

# Synthesis, Characterization and Thermal Behaviour of 2,4,6,8-Tetranitro-2,4,6,8-Tetraazabicyclo[3.3.1]Nonane-3,7-Dione (TNPDU) and one of its Methylene Analogues

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## Summary

2,4,6,8 - Tetranitro - 2,4,6,8 - tetraazabicyclo[3.3.1]nonane-3,7-dione (TNPDU) has been synthesized from propane diurea by nitration with nitric acid–acetic anhydride with a yield of 85%. The molecular structure of the compound has been determined by elemental analysis, IR and <sup>1</sup>H-NMR spectroscopy. Some of the properties including thermal and explosion delay behaviour of the compound and its mixtures with high explosives, are reported. An analogous compound 2,5,7,9-tetranitro-2,5,7,9-tetraazabicyclo[4.3.0]nonane-8-one (TNABN) has also been evaluated for some of the explosive properties considering its good stability and insensitiveness as compared to other nitrodiurea derivatives.

## 1. Introduction

Explosives like TNT, RDX and HMX considered to be adequate for all weapon applications, have become less attractive due to a number of accidents involving initiation of munitions by impact or shock aboard ships, aircraft carriers and munitions trains. There is a need for the development of new explosives with improved stability and insensitivity without a decrease in energy. Significant attention has been paid in this direction during the recent past.

Our interest in azaheterocyclic nitramineureas arise from the fact that the urea moiety has an inherent high molecular density<sup>(1–3)</sup> and these compounds are considered as high explosives which can be made conveniently from inexpensive raw materials. Among the investigated compounds tetranitropropanediureas appear to be of renewed interest with a unique combination of properties like thermal stability as well as impact and friction sensitivity. In spite of the abundance of early literature on nitroureas<sup>(4–7)</sup>, details of the experimental procedure, the characterization and their applications are not found until more recent reports<sup>(8,9)</sup>.

With this goal in mind and as the next progression in the study of high-density compounds, the current research effort concentrates on preparing, characterizing and evaluating

tetranitropropanediurea (TNPDU) and an analogous tetranitromonourea compound in order to mediate some of the less desirable characteristics of TNPDU. We also report here the thermal properties of the compound and its mixtures for thermally stable and insensitive high explosives in order to assess their compatibility and sensitivity properties.

## 2. Experimental

Melting points were determined on a melting point apparatus and were not corrected. IR spectra were recorded on a Perkin-Elmer FTIR usually as KBr pellets. <sup>1</sup>H-NMR spectra were taken on Bruker-90 M with a pulsed Fourier transform (FT) system. Spectra were recorded at ambient temperature using tetramethylsilane (TMS) as an internal standard. Thin layer chromatography (TLC) was performed on silicagel 'g' plate.

The impact sensitivities were determined on an impact machine using a 2 kg weight dropped from heights which were varied according to the Bruceton "stair case" method<sup>(10)</sup>. The friction sensitivity measurements were carried out with an apparatus from Julius Peters, Berlin. Vacuum thermal stabilities were determined by holding 0.2 g of the explosive under vacuum at constant elevated temperature and measuring the volume of the evolved gas. The particle size was determined by Malvern Instrument SB 22 using water as a dispersion medium. The velocity of detonation<sup>(11)</sup> and the detonation pressure<sup>(12)</sup> were calculated by the methods reported in the literature.

### 2.1 Materials

Vinylethylether, ethyl orthoformate and BF<sub>3</sub>-ether complex were purchased from Fluka Chemie AG, Switzerland. 1,1,3,3-Tetraethoxypropane was purchased from Aldrich Chemical Co., USA and was also prepared in our laboratory. Anhydrous sodium carbonate, urea and hydrochloric acid were purchased from Qualigens Fine Chemicals. Fuming nitric acid was obtained from Ammunition Factory, Khadaki, Pune.

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## 2.2 Synthesis

The synthesis of tetranitropropane diurea consists of three steps:

- (1) the preparation of tetraethoxypropane,
- (2) the condensation of tetraethoxypropane with urea and
- (3) the nitration of propane diurea.

## 2.3 Preparation of 1,1,3,3-Tetraethoxypropane (TEP)

In a three-necked round bottom flask equipped with a pressure equalizer dropping funnel fitted with a calcium chloride tube at the top, a mixture of 10 g (0.067 mol) ethyl orthoformate and 0.09 ml of  $\text{BF}_3$ -ether complex was given to which 3 g (0.42 mol) vinyl ethylether was added dropwise during 15 min at a temperature below  $45^\circ\text{C}$ . After the addition, the mixture was stirred constantly at  $33^\circ\text{C}$  for 1 h. This was followed by the addition of 0.3 g sodium carbonate and the stirring was continued for an additional 3 h at room temperature. The precipitate was filtered and the filtrate was fractionated in vacuum in the presence of a small quantity of sodium carbonate as an acid quencher to yield 2.5 g (85 %) 1,1,3,3-tetraethoxypropane, b.p.  $90^\circ\text{C}$  at 800 Pa. The product was characterized by spectral data and elemental analysis.

Analysis Calcd for  $\text{C}_{11}\text{O}_4\text{H}_{24}$ : C 60.0%; H 10.90 %  
Found: C 59.5%; H 10.44 %

IR (KBr)  $\nu$ : 3000, 2950, 1444, 1380, 1116, 1064, 994  $\text{cm}^{-1}$

$^1\text{H-NMR}$  ( $\text{CD}_3\text{COCD}_3$ )  $\delta$ : 1.0 (t, 12H), 1.75 (t, 2H), 3.2–3.55 (m, 8H) 4.25–4.5 (t, 2H) ppm.

## 2.4 Preparation of 2,4,6,8-Tetraazabicyclo[3.3.1]Nonane-3,7-Dione (Propane diurea)

36 g (0.6 mol) of urea was dissolved in a mixture consisting of 30 ml of hydrochloric acid and 60 ml of water in round bottom flask. After the reaction the content was heated to  $50^\circ\text{C}$ . Then 44 g (0.2 mol) of 1,1,3,3-tetraethoxypropane was added dropwise while stirring. The resulting mixture was held at  $50^\circ\text{C}$  for 3 h and then was allowed to stand overnight at room temperature. The product obtained was filtered and dried to yield 14 g (45 %). Propane diurea thus obtained was recrystallized from water and offered fine colourless crystals with a melting point at  $312^\circ\text{C}$  (decomp). It was characterized by spectral data (IR, UV,  $^1\text{H-NMR}$ ) and elemental analysis. The differential thermal analysis (DTA) of the compound showed the endotherm at  $315^\circ\text{C}$ .

Analysis Calcd for  $\text{C}_5\text{H}_8\text{O}_2\text{N}_4$ : C 38.48%; H 5.16%; N 35.88 %  
Found: C 38.78%; H 5.23%; N 36.34 %

IR(KBr)  $\nu$ : 3258, 3095, 2985, 2900, 2850, 1636, 1628, 1528, 1425, 1368  $\text{cm}^{-1}$

$^1\text{H-NMR}$  ( $\text{CF}_3\text{COOD}$ , TMS)  $\delta$ : 7.40 (4H, br, -NH), 4.68(2H, br, -CH), 2.0 (2H, br,  $-\text{CH}_2-$ ) ppm.

## 2.5 Preparation of 2,4,6,8-Tetranitro-2,4,6,8-Tetraazabicyclo[3.3.1]Nonane-3,7-Dione (Tetranitropropane diurea, TNPDU)

The compound was prepared by adopting the method of Hong Guanlin *et al.*<sup>(8)</sup> with slight modifications of the reaction parameters.

A 500 ml round bottom flask equipped with thermometer and overhead stirrer containing 150 ml of nitric acid (98 %) was cooled to  $10^\circ\text{C}$  to which propane diurea 10 g (0.064 mol) was added slowly in small portions under constant stirring and cooling below  $18^\circ\text{C}$ . The reaction mixture was stirred at this temperature for 5 min and then 75 ml of acetic anhydride (97 %) was added dropwise at  $21^\circ\text{C}$  to  $23^\circ\text{C}$ . Under this condition the stirring was continued for 8–9 h and finally filtered to yield a white compound which was washed thoroughly and dried. The reaction was monitored by IR spectrum in KBr matrix till the disappearance of the NH peak at  $3258\text{ cm}^{-1}$ . The yield of the fully converted nitramine product was 17.6 g (82 %). Recrystallization from nitromethane gave a compound of m.p.  $>220^\circ\text{C}$  (deflagration). With this optimized conditions the batch size was enhanced to 10–15 g. The compound was fully characterized by IR,  $^1\text{H-NMR}$  and elemental analysis. DTA results showed the decomposition peak temperature at  $235^\circ\text{C}$ .

Analysis Calcd for  $\text{C}_5\text{H}_4\text{N}_8\text{O}_{10}$ : C 17.84%; H 1.19%; N 33.33 %  
Found: C 18.01%; H 1.15%; N 32.89 %

IR(KBr)  $\nu$ : 3026, 2995, 1762, 1604, 1528, 1425, 1356, 1128, 1010  $\text{cm}^{-1}$

$^1\text{H-NMR}$  ( $\text{CD}_3\text{COCD}_3$ , TMS)  $\delta$ : 7.41(2H, t, CH), 3.55(2H, m,  $\text{CH}_2-$ ) ppm.

## 2.6 Hydrochloride of 2,5,7,9-Tetraazabicyclo[4.3.0]Nonane-8-One (TABN)

In a 500 ml two-necked round-bottomed flask, 16 ml (0.1 mol) of glyoxal (30 %) were placed and ethylenediamine (70 %) (10.5 ml, 0.1 mol) was added with stirring. The pH of the reaction mixture was adjusted to 8.5–9.5. The reaction mixture was then stirred for 40 min and cooled to  $10^\circ\text{C}$ . After the addition of 6.2 g (0.1 mol) urea concentrated HCl (50 ml) was dropped slowly at  $15^\circ\text{C}$  for one hour. The solution was stirred for additional 2 h and

allowed to stand overnight. Yellow crystals of TABN precipitated. The product was filtered, washed with water and ethanol, and finally dried to yield 2.5 g (10.4%) of a light yellow solid, m.p. 183 °C to 185 °C.

Analysis Calcd for  $C_5H_{14}Cl_2N_4O_2$ : C 25.74%; H 6.05%; N 24.24%

Found: C 25.20%; H 5.79%; N 23.69%

IR(KBr)  $\nu$ : 3190, 2362, 2136, 1764, 1504, 1414, 1340, 1250, 1122  $cm^{-1}$

$^1H$ -NMR (DMSO- $D_6$ )  $\delta$ : 8.30 (2H, NH), 7.50 (2H, NH), 4.9 (2H, -CH-), 3.8 (4H, -CH<sub>2</sub>-) ppm.

### 2.7 Preparation of 2,5,7,9-Tetranitro-2,5,7,9-Tetraazabicyclo[4.3.0]Nonane-8-One (TNABN)

To 30 ml of acetic anhydride 45 ml of concentrated nitric acid (99.5%) were added at 25 °C with constant stirring. A quantity of 4.0 g (0.02 mol) of HCl-salt of TABN were added in small portions to keep the temperature of the reaction mixture below 45 °C. The mixture was stirred for 6 h and cooled to room temperature. The product precipitated was filtered, washed and dried to yield 2.8 g (50.5%). Crystallization from nitromethane produced white crystals, m.p. 194 °C–196 °C.

Analysis Calcd for  $C_5H_6N_8O_9$ : C 18.64%; H 1.88%; N 34.78%

Found: C 19.16%; H 1.44%; N 34.6%

IR (KBr)  $\nu$ : 3028, 2342, 1772, 1568, 1424, 1360, 1178, 870, 738  $cm^{-1}$

$^1H$ -NMR (DMSO- $D_6$ )  $\delta$ : 4.40–4.93 (4H, CH<sub>2</sub>-CH<sub>2</sub>), 7.97 (2H, -CH-) ppm.

### 2.8 Thermal Decomposition and Explosion Delay Measurements

Thermal decomposition studies of TNPDU and its mixtures were carried out using a micro differential thermal analyzer (m-DTA) fabricated in our laboratory. Details of the apparatus are given elsewhere<sup>(13)</sup>. The mixtures of the TNPDU with 3-amino-5-nitro-1,2,4-triazole (ANTA),

triaminotrinitrobenzene (TATB), 5-nitro-1,2,4-triazole-3-one (NTO) and TNABN were made in 1 : 1 proportion with the help of pestle and mortar. A sample of 10 mg was heated at a heating rate of 10 °C/min against the equal amount of reference material (calcined alumina). The magnitude of exothermicity was considered as the ratio of peak height to the corresponding weight of the sample.

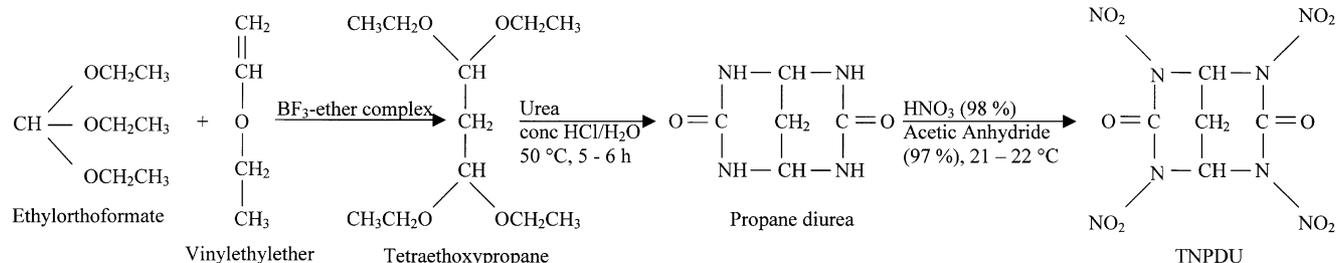
The deflagration temperature was determined by heating a sample of 0.02 g in a glass tube in a Woods metal bath at a rate of 5 °C/min. The temperature of ignition was recorded<sup>(14)</sup>.

The explosion delay measurements for TNPDU were carried out using a Wood's metal bath fabricated indigenously and following the method reported by Agrawal and Agrawal<sup>(15)</sup>. A sample of about 5 mg was taken in a cup tightly covered with lid and was dropped in a Wood's metal bath maintained at the required temperature. The measurements were made by the help of an automatic clock mechanism which starts at the time of dropping and stops at the time of explosion. The start and the stop mechanisms were achieved with an optical and a sound sensor, respectively. The explosion delay was measured at different temperatures using the same quantity of explosives.

## 3. Results and Discussion

At the start of our 2,4,6,8-tetranitro-2,4,6,8-tetraazabicyclo[3.3.1]nonane-3,7-dione, commonly called tetranitropropane diurea (TNPDU), synthesis and scale up, we followed the procedure of Hong Guanlin *et al*<sup>(8)</sup>. TNPDU was prepared in our laboratory by the condensation of 1,1,3,3-tetraethoxypropane with urea according to Mannich reaction, followed by the nitration in acidic medium with nitric acid–acetic anhydride (Scheme 1). Initially the 1,1,3,3-tetraethoxypropane for the preparation of propane diurea was taken from a commercial source. However, in due course, it was synthesized successfully in our laboratory with the aim of a cost effective production of the target compound. The compound has been satisfactorily characterized by spectral data and elemental analysis.

Following the procedure propane diurea was prepared in different batches with an average yield of 26 to 29% and subsequently converted to tetranitropropane diurea. The slow nitration procedure reported here has the advantage of a significant higher yield (79–84%) and excellent product



Scheme 1. Synthesis of TNPDU.

**Table 1.** Physico-chemical and Explosive Properties of Tetranitropropane Diurea (TNPDU) and TNABN

Ser. No.	Property	TNPDU	TNABN
1	Melting point, °C	> 220	> 230
2	Density, g/cm <sup>3</sup> (experimental)	1.93	1.92
3	Particle size, μm	32–33	14
4	DTA, peak temp. °C	220	235
5	Deflagration temp. °C	252–255	202
6	Impact sensitivity, cm (height for 50 % explosion with 2 kg wt.)	27.5	115
7*	F of I	30.31	92
8	Friction sensitivity (Julius Peters Apparatus)	Insensitive upto 8 kg	Insensitive upto 36 kg
9	Velocity of detonation, m/s (calcd.)	9034 ( $\rho = 1.93 \text{ g/cm}^3$ )	9015 ( $\rho = 1.92 \text{ g/cm}^3$ )
10	Detonation pressure, GPa (calcd.)	39.38	37.0
11	Oxygen balance, %	–9.5	–19.9
12**	Heat of formation ( $\Delta H_f$ ), kJ/mol	–81.39	+ 70.313

\*The sensitivity of explosives is also expressed by the Figure of Insensitivity (F of I) where Tetryl (CE) is chosen as standard<sup>(16)</sup> (F of I  $\approx$  70). The value obtained shows that TNPDU is more sensitive than CE.

\*\*Heats of formation (unpublished data) were calculated using G. DePaz and Ciller empirical equations<sup>(17)</sup> where  $\Delta H_f$  in gas phase was considered from the parametrization method 3 (PM3) using GAUSSIAN-94 program.

purity offset by the lengthy “digestion” period, a not insignificant inconvenience for scale-up efforts. During the nitration reaction, the formation of the product was monitored by IR spectroscopy. The disappearance of the  $> \text{NH}$  stretching band in the spectra indicates the complete conversion of propane diurea to tetranitropropane diurea. The peaks at 3026, 2995 and 1762  $\text{cm}^{-1}$  are due to  $> \text{CH}$  and  $> \text{C}=\text{O}$  stretchings whereas the strong absorptions of  $\text{N}-\text{NO}_2$  stretching frequencies are observed at 1604 and 1356  $\text{cm}^{-1}$ , respectively. In the NMR spectrum, the signal for the methylene protons appears as a triplet at 7.41 ppm and the second triplet at 3.55 ppm is assigned for the  $-\text{CH}_2$  protons.

Tetranitropropane diurea is a white crystal solid with a density of 1.93  $\text{g/cm}^3$ . This compound exhibits better hydrolytic stability than similar compounds. It is stable in neutral and acidic medium while immediate decomposition was observed in alkaline medium (0.1 M NaOH). The compound was further characterized for its preliminary explosive properties (Table 1). The results show that the compound itself is sensitive to both impact and friction but it has high thermal stability. TNPDU has a relatively small particle size of 32  $\mu\text{m}$  with a typical broad distribution and exhibits often two distinct modes. The size meets the requirements for propellant and explosive formulations.

In order to explore its suitability in propellant and explosive formulations, different compositions were made by uniform coating with polyurethane and paraffin wax, and evaluated for preliminary explosive properties. The data

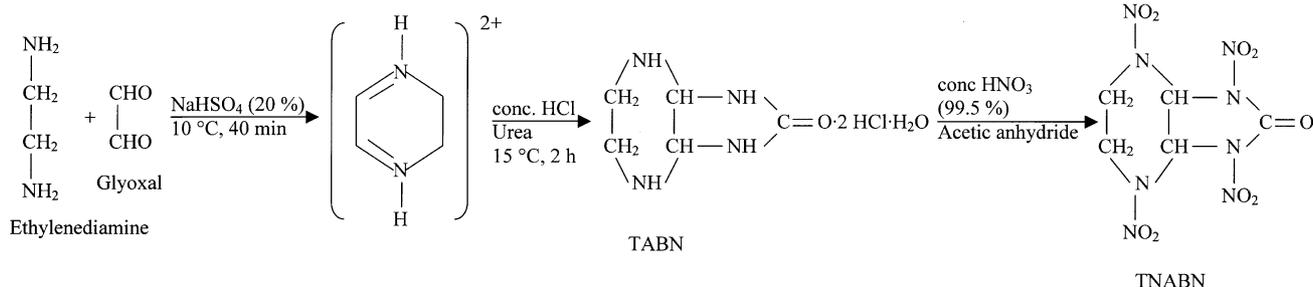
given in Table 2, are the average of two independent tests under identical conditions. Out of which, the composition containing TNPDU – paraffin wax (85 : 15) is found with substantial decrease in sensitivity to impact and friction, thereby revealing its suitability for the next progression in the study of propellant formulations.

Further, in order to improve the hydrolytic stability of compounds containing carbonyl groups we prepared 2,5,7,9-tetranitro - 2,5,7,9 - tetraazabicyclo[4.3.0]nonane - 8 - one, TNABN (Scheme 2) which possesses better properties in terms of sensitivity to impact and friction than those of tetranitropropane diurea (Table 1). Both TNPDU and TNABN are powerful explosives with high densities and high detonation velocities. These compounds are significantly more resistant to hydrolytic destruction than tetranitroglycoluril (TNGU). TNGU has one of the highest densities of the organic explosives ( $\rho = 2.04 \text{ g/cm}^3$ ), but in an aqueous suspension it is completely hydrolysed in less than 4 h. The comprehensive properties of TNPDU are superior to other similar compounds like Sorguyl (TNGU) or Dinitroglycoluril (DINGU). In addition, the compounds have a better oxygen balance than cyclotetramethylenetetranitramine (HMX) (Table 1). A detailed investigation of the compound is under study. The compound was characterized by spectral (IR and <sup>1</sup>H-NMR) and elemental analysis.

The single component TNPDU and a binary system formed with an insensitive class of explosive have been subjected to vacuum stability tests at 90 °C for 48 hours.

**Table 2.** Impact and Friction Sensitivity Data of TNPDU and Phlegmatized TNPDU

Ser. No.	Composition	Impact sensitivity		Friction sensitivity, kg (Insensitive upto)
		Height for 50 % explosion, cm (2 kg)	F of I	
1	TNPDU,	20	18	8
2	TNPDU/Polyurethane, 90/10	25	19	12
3	TNPDU/Polyurethane, 85/15	26	23	19.2
4	TNPDU/Polyurethane, 80/20	40	35	16
5	TNPDU/Paraffin wax, 90/10	26	20	21.6
6	TNPDU/Paraffin wax, 85/15	47	41	36



**Scheme 2.** Synthesis of TNABN.

The measured results of the study (Table 3) show that TNPDU is exceedingly compatible with ANTA, TATB, NTO and TNABN (values are much less than 1 ml/5 g in all cases).

### 3.1 Thermal and Delay Studies

Figure 1 represents the DTA curve of TNPDU. It is seen that there is only one sharp exotherm with a temperature of initiation at  $T_i=194^\circ\text{C}$  and a temperature of the peak maximum at  $T_m=220^\circ\text{C}$ . The magnitude of exothermicity was found to be 10.5 (Table 4) which indicates the highly exothermic nature of the decomposition reaction.

From the DTA curves, the initiation temperatures and the peak or maximum temperatures for the decomposition of the compounds and their equiproportion mixtures with other insensitive explosives are calculated and presented in Table 4. In every case the begin of the exothermic reaction and the maximum are shifted to higher temperatures. The data in Table 4 show that high explosives with lower thermal sensitivity bring down the exothermicity of TNPDU suggesting thereby that the mixtures might be safer from the processing point of view.

Table 5 shows the delay measurement data on TNPDU. It has been observed that explosion delay decreases as the temperature increases revealing the rapidity of the reaction with high temperature. The activation energy of TNPDU was calculated from delay measurements using the following equation. It was found to be 40.5 kJ/mol.

$$E_a = \frac{4.576 \cdot (\log[t_1] - \log[t_2]) T_1 \cdot T_2}{T_2 - T_1}$$

**Table 3.** Compatibility of Vacuum Stability Data on TNPDU and its Mixtures with ANTA, TATB, TNABN and NTO

Ser. No.	Composition	Vacuum stability at 94 °C for 48 h, ml/5 g
1	TNPDU (crystalline)	0.7597
2	TNPDU (amorphous)	0.6191
3	TNPDU : ANTA (1 : 1)	0.4929 (0.3104)
4	TNPDU : TATB (1 : 1)	0.4369 (0.206)
5	TNPDU : TNABN (1 : 1)	0.5245 (0.3395)
6	TNPDU : NTO (1 : 1)	0.4098 (0.2139)

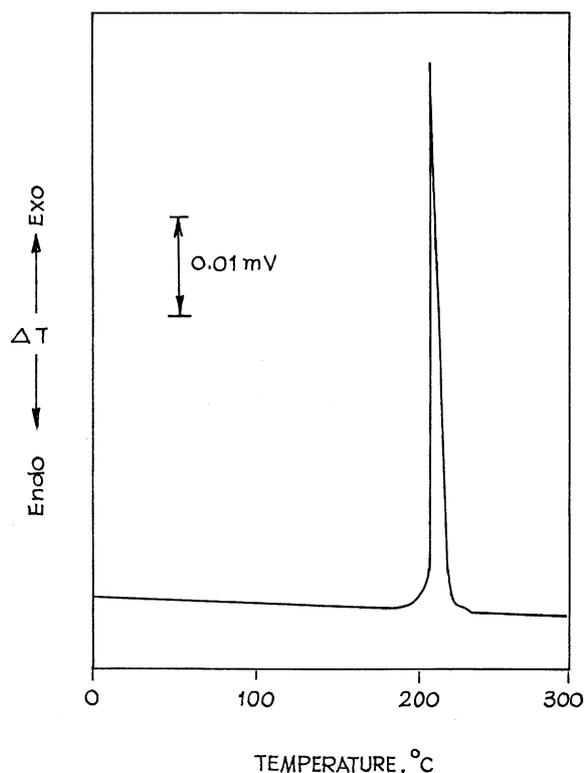
Note: Values in parentheses indicate the vacuum stability data of the single components: ANTA, TATB, TNABN and NTO

where  $E_a$  = activation energy  
 $t_1, t_2$  = delay times in seconds  
 $T_1, T_2$  = temperatures for the above delay times in K

The combination of thermal stability with the results of preliminary explosive properties is unique and thus creates a renewed interest in its suitability for further studies in explosive and propellant formulations.

### 4. Conclusion

Tetranitropropane diurea (TNPDU) has been prepared from the condensation reaction of urea with tetraethoxypropane followed by nitration with nitric acid – acetic anhydride. The data on thermal analysis and preliminary



**Figure 1.** DTA curve of TNPDU.

**Table 4.** Differential Thermal Analysis (DTA) Data on High Explosives and their Mixtures

Ser. No	Compound/Mixture	$T_i$ (°C)	$T_m$ (°C)	Exothermicity
1	TNPDU	194	220	10.5
2	NTO	254	260	7.47
3	ANTA	222	230	12.95
4	TATB	235	360	7.36
5	TNABN	199	205	1.15
6	TNPDU + NTO	220	240	10
7.	TNPDU + ANTA	220	245	3.9
8.	TNPDU + TATB	218	235	3.57
9	TNPDU + TNABN	199	220	2.65

**Table 5.** Explosion Delay Measurements of TNPDU

Ser. No.	Temperature (°C)	Explosion delay (s)
1	220	12.0
2	230	9.4
3	240	7.4
4	250	6.8

explosive properties of TNPDU show its suitability for further studies in propellant and explosive formulations.

An analogous compound 2,5,7,9-tetranitro-2,5,7,9-tetraazabicyclo[4.3.0]nonane-8-one has also been prepared and evaluated for preliminary explosive properties. This compound gives a promising blend of explosive properties and insensitivity to impact and friction.

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## Symbols and Abbreviations:

$\delta$	delta
$\mu\text{m}$	micrometer
mm	millimeter
$\nu$	wave number (nu)
$\Delta H_f$	heat of formation
$E_a$	activation energy
m.p.	melting point
b.p.	boiling point
ppm	parts per million
Pa	Pascal
br.	broad
$T_i$	temperature of initiation
$T_m$	temperature of maximum
F of I	figure of insensitivity
DTA	differential thermal analysis
m-DTA	micro differential thermal analyzer
$\text{BF}_3$	boron trifluoride
TNT	trinitrotoluene
RDX	1,3,5-trinitro-1,3,5-triazacyclohexane
HMX	1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane
DINGU	1,4-dinitroglycoluril
SORGUYL	1,3,4,6-tetranitroglycoluril(TNGU)
TNPDU	Tetranitropropane diurea
TNABN	Tetranitrotetraazabicyclononanone
ANTA	3-Amino-5-nitro-1,2,4-triazole
TATB	1,3,5-Triamino-2,4,6-trinitrobenzene
NTO	3-Nitro-1,2,4-triazole-5-one

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