aromatic nitrate esters and their precursors

Compound	Assignment of major bands ( $\text{cm}^{-1}$ )						
	–OH	–NH	Ar–H	–CH <sub>2</sub>	–ONO <sub>2</sub>	–C=C–	–NO <sub>2</sub>
1-(2-hydroxyethylamino)-2,4,6-trinitrobenzene ( <b>I</b> )	3576	3296	3090	2956, 2896		1586	1528, 1360
1-(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene ( <b>I-A</b> )			3098	2960, 2890	1640	1608	1548, 1342
1,3-bis(2-hydroxyethylamino)-2,4,6-trinitrobenzene ( <b>II</b> )	3534	3244	3100	2946, 2896		1584	1548, 1358
1,3-bis(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene ( <b>II-A</b> )			3108	2906, 2890	1644	1580	1576, 1338
1,3,5-tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene ( <b>III</b> )	3538	3232		2948, 2898		1594	1526, 1356
1,3,5-tris(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene ( <b>III-A</b> )				2948, 2898	1648	1594	1526, 1342

experimental values of C, H and N closely match with calculated values in both compounds.

The <sup>1</sup>H NMR spectra of compounds **II** and **II-A** are given in Fig. 4A and B and different chemical shifts are given in Table 3. In the case of compound **II**, protons of –CH<sub>2</sub> groups attached to –OH and –NH groups appear at 3.5 and 3.0 ppm, respectively. The aromatic proton appear at 8.8 ppm while that of –NH proton appear at 9.0 ppm [7]. The hydroxyl protons of –CH<sub>2</sub>OH appear at 4.5 ppm. In the case of compound **II-A**, protons of –CH<sub>2</sub> groups attached to –O–NO<sub>2</sub> and –N–NO<sub>2</sub> appear at 4.6 and 4.4 ppm, respectively. The aromatic proton appears at 9.3 ppm. The absence of protons of –OH and –NH groups indicate full conversion of these protons to corresponding –NO<sub>2</sub> groups.

Table 2

Elemental analysis data of aromatic nitrate esters and their precursors

Compound	Experimental (%)			Calculated (%)		
	C	H	N	C	H	N
1-(2-hydroxyethylamino)-2,4,6-trinitrobenzene ( <b>I</b> )	35.60	3.24	20.23	35.29	2.94	20.58
1-(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene ( <b>I-A</b> )	26.86	1.87	22.69	26.51	1.65	23.10
1,3-bis(2-hydroxyethylamino)-2,4,6-trinitrobenzene ( <b>II</b> )	36.28	3.78	20.58	36.25	3.9	21.14
1,3-bis(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene ( <b>II-A</b> )	23.97	1.78	24.06	23.48	1.76	24.65
1,3,5-tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene ( <b>III</b> )	36.57	4.82	21.37	36.92	4.61	21.53
1,3,5-tris(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene ( <b>III-A</b> )	22.22	1.90	24.98	21.81	1.81	25.45

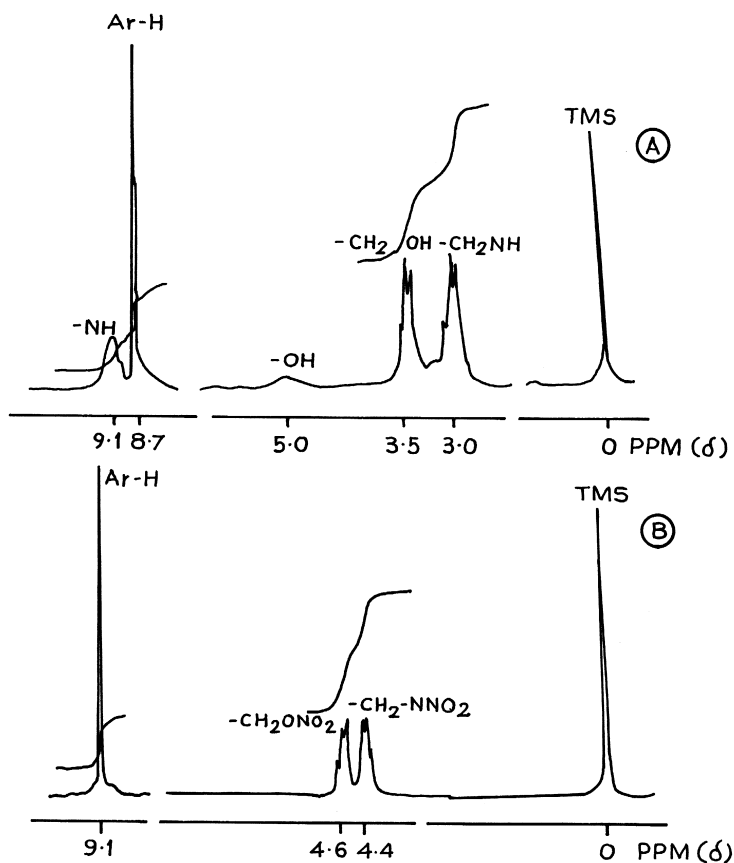
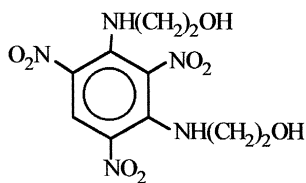
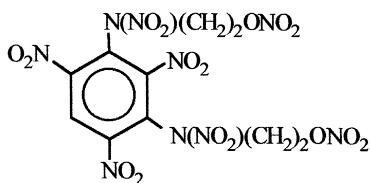


Fig. 2.  $^1\text{H}$  NMR spectra of: (A) 1-(2-hydroxyethylamino)-2,4,6-trinitrobenzene (**I**); (B) 1-(2-nitroxyethyl-nitramino)-2,4,6-trinitrobenzene (**I-A**).

Similar to **I-A**, based on FTIR, the elemental analysis and  $^1\text{H}$  NMR structures of compounds **II** and **II-A** may be assigned as :



(**II**)



(**II-A**)

Table 3  
Chemical shifts in aromatic nitrate esters and their precursors

Compound	Chemical Shifts, ppm						
	Ar–H	–NH	HN–CH <sub>2</sub>	CH <sub>2</sub> –OH	CH <sub>2</sub> ONO <sub>2</sub>	(O <sub>2</sub> N)N–CH <sub>2</sub>	–OH
1-(2-hydroxyethylamino)-2,4,6-trinitrobenzene ( <b>I</b> )	8.7 (s, 2H)	9.1 (s, 1H)	3.0 (t, 2H)	3.5 (t, 2H)			5.0
1-(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene ( <b>I-A</b> )	9.1 (s, 2H)				4.6 (t, 2H)	4.4 (t, 2H)	
1,3-bis(2-hydroxyethylamino)-2,4,6-trinitrobenzene ( <b>II</b> )	8.8 (s, 1H)	9.0 (t, 2H)	3.0 (t, 4H)	3.5 (t, 4H)			4.5 (m, 2H)
1,3-bis(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene ( <b>II-A</b> )	9.3 (s, 1H)				4.6 (t, 4H)	4.4 (t, 4H)	
1,3,5-tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene ( <b>III</b> )		10.8 (m, 3H)	3.3 (d, 6H)	3.5 (d, 6H)			4.1 (m, 3H)
1,3,5-tris(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene ( <b>III-A</b> )					4.6 (t, 6H)	4.3 (t, 6H)	

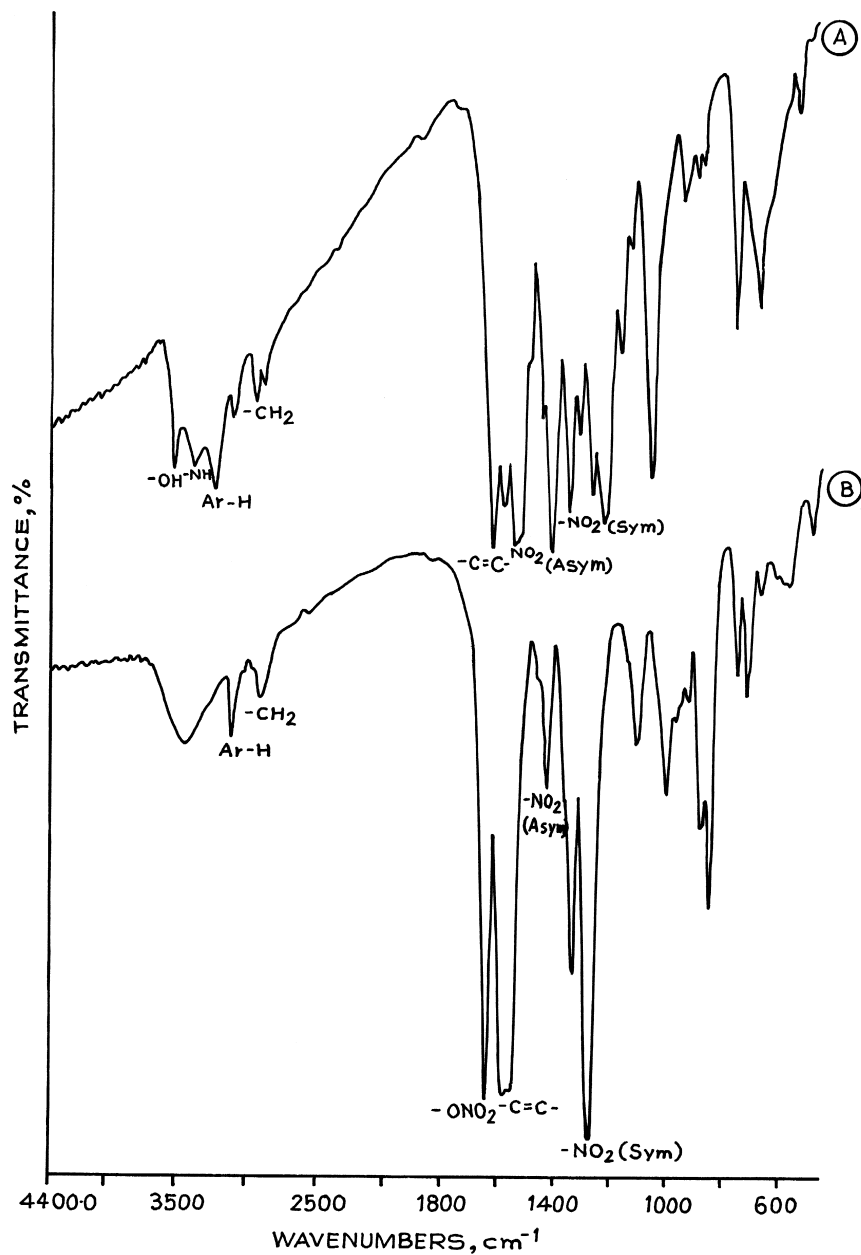
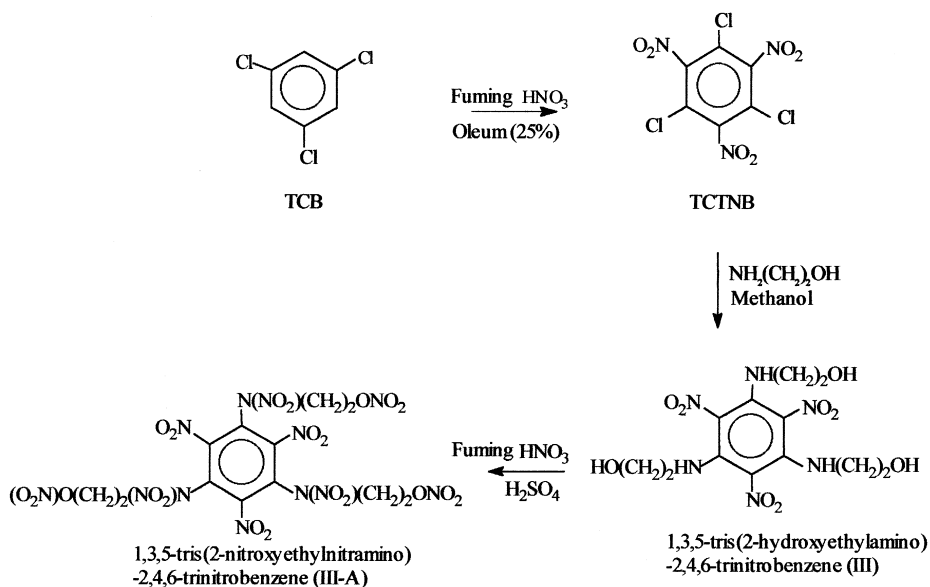


Fig. 3. FTIR spectra of: (A) 1,3-bis(2-hydroxyethylamino)-2,4,6-trinitrobenzene (II); (B) 1,3-bis(2-nitroxyethyl-nitramino)-2,4,6-trinitrobenzene (II-A).

(III) The reaction scheme for synthesis of 1,3,5-tris(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene is as follows:

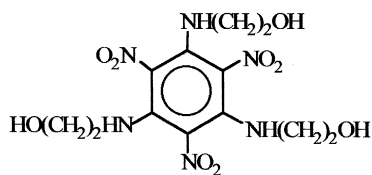


The FTIR spectra of **III** and **III-A** are given in Fig. 5A and B and their major bands are summarized in Table 1. It is clear from Table 1 that in the case of compound **III-A**, absence of bands at 3538 and 3232 cm<sup>−1</sup>, which correspond to –OH and –NH groups, respectively, and presence of additional band at 1648 cm<sup>−1</sup> indicate complete conversion of –NH and –OH groups to corresponding –N–NO<sub>2</sub> and –O–NO<sub>2</sub> groups [7].

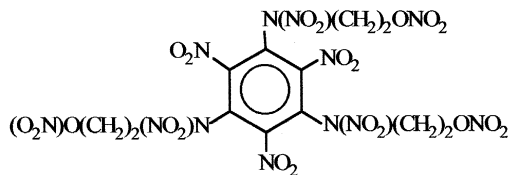
The experimental and calculated (based on assigned structures) values of the elemental analysis of the compounds **III** and **III-A** are given in Table 2. It is clear from the table that the experimental values of C, H and N closely match with the calculated values in both compounds.

The <sup>1</sup>H NMR spectra of compounds **III** and **III-A** are given in Fig. 6A and B and their chemical shifts are given in Table 3. In the case of compound **III**, protons of –CH<sub>2</sub> groups attached to –OH and –NH groups appear at 3.5 and 3.3 ppm, respectively [7]. Protons of –NH appear at 10.8 ppm and hydroxyl protons of –CH<sub>2</sub>OH group appear at 4.1 ppm, while in the case of compound **III-A**, protons of –CH<sub>2</sub> group attached to –O–NO<sub>2</sub> and –N–NO<sub>2</sub> appear at 4.6 and 4.3 ppm, respectively. The absence of –OH and –NH protons indicates full conversion of these protons to corresponding –NO<sub>2</sub> groups.

The data on FTIR, the elemental analysis and  $^1\text{H}$  NMR suggest the following structures of compounds **III** and **III-A**:



(III)



(III-A)

### 5.2. Thermal properties

Thermal properties of the nitrate esters are given in Table 4.

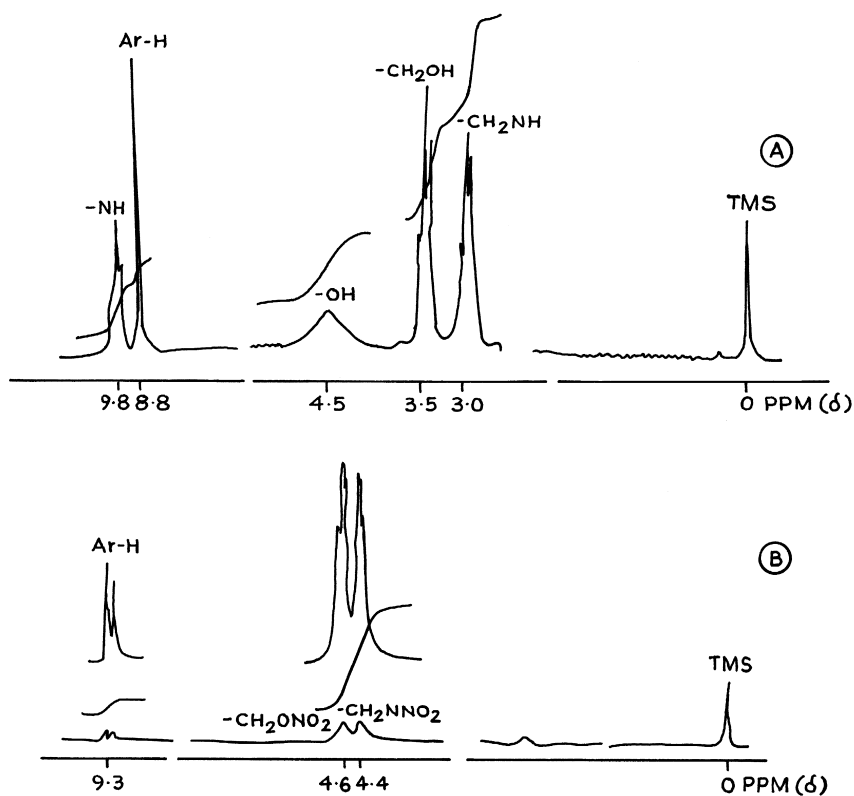


Fig. 4.  $^1\text{H}$  NMR spectra of: (A) 1,3-bis(2-hydroxyethylamino)-2,4,6-trinitrobenzene (**II**); (B) 1,3-bis(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (**II-A**).

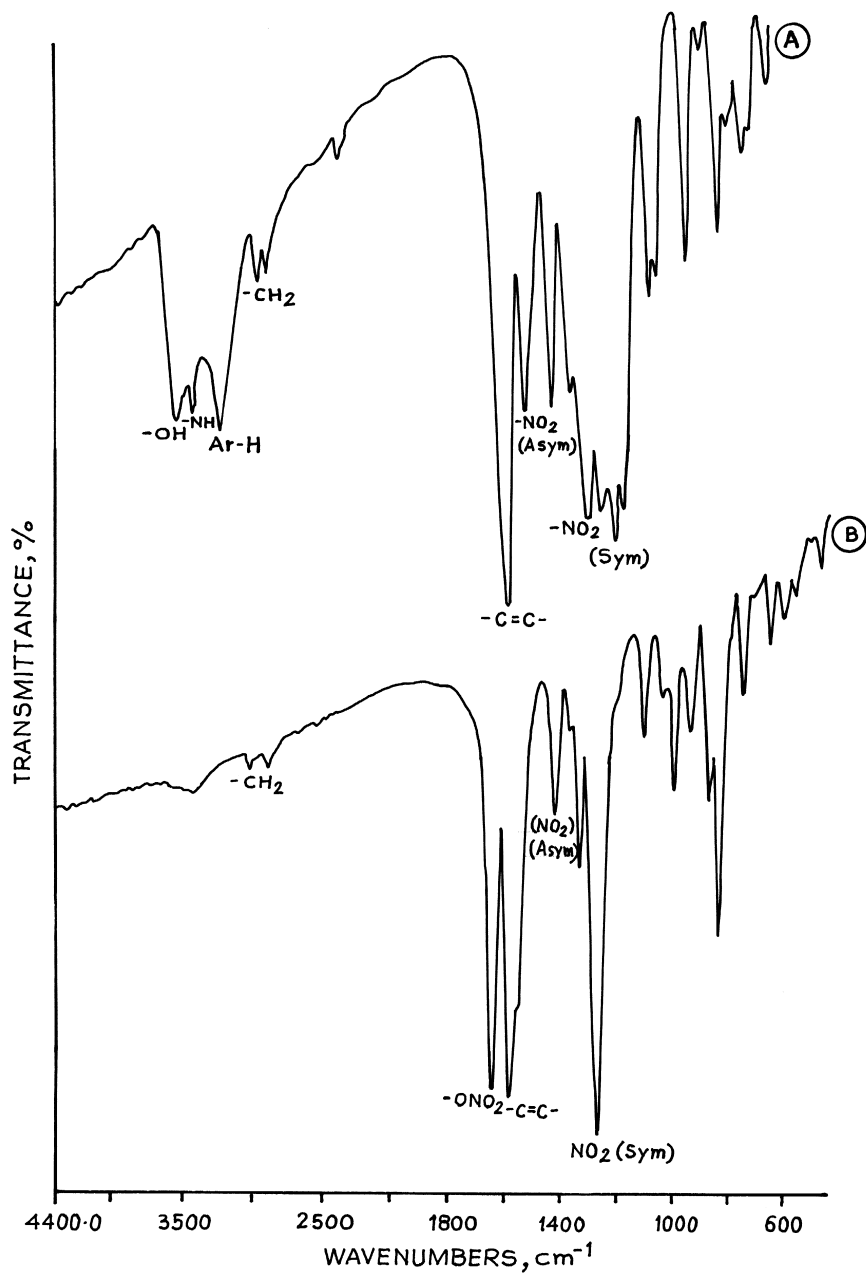


Fig. 5. FTIR spectra of: (A) 1,3,5-tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene (III); (B) 1,3,5-tris(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (III-A).

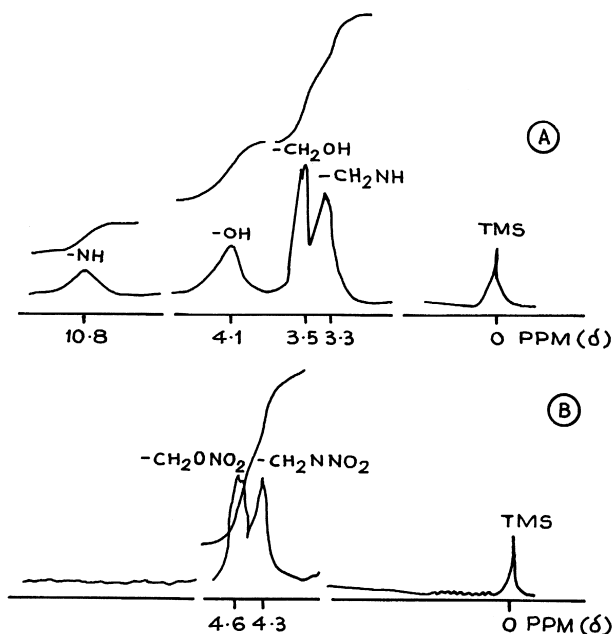


Fig. 6.  $^1\text{H}$  NMR spectra of: (A) 1,3,5-tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene (**III**); (B) 1,3,5-tris(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (**III-A**).

### 5.2.1. Differential thermal analysis

DTA curves of compounds **I** and **I-A** are shown in Fig. 7A and B. It is clear from the figures that endothermic peaks obtained at 109.5°C and 128°C for compounds **I** and **I-A** are due to melting while exothermic peaks obtained at 227–275°C and 164–184°C, respectively, are due to their thermal decompositions.

Table 4

Thermal properties of aromatic nitrate esters and their precursors

Compound	$T_i$ (°C)	$T_m$ (°C)	Activation energy (kcal/mol)	
			Ozawa	Kissinger
1-(2-hydroxyethylamino)-2,4,6-trinitrobenzene ( <b>I</b> )	227	275		
1-(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene ( <b>I-A</b> )	164	184	51.8	51.1
1,3-bis(2-hydroxyethylamino)-2,4,6-trinitrobenzene ( <b>II</b> )	221	238		
1,3-bis(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene ( <b>II-A</b> )	164	166	47.4	48.0
1,3,5-tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene ( <b>III</b> )	175	199		
1,3,5-tris(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene ( <b>III-A</b> )	149	158	76.9	78.0



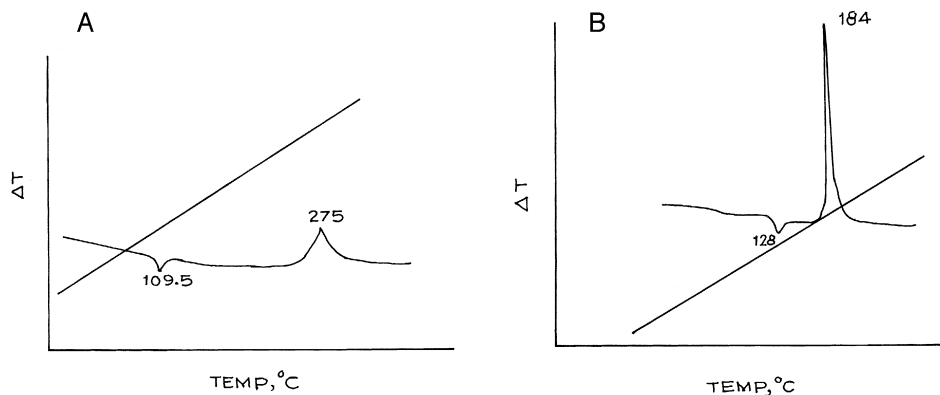


Fig. 7. (A) DTA curve of 1-(2-hydroxyethylamino)-2,4,6-trinitrobenzene (**I**); (B) DTA curve of 1-(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (**I-A**).

In the same way, compounds **II** and **II-A** were also subjected to DTA (Fig. 8A and B). The endotherms obtained at 199.0°C and 120.1°C for compounds **II** and **II-A**, respectively, are attributed to melting where as exothermic peaks obtained at 221–238°C and 166°C are due to their thermal decompositions.

The DTA curve of compound **III** (Fig. 9A) shows no endothermic peak, indicating no melting of the compound, while compound **III-A** (Fig. 9B) gives sharp endotherm at 149°C due to melting. The exothermic peaks obtained at 175–199°C and 158°C for compounds **III** and **III-A**, respectively, are due to their thermal decompositions similar to other compounds.

#### 5.2.2. Activation energy( $E_a$ )

The DTA curves were recorded at four different heating rates ( $\beta$ ), i.e. 5, 10, 15, 20 °C/min for compounds **I-A**, **II-A** and **III-A** and values of peak maxima ( $T_m$ ),  $\log \beta$ ,  $\ln(\beta/T_m^2)$  and  $1/T_m$  corresponding to the different heating rates have been calculated. In the Ozawa method, a graph was plotted between  $\log \beta$  vs.  $1/T_m$  (Fig. 10), while in the Kissinger method, a graph was plotted between  $\ln(\beta/T_m^2)$  vs.  $1/T_m$  (Fig. 11). With

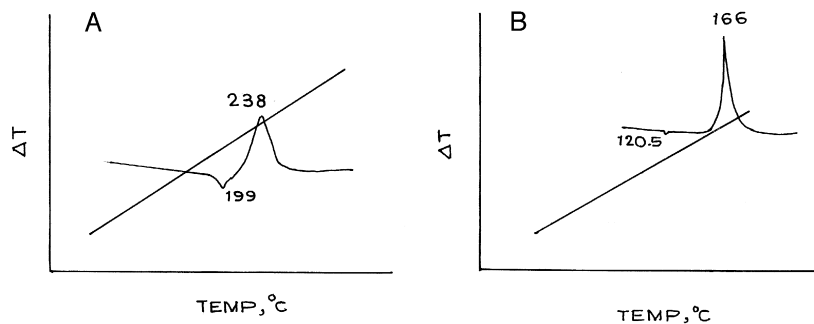


Fig. 8. (A) DTA curve of 1,3-bis(2-hydroxyethylamino)-2,4,6-trinitrobenzene (**II**); (B) DTA curve of 1,3-bis(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (**II-A**).

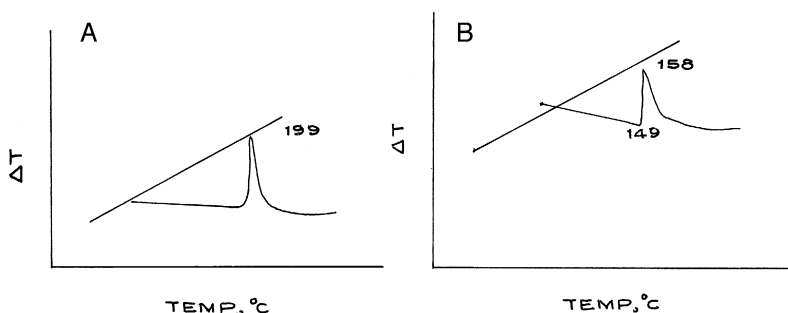


Fig. 9. (A) DTA curve of 1,3,5-tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene (**III**); (B) DTA curve of 1,3,5-tris(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (**III-A**).

the use of slopes of these lines activation energy has been calculated and data is given in Table 4. The decrease in activation energy in the case of compound **II-A**, as compared with compound **I-A**, is perhaps attributed to asymmetric substitution in benzene ring in compound **II-A**.

### 5.3. Explosive properties

#### 5.3.1. Impact sensitivity

The impact sensitivity of compounds **I-A**, **II-A** and **III-A** and their precursors is given in Table 5. In the case of compounds **I**, **II**, and **III**, i.e. precursors, it is seen that the impact sensitivity decreases as number of  $-\text{OH}$  groups increases from compounds **I** to **III**. It is mainly due to intra-hydrogen bonding [16,17], which increases in these molecules from compound **I** to compound **III** through compound **II**. On the contrary, in the case of compounds **I-A**, **II-A** and **III-A** (Table 5), the trend in impact sensitivity is reversed, i.e. it increases from compound **I-A** to compound **III-A**. It is due to the

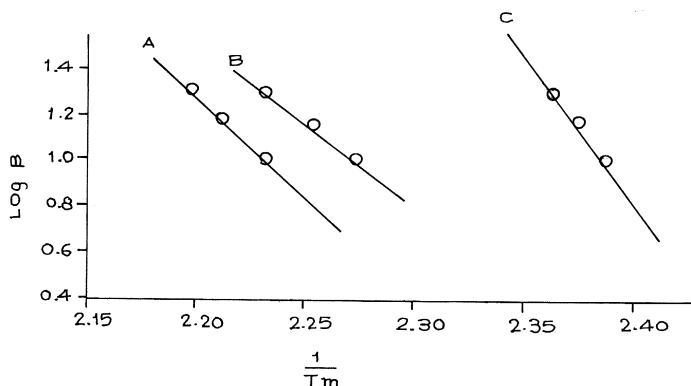


Fig. 10. A plot of  $\log \beta$  vs.  $1/T_m$  (Ozawa method) for (A) 1-(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (**I-A**); (B) 1,3-bis(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (**II-A**); (C) 1,3,5-tris(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (**III-A**).

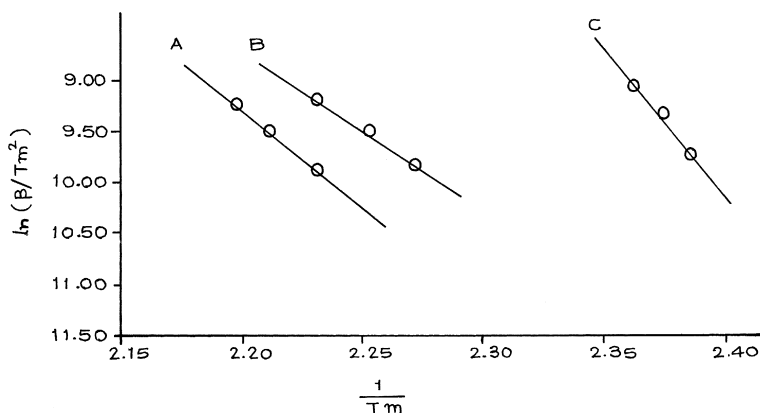


Fig. 11. A plot of  $\ln(\beta/T_m^2)$  vs.  $1/T_m$  (Kissinger method) for (A) 1-(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (**I-A**); (B) 1,3-bis(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (**II-A**); (C) 1,3,5-tris(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (**III-A**).

increase in the number of  $-\text{N}-\text{NO}_2$  and  $-\text{C}-\text{NO}_2$  groups in these molecules. This is also supported by oxygen balance and the oxidant balance data, which increase in the case of compounds of **I-A**, **II-A** and **III-A** and decrease in the case of compounds **I**, **II** and **III** (Table 5).

### 5.3.2. Friction sensitivity

Friction sensitivity of precursors and compounds **I-A**, **II-A** and **III-A** is given in Table 5. It is clear that the friction sensitivity follows a pattern similar to impact

Table 5

Some explosive properties of aromatic nitrate esters and their precursors

Compound	Density (g/cc)	Oxygen balance (%)	Impact sensitivity, height for 50% explo- sion (cm)	Friction sensitivity, i.e., does not ignite up to (kg)	VOD (m/s)	Detonation pressure (GPa)
1-(2-hydroxyethylamino)-2,4,6-trinitrobenzene ( <b>I</b> )		−76.47	150	36	6727	21.03
1-(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene ( <b>I-A</b> )	1.81	−35.35	98.5	32.4	8100	29.68
1,3-bis(2-hydroxyethylamino)-2,4,6-trinitrobenzene ( <b>II</b> )		−89.41	160	36.0	6403	19.6
1,3-bis(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene ( <b>II-A</b> )	1.82	−26.61	60	19.2	8500	32.87
1,3,5-tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene ( <b>III</b> )		−98.46	170	36.0	6209	19.04
1,3,5-tris(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene ( <b>III-A</b> )	1.82	−21.81	32.0	12.6	8650	34.11

sensitivity, i.e. a decrease in the friction sensitivity in the case of precursors **I**, **II** and **III** and an increase in the friction sensitivity of final compounds, i.e. **I-A**, **II-A** and **III-A** and may be explained accordingly.

### 5.3.3. Velocity of detonation (VOD) and DP

The calculated VOD and DP of precursors and compounds **I-A**, **II-A** and **III-A** are given in Table 5. It is clear that VOD and DP decrease from compounds **I** to **III**. It is due to the introduction of more hydrogen and carbon atoms in the molecule, which increase from compounds **I** to **III**. On the other hand, VOD and DP increase from **I-A** to **III-A** and is due to introduction of  $-N-NO_2$  and  $-O-NO_2$  groups in the benzene ring. The VOD of compound **I-A** is 8100 m/s, while that of compounds **II-A** and **III-A** are 8500 and 8650 m/s, respectively. It means that VOD of compound **II-A** is more than PETN (8300 m/s), while that of compound **III-A** is comparable to RDX (8750 m/s).

The prime interest to synthesize and characterize these explosive molecules was to explore the possibility of their use as booster/base charge for detonators in the place of PETN. The data on explosive properties of compounds **II-A** and **III-A** indicate that these are comparatively more powerful than PETN (VOD  $\cong$  8300 m/s), while less sensitive towards impact and friction (height for 50% explosion is  $\cong$  28.5 cm and 6.0 kg for friction sensitivity). This suggests that it is safe to handle and transport compounds **II-A** and **III-A**.

The evaluation of these explosives as base charges in detonators in the place of PETN is in progress.

## 6. Conclusion

The data on thermal and explosive properties of 1-(2-nitroxyethylnitramino)-2,4,6 trinitrobenzene (**I-A**), 1,3-bis(2-nitroxyethylnitramino)-2,4,6 trinitrobenzene (**II-A**) and 1,3,5-tris(2-nitroxyethylnitramino)-2,4,6 trinitrobenzene (**III-A**) indicate that the compound **III-A** is a potential substitute for PETN. However, exhaustive trials are required for this purpose.

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