

1,3,3-Trinitroazetidine (TNAZ), a melt-cast explosive: synthesis, characterization and thermal behaviour

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Abstract

1,3,3-Trinitroazetidine (TNAZ) has been prepared at a laboratory scale in HEMRL. The structure of the compound has been confirmed by IR, NMR, mass, elemental analysis and by X-ray crystallography. HPLC technique has been employed to confirm the purity of TNAZ (>99%). The compound is further characterized by thermal techniques and is found to undergo limited decomposition at its melting point. Small scale sensitivity tests have also been carried out and the results show that TNAZ is significantly more sensitive to mechanical stimuli than TNT.

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1. Introduction

Improvements to high explosive performance are of increased importance to defeat the growing number of complex and hardened targets. The most common way to improve the performance of metal accelerating warheads is through the use of PBXs with high solid loadings of RDX or HMX. Such warheads however, are typically used only in small missiles that are volume restricted. They are unsuitable either technically, due to cost or due to IM issues for large (GP Bombs) or high usage (artillery rounds) articles. For such kind of systems melt-cast explosives or cast cured PBX are more suitable.

1,3,3-Trinitroazetidine (TNAZ) is a high performance, melt castable explosive that has been proposed as potential replacement for TNT [1]. The low melting point of TNAZ enables processing of formulations on modified production lines whilst its performance is approximately 30% greater than TNT [1]. It is also reported that TNAZ is highly energetic material more powerful than RDX, and it is less

vulnerable than most other nitramine [2]. Further, TNAZ has many added advantages over known explosives [3]. Unlike HMX, TNAZ is soluble in molten TNT, and is compatible with aluminium, steel, brass and glass. TNAZ provides up to 10% increased energy relative to RDX in the low vulnerability ammunition (LOVA) XM-39 gun propellant formulation. A comparison of the energetics in XM-39 gun propellant formulation [3,4] is; RDX, 1069 J/g, HMX, 1063 J/g and TNAZ, 1160 J/g. Hence, it is a steam-castable material which is attractive as an explosive or as a near-term candidate component for explosives/propellants with low sensitivity, good stability and enhanced performance over existing military formulations.

In view of the above, it was considered worthwhile to undertake the synthesis of 1,3,3-trinitroazetidine. Of course, the efficient and environmentally benign methods for large scale synthesis of TNAZ have been the challenging tasks for all over the globe. Although, there have been several reports [5–13] for the synthesis of TNAZ but every method is limited by steps to afford good yields and up-scaling of the product. In the following section we describe an efficient procedure for the synthesis of TNAZ along with the results of the instrumental techniques employed for characterization, thermal and explosive behaviour of TNAZ.

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2. Experimental

2.1. Materials

Unless otherwise stated, all common reagents and solvents were used as supplied from commercial sources without further purification. Triphenyl phosphine, *tert*-butylamine and ammonium nitrate were supplied by E. Merck (India), diisopropyl azodicarboxylate (DIAD) was a product from Lancaster (India), paraformaldehyde, sodium hydroxide, nitromethane, sodium nitrite were purchased from Qualigens Fine Chemicals, Potassium ferricyanide, acetic anhydride and sodium persulphate were commercially purchased from S.D. Fine Chemicals.

2.2. General methods

Melting points were run at 3 °C/min on a Mettler FP-61 automatic melting point apparatus and are uncorrected. All chemicals were obtained from commercial suppliers and were used without further purification. Triphenyl phosphine and diisopropyl azodicarboxylate were distilled before use. TLC was carried on precoated plates (Merck Silica gel-60, F₂₅₄) and the spots were visualized with UV-light. The IR spectra were recorded on Perkin–Elmer Infra red Spectrophotometer using KBr Matrix. ¹H and ¹³C NMR spectra were recorded on a Bruker-300 MHz instrument and chemical shifts were recorded in δ units parts per million with reference to tetramethyl silane (TMS) as internal standard. Electron impact mass spectrum (EIMS) were measured on a double focusing JEOL-DS mass spectrometer at 70 eV using direct insertion technique. The chemical ionization mass spectrometry in methane was carried on Finnigan mass spectrometer.

The deflagration temperature was determined by heating 0.02 g of sample in a glass test tube in Wood's Metal Bath at a heating rate of 5 °C/min and the temperature at which sample ignited/decomposed, was recorded as deflagration temperature. Differential thermal analysis (DTA) was recorded by heating 10 mg of sample at a rate of 10 °C/min in presence of static air. The impact sensitivity was determined by the Fall Hammer Method using 2 kg drop weight while friction sensitivity was determined on Julius Peter's Apparatus.

2.3. Synthesis

The synthesis of TNAZ consist of:

2.3.1. 3-*tert*-Butyl-5-hydroxymethyl-5-nitrotetrahydroxy-1,3-oxazine, **1**

To a solution of paraformaldehyde (104 g, 3.46 mol) and 40% NaOH (48 drops in 480 mL water) was slowly added nitromethane (48 g, 0.78 mol) at room temperature. The mixture was stirred at 60 °C for 1 h, followed by dropwise addition of *tert*-butylamine (56 g, 1.05 mol) in 144 mL water at 60 °C. The precipitate began to appear during the addition.

The mixture was held at 60 °C for 5 h, cooled and filtered. The precipitate was washed with water and dried to give 3-*tert*-butyl-5-hydroxymethyl-5-nitrotetrahydro-1,3-oxazine. Yield: 145 g (81.2%), mp: 135–138 °C.

IR (KBr) ν (cm⁻¹): 3416 (OH), 2976 (N–CH₂), 1546 (NO₂), 1370 (OH), 1094 (COC), 946.

¹H NMR (DMSO-d₆) δ : 0.94 (s, 9H), 2.7 (d, 1H), 3.56 (d, 1H), 3.56 (d, 1H), 3.6 (d, 1H), 3.7 (s, 2H), 3.9 (d, 1H), 4.36 (d, 1H), 4.4 (d, 1H).

Elemental analysis for C₉H₁₈N₂O₄: Calcd.: C-49.54; H-8.25; N-12.84. Found: C-49.18; H-8.01; N-12.62.

2.3.2. 2-*tert*-Butyl-aminomethyl-2-nitro-1,3-propandi-ol-hydrochloride, **2**

To a solution of concentrated Hydrochloric acid (54 mL, 0.65 mol) in Methanol (500 mL) was added 3-*tert*-butyl-5-hydroxymethyl-5-nitrotetrahydro-1,3-oxazine (140 g, 0.64 mol). The resulting solution is heated under gentle reflux for 20 h. The solvent was removed in a solvent evaporator and the residue was stirred in 100 mL of isopropyl alcohol. The mixture is chilled in ice-salt mixture for 2 h and the solid is collected by filtration, washed with cold isopropyl alcohol and dried. Yield: 108 g (70%), mp: 175–177 °C.

IR (KBr) ν (cm⁻¹): 3322, 2982, 1550, 1402, 1104, 1018, 846.

¹H NMR (D₂O) δ : 1.27 (s, 9H), 3.85 (s, 2H), 3.97 (d, 2H), 4.21 (d, 2H).

Elemental analysis for C₈H₁₉N₂O₄Cl: Calcd: C-39.5; H-7.83; N-11.54. Found: C-39.26; H-7.91; N-10.86.

2.3.3. 1-*tert*-Butyl-3-hydroxymethyl-3-nitro-azetidine-hydrochloride, **3**

To a vigorously stirred mixture of diol, **2** (41 g, 0.17 mol) and diisopropyl azodicarboxylate (37.7 g, 0.19 mol) in butanone (66 mL) at 50 °C a solution of triphenylphosphine (48.4 g, 0.21 mol) in 125 mL butanone was added dropwise, maintaining the solution temperature of 50–55 °C. The mixture was stirred at 50 °C for 3 h, filtered, washed with cold butanone (25 mL) and dried to give **3**.

Yield: 27.0 g (69.5%), mp: 158–161 °C.

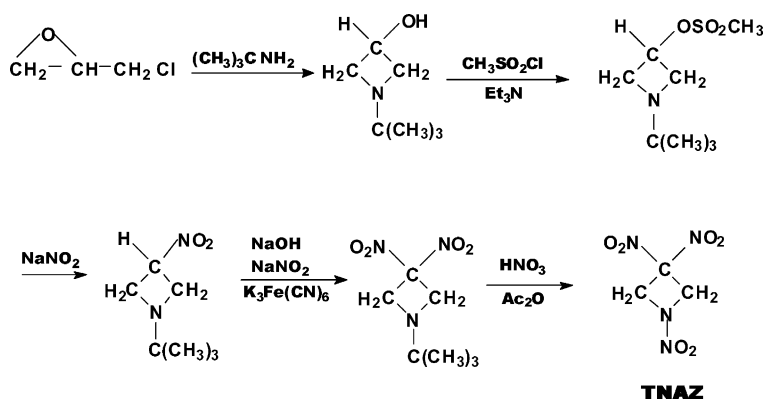
IR (KBr) ν (cm⁻¹): 3276, 3030, 1554, 1194, 1078, 994, 864.

¹H NMR (D₂O) δ : 1.17 (s, 9H), 4.06 (bs, 2H), 4.6 (bs, 4H).

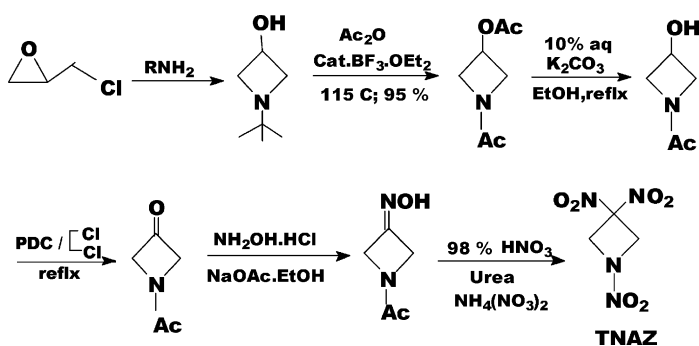
Elemental analysis for C₈H₁₇H₂O₃Cl: Calcd.: C-42.7; H-7.57; N-12.47. Found: C-42.10; H-7.45; N-11.67.

2.3.4. 1-*tert*-Butyl-3,3-dinitrozetidine, **4**

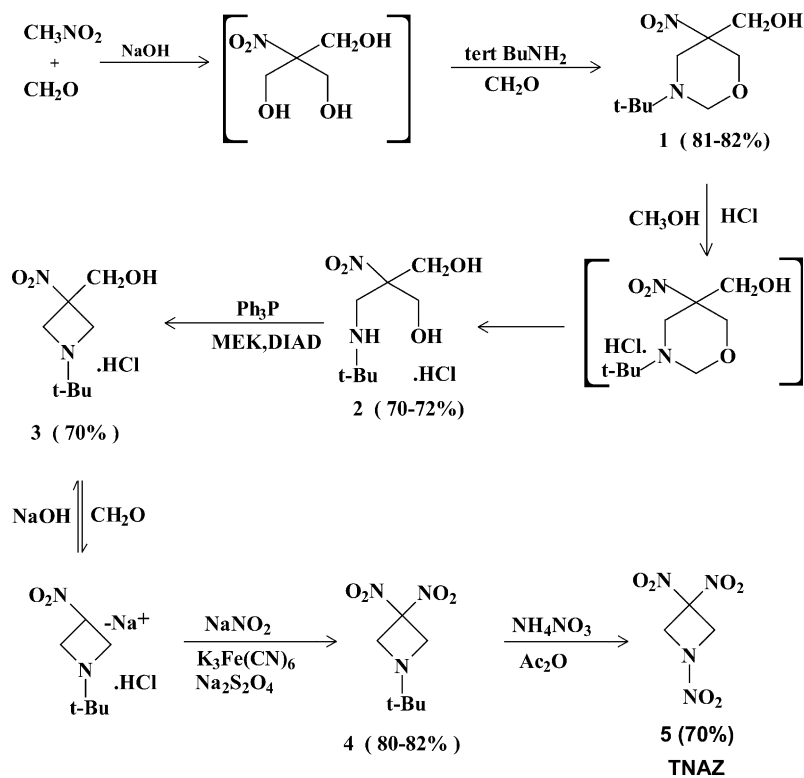
To a solution of (33.5 g, 0.148 mol) in water (148 mL) was added aqueous NaOH (17.82 g, 0.445 mol) in 74 mL water and resulting solution stirred at room temperature for 3 h. The reaction mixture was cooled to 10 °C and a chilled solution of sodium nitrite (41.0 g, 0.594 mol) and potassium ferrocyanide (4.9 g, 0.148 mol) in 113 mL water was slowly added. Solid sodium persulphate (44.25 g, 0.187 mol) was



Scheme 1.



Scheme 2.



Scheme 3.

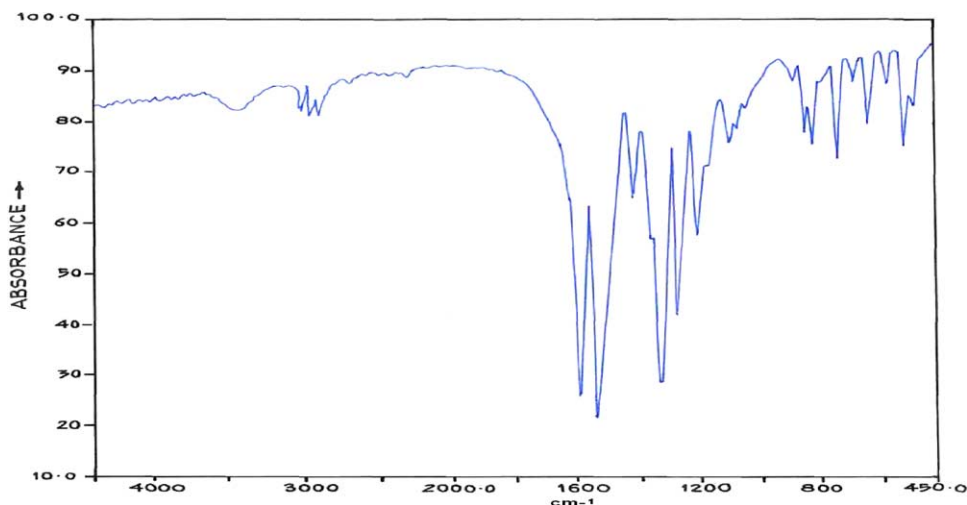


Fig. 1. IR (KBr) spectrum of TNAZ.

added in a single portion and the yellow solution warmed to ambient temperature when the solution gradually turns to light orange colour. The solution was stirred for 1 h and extracted with dichloromethane (150 mL). The organic phase is dried with MgSO_4 and solvent was evaporated to give **4** as a yellow oil. Yield: 25 g (83%).

IR (KBr) $\nu(\text{cm}^{-1})$: 2998, 1574, 1364, 1241, 1070, 838.

^1H NMR (CDCl_3) δ : 1.0 (s, 9H), 4.05 (s, 4H).

Elemental analysis for $\text{C}_7\text{H}_{13}\text{N}_3\text{O}_4$: Calcd.: C-41.3; H-6.40; N-20.68. Found: C-40.8, H-6.50; N-19.87.

2.3.5. 1,3,3-Trinitroazetidine, **5**

To a vigorously stirred solution of **4** (25 g, 0.124 mol) in a distilled acetic anhydride (103 mL) was added ammonium nitrate (15.1 g, 0.188 mol) over 15 min period. The

suspension was heated to 80°C to complete dissolution, stirred for 5 h, cooled to ambient temperature and stirred further for 16 h. The mixture is poured in crushed ice and stirred to get precipitate of TNAZ. Yield: 16.6 g (70%), mp: 101°C .

IR (KBr) $\nu(\text{cm}^{-1})$: 3036, 1596, 1540, 1332, 1278, 1016, 842, 762, 665.

^1H NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$) δ : 5.14 (s, 4H, 2 CH_2).

^{13}C NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$) δ : 103 (w, 1C, C_3), 63.2 (s, 2C, C_2 & C_4).

Elemental analysis for $\text{C}_3\text{H}_4\text{N}_4\text{O}_6$: Calcd.: C-18.75; H-2.08; N-29.16. Found: C-18.64; H-1.67; N-30.4.

EIMS, 70 eV, m/z : 146, 145, 116, 99, 100, 68, 57, 56, 54, 53, 52.

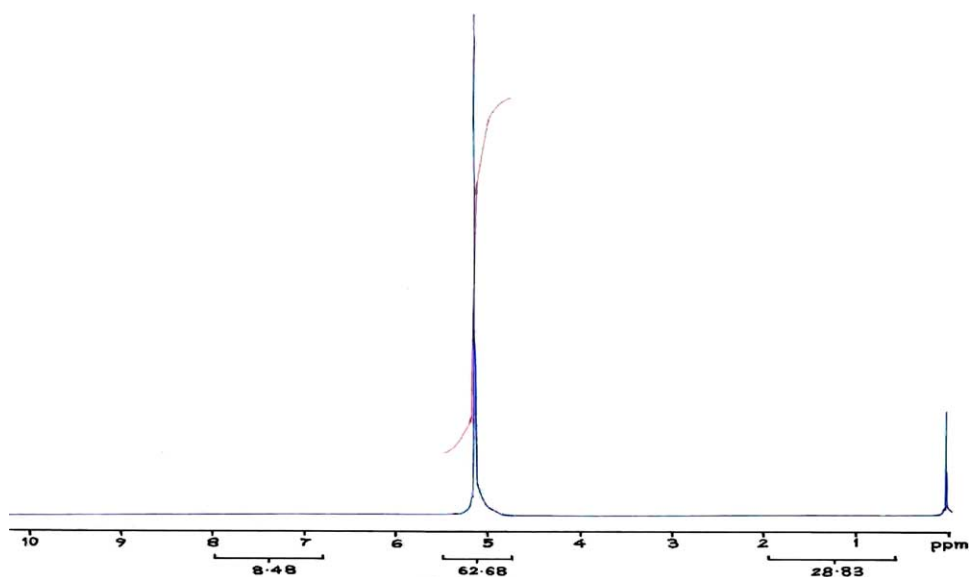


Fig. 2. ^1H NMR Spectrum (300 MHz) of TNAZ in CDCl_3 .

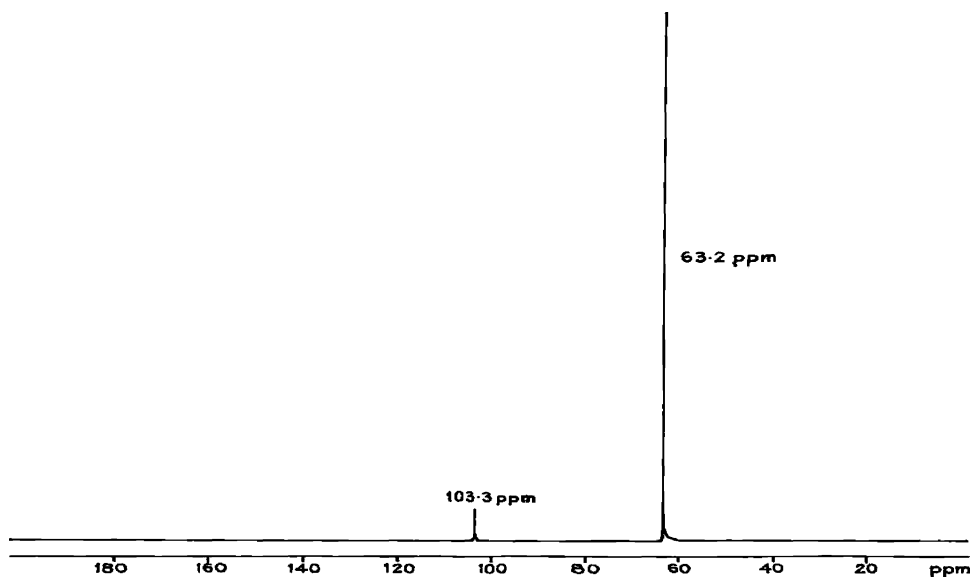


Fig. 3. ^{13}C NMR Spectrum (300 MHz) of TNAZ in $\text{d}_6\text{-DMSO-CDCl}_3$.

CIMS (CH_4), m/z (M.wt. 192[P]): 221 (P- C_2H_5), 193 (base peak, P + 1), 188 (P + 1- NO_2 + C_3H_5), 161 (P + 1- H_2NO), 160 (P- H_2NO), 158 (188-NO), 147 (P + 1- NO_2), 146 (P- NO_2), 117 (193- NO_2 -NO), 101 (P + 1- 2NO_2), 100 (P + 1- HNO_2 - NO_2), 70 (P- 2NO_2 -NO), 68 (P- 2HNO_2 -NO), 56, 55, 54, 52 (Azetidine ring), 46 (NO_2), 30 (NO).

3. Results and discussion

3.1. Synthesis

There are almost 50 synthetic routes reported as of today in the literature to make the compound available with

sufficient quantity. However, every method has some limitations in terms of yield of TNAZ or of its synthetic intermediates, product purity and by multiple steps-synthetic routes. We have made TNAZ in the laboratory following three different routes (Schemes 1–3). The first method follows the original synthetic route of Archibald et al. [5] starting from *tert*-butylamine and epichlorohydrin to form 1-*tert*-butyl-3-azetidinol. The overall yield in this synthesis is very poor, being principally limited by the steps involving the formation of the intermediate, 1-*tert*-butyl-3-mesyloxyazetidine and the SN^2 nitrite ion displacement of mesylate ion in the latter to introduce the first C- NO_2 group. The inconvenience and economics of benzhydrylamine in an eventual scale-up were deemed unfavourable and thus, this approach was abandoned presently.

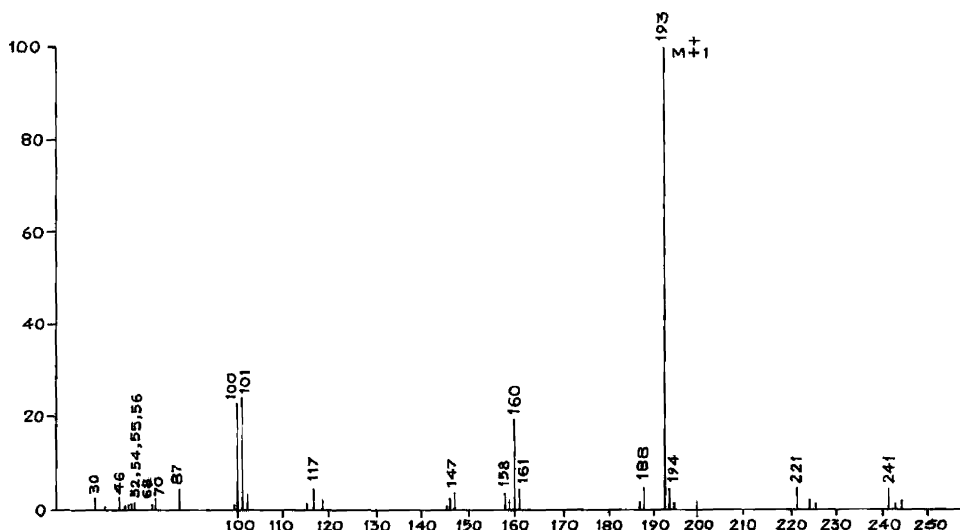


Fig. 4. CIMS (CH_4) of TNAZ.

A major limitation of the second method [14] (Scheme 2) is the multistep synthesis recorded overall poor yield of the final product and thus, this method cannot claim wide applicability. This synthetic route is tedious, lengthy and more expensive. However, the synthetic route described herein and presented in Scheme 3, provides a new efficient and expeditious procedure for synthesis of TNAZ starting from inexpensive and commercially available starting materials. The reaction of nitromethane with excess formaldehyde in aqueous solution follows Mannich condensation procedure to afford **1**, which undergoes further condensation reaction and subsequent ring cyclization due to effect of tertiary butylamine to form oxazine with excellent purity (>95%). Mineral acidification in methanol effected ring opening with elimination of formaldehyde to give 2-*tert*-butyl-aminomethyl-2-nitro-propanediol-hydrochloride in 82% yield. The cyclised azetidine ring was achieved with excellent reproducibility by the effect of DIAD in presence of triphenyl phosphine. Deformylation reaction followed by nitration reactions were carried out in situ to afford amine which on nitrolysis gave crude TNAZ with 70% yield. An attractive feature of this route is that the HNO₃ oxidation leading to the formation of the C(NO₂)₂ with the nitrolysis of the N-substituent to produce the NNO₂ function. An added benefit of this approach is that all energetic nitro-groups are introduced stepwise which is an important safety consideration. TNAZ is a white crystalline compound crystallized from Chloroform. The compound has a density of 1.85 g/cm³ (confirmed by X-ray crystallography) further suggests stability of the compound with compactness. TNAZ is relatively thermally stable, showing no measurable decomposition in the melt up to 132 °C and has short term stability to higher temperature.

3.2. Characterization

All important intermediate compounds prepared in the course of achieving the target compound, TNAZ have been fully characterized by IR, ¹H and ¹³C NMR, mass and elemental analysis and X-ray crystallographic structure. The ultraviolet wavelength maxima are in nm, IR frequencies are in cm⁻¹, and chemical shifts are in δ (ppm). The purity

of compound was determined by HPLC with a mobile phase methanol–water (70:30) at a flow rate 1 mL/min in C-18 micro-bondapack column with UV detector at 232 nm and was found >99% pure. IR vibrational stretching signals at 3000 cm⁻¹ are due to high ring tension of the heterocyclic system with the evidence of NO, NO₂ and N–N stretching vibration (Fig. 1). The ¹H NMR spectra of TNAZ were recorded in both CDCl₃ and d₆-DMSO solvents with tetramethyl silane as internal standard. A chemically and magnetically equivalent four protons of the ring occur as singlet at δ 5.25 (Fig. 2). In ¹³C NMR spectrum, the secondary ring two carbon atoms resonate as singlet at δ 63.5 ppm while a typical weak signal can be found for a quaternary carbon at δ 103 ppm (Fig. 3). The direct inlet probe electron impact mass spectrum showed no molecular ion peak but nevertheless, some interesting ions which are of diagnostic value for structural information were observed at *m/z* 146 (s, P–NO₂), 145 (s, P–HNO₂), 116 (t, P–NO₂–NO), 100 (t, P–2NO₂), 99 (s, P–HNO₂–NO₂), 68 (t, P–2HNO₂–NO), 56, 54, 53, 52 (azetidine ring). The major pathways involve the loss of NO₂ or nitrous acid from the dinitromethylene group followed by a loss of a nitro group or NO from the nitramine group. The peak at *m/z* 46 (NO₂)⁻ arises primarily from N–N bond

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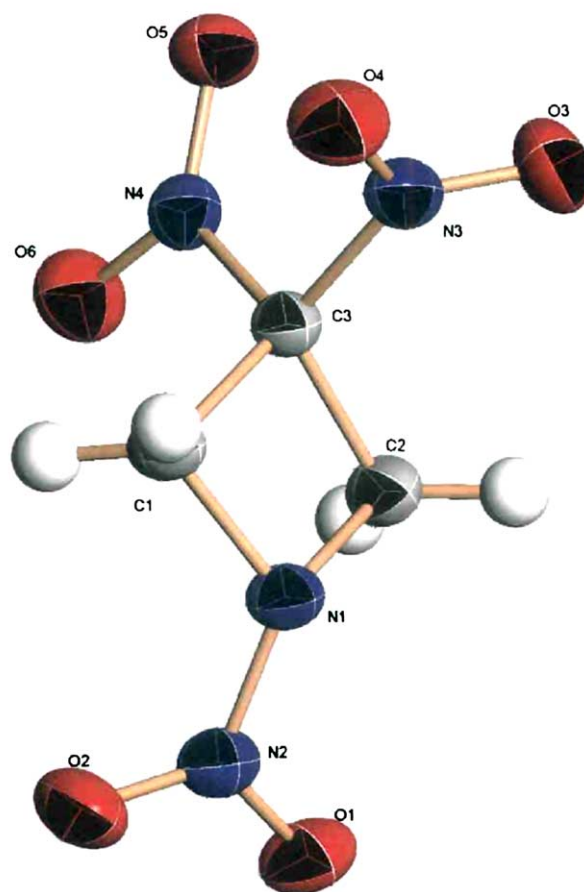


Fig. 5. X-ray crystallography structure of TNAZ.

Table 1
X-ray structure data of TNAZ

Formula	C ₃ H ₄ N ₄ O ₆
Space group	
<i>a</i> (°A)	5.7580 (6)
<i>b</i> (°A)	11.1309 (12)
<i>c</i> (°A)	21.524
α (°)	90
β (°)	90
γ (°)	90
Volume (°A ³)	1379.5 (3)
<i>Z</i>	8
<i>D_c</i> (g/cm ³)	1.850

scission of the azetidine ring. The chemical ionization mass spectrometry in methane was also carried on finningan mass spectrometer where $m + 1$ peak (100%) along with other diagnostic peaks with rich abundance were observed (Fig. 4).

Structure of TNAZ was elucidated by X-ray crystallography. A clear colourless crystal recrystallised from carbon tetrachloride was used for data collection on an automated Nicolet R 3 m/V diffractometer with incident beam monochromator, 25 centred reflections with $20 < 2\theta < 60^\circ$ were used for determining lattice parameters. Data provided in Table 1, was corrected for Lorentz and polarization effect and an empirical absorption correction was applied. The maximum and minimum transmission values were 0.94 and 0.41. Structure was solved by direct method and the model was refined by using Full matrix least-square techniques. The geometry of TNAZ is illustrated in Fig. 5 and the bond distance and angles are given in Table 2. The ring is significantly puckered with an angle between the C–C–C and C–N–C planes, θ of $13.6(5)^\circ$. The amino nitrogen N(1) is pyramidal, and the 'out of plane bend' angle between the N–N bond and the C–N–C plane, is 39.4° . This bend is much larger than the normally observed nitramines. The N–N bond length in TNAZ is 1.351 \AA . This is consistent with N–N bond lengths observed for nitramines in 5- and 6-membered rings. The

various bond lengths and other parameters of crystal lattice determined are identical with the data published earlier [10].

3.3. Thermal analysis

The thermal behaviour of TNAZ has been studied by using differential thermal analysis, differential scanning calorimetry (DSC) and thermogravimetry (TG) analysis. The DTA was recorded by taking 10 mg of sample at a heating rate of $10^\circ\text{C}/\text{min}$ in presence of static air. Unlike most nitramines, pure TNAZ has a melting endotherm without decomposition at 100°C (Fig. 6). It may be hypothesized that low temperature melt phase may enhance the resistance of TNAZ based explosive to form hot spots during mechanical loading and thus, may be less vulnerable in practical applications. DSC thermogram obtained at $10^\circ\text{C}/\text{min}$ heating rate and using TNAZ sample 2 mg closed in sealed aluminium sample pan has shown a sharp melting even at $99.5/100^\circ\text{C}$ (onset/peak) with an associated heat of fusion of 6.405 kcal/mole (Fig. 6). The slight gradual endothermic behaviour observed for the melt transition can be explained as latent heat [10,15]. DSC results also showed a weak exothermic decomposition of $225/241^\circ\text{C}$ (on set/peak) with an associated energy of 115.9 J/g . This weak exotherm can be accounted due to evaporation (loss) of TNAZ after melting a temperature. By applying multiple heating rate DSC measurements and Ozawa method the activation energy of 39 kcal/mole was calculated from DSC peak maximum temperature heating rate relationship.

The DTA, TG and DTG analysis on pure TNAZ was performed on Mettler TOLEDO Star System at CMET, Pune with 2.86 mg of sample (Fig. 7). The analysis provides a clear picture of thermal behaviour of TNAZ. The endothermic melt is seen peaking at 100°C accompanied by a steady evaporation TGA weight loss. The DTA base line decreases steadily between approximate 120 and 180°C reflecting the endothermic nature of TNAZ evaporation. The curve reveals decomposition of TNAZ at 105 – 134°C with weight loss 10%. The complete loss of sample was observed due to evaporation/decomposition process over the temperature

Table 2
Bond lengths (\AA) and angles ($^\circ$) of TNAZ

O(3)–N(3)	1.2103 (15)
O(1)–N(2)	1.2210 (15)
O(5)–N(4)	1.2119 (14)
N(3)–O(4)	1.2124 (16)
N(3)–C(3)	1.5014 (16)
N(1)–N(2)	1.3564 (15)
N(1)–C(1)	1.4722 (16)
N(1)–C(2)	1.4730 (18)
N(4)–O(6)	1.2107 (15)
N(4)–C(3)	1.5120 (17)
N(2)–O(2)	1.2236 (16)
C(3)–C(1)	1.5344 (18)
C(3)–C(2)	1.5376 (17)
O(3)–N(3)–O(4)	126.40 (12)
O(3)–N(3)–C(3)	116.74 (12)
O(4)–N(3)–C(3)	116.84 (11)
N(2)–N(1)–C(1)	121.55 (11)
N(2)–N(1)–C(2)	121.17 (11)
C(1)–N(1)–C(2)	95.10 (9)
O(6)–N(4)–O(5)	126.49 (12)
O(6)–N(4)–C(3)	115.23 (11)
O(5)–N(4)–C(3)	118.28 (11)
O(1)–N(2)–O(2)	126.22 (12)
O(1)–N(2)–N(1)	116.67 (12)
O(2)–N(2)–N(1)	116.98 (12)
N(3)–C(3)–N(4)	105.96 (9)
N(3)–C(3)–C(1)	116.26 (11)
N(4)–C(3)–C(1)	114.03 (11)
N(3)–C(3)–C(2)	115.37 (11)
N(4)–C(3)–C(2)	115.08 (11)
C(1)–C(3)–C(2)	90.05 (9)
N(1)–C(1)–C(3)	86.79 (9)
N(1)–C(2)–C(3)	86.64 (9)

Table 3
Some characteristic explosive and thermal properties of TNAZ

1	Melting point ($^\circ\text{C}$)	101 ($3^\circ\text{C}/\text{min}$)
2	Thermal stability DSC	
	Endotherm	97/101 $^\circ\text{C}$ (onset/peak)
	Exotherm	226/241.3 $^\circ\text{C}$ (onset/peak)
3	Activation energy (kcal/mol)	39
4	TGA (wt. loss %)	103–194 $^\circ\text{C}$ (100%)
5	Density (g/cm^3)	1.85
6	Impact sensitivity ($h_{50}\%$) (cm)	32
7	Friction sensitivity (kg) (insensitive up to)	36
8	F of I	39
9	Particle size (μ)	23
10	Vacuum stability, 48 h, 100°C	0.66 (mL/g)

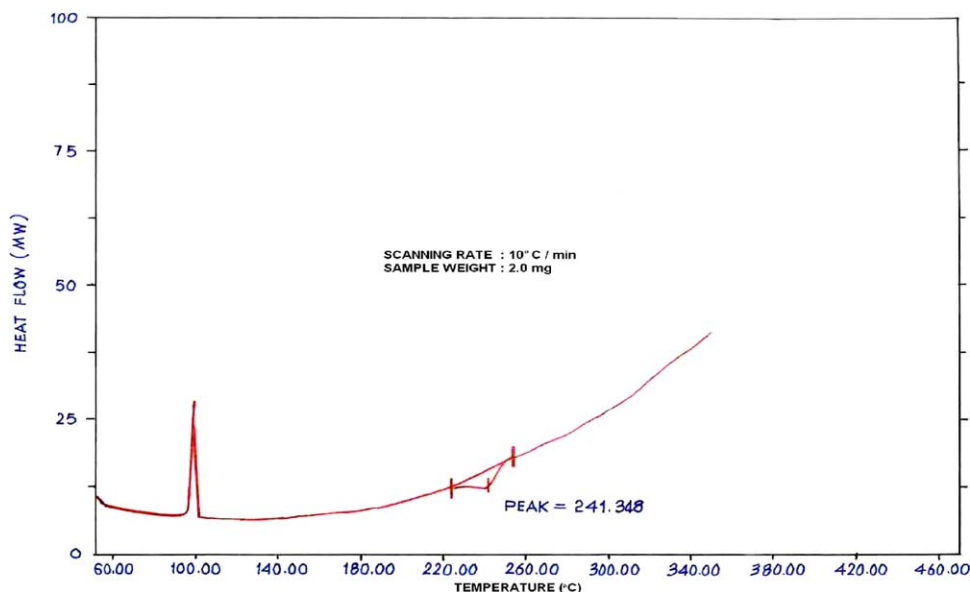


Fig. 6. DSC thermogram of TNAZ.

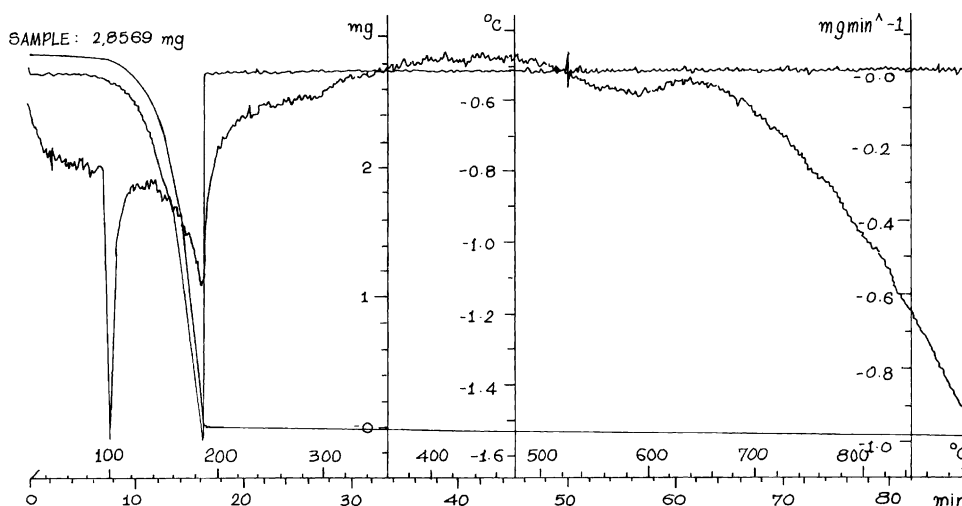


Fig. 7. DSC, TG and DTG of TNAZ.

range 103–194 °C. However, the reaction of intense thermal decomposition starts at 184 °C while first exothermic reaction starts at 170 °C at a heating rate of 10 °C/min. This rapid rate of evaporation of TNAZ from the molten phase is of concern from an explosive safety and processing view point.

The vacuum stability test conducted in duplicate with 1.0 g sample and the average evolved gas volume was recorded. Samples were run at 100 °C for 48 h. The results (Table 3) showed significantly gas evolution (0.66 mL/g) compared to results obtained for other common explosives, although it is still well below a commonly accepted upper limit of 2 mL/g. In addition, significant vapourization of TNAZ was observed and considerable quantities of material were deposited at the pressure transducer at the top of the tube. This behaviour may create difficulties in obtaining high quality castings and

also may result in matrices of poor mechanical properties and reduced density [16].

3.4. Sensitivity tests

The sample of TNAZ was subjected to a preliminary explosion tests for impact and also for friction sensitivity. Table 3 summarizes the small scale safety data along with other physicochemical characteristics obtained from TNAZ. The impact response determined for TNAZ was very good with excellent purity of the sample and the value was found to be similar to that of HMX [17]. In contrast to the impact response, the apparent friction sensitivity, as determined by the Julius Apparatus, showed purer TNAZ is less sensitive. Impact and Friction testing of crystallized TNAZ showed

the sample to be significantly more sensitive to mechanical stimuli than TNT [18,19].

4. Conclusion

TNAZ, a powerful strained ring explosive with favourable properties of moderate density, good thermal stability and low sensitivity, has been prepared via a five-step synthesis route. The compound has been fully characterized and the batch size is enhanced to 50 g. Small scale sensitivity tests show that TNAZ is significantly more sensitive as compared to TNT but more powerful, and it is less vulnerable than most other nitramines. The compound has the greatest promise for technological advances in future weapon system if the cost of production and volatility can be reduced to some extent.

Acknowledgements

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