

## Alternate method for synthesis of 1,3,3-trinitroazetidine (TNAZ): Next generation melt castable high energy material

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The synthesis of 1,3,3-trinitroazetidine (TNAZ) from 2,2-dinitropropane-1,3-diol precursor derived from nitromethane is described. The cyclization of 1,3-dichloro-2,2-dinitropropane in presence of *t*-butyl amine to *t*-butylated azetidine ring, followed by its nitration afforded target molecule TNAZ in minimum number of synthesis steps. TNAZ was characterized by elemental analysis, Spectral Energy Dispersive Analyser-X-ray (EDAX), and Scanning Electron Microscope (SEM) techniques. Thermolysis studies on TNAZ were undertaken using Differential Scanning Calorimetry (DSC) and Thermo Gravimetric (TG) techniques. The Fourier Transform Infrared (FTIR) of decomposition products of TNAZ revealed the evolution of oxides of nitrogen and –CN containing species suggesting the cleavage of C/N-NO<sub>2</sub> bond accompanied with the collapse of the ring structure. The sensitivity data obtained for the TNAZ indicated its sensitive nature towards external stimuli (Impact height ( $h_{50\%}$ ) for explosion > 47 cm; Friction insensitive up to > 36 kg). The theoretically predicted performance parameters suggest that TNAZ is energetically superior in terms of velocity of detonation (VOD: 8.6 km/s) and power index (PI: 182) compared to the conventionally used melt castable high explosive 2,4,6-trinitrotoluene (TNT) (VOD-6.66 km/s and PI-125).

**Keywords:** Trinitroazetidine, Melt cast explosive, Synthesis, Thermolysis

**IPC Code:** Int.Cl.<sup>7</sup> C06B25/00

The nitramine class of compounds characterised by high energy content continue to be the source of new explosives. The search for more powerful and less sensitive energetic materials has brought strained polynitro cyclic compounds into focus<sup>1</sup>. Such materials have potential of application as an energetic component of high performance explosives and propellants. One of the molecules of this class that has evinced interest since 1990 is 1,3,3-trinitroazetidine (TNAZ)<sup>2,3</sup>. The compound has attracted considerable attention as melt castable energetic material due to an attractive combination of moderately low melting point (101°C) and thermal stability up to 180°C). Its advantages compared to the today's most sought after melt castable explosive, 2,4,6-trinitrotoluene (TNT) are superior density (1.89 g/cm<sup>3</sup>) and velocity of detonation (> 8500 m/s). TNAZ is close to hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in terms of energetics and yet is less vulnerable than it ( $h_{50\%}$  explosion, 45-47 cm) compared to RDX<sup>4,5</sup>. Unlike octahydro-1,3,5,7-tetranitro-1,3,5,7-

tetrazocine (HMX), TNAZ is soluble in molten TNT, and is compatible with aluminium, steel, brass and glass<sup>6</sup>. TNAZ is reported to offer low vulnerable ammunition (LOVA) gun propellant formulation<sup>7</sup> having 10% higher energy content compared to corresponding RDX based composition XM-39. TNAZ was first synthesized<sup>8</sup> in 1983 and since then continued work is being done on its synthesis<sup>8-22</sup>. However, the overall yield obtained from different synthesis routes is poor<sup>8-19</sup>. This coupled with multistep process results in high cost of the TNAZ, which is the greatest hindrance for large-scale adoption in its military applications.

Recently, Shu<sup>9</sup> reported five steps synthesis of TNAZ from nitromethane resulting in 34% yield. In view of the emergence of TNAZ as a next generation high energy material (HEM), it was considered worthwhile to search for alternative synthesis approach for TNAZ with improved yields in minimum number of synthetic steps. Most of the reported methods<sup>8-22</sup> involve construction of the

azetidine ring in the first step, followed by its nitration. In the present synthesis approach, first the precursor with gem dinitro functionality is prepared and then it is cyclized to an azetidine ring.

## Experimental Procedure

### Methods

The starting materials used in the present study were of AR grade and used directly as purchased from the trade. The reactions were carried out in oven-dried glassware under dry N<sub>2</sub> environment. After work-up, organic layer was washed with water, brine and dried over anhydrous sodium sulphate. The product was isolated by evaporating the solvent at reduced pressure. Thin Layer Chromatography (TLC) was performed on pre-coated plates (0-25 mm, silica gel 60 F<sub>254</sub>). Column chromatography was carried out using 100-200 mesh silica gel. The melting point of the synthesized compound was measured using Thomas Hoover capillary melting point apparatus. The SEM and EDAX of the sample was recorded using Instrument of Philips make (FEI XL-30 model). The energy of electron beam impinged on the samples was of the order of 5 kV. The IR spectra were determined as nujol mull on a Perkin-Elmer-1600 FTIR spectrophotometer. Proton NMR spectra were recorded on Varian 300 MHz spectrometer with tetramethyl silane (TMS) as an internal standard. Elemental analysis was carried out on Perkin-Elmer instrument. TG-FTIR of the product was undertaken on simultaneous thermo-gravimetry-differential thermal analyzer (TG/SDTA-Mettler Toledo 851) in conjunction with FTIR of Bruker make (Equinox Model-55) system at the heating rate of 10°C/min in nitrogen atmosphere at a flow rate of 80 cm<sup>3</sup>/min. DSC was obtained on Perkin-Elmer-7 system at the heating rate of 10°C/min in nitrogen atmosphere. The impact sensitivity test was conducted using a set-up similar to that used in Naval Ordnance Laboratory (NOL), USA. Test specimens (30-35 mg of powder) were kept between two hardened stainless steel anvils and a 3 kg drop weight was allowed to fall freely from different heights. Both open and aluminum foil encapsulated specimens were used for evaluation. Ten tests were conducted for each compound. The results are reported in terms of height for 50% probability of explosion (h<sub>50%</sub>) of the sample. The friction test was also conducted in a test set-up similar to the one employed by NOL. The sample was kept between a fixed corrugated (rough) and a movable stainless steel

plate. Pulling of the movable plate at varying lever loads subjected sample to friction stimuli. The sample size and the procedure was same as followed for impact testing. The impact and friction sensitivity studies of bench mark explosives RDX, HMX and teryl were also carried out under identical conditions to validate the experimental set-up as well as to obtain relative data. The performance parameters of the newly synthesized compounds were predicted using Linear Output Thermodynamic User Friendly Software for Energetic Systems (LOTUSES) code<sup>23-25</sup>.

### Synthesis of compounds

#### *Preparation of 2,2-dinitropropane-1,3-diol, (2)*

A mixture 6.82 g (0.11 mol) of nitromethane and 18.88 g of 37% formaldehyde in 17.2 g of water was cooled down to 0°C. A few drops of solution of 5.75 g of NaOH in 15 mL of water were added to the reaction mixture with vigorous shaking. The cooling was stopped and temperature was allowed to rise to 40°C. The contents were again cooled to 0°C and remaining sodium hydroxide solution was added in a steady stream maintaining the temperature of the reaction mixture between -5 to + 5°C. After the completion of the addition, the mixture was allowed to stand for 1-2 h, at 0°C and then 8.65 g of NaNO<sub>2</sub> (0.125 mol) was added. This entire mixture was added to a solution of 42.56 g (0.250 mol) of AgNO<sub>3</sub> in 56 mL of distilled water kept at a temperature below 25°C. The contents were stirred for 2 h at 0°C. The silver precipitate salt was removed by filtration and the filtrate was extracted with three portions of 1:1 ether-water mixture. The extracts were dried on sodium sulphate, and the ether was evaporated to obtain yellow coloured liquid. Methylene chloride was added to product, and the resulting solution was cooled to precipitate the colourless compound **2** (9.83 g, 53% yield) having a melting point of 144-145°C, (Reported, 146-147°C). IR ν<sub>max</sub> nujol/cm<sup>-1</sup> 765, 843, 873, 924, 1068, 1158, 1260, 1319, 1374, 1594, 2457, 2565, 2923, 3259, 3350. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) δ: 4.37 (4H, s), 3.6 (2H, bs, -OH). Anal. Calcd for C<sub>3</sub>H<sub>6</sub>N<sub>2</sub>O<sub>6</sub> (166): C, 21.68; H, 3.61; N, 16.86; Found: C, 22.01; H, 3.43; N, 16.42.

#### *Preparation of 1,3-dichloro-2,2-dinitropropane, (3)*

Five grams of 2,2-dinitropropane-1,3-diol (**2**) (0.030 mol) was dissolved in 12.5 mL of thionyl chloride. Pyridine hydrochloride (0.750 g) was added

to the solution and the contents were refluxed for 72 h. The excess of thionyl chloride was removed *in vacuo* and the oily residue was fractionated under reduced pressure resulting in 4.95 g (81%) of product having boiling point of 60°C (60-62°C). Sublimation of the liquid product afforded **3** as a white solid having melting point of 38-39°C. IR  $\nu_{\text{max}}$  nujol/cm<sup>-1</sup>: 769, 772, 843, 873, 924, 1035, 1068, 1158, 1260, 1319, 1374, 1460, 1545, 2865, 2927. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 4.53 (4H, s). Anal. Calcd for C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>O<sub>4</sub>Cl<sub>2</sub> (202): C, 17.82; H, 1.98; N, 13.86; Found: C, 17.64; H, 1.92; N, 13.98.

#### Preparation of 1-tert-butyl-3,3-dinitroazetidine, (**4**)

To a solution of 0.59 g of *t*-butyl amine (0.0081 mol), in dry methanol (10 mL), 4.17 g of potassium carbonate (0.030 mol) was added and the reaction mixture stirred for 1 h. Subsequently, 1.64 g of compound **3** (0.0081 mol) in dry methanol (5-7 mL) was added slowly. The reaction mixture was refluxed for 24 h. The contents were allowed to cool down and the excess of methanol was evaporated. The residue was extracted with ethyl acetate/water and dried on sodium sulphate. Evaporation of the excess of solvent followed by purification by column chromatography (hexane/ethyl acetate 2:8) afforded compound **4**, (0.10 g, 21.00%). IR  $\nu_{\text{max}}$  nujol/cm<sup>-1</sup>: 808, 852, 882, 943, 1029, 1083, 1122, 1207, 1241, 1303, 1364, 1479, 1569, 2972. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.6 (4H, s), 1.1 (9H, s); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 26.38, 50.82, 63.12, 118.7. Anal. Calcd for C<sub>7</sub>H<sub>13</sub>N<sub>3</sub>O<sub>4</sub> (203): C, 41.38; H, 6.40; N, 20.69; Found: C, 41.59; H, 6.50; N, 20.64.

#### Preparation of 1,3,3-trinitroazetidine, (**1**)

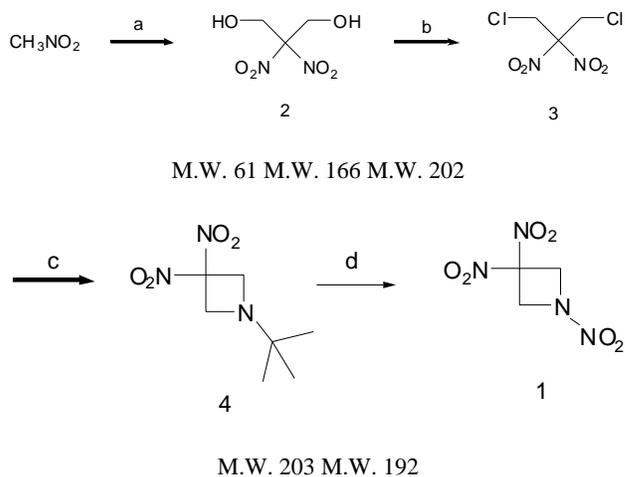
Acetic anhydride (10 mL) was allowed to cool down to 2°C in an ice bath, and 98% nitric acid (3.0 mL) was added, dropwise, at a rate such that the temperature was maintained at 10°C. The solution was stirred for 5 min, and then 0.753 g compound **4** was added dropwise. The stirring was continued for 1 h. Subsequently, dichloromethane (50 mL) was added, and the solution was washed with water followed by 10% aqueous sodium bicarbonate (50 mL). It was then dried over sodium sulphate. The solvent was evaporated, and the solid residue was recrystallised with carbon tetrachloride to yield 0.20 g, (28%) of TNAZ **1**, having melting point of 101°C. IR  $\nu_{\text{max}}$  nujol/cm<sup>-1</sup>: 662, 712, 762, 840, 868, 908, 1086, 1112, 1216, 1278, 1334, 1426, 1461, 1539,

1594, 2910, 2970, 3036. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 5.19 (4H, s); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>)  $\delta$ : 104, 63.2; Anal. Calcd for C<sub>3</sub>H<sub>4</sub>N<sub>4</sub>O<sub>6</sub> (192): C, 18.75; H, 2.09; N, 29.17; Found: C, 18.89; H, 2.10; N, 29.43.

## Results and Discussion

### Synthesis and structure

The base catalyzed reaction between nitromethane and formaldehyde gave 2,2-dinitropropane-1,3-diol (**2**). The compound has been characterized by elemental analysis and spectroscopy to confirm its formation. The IR spectrum of **2** clearly indicated the presence of gem dinitro functional group at 1595 cm<sup>-1</sup>, and the alcoholic band appeared at 3350 cm<sup>-1</sup>. Compound **2** on chlorination gave compound **3**. Its formation was confirmed by <sup>1</sup>H NMR. The presence of chlorine resulted in downfield shift of the signal attributed to four methylene protons ( $\delta$  4.53) compared to **2** ( $\delta$  3.6) due to the high electronegativity of the chlorine. Condensation of **3** with *t*-butyl amine afforded the cyclized *t*-butyl azetidine (**4**). The subsequent nitration of **4** with 98% nitric acid resulted in TNAZ (**1**). The yield of TNAZ obtained during the present work was 28-30%. The compound **4** and TNAZ could be well distinguished by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectral data. The methyl protons resonated at  $\delta$  5.19 (4H, s, 2 X CH<sub>2</sub>) in the proton spectrum of TNAZ. The IR spectrum of TNAZ displayed major IR stretching vibrations at 3036, 2970, 2910 (CH); 1594, (N-NO<sub>2</sub>); 1540 (C-NO<sub>2</sub>) and 1426 (C-N). The elemental analysis further confirmed



Scheme 1: (a) NaOH-H<sub>2</sub>O, HCHO, AgNO<sub>3</sub>, NaNO<sub>2</sub>; (b) Pyridine hydrochloride, SOCl<sub>2</sub>; (c) *t*-Butyl amine, K<sub>2</sub>CO<sub>3</sub>, dry MeOH; (d) Ac<sub>2</sub>O, HNO<sub>3</sub> CH<sub>2</sub>Cl<sub>2</sub>.

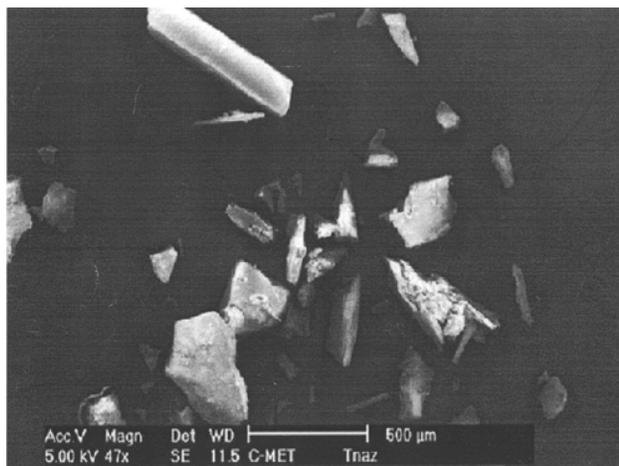


Fig. 1—SEM of TNAZ

the synthesis of the compound. The EDAX of TNAZ gave nitrogen (29.27%) and oxygen (48%) content in close agreement with the theoretical values (nitrogen: 29.17%; oxygen: 50%). The SEM of TNAZ revealed rod and square shaped morphology (Fig. 1).

#### Thermal and sensitivity studies

The thermal and sensitivity characteristics of TNAZ determined during this work are given in Table 1. The DSC of TNAZ (Fig. 2) exhibited a sharp endotherm at 100°C corresponding to its melting point ( $\Delta H$  158.4 J/g). It was followed by an exotherm having ( $T_{max}$ ) at 214°C ( $\Delta H$  of 68.41 J/g). A minor exotherm was also observed at 194°C ( $\Delta H$  of 9.3 J/g). The enthalpy derived from the DSC peaks at 100°C may not be only due to melting but may represent integrated effect of fusion and vaporization. This calls for the further in-depth DSC studies to confirm the integrated effect of fusion and vaporization. In TGA, TNAZ recorded two step weight loss in the temperature region of 100-130 and 130-170°C. The weight loss in the first step may be attributed to its volatilization, whereas the evaporation accompanied with partial decomposition may be occurring during second step. Owing to the complexity of phenomenon due to interplay between evaporation and decomposition, the results are expected to be valid for a given experimental set-up. The rapid rate of evaporation of TNAZ from the molten phase is of concern from safety and processing viewpoint. The sensitivity test results brought out that TNAZ is impact insensitive up to 47 cm ( $h_{50\%}$  explosion) and it is friction insensitive up to load of > 36 kg (Table 1).

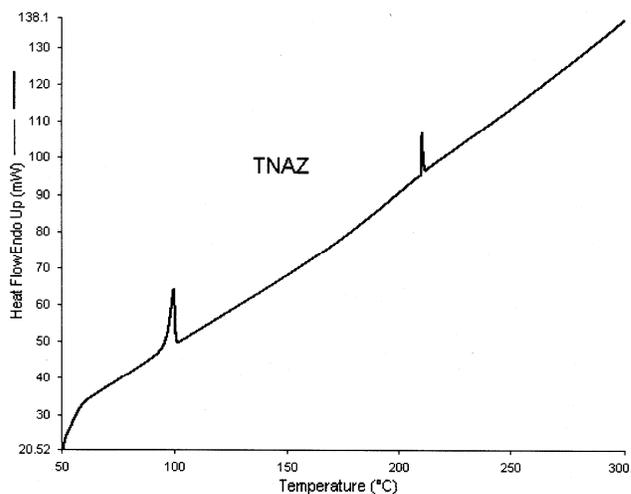


Fig. 2—DSC of TNAZ

Table 1—Explosive and thermal properties of TNAZ

Melting point (°C)	101
Thermal stability (DSC), (°C) Endotherm	101
Exotherm	194
TGA (weight loss%) 1 <sup>st</sup> step	97-130 (27%)
2 <sup>nd</sup> step	130-170 (73%)
Activation energy (kJ/mol): 1 <sup>st</sup> step	55
2 <sup>nd</sup> step	75
Impact sensitivity ( $h_{50\%}$ ), cm	45-47
Friction sensitivity (kg)	36

Sensitivity to impact: RDX, 28-30; HMX, 23-25; Tetryl, 74-78 cm; Sensitivity to friction: RDX: 19; HMX: 16; Tetryl, 36 kg.

These trends suggest its overall low vulnerability to mechanical stimuli compared to that of other nitramine explosives such as RDX and HMX ( $h_{50\%}$  friction insensitive up to 16 and 19 kg, respectively).

#### Hyphenated TG-FTIR studies

The FTIR of gaseous decomposition products of TNAZ evolved during TG revealed the presence of oxides of nitrogen (1521 and 1651  $\text{cm}^{-1}$ ), OH<sup>-</sup> containing species (3842, 3743 and 3675  $\text{cm}^{-1}$ ) and -CN containing species (2358, 1464  $\text{cm}^{-1}$ ), as well as CO (2424  $\text{cm}^{-1}$ ). The oxides of nitrogen may result from the cleavage of the both N-NO<sub>2</sub> and C-NO<sub>2</sub> linkages, whereas evolution of -CN containing species like HCN may be an outcome of the cleavage of the ring structure. The strained structure of TNAZ is expected to favour the collapse of the heterocyclic ring. The results obtained are in line with the data reported by other researchers. Various researchers identified 1-nitroso-3,3-dinitroazetidene (NDNAZ) as

Table 2—Performance parameters of TNAZ and other conventional explosives

Sl No	MW	Composition (wt. %)				OB (%)	DF	VOD (km/s)	C-J-P (Gpa)	SI (db)	$\rho$ (g/cm <sup>3</sup> )	$H_e$ (kJ/kg)	RS	PI (%)
		C	H	N	O									
TNAZ	192.1	18.76	2.10	29.17	49.97	-16.66	5.03	8.68	34.25	345	1.76	5733	175.4	182.7
TNT	227.1	37.01	2.21	18.50	42.26	-73.96	3.92	6.66	19.26	275	1.66	2953	120.1	125.1
RDX	222.1	16.22	2.72	37.84	43.21	-21.61	5.18	8.93	36.48	353	1.77	4777	162.6	169.4
HMX	296.1	16.22	2.72	37.84	43.21	-21.61	5.24	9.04	39.49	355	1.77	4777	162.6	169.4
Tetryl	287.2	29.2	1.75	24.39	44.57	-47.35	4.53	7.77	27.32	317	1.75	3567	125	130.4

TNAZ: 1,3,3-Trinitroazetidide; TNT: 2,4,6-trinitrotoluene; RDX: Hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX: Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; Tetryl: *N*-methyl-*N*-nitro-2,4,6-trinitrotoluene; MW = Molecular weight of HEM; OB = Oxygen balance; DF = Detonation factor; VOD = Velocity of detonation; CJ-P = Chapman Jouget Pressure; SI = Sound intensity;  $\rho$  = Density; RS = Relative strength (as per Bertlot approximation as compared to TNT on a mass basis);  $H_e$  = Heat of explosion; PI = Power index (in comparison to picric acid).

the stable intermediate of thermal decomposition of TNAZ in condensed phase<sup>26</sup>. The SCF-MO-AM1 calculations<sup>27</sup> suggest the homolysis of N-NO<sub>2</sub> bond as the primary step of thermolysis of secondary nitramines in a condensed phase<sup>28</sup>.

#### Explosive properties

The theoretically predicted performance parameters of TNAZ indicated its superior energy levels in comparison to conventional explosives such as TNT and tetryl in terms of velocity of detonation. Its performance level appears to be close to that of the well known bench mark explosive RDX. However, the predicted power index of TNAZ appears to be higher than that of not only RDX but also of HMX (Table 2).

#### Conclusion

The present investigation demonstrates an efficient alternate method of synthesis of TNAZ from inexpensive starting materials. The formation of the compound was confirmed by elemental analysis and spectroscopic techniques. The sensitivity data obtained for the synthesized TNAZ indicated its relative safe nature towards external stimuli (Impact height,  $h_{50\%}$  explosion 45-47 cm; Friction insensitivity up to > 36 kg) compared to RDX and HMX. The FTIR of decomposition products of TNAZ revealed the evolution of oxides of nitrogen and -CN containing species suggesting the cleavage of C/N-NO<sub>2</sub> bond accompanied with the collapse of ring structure. The theoretically predicted performance parameters suggest that TNAZ is a potential energetic molecule superior in terms of velocity of detonation, Cj pressure, heat of explosion, sound intensity, and power index for wide range of applications in the area

of HEMs.

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