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TNAZ Based Melt-Cast Explosives: Technology Review and AMRL Research Directions

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ABSTRACT

1,3,3-Trinitroazetidine (TNAZ) is a high density, melt-castable explosive with the potential to replace TNT in melt-cast systems. The purpose of this review is to examine work performed to date and to identify technology gaps AMRL needs to address to permit its use in Australian Defence Force applications.

Synthetic work is well advanced, with pilot-plant scale operations in use. Chemical and physical characterisation has been extensively performed, as has hazard assessment; however, certain sensitiveness results vary and will require further evaluation.

Three studies of thermal decomposition have been performed and show similar trends with decomposition occurring *via* consecutive NO_2 losses. The decomposition gases have largely been identified.

Calculated and experimentally measured explosive properties show TNAZ to have an explosive performance similar to HMX and substantially improved over that of TNT. High quality pressed charges can be consistently produced, but melt-casting of TNAZ has not yet been perfected. Identified AMRL research directions include addressing melt-cast technology and examining TNAZ as a TNT-replacement in TNT/nitramine melt-cast fillings.

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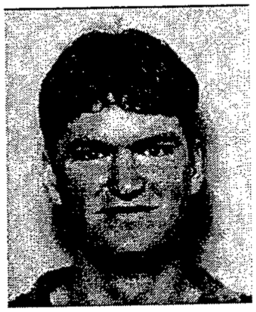
Executive Summary

1,3,3-Trinitroazetidine (TNAZ) is a new melt-castable explosive with the potential to replace TNT in melt-cast munition fillings. TNAZ possesses an extremely high energy density and, if used in melt-cast systems, could substantially increase the performance of currently used munitions. The purpose of this review is to examine work performed to date and identify technology gaps AMRL can address to further this technology.

The chemical synthesis of TNAZ is well advanced with pilot plant production underway in the United States. Chemical and physical characterisation has been extensively performed, however, certain sensitiveness results vary and will require further examination. Thermal decomposition studies have been performed and show similar trends with decomposition occurring *via* consecutive NO_2 losses.

Calculated and experimentally measured explosive properties show TNAZ to have performance similar to HMX, the most powerful commonly used energetic material, and offer a 30–40% improvement over TNT. High quality pressed TNAZ charges have been produced, but melt-casting of TNAZ has not yet been perfected. It is suggested that future AMRL research directions should include an examination of some of the technological problems existing with TNAZ; in particular, overcoming melt-cast difficulties, examining TNAZ as a TNT replacement in TNT/nitramine melt-cast fillings, and assessing the performance and sensitiveness/sensitivity of TNAZ/nitramine compositions.

Authors



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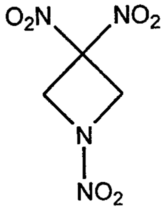
Contents

1. Introduction

1,3,3-Trinitroazetidine (TNAZ) is a new potential melt-castable energetic material under investigation primarily in the United States. TNAZ is a highly ring-strained cyclic nitramine, possessing both nitramine and geminal nitro groups. First synthesised in 1984 by Archibald and Baum [1], TNAZ possesses attractive properties that make it a candidate as a melt-castable replacement for TNT as well as a possible propellent component possessing a high energy density. TNAZ has the symmetrical structure shown below.



TNAZ
(1)

TNAZ is built on a highly strained ring structure, which adds around 37 kcal/mol to the internal energy of the material, in addition to its 'explosophore' moieties [2]. The energy density of TNAZ is comparable to that of HMX, currently the most powerful commonly used energetic material [3]. Unlike other nitramines, such as RDX and HMX, TNAZ exhibits a low melt transition with no decomposition evident. The low melting point (101°C) potentially enables TNAZ to be melt-cast using existing TNT facilities with minimal alteration. TNAZ potentially offers a 30-40% improvement in explosive performance as a TNT replacement in melt-cast formulations such as Composition B (RDX/TNT/wax: 60/40/1) [4].

The aim of this report is to review the development of TNAZ as an energetic material. Much of the work to date has been directed towards synthetic efforts and preliminary assessment of performance and sensitiveness properties. Later studies have involved the development of low temperature melting eutectics and technological developments. This review will examine work performed to date, and identify areas of research that need to be addressed by AMRL to fill technology gaps.

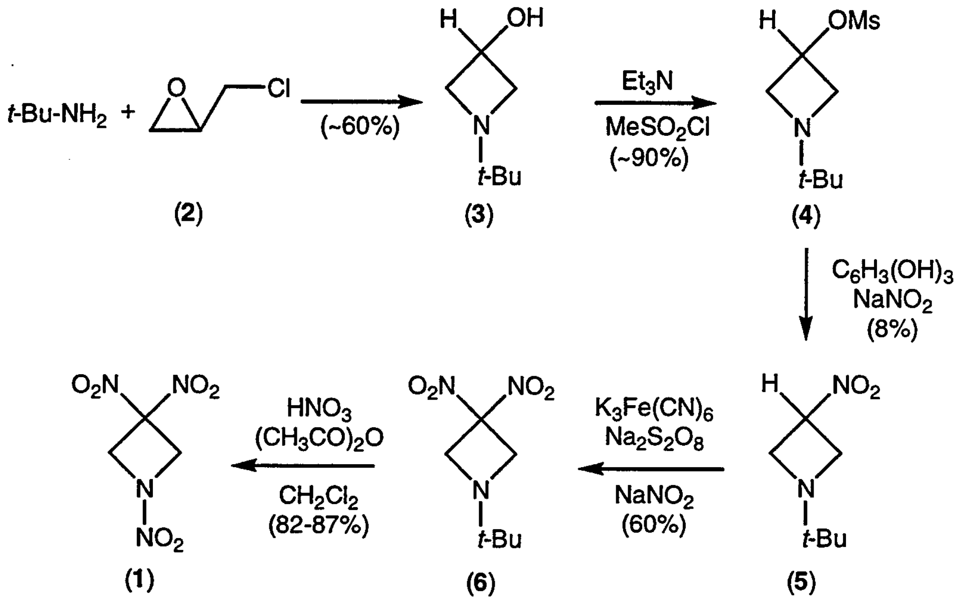
2. Synthesis of TNAZ

Although possessing only two simple functional arrays and being of high symmetry, TNAZ has none-the-less proven to be a challenging molecule to synthesise in commercially acceptable yields. Research groups at the City University of New York, the University of Florida, Aerojet, Fluorochem, Geo-Centers Inc., Los Alamos National Laboratory (LANL) and the University of North Texas have all tackled the synthesis of

TNAZ in an effort to develop a commercially viable method which is simple, high yielding and results in the production of minimal quantities of waste materials.

2.1 Fluorochem Process

The first synthesis for TNAZ was achieved in 1984 by Archibald and Baum working at Fluorochem [1, 5, 6]. The reaction scheme was improved over a number of years, and it first appeared in the open literature in 1990 (Scheme 1). This strategy employs the stepwise introduction of C-NO_2 moieties, followed by the incorporation of the N-NO_2 functional group to the azetidine (4). *tert*-Butyl-3-azetidol (3) was prepared from epichlorohydrin (2) and *tert*-butylamine using a method described earlier by Cichra with a reaction period of one to three days [2]. Condensation of the amine and epoxide formed a 1-amino-3-chloropropanol derivative, which then cyclised to give **3**. The resulting alcohol (3) was then converted to the mesylate (4) using methanesulfonyl chloride in the presence of triethylamine base. Subsequent S_N2 displacement of the mesylate ion, $CH_3SO_2O^-$, by the nitrite ion, NO_2^-, gave the corresponding 3-nitro compound (5) in poor yield. Only an 8% yield of **5** was obtained after reaction of the mesylate (4) with a methanolic solution of sodium nitrite and phloroglucinol dihydrate for 16 hr at 0°C. This step can also be performed in a two-phase, water/Freon 113 medium, with the low yield warranting significant improvement for scale-up development [7]. Oxidative nitration of **5** with potassium ferricyanide/sodium persulphate/sodium nitrite gave *tert*-butyl-3,3-dinitroazetidine (TBDNAZ) (6) in 60% yield. Nitrolysis of the trifluoroacetate salt of **6** with 98% nitric acid and acetic



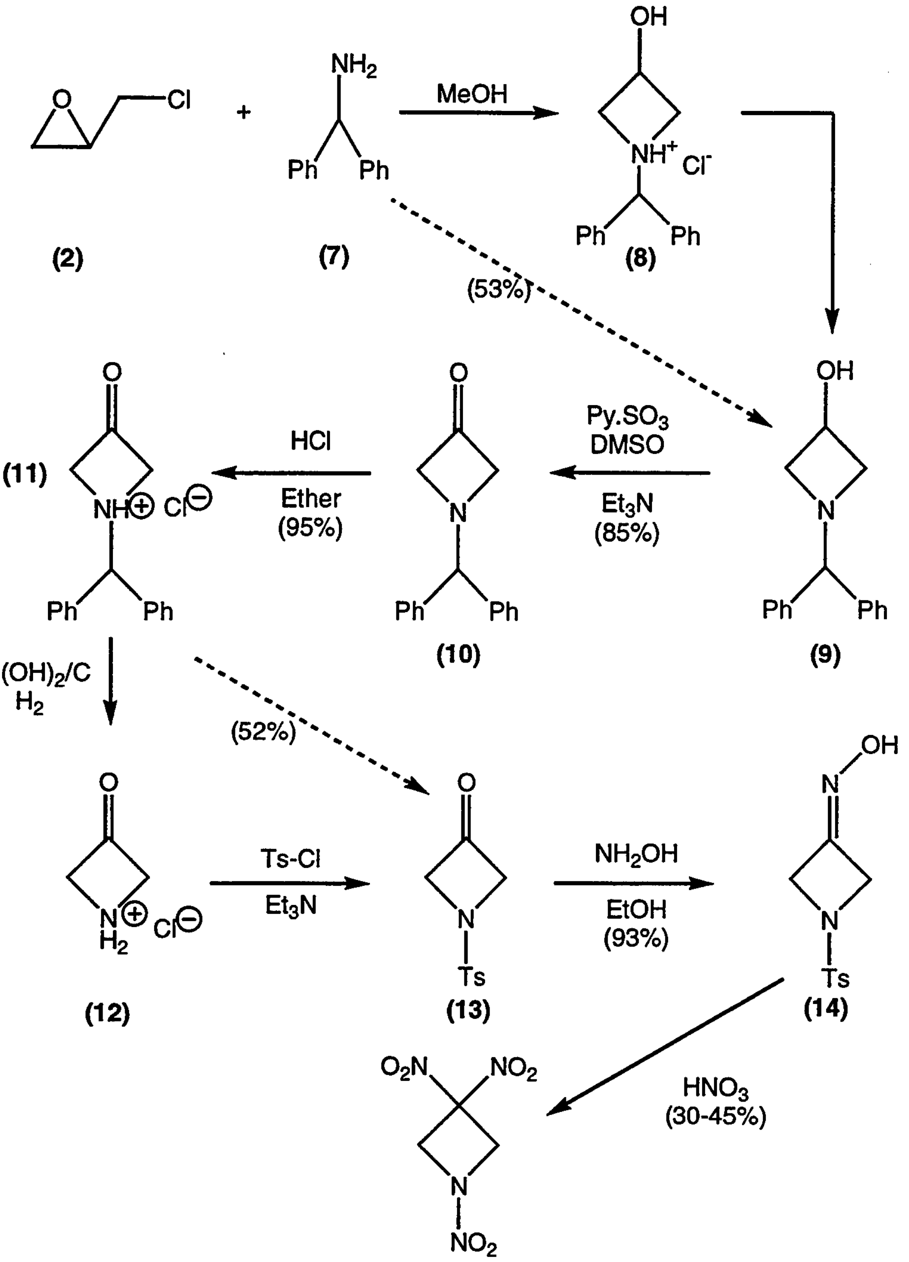
Scheme 1: Fluorochem Synthetic Strategy (1990)

anhydride in dichloromethane gave TNAZ (**1**) in high yield (82-87%). While this method allowed the first synthesis of TNAZ, the overall yield was poor, with a number of steps requiring technical and/or economic improvements.

An improved procedure for the initial condensation step to form the azetidine (3) was developed at LANL. This alternative method resulted in a reduction of reaction time from 1-3 days to 5-8 hr [8]. Using a simplex optimisation method, it was found that the reaction time could be significantly reduced, while maintaining a high yield. The improved procedure to form **3** involved reaction in a high pressure vessel at 90°C. A yield of 68% for **3** is possible with a reaction time of 5.5 hr, using hexane as reaction solvent in an inert atmosphere of argon. The final nitrolysis reaction was also improved by Iyer *et al.*, at Picatinny Arsenal [9]. Use of the nitrate salt of *tert*-butyldinitroazetidine (**6**) in place of the original trifluoroacetate derivative resulted in a less costly procedure and elimination of toxic and expensive trifluoroacetic anhydride. By continuously extracting TNAZ from the reaction vessel, the production of TNAZ was driven to completion by pushing the nitrate salt / TNAZ equilibrium towards TNAZ production. Although many advances were made, the highest production yields that could be obtained were still only around 20%, with over 1200 kg of waste generated per kilogram of TNAZ produced, including large quantities of halogenated solvents [4].

2.2 Alternative synthesis from epichlorohydrin

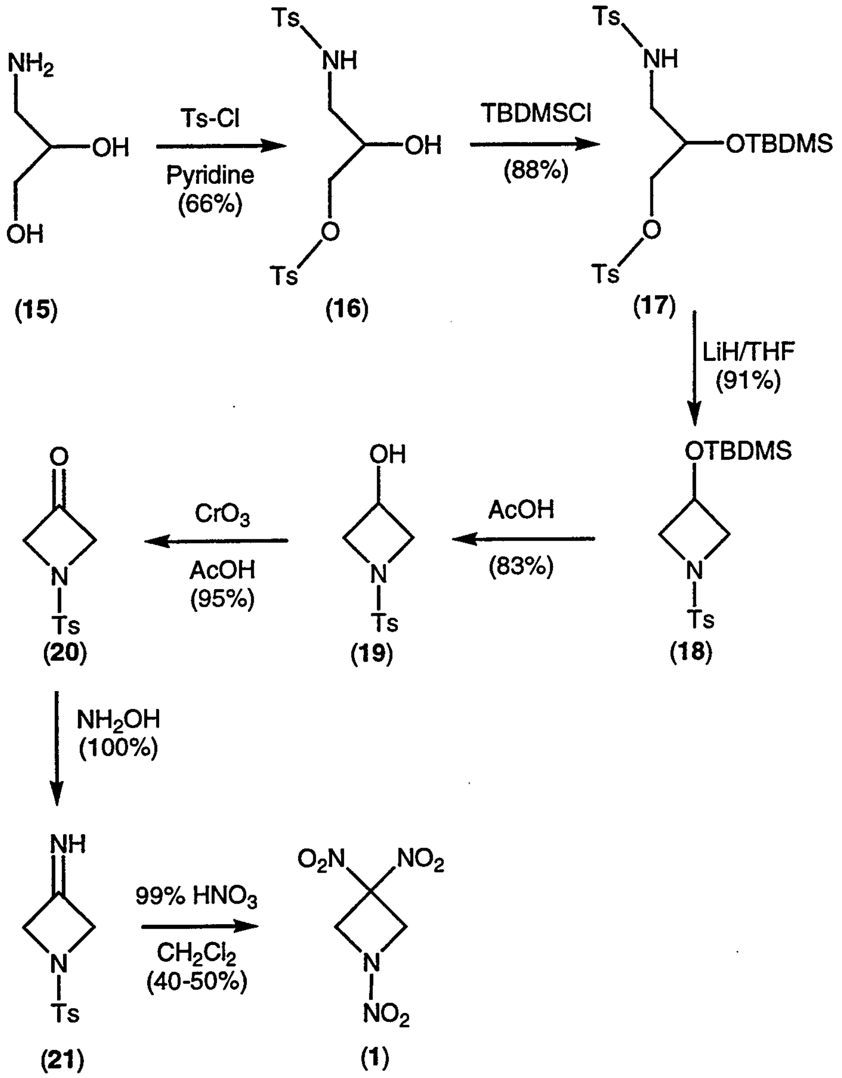
Researchers from the University of Florida have developed an alternative synthetic strategy starting with epichlorohydrin (2) and benzhydrylamine (7) (Scheme 2) [10]. Condensation of epichlorohydrin (2) with benzhydrylamine (7) gave *N*-benzhydryl-azetidin-3-ol hydrochloride (8) which was subsequently neutralised to *N*-benzhydrylazetidin-3-ol (**9**) in 53% yield from **2**. Swern oxidation of **9** gave *N*-benzhydrylazetidin-3-one (**10**) in good yield (85%). Treatment of **10** with HCl gas in a cooled ether solution gave the hydrochloride salt (**11**) in excellent yield (95%). Hydrogenation of **11** over Pearlman's catalyst gave the hydrochloride (**12**) which was immediately treated with tosyl chloride to give the *N*-protected species (**13**) in 52% yield from **11**. Conversion of **13** to **14** was achieved in 93% yield using hydroxylamine hydrochloride and NaOH in an ethanolic solution. Nitrolysis of **14** with fuming nitric acid gave TNAZ (1) in 30-45% yield after recrystallisation from carbon tetrachloride. While the average reaction yields were superior to those obtained using Archibald's method (approx. 75% versus <50%), additional synthetic steps were required resulting in no significant improvement in overall yield. Additionally, the high cost of benzhydrylamine (7) greatly undermines the value of this procedure in terms of its commercial applicability.



Scheme 2: University of Florida Synthetic Strategy (1994)

2.3 Alternative syntheses using different starting materials

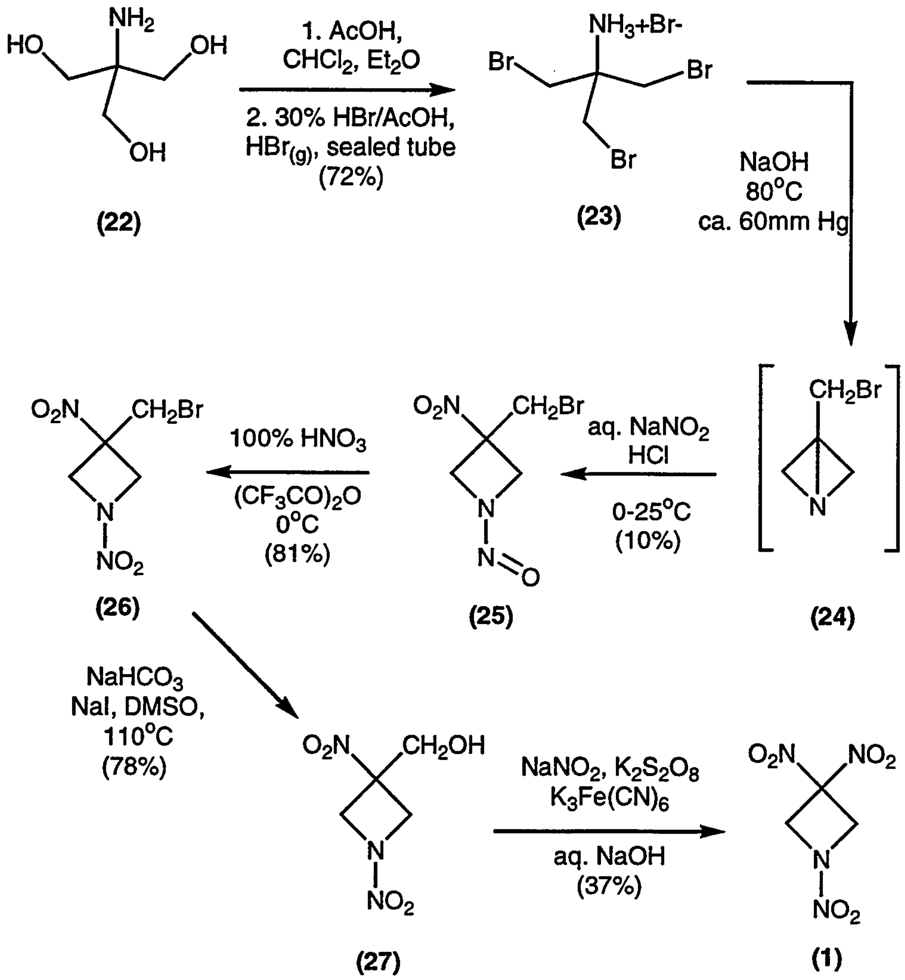
A major disadvantage of the synthetic strategies developed at Fluorochem and the University of Florida is the utilisation of expensive epichlorohydrin (2) as a starting material. An alternative synthesis, developed through collaboration between the City University of New York and Geo-Centers Inc., uses 3-amino-1,2-propanediol **(15)** as a starting material (Scheme 3) [11-14].



Scheme 3: City University of New York / Geo-Centers Synthetic Strategy (1993)

The key steps in this synthetic strategy are the use of lithium hydride to induce ring closure of the protected diol **(17)** to form the azetidine **(18)**, and oxidative nitrolysis of **21** to simultaneously introduce N-NO_2 and C-NO_2 moieties. Yields for this sequence range from good to excellent, with an average yield of 80%. An important point to note is that, like the Katritzky procedure [10], all three nitro groups are induced simultaneously in the final step. This may mean that safety concerns involved with dealing with highly nitrated reaction intermediates are eliminated.

A novel approach to the TNAZ synthesis was developed by Marchand *et al.*, at the University of North Texas, in conjunction with Aerojet (Scheme 4) [15, 16]. Electrophilic addition of NO^+ NO_2^- across the highly strained C(3)-N sigma-bond in 1-azabicyclo[1.1.0]butane (**24**) gave the nitrosamine (**25**) in very low yield (~10%). Conversion to the nitramine (**26**) moiety was effected using neat nitric acid in trifluoroacetic anhydride in 81% yield. Hydrolysis of **26** with sodium bicarbonate and sodium iodide in DMSO gave **27** in 78% yield. Treatment of **27** in a retro-Henry reaction, followed by oxidative nitration of the *in situ* generated carbanionic intermediate gave TNAZ (**1**) in a moderate 37% yield.

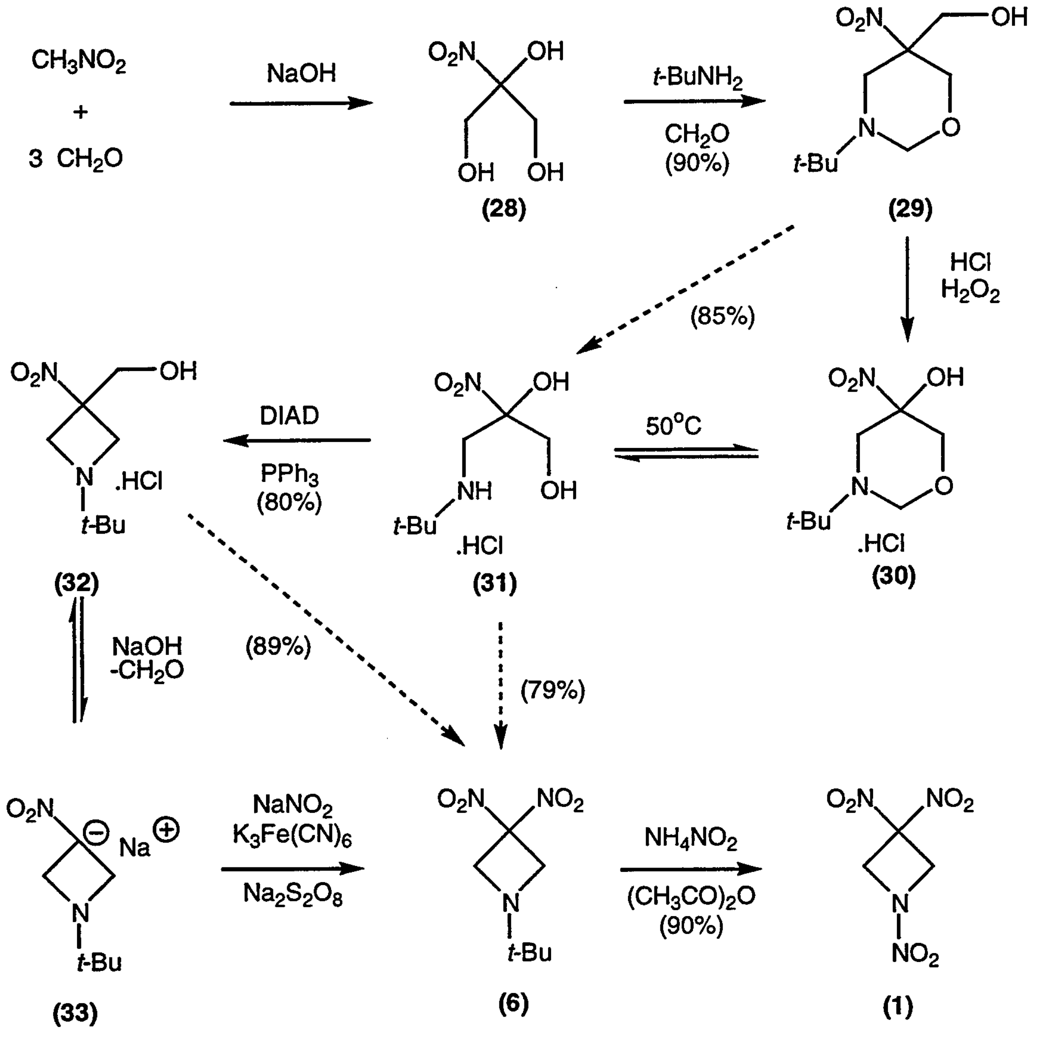


Scheme 4: University of North Texas / Aerojet Synthetic Strategy (1995).

Although using inexpensive tris(hydroxymethyl)amino-methane (**22**) as a starting material, this method provides little hope for commercial application, with the formation and trapping of the azabicyclobutane intermediate being achieved in only around 10% yield. In an attempt to increase yields, Marchand *et al.* are currently investigating an alternative route using allylamine, a readily available and inexpensive starting material, to form the azabicyclobutane derivative [16, 17]. (Azabicyclobutane derivatives, however, have fundamental disadvantages - they are difficult to prepare, decompose readily and can be dangerous to handle as solids).

2.4 LANL Process

An alternative route to the original Archibald method was developed by Coburn and Hiskey at LANL, in conjunction with workers at Aerojet (Scheme 5) [18, 19]. The key steps in this pathway are the Mannich condensation reaction to give **28** and cyclisation of **31** to give the azetidine **32** *via* a Mitsunobu reaction.

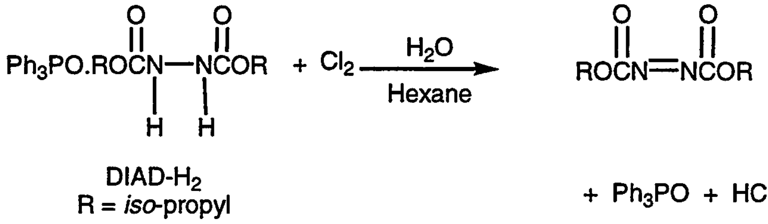


Scheme 5: LANL Synthetic Strategy (1994)

Condensation of nitromethane and paraformaldehyde in aqueous NaOH gave the triol (**28**). Addition of *tert*-butylamine and formaldehyde to the reaction mixture effected cyclisation to afford the six-membered heterocyclic (**29**) in 90% overall yield and 98% purity. Hydrochloric acid-induced ring opening gave the amino-glycol (**31**) in 85% yield. This reaction is governed by the rapid equilibrium established between amino-glycol and formaldehyde. To drive the reaction to completion, hydrogen peroxide is added to convert the formaldehyde to formic acid. Subsequent Mitsunobu reaction resulted in ring closure to give the azetidine (**32**) in 80% yield. The yield for this step is highly dependent upon the order of reagent addition, solvent and temperature: with care, high yields are readily possible on a production scale. Deformylation of **32** with NaOH gave the sodium salt (**33**), which was subjected to an oxidative nitration to give TBDNAZ (**6**) in 85-90% yield (52% overall yield of TBDNAZ from nitromethane). Nitrolysis of **6** using ammonium nitrate and acetic anhydride gave TNAZ (**1**) in 90% yield.

The process has been successfully scaled-up, with a 450 kg production demonstration being completed at Aerojet, in 57% overall yield on production scale. The amount of waste produced is around 10% that of the original Fluorochem process (120 kg per kg TNAZ *cf.* ~1200 kg for the Fluorochem process). With implementation of solvent and acetic acid/anhydride recycle processes, developed at the Holston Army Ammunition Plant, waste for the process may be reduced to ~15.7 kg per kg of TNAZ [4]. Despite being high yielding, a notable drawback in using this method on a commercial scale is the cost of the reagents required for the Mitsunobu reaction, with diisopropyl azodicarboxylate (DIAD) costing approximately Aus$80/100g. Significant amounts of the stable complex of di-*iso*-propylhydrazodicarboxylate and triphenylphosphine oxide ($DIAD\text{-}H_2.Ph_3PO$) and Na_2SO_4 are produced as waste; recovery and recycling of these waste products could result in considerable cost savings.

To address this problem a method to regenerate DIAD was developed through cooperation between LANL and Aerojet [4]. Treatment of $DIAD\text{-}H_2.PH_3PO$ with gaseous chlorine enables a 96% recovery of pure DIAD, with Ph_3PO and aqueous HCl produced as by-products (Scheme 6). The DIAD recycling process has been successfully demonstrated in a 378 l reactor at Aerojet.



Scheme 6: Regeneration of DIAD

Work is currently being carried out at Aerojet to address Na_2SO_4 waste. Electrochemical oxidative nitration is being developed to avoid the use of sodium bisulphate and hence generation and subsequent recovery of Na_2SO_4 waste. It is estimated that introduction of the DIAD recycling process and the electrolytic oxidative nitration will result in a reduction of waste produced to less than 3.8 kg per kg of TNAZ [4]. Preliminary research has been directed at combining the beneficial features of both the LANL and original Fluorochem route [20]. At the date of writing this report, the two processes are yet to be fully integrated.

2.5 Suggested Synthetic Procedure

At least five potential routes are available for the synthesis of TNAZ, with the Fluorochem and LANL routes both having been scale-up to a pilot plant level. The Fluorochem method is severely limited by the mesylate displacement reaction, this reaction is affected in around 10% yield with the major reagent phloroglucinol dihydrate costing approximately Aus$50/100g. The LANL procedure involves relatively simple methodology and the cost of most materials is low. The most expensive compound required is DIAD, at around Aus$80/100 g. By using the DIAD regeneration method the cost could be kept to a minimum. It is therefore recommended that any synthetic program conducted by AMRL should implement the LANL procedure. The estimated material cost for producing TNAZ on a laboratory scale was calculated at Aus $840/100g TNAZ (Table 1). The costing includes the use of

Table 1: Costing for TNAZ production using LANL Synthetic Strategy

Compound	Mass required (g)	Cost (Aus $)[a]	Product	Amount
CH_2O	135	21		
NaOH	.1	0.5		
CH_3NO_2	61	4		
t-Butylamine	73	2.5		
			Oxazine	0.9mol
HCl	33	1		
H_2O_2	100ml	5.2		
			Aminoglycol	0.82mol
DIAD	182	142		
2-Butanone	615ml	16.5		
PPh_3	236	58.4		
NaOH	100	3.5		
Celite		5		
$NaNO_2$	210	11.4		
Methyl-*t*-butyl ether	1230ml	31		
			TBDNAZ	0.65mol
TFAA	650ml	300		
DCM	975ml	5.6		
100%nitric acid	200ml	31.6		
			TNAZ	0.5mol
Auxiliary costs[b]		200		
	Total Cost of TNAZ:100g produced		**Aus$ 839.2**	

a Cost based upon prices gained from Sigma, Fluka and Riedel-de Haën product catalogues.

b Auxiliary costs include estimated TSS services, general laboratory supplies, etc.

TFAA in the final nitrolysis step, although other potentially more economical options should be investigated. Additionally, purchase of reagents on a bulk scale could significantly reduce the actual total cost.

3. Physical and Chemical Properties

3.1 Instrumental analysis

^{1}H and ^{13}C NMR spectra for TNAZ are very simple [1]. The ^{1}H spectra shows only one resonance, a singlet occurring at δ 5.2 ppm. The ^{13}C NMR shows two resonances at δ 103.4 (C3) and 63.4 ppm (C2 & C4).

The infrared spectrum of TNAZ shows three major absorbances at 3050, 1580 and 1420 wavenumbers [1]. Vibration of the nitro groups is responsible for the two latter peaks. The strong singlet at 3050 cm^{-1} is typical of that observed for C-H stretch. The UV spectrum for TNAZ has been found to have a maximum at 240nm, ε 3600 [1]. Thompson *et al.* performed extensive work to assign 24 of the 45 fundamental molecular vibrations of TNAZ [21]. This was achieved through use of matrix-isolation and isotopically labelled TNAZ, along with quantum chemical calculations.

X-ray crystal structure analysis has been performed on TNAZ [1]. The results of this study showed the azetidine ring to be significantly puckered, with the angle between the C-C-C and the C-N-C planes, ϕ, being 13.6°. The studies also revealed that the two geminal nitro groups are essentially perpendicular to one another (Figure 1).

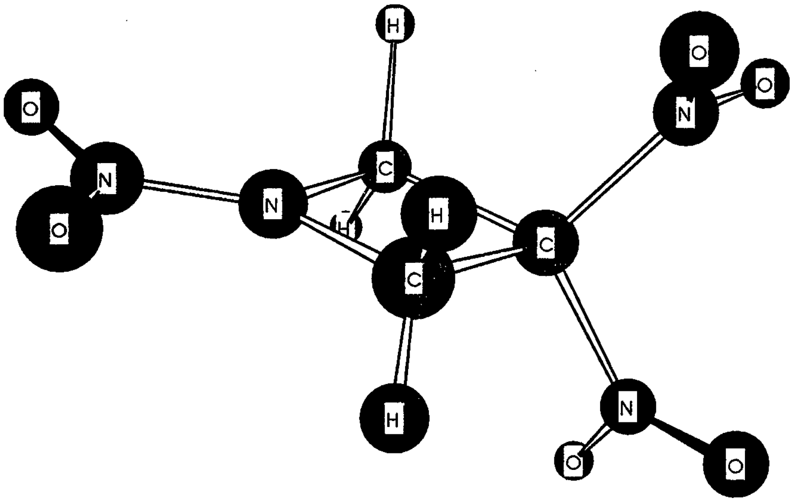
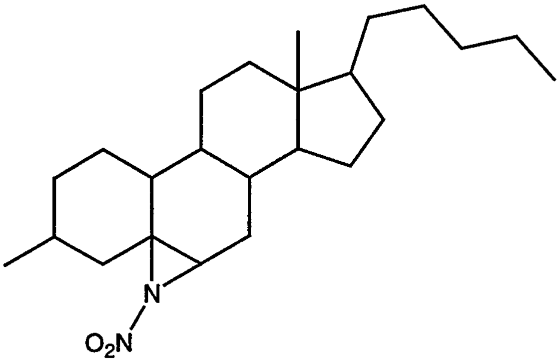


Figure 1: TNAZ 3D structure based upon X-ray data.

One feature of note is the bend observed in the ring nitrogen. In general, it has been observed that the "out-of-plane-bend" in nitramines averages 12.2°. In TNAZ this value is 39.4°, suggesting that the nitrogen is essentially pyramidal, with 'pseudotetrahedral' sp^3 hybridisation. Ring size plays a crucial role in the size of the bend. It has been reported that 3-nitrato-1-nitroazetidine has a bend of $\phi = 39.5°$, along with significant puckering of the azetidine ring [22]. The only nitramine reported to have a significantly greater bend, at $\phi = 59°$, has the nitramine as part of an aziridine moiety (34).



(34)

The length of the N-N bond in the nitramine, 1.351 Å, is around the same as that observed for other nitramines (eg. β-RDX N-N = 1.354 Å), but shorter than that expected considering the large twist and bend between the C-N-C plane and the NO_2 plane. The shortened length, relative to other strained nitramines, has been attributed to inductive effects produced by the strongly electron withdrawing geminal dinitro grouping [1].

3.2 Chromatographic Analysis

Analysis of TNAZ in the presence of other explosive components has been successfully performed using reverse-phase high performance liquid chromatography (HPLC) with photodiode array (PDA) detection [23]. Baseline resolution of 16 energetic compounds in under 30 min was achieved using a Nova-Pak™ C_8 column and water: *iso*-propanol (82:18) as the eluent. An alternative HPLC analysis method was developed at the National Defence Research Establishment, Sweden [24]. This method used a Supelco 5-2880 packed column with $MeOH:THF:H_2O$ (49:6:45) as the mobile phase and UV absorbance detection at 210 nm. This system allowed separation of nine components including TNAZ, CL-20, TNT and RDX, in under seven minutes. Detection limits for TNAZ were reported as <5 ng per injection. Use of Micellar Electrokinetic Capillary Chromatography (MEKC) has also enabled separation of 14 nitroaromatic and nitramine compounds, including TNAZ, TNT and CL-20 in under seven minutes [25]. The electrolyte buffer consisted of 2.5 mM sodium borate, 12.5 mM boric acid and 50 mM sodium dodecylsulphate. A 50 μm I.D. × 60 cm effective length AccuSep™ polyimide fused silica capillary was used with UV_{254} or UV_{185} absorbance detection.

3.3 Chemical Properties

TNAZ is a highly symmetrical molecule with a molecular weight of 192.0131 mass units and formula of $C_3H_4N_4O_6$. The calculated elemental analysis is C, 18.76; H, 2.10; N, 29.16; O, 49.98. TNAZ shows varied solubility in common organic solvents (Table 2) [26]. At ambient temperature, TNAZ has high solubility in polar aprotic solvents such as ethyl acetate and acetone but has only moderate solubility in alcohols and non-polar hydrocarbons.

The crystal density of TNAZ is 1.83 g/cm^3 while the molten form has a lower density of approximately 1.59 g/cm^3, thus resulting in shrinkage of ~15% upon solidification. Additionally, TNAZ is believed to exist in at least two polymorphic forms.[27, 28] Upon cooling to the solid state, it has been proposed that TNAZ transitions between its polymorphs, thereby developing defects within the polycrystalline lattice.

Table 2: Solubility of TNAZ at ambient temperature

Solvent	Solubility (g/mL)
Ethyl Acetate	0.436
Absolute Ethanol	0.055
Iso-propanol	0.026
Acetone	0.442
Toluene	0.038
Iso-octane	0.014

3.4 Genetic toxicity

Preliminary toxicity studies have been conducted by the U.S. Army Environmental Hygiene Agency. The results of these studies show that TNAZ is non-irritating to the skin, has no sensitisation potential and is only mildly toxic following oral administration in rats. However TNAZ was seen to cause transient irritation to the conjunctiva of rabbit eyes, with a severity similar to that caused by TNT [29].

The mutagenic activity of TNAZ has been examined by both the salmonella reverse mutation assay and the Chinese hamster ovary cell/hypoxanthine-guanine phosphoribosyl transferase (CHO/HGPRT) forward mutation assay [30]. TNAZ was observed to induce no significant increase in mutant colonies at the HGPRT locus. Analysis of these results, and additional independent confirmatory Ames and CHO/HGPRT assays indicate that TNAZ is non-mutagenic.

The clastogenic potential of TNAZ was investigated by examining its effects upon mice bone marrow cells [30]. In the presence of TNAZ, the number of micronucleated cells was not increased. From this data, the authors concluded that TNAZ is non-clastogenic.

4. Hazards Characterisation of TNAZ

Characterisation of TNAZ using standard small scale sensitiveness tests has shown that the sensitiveness of TNAZ is between that of RDX and TNT, depending upon the purity, source and particle size being examined.

4.1 Impact Sensitiveness

It has been observed that impact sensitivities vary greatly, depending upon the TNAZ particle size. In general it is found that the impact sensitiveness of large particle size TNAZ is comparable with those of HMX and RDX, while smaller particle sizes exhibit impact sensitiveness similar to that of TNT. Data from LANL shows a drop height of ~29 cm *cf.* 28 and 32 cm for HMX and RDX respectively (type 12A tools, 2.5 kg drop weight with 35 mg pressed pellets) [26]. In contrast to the above results, tests conducted at Eglin Air Force Base (AFB) showed an impact sensitiveness of 21.1 cm using the same testing procedure [31].

Tests performed at Picatinny Arsenal found a 50% go/no-go point of approximately 66 cm when smaller average particle size(~5.4 μm) TNAZ samples were used [32]. For comparison, the sensitiveness for HMX, RDX and TNT are typically 23, 15 and 98 cm respectively. It was observed that 5-10 μm particle size TNAZ has an impact sensitiveness closer to that of TNT, than conventional nitramines.

4.2 Friction Sensitiveness

The friction sensitiveness of TNAZ was examined using a BAM friction testing apparatus. The friction sensitiveness reported by LLNL was in the range of 54-116 N, compared to 116 N for a HMX reference standard [26]. Results obtained by researchers at Eglin AFB, using the same testing procedure, found the friction sensitiveness to be lower, at 160 N [31]. The results appear to vary depending upon the source and purity of the TNAZ sample, with friction sensitiveness decreasing for pure, recrystallised TNAZ samples. No data was found regarding the effect of particle size.

4.3 Electrostatic Spark Sensitiveness

Using a modified Naval Surface Weapons Centre (NSWC)/White Oak electrostatic sensitiveness test, researchers at Eglin AFB determined TNAZ to be insensitive to a discharge of 0.6125 J (no observed ignitions during 10 trials) [31].

4.4 Chemical Reactivity/ Vacuum Stability Test

Unlike other nitramines such as RDX, TNAZ does not undergo decomposition at its melting point (101°C). Chemical reactivity testing also showed insignificant gas evolution when pure TNAZ is held at 120°C for 22 hr under 1 atmosphere of helium gas. Significant gas evolution was observed under similar reference test conditions for some industrially produced samples, suggesting possible contamination with low levels of impurities for this material. Vacuum thermal stability tests on TNAZ were also performed using a 0.5 g sample at 100°C for 48 hr in a vacuum of less than 10^{-4} millitorr [31]. In these tests it was observed that gas evolution was around 0.11 cm^3/g of TNAZ; this may be compared with evolution seen from other commonly used energetic materials (Table 3) [33].

Table 3: Gas evolution from common explosives

Energetic Material	Gas Evolution (cm^3/g)	Experimental Conditions
NTO[34]	0.3	48hours@120°C
RDX[35]	0.12-0.9	48hours@120°C
HMX[35]	0.07	48hours@120°C
TNAZ[31]	0.11	48hours@100°C
Composition B [35]	0.05-0.16	48hours@120°C
PETN[35]	0.1-0.14	22hours@120°C

4.5 Shock Sensitivity

A small scale insensitive high explosive gap test has been performed on TNAZ using the procedure established at NSWC [31]. A modified Bruceton up-down procedure was used with the boosting system being the same as that employed in the Naval Ordnance Laboratory (NOL) large-scale gap test. Results of this test showed cast TNAZ shock sensitivity to be around 4.3 kbar (ρ=89.4%TMD). In studies conducted at Picatinny Arsenal the crystal size was seen to greatly affect shock sensitivity for pressed samples [32]. Pressed Class 5 TNAZ, with 5-10 µm particle size, showed an approximately one third reduction in shock sensitivity over cast samples, despite the pressed samples having higher porosity (16.9% *cf.* 8.2% for cast sample). In NOL large-scale gap tests conducted at Eglin AFB, a shock sensitivity of 10.5 kbar was found for a pressed sample of TNAZ (ρ=98.4%TMD) [31]. These results show that TNAZ has a shock sensitivity moderately greater than that of LX-14 (HMX:estane; 95.5%:4.5%).

4.6 Thermal Properties

The thermal stability of TNAZ, over the temperature range of 160-280°C, has been shown to be greater than that of RDX but inferior to that HMX or TNT [36]. Thermal decomposition in the temperature range 160-250°C was shown to follow a first order rate law, with the rate constant at 240°C reported as being 4.6-4.8E-03 [36, 37]. The activation energy, measured by several methods, has been reported in the range 130-200 kJ/mol [36, 38].

Differential scanning calorimetry of TNAZ showed a melting endotherm at approximately 100°C [26]. A gradual endotherm was observed after the melt transition, which was attributed to 'latent heat' by the author. The principal exotherm due to thermal decomposition begins at approximately 240°C and reaches a maximum at 245°C. The onset of the principal exotherm is around 30°C lower than that observed for HMX. Figure 2 shows a typical DSC trace found for TNAZ.

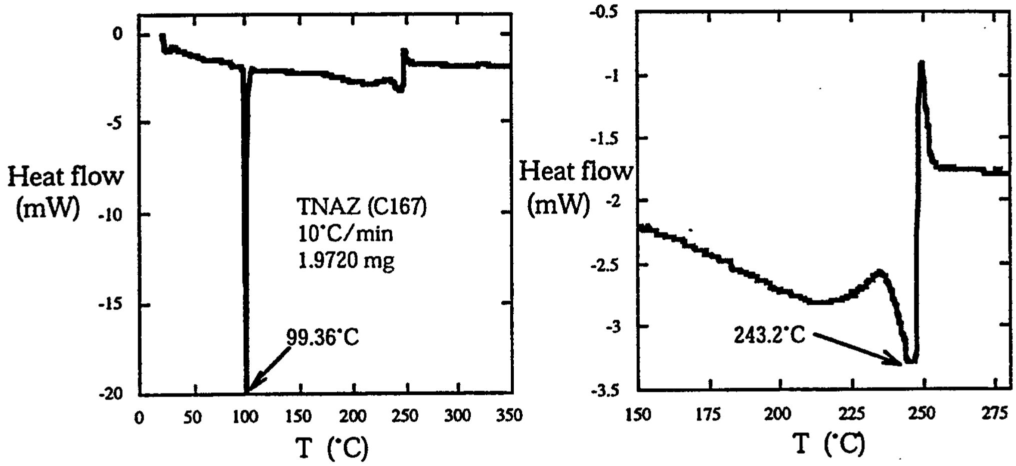


Figure 2: DSC trace for TNAZ

One dimensional time to explosion (ODTX) experiments were performed to establish a thermal response model [26]. The time between sample introduction and explosion was determined at temperatures down to that at which no reaction occurred. Using pressed TNAZ samples at 97-99% of theoretical maximum density (TMD), the minimum temperature required for an event to occur was 201°C. This critical ODTX temperature is higher than that for RDX (184°C), HMX (190°C) and CL-20 (163°C).

The time-to-explosion response of TNAZ is similar to RDX and CL-20 at moderate to high temperature while at lower temperatures the time-to-explosion is more similar to that of observed for HMX. All of the reactions observed, however, were probably high order events.

5. Thermal Decomposition Mechanism

As part of the evaluation of TNAZ for use as a military explosive, characterisation of the products of thermal decomposition is required. A large number of studies, using electron impact mass spectrometry, photofragmentation translational spectroscopy, gas chromatography and infrared spectroscopy have been completed in an attempt to fully characterise the decomposition pathway(s).

5.1 Decomposition Gases

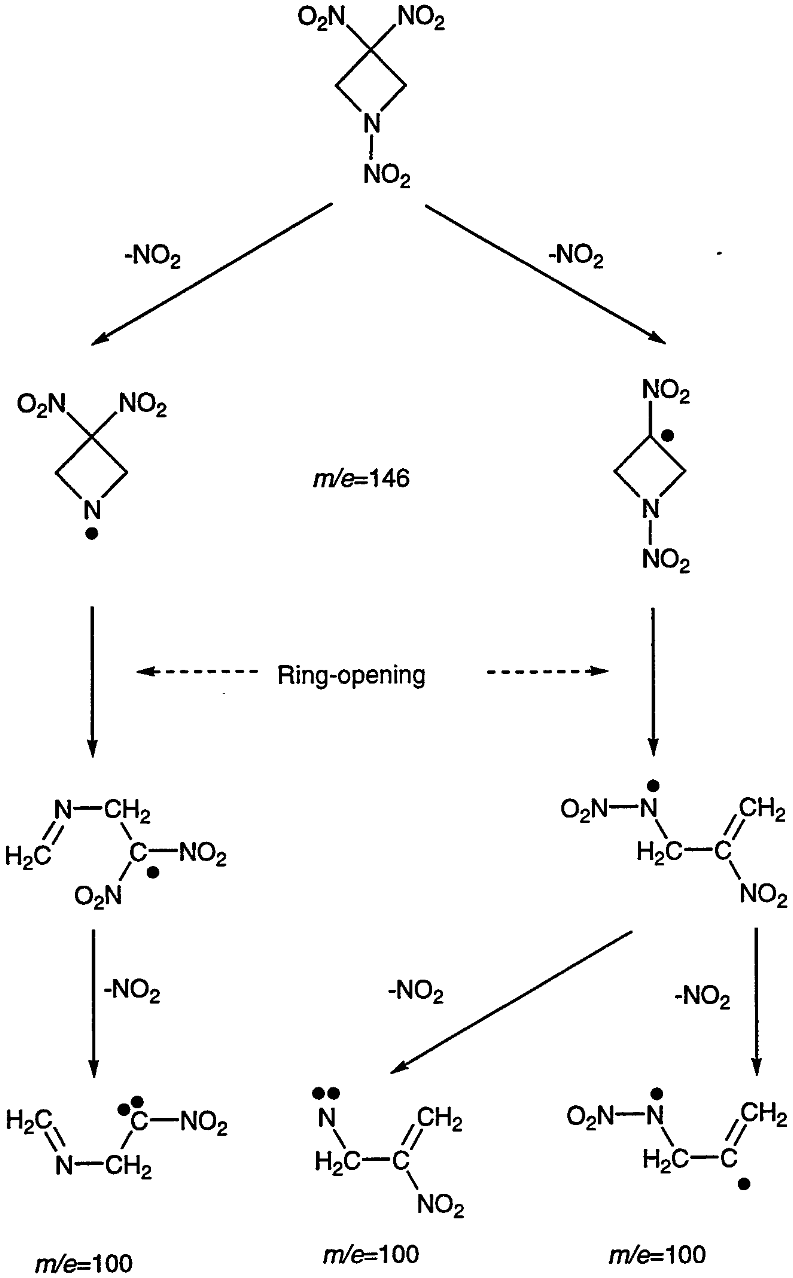
The gaseous products formed during thermal decomposition are those typically observed from other simple nitramines. The most commonly observed decomposition gas is NO_2, with other major components being CO_2, CO, N_2O, N_2 and NO, and HCN and cyanogen have also been observed [39, 40]. Oyumi and Brill suggested that CH_2O may also be present, although its existence has not been confirmed. Nitrogen and NO gases are produced in roughly equal proportions and are present in larger quantities than N_2O. During the initial thermal decomposition, NO_2 is observed as the major decomposition product. The quantity of CO_2 produced is approximately 2.5 times that of CO.

Decomposition studies using carbon-labelled TNAZ showed equal inclusion of all three carbon atoms of the ring in both CO_2 and CO [36]. ^{15}N studies have shown that the majority of evolved NO originates from the nitramine nitro. The N_2O is mostly evolved from the geminal nitro groups interacting with each other, while the majority of the N_2 contained one nitrogen from the ring.

5.2 Decomposition Pathway

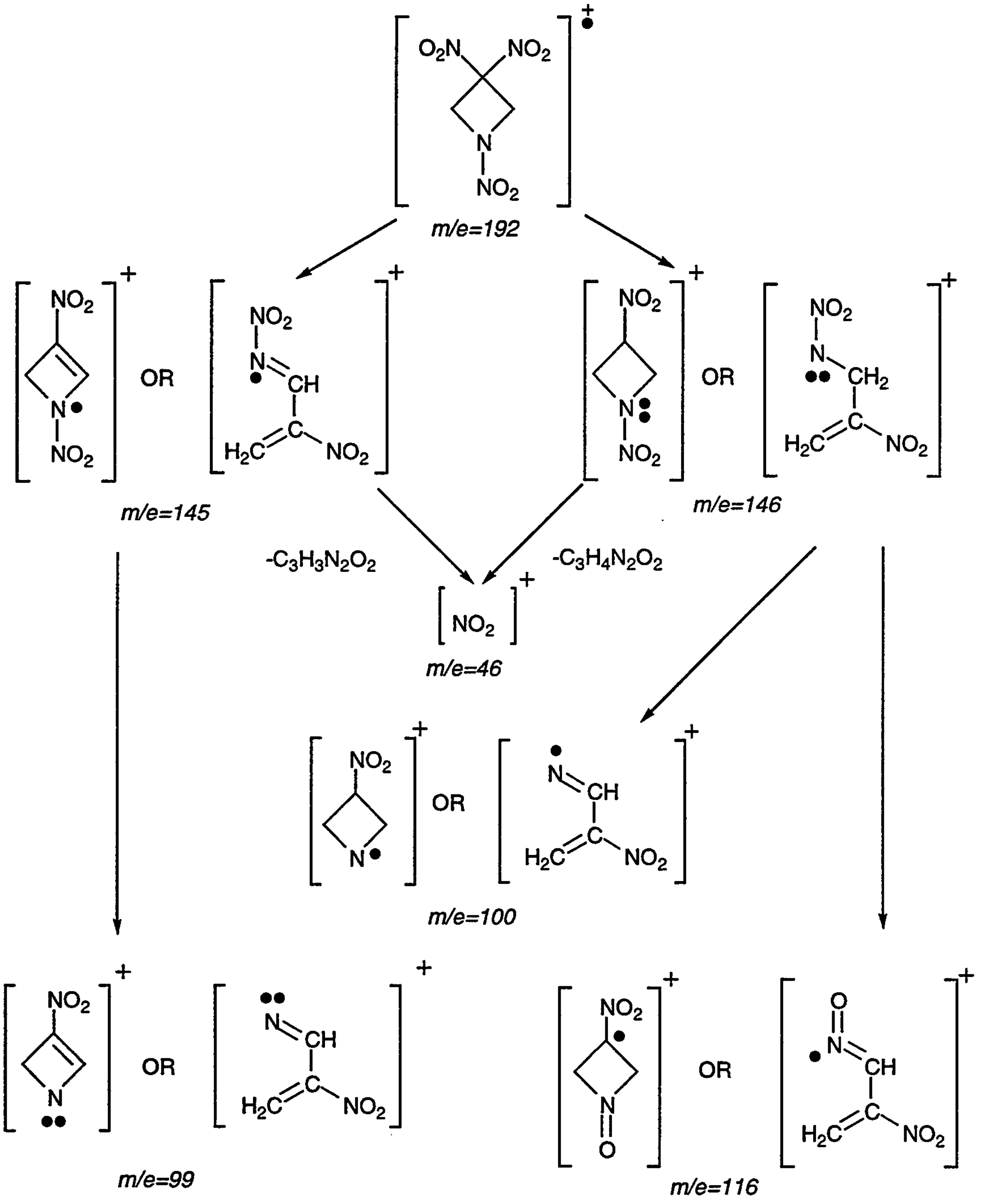
Photofragmentation translational spectroscopy studies by Anex provide an insight into the thermal decomposition pathway of TNAZ (Scheme 7) [41]. In this study TNAZ was expanded from an inlet nozzle into a vacuum, and collimated to form a molecular beam. The molecules were then excited above the dissociation threshold using a pulsed CO_2 laser, inducing decomposition *via* infrared multiphoton excitation. The decomposition products then entered the mass spectrometer, were ionised and separated by a quadrupole mass spectrometer and subsequently detected with an ion counter.

The results suggest that initial decomposition involves the loss of two NO_2 groups, with mass fragments $m/e = 146$ ($M-NO_2$) and $m/e = 100$ ($M-2NO_2$). The remaining ring-opened fragment decomposes into C_3H_4 and N_2O_2. Time-of-flight data shows that C_3H_4 must have recoiled from a larger fragment, rather than being produced from the collision of smaller fragments. The presence of this tertiary degradation step lead to the conclusion that in TNAZ, some of the initial NO_2 loss is from the *gem*-dinitro groups. The decomposition of TNAZ was seen as being different to, and far simpler than, that of other nitramines such as RDX, in that no evidence of HONO elimination, nitro-nitrite rearrangement or a concerted ring scission was observed.



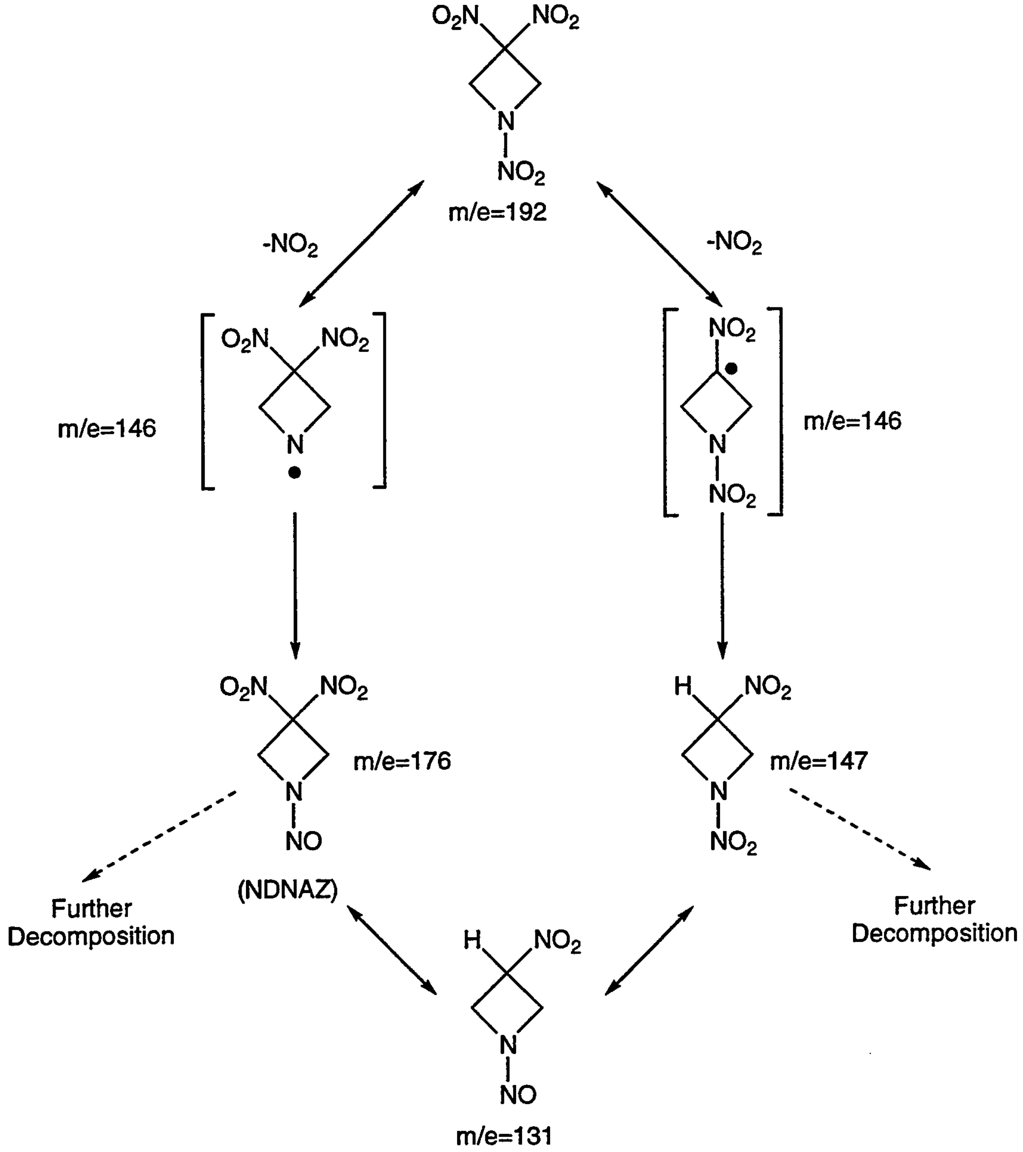
Scheme 7: Anex D.S. (1991). Thermal Decomposition Pathway

Zheng *et al.* have suggested that initial thermal fragmentation results in the loss of either NO_2 or HNO_2 from the *gem*-dinitro group [42]. Mass spectral analysis of the decomposition showed a large fragmentation peak at *m/e* = 145, corresponding to the $[M\text{-}NO_2]^+$ fragment. Mass spectral data has shown that this is followed by loss of NO_2 or NO from the nitramine group. The *m/e* = 46 $[NO_2]^+$ fragment was found to primarily result from N-N scission while the peak at m/e = 30, $[NO]^+$, was seen to result from both alkyl and nitramine NO_2 groups. The thermal decomposition proposed by Zheng *et al.* is shown in Scheme 8.



Scheme 8: Zheng *et al.* (1997). TNAZ Thermal Decomposition Pathway

In a study by Oxley *et al.* it was proposed that the decomposition of TNAZ occurs by two competitive pathways (Scheme 9) [36]. Oxley *et al.* concluded that the initial step is the loss of NO_2 to give either di-nitroazetidine isomer. There are two possible pathways; the first pathway proceeds *via* N-NO_2 bond homolysis and the second *via* C-NO_2 cleavage. It was found that N-NO_2 homolysis was slightly favoured over C-NO_2 bond cleavage. In research conducted at the University of Rhode Island, both of these pathways were reported, with the conditions of the experimental design effecting which of the pathways is the most favoured [36, 40]. With a calculated



Scheme 9: Oxley et al. (1997) Thermal Decomposition Pathway

energy difference of only ~2 kcal/mol for the products formed as a result of NO_2 loss from the azetidine or C-NO_2 bond cleavage [43], these experiment-dependent results would not be unexpected. In these studies it has been suggested that TNAZ may thermally decompose *via* the mononitroso analogue of TNAZ, 1-nitroso-3,3-dinitroazetidine (NDNAZ) [36]. It has been shown that the nitroso derivative is significantly less stable than TNAZ, resulting in the suggestion that NDNAZ may play a pivotal role in the TNAZ decomposition process [44].

The general conclusion from the above studies is that TNAZ decomposes *via* an initial loss of NO_2 from either the nitramine or C-NO_2 moieties with a subsequent loss of further NO_x species following. The role of other TNAZ based species, such as NDNAZ, in the decomposition process has not been fully examined. The mechanism for the formation of NDNAZ is also not yet clear, whether NO reacts with TNAZ or DNAZ to form NDNAZ has not been proven.

Further work in this area may involve identification of the role NDNAZ plays in the decomposition of TNAZ, along with investigating the intermolecular reaction occurring during degradation. As seen, all the reported studies are based upon the instrument induced degradation of TNAZ. The thermal degradation of TNAZ under conditions likely to be experienced in a munition environment has not been studied; such studies will be required before TNAZ is used in munition applications.

6. TNAZ as an Energetic Material

The processing of TNAZ for use as an energetic material is in the early stages of investigation. An important physical property of TNAZ for use as an energetic material is its low melting point. It is predicted that TNAZ might be processed in the liquid phase, using existing steam-jacketed vessels currently used for producing TNT based melt-cast fills. Bottaro (SRI International) has predicted that "TNAZ will find applications in every system that now uses TNT" [45]. Consistent, high density melt-cast TNAZ charges have not been produced to date probably due to its complicated crystallisation process as discussed earlier, (Section 3.3). However, pressed TNAZ charges with densities of greater than 99% TMD can be consistently achieved. It is believed that TNAZ partially melts and sinters while being pressed at elevated temperatures, resulting in high quality, machineable pellets [46].

It has been observed that small particle size TNAZ allows the production of higher quality charges. Class 5 TNAZ, with an average particle size of 10-15 μm in the form of irregular crystals, has been found to give consistent charge quality. Class 5 TNAZ can be readily produced by using crash precipitation techniques [46], by dissolving the TNAZ in a minimum quantity of hot solvent (ethanol or *iso*-propanol) followed by immediate addition to an ice/water slurry.

For other applications, such as in LOVA propellants, larger diameter (>125 μm) spherical particles are required. In a process developed by Stec *et al.*, oblong crystals of 100 μm average size are produced by recrystallisation from an aqueous ethanol/methyl cellulose medium [46]. Rapid agitation was required to prevent the formation of needle shaped crystals. NMR spectrometry showed no inclusion of methyl cellulose within the crystal structure.

6.1 Explosive properties

Detonation calorimetry performed at LLNL found TNAZ to have a heat of detonation of 1466 ± 15 cal/g [26]. This figure compares favourably to HMX (1480 cal/g) and PETN (1490 cal/g) and is significantly higher than TNT (1090 cal/g). The major gases that were produced during TNAZ detonation were N_2, H_2O, CO_2 and CO. The energy densities of TNAZ and several other explosives are given in Table 4. Of particular note is that TNAZ possesses a 50% higher energy density than TNT, for which it is seen as a possible replacement (Table 4).

The heat of formation of TNAZ is generally regarded as being high, about 8.7 kcal/mol, largely due to its highly strained azetidine ring. Although this figure is commonly quoted, the authors were unable to find an original source for this data. In tests performed at LLNL, the heat of formation was measured as 2.81 kcal/mol [26]. These measurements were performed using a Parr isothermal calorimeter. The TNAZ was sublimed prior to analysis and thus samples were around 99.8% pure, as determined by HPLC, GC-MS, IR and direct inlet probe mass spectrometry.

Table 4: Energy Density of representative materials

Explosive	**Density** (g/cm^3)	**Energy** (cal/g)	**Energy Density** (cal/cm^3)	**Energy Density relative to TNAZ** (%)
TNT	1.53	1090	1670	62
TNAZ	1.83	1466	2700	100
HMX	1.89	1480	2797	104
ε-CL-20	1.96	1500	2940	109
PETN	1.73	1490	2580	96

The explosive performance of TNAZ has been calculated using various computational models. The TIGER code calculated the velocity of detonation (VoD) and detonation pressure (P_{CJ}) as 8846 m/s and 372 kbar respectively at TMD [46]. Similar calculations for TNAZ in its liquid state (ρ=1.51 g/cm^3) gave VoD and P_{CJ} values of 7897 m/s and 266 kbar respectively. Using CHEETAH code the VoD and P_{CJ} were calculated as 9000 m/s and 364 kbar respectively [31]. The calculated VoD figures compare favourably with the VoD=8730 m/s found experimentally by Aubert [47].

A summary of the explosive performance of TNAZ compared to some commonly used explosives is presented in Table 5. TNAZ has performance properties in the range of the most highly energetic explosives commonly used. Its performance is significantly higher than that of TNT, for which it is a potential replacement in melt-cast systems.

Recent computational chemistry has been performed at Picatinny Arsenal for two TNAZ based compositions, PAX-T99 and PAX-T98, containing 99 and 98% TNAZ respectively [48]. The results of these JAGUAR calculations showed high VoD (>8625 m/s) and detonation pressures (P_{CJ} >327 kbar). The expected explosive performance, along with their calculated densities, 1.824 and 1.815 g/cm^3 respectively, suggests that further development may be profitable.

Table 5: Explosive performance of common energetic materials

Explosive	Density (g/cm^3)	VoD (m/s)	P_{CJ} (kbar)	ΔHf (kcal/mol)	Energy Density (cal/cm^3)	Oxygen Balance (%)	M.P. (°C)
TNAZ[26, 29, 31]	1.83	8730	372	2.8	2700	-16.7	99-101
NTO[33, 49]	1.93	8585	349	-20	2780	-24.6	273^a
RDX[35]	1.81	8700	338	14.71	2610	-21.6	205^a
HMX[35]	1.89	9110	390	17.93	2797	-21.6	285^a
PETN[35]	1.73	8300	335	-128	2652	-10.0	140
TNT[35]	1.65	6900	210	-15	1670	-21.6	80.9

a: Decomposition

6.2 Utilisation of TNAZ in HE formulations

The relatively low melting point of TNAZ suggests that melt-casting of TNAZ-based HE charges using existing TNT equipment is a possibility. It has been observed, however, that the vapour pressure is much higher than that of TNT. High concentrations of energetic vapours are potentially hazardous during melt-cast processing operations in open, steam-jacketed melt kettles. In addition it has been observed that the resolidification process is a complicated one. This results in the formation of porous charges of an unacceptable quality for use in military stores. Densities above 90% TMD have proved to be difficult to obtain in cast TNAZ charges. If TNAZ is to be processed in the liquid phase then additives will be needed to lower the melt temperature and vapour pressure, and also modify the crystal morphology to assist in the production of high quality cast charges.

In work carried out by Reich *et al.* at Eglin AFB, a number of TNAZ compositions were examined [31]. The physical, chemical and sensitivity properties of TNAZ and various compositions containing TNB (1,3,5-trinitrobenzene), TNT (2,4,6-trinitrotoluene), MNA (*N*-methyl-*p*-nitroaniline), DNA (2,4-dinitroaniline) and CAB (cellulose acetate butyrate) were examined. Tests performed on these mixtures included thermal analysis, Henkin time to explosion (HT_c), impact, friction and electrostatic sensitivity, vacuum thermal stability (VTS) and NOL large scale gap testing (NOL LSGT) (Table 6).

The results of these studies suggest that mixtures containing MNA or DNA, both of which are aromatic amines, could be useable melt-cast formulations. The modified crystal morphology greatly enhanced the quality of the cast charges. Charge density increased from (typically) 89.4% TMD for pure cast TNAZ to 97.7% TMD for a 90/10 TNAZ/MNA composition. Although dilution with the aromatic amines reduces performance at TMD, the greater achievable melt-cast density (>95% TMD) of the mixture compared to that for neat cast TNAZ (~90% TMD), ensures calculated performance is within 1-4% of that of cast TNAZ. In this work it was concluded that a composition of TNAZ/MNA, 80/20 weight percent, resulted in the greatest improvement of charge quality and reduction in shock sensitivity, and thus has the most future as an explosive composition.

Table 6: TNAZ composition properties

Eutectic	**% TNAZ**	**TMD** (g/cm^3)	**Cast density** (g/cm^3)	**M.P** (°C)	**HT_c** (°C)	**VTS** (cm^3/g)	**NOL LSGT** (kbar)	**Impact** $H_{50\%}$ (cm)	**VoD^a** (m/s)
TNT	0	1.65	1.63	80.9		0.10	44	>80	6970
TNAZ	100	1.84	1.64	101	251	0.11	10.5	21.1	9000
TNAZ/ TNB	53.7	1.77	1.71	69	266	0.05	7.4	36.1	8250
TNAZ/ TNT	37.1	1.72	1.66	60	260	0.10	10.4	52	7600
TNAZ/ MNA	90	1.75	1.66	93	239	0.20	***	38.6	8320
TNAZ/ MNA	80	1.66	1.62	93	230	0.06	10.8	34.9	7730
TNAZ/ DNA	92	1.82	1.69	95	234	0.04	***	30.8	8770
TNAZ/ CAB	97	1.81	1.72	100	243	0.24	0.73	22.6	8800

a: Calculated performance (CHEETAH code)
*** Data not available

A composition that has received some attention is that between TNAZ and HMX [50, 51]. In work performed Chapman *et al.* at TPL Inc. it was observed that TNAZ/HMX had only very limited eutectic interaction. For the TNAZ-HMX system, compositions having mole ratios of 95:5, 75:25, 50:50, 25:75 and 5:95 were prepared and analysed using DSC. It was found that there is only a very slight depression in the melting point, ~3°C. This slight melting point depression suggests that only a small HMX content is present in the melting TNAZ throughout the composition range. RDX, having a lower melting point than HMX, is expected to have a greater eutectic interaction with TNAZ. This study also showed that TNAZ-tetryl forms a very good composition (M.P. ~80°C) in a 50/50 TNAZ/tetryl mix. Use of this composition is unlikely, however, as tetryl has prohibitive OH&S problems and production has ceased.

Another eutectic that has shown some promise is that of TNAZ with *N*-acetyl-3,3-dinitroazetidine (ADNAZ) [52]. In this work it was seen that from being totally miscible in the liquid phase, TNAZ & ADNAZ forms a eutectic mixture upon cooling, the composition being TNAZ:ADNAZ 2:1. This composition possesses a melting point of 78°C, similar to that of TNT (80.5°C).

Considerable effort at LANL has been directed to the investigation of the eutectic formed between TNAZ and 1-nitroso-3,3-dinitroazetidine (NDNAZ, **6**). The eutectic composition contains 58 mole % TNAZ, and has a melting point of 83°C. The vapour pressure of this eutectic is only 0.65 torr at 90°C. NDNAZ has explosive properties not dissimilar to that of TNAZ. NDNAZ has a calculated VoD and P_{CJ} of 8400 m/s and 316 kbar respectively compared to 8730 m/s and 372 kbar respectively for TNAZ. The stability of this eutectic, however, is questionable. NDNAZ is suspected to be one of the initial decomposition products of TNAZ and may reduce the thermal stability of such eutectic mixtures [36]. Other eutectics investigated at LANL include the 3-halo-1,3-dinitroazetidine series; the addition of small quantities (<5%) of these compounds increases the impact sensitiveness drop height of these mixture by 30-50% above that measured for neat TNAZ.

Recent work into the use of TNAZ has been concentrated upon the use of the TNAZ/CAB mixture, a composition that is seen as readily cast-loadable or pressable to very close to TMD [53, 54]. This composition has been formed by heating TNAZ to around 115°C and then adding the required weight of powdered CAB. It is observed that with stirring the powdered CAB becomes completely dissolved and/or plasticised by the liquid TNAZ. Upon cooling it is observed that the crystal structure of the solidified sample is finer than that of pure TNAZ. This finer structure gives both greater mechanical strength and improved sensitiveness towards impact *cf.* pure TNAZ. The eutectic does however possess a moderate shock sensitivity, suggesting usage within secondary explosive applications may be difficult [55].

It has also been shown that other explosives can be readily incorporated into TNAZ/CAB compositions. Addition of such energetic materials at a temperature of about 115°C resulted in uniformly distributed explosive within the primary matrix. A mixture of 60% by mass HMX was added to a melted composition of TNAZ/CAB (97%/3%), resulting in complete distribution. It is foreseen that this method could be investigated to produce RDX based HE, as a possible TNAZ based Composition B analogue.

In this work, pressing has occurred at temperatures greater than the melting point of TNAZ (pressing temperatures: 120-169°C). Although not stated explicitly, it is obvious that initially the TNAZ/CAB composite is pressed in the liquid state. The composition is kept under pressure during cooling and recrystallisation giving higher quality charges with minimal voids and defects.

6.3 Pressed Polymer Bonded Explosives (PBXs)

An alternative method to overcome the melt-cast problems encountered with TNAZ may be the development of polymer bonded TNAZ formulations. Simpson *et al.* at LLNL have developed six PBXs containing TNAZ [26]. The binders that were considered in these investigations were Viton A, Estane 5703P and Fluorel L-9035. These binders were found to increase the friction sensitiveness of the composition compared to pure TNAZ. It was also shown that Viton A results in increased impact sensitiveness and that estane PBXs showed significant decomposition above 120°C in the vacuum stability tests.

TNAZ has been utilised as a plasticiser in HMX formulations, (HMX/Eypel/TNAZ 85/9/6) 46. TNAZ is used in place of more conventional plasticisers such as NENA and BDNDA/F, both of which possess lower performance (Table 7). The application of TNAZ as a plasticiser may be of particular importance when components are know to be incompatible (*eg*. NTO with NENA).

Table 7: TIGER Calculations of Thermodynamic Properties

Material	VoD (m/s)	P_{CJ} (kBar)
BDNPA/F	6611	165
Et/Me NENA (3:1)	7015	166
TNAZ (solid)	8846	372
TNAZ (liquid, $\rho = 1.52$ g/cm^3)	7897	266

6.4 TNAZ as a potential propellant ingredient

Along with many other compounds, TNAZ is currently being investigated as an energetic propellant ingredient in the hope of forming the basis for the next generation of gun propellents. Future propellants are sought with impetus values of greater than 1400 J/g and flame temperatures of less than 3500 K [56]. Impetuses of around 1200-1300 J/g are also considered useful if average molecular weights (MW) of the product gases are less than 18 g/mol.

BLAKE code calculated impetus and flame temperatures for pure TNAZ are 1399 J/g and 4466 K respectively [56]. ICT-Thermodynamic Code has these figures calculated as 1357 J/g and 4259 K respectively [57]. The impetus of pure TNAZ has been measured at 1428 J/g, however it is unable to be used neat as the flame temperature is excessively high (~4100 K) leading to increased gun barrel wear and the potential for cook-off. Through the usage of a 76% TNAZ/24% AMMO/BAMO composite, an impetus of

1375 J/g, flame temperature of 3500 K and an average gas MW of 21.46 g/mol has been calculated as being achievable.

A promising propellant formulation reported by Simmons contains TNAZ/DANPE (40:60) [56]. Calculated performance of this composition showed an impetus of 1439 J/g, flame temperature of 3490 K and gas MW = 20.16 g/mol. With further formulation optimisation similar blends could prove to be useful propellant formulations. Another possible application of TNAZ is to replace conventional nitramines in low vulnerability ammunition (LOVA) propellant such as XM-39.
The composition of XM-39 is as follows:

NC	4.0%
CAB	12.0%
Plasticiser (ATEC)	7.6%
EC (stabiliser)	0.4%
RDX	76.0%

BLAKE code calculations showed that substituting TNAZ for RDX would result in a substantial 10% increase in impetus to around 1160 J/g [32, 57]. Concurrent replacement of the presently-used ATEC plasticiser with an energetic binder could result in even greater improvement in performance [58].

7. Future Investigations

A great deal of research has gone into optimising the synthesis of TNAZ with further work currently being carried out at Aerojet, LANL, and Fluorochem. Future research directions for AMRL are best directed away from synthetic efforts and concentrated rather towards applications in explosive formulations. This work should address potential melt-cast issues and the possibility of utilising TNAZ as a TNT replacement.
A suggested future research program could include:

- Synthesis of a limited quantity of TNAZ to allow small-scale hazard testing (using the AMRL standard techniques) and chemical, materials and sensitiveness characterisation. The synthetic method of choice is that developed by Coburn and Hiskey at LANL, and currently employed by Aerojet on a pilot plant scale.
- Purchasing of TNAZ from a US source, or scaling up of laboratory synthesis, to obtain sufficient quantities for further studies.
- Investigation of TNAZ behaviour during crystallisation from the liquid phase (eg. shrinkage rate, voidage, crystalline microstructure).
- Application of TNT casting technology (eg. "clear" or "cloudy" casting techniques) to examine effect on cast charge quality and produce high density charges. Examination of TNAZ melt-cast charges (eg. density measurements and microstructure determination of sectioned charges, mechanical properties).
- Examination of TNAZ melt-cast charges containing other nitramines (RDX and HMX)

- Thermal analysis of TNAZ/nitramine compositions
- Performance (VoD) and sensitiveness/sensitivity testing of TNAZ/nitramine compositions

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19. ABSTRACT

1,3,3-Trinitroazetidine (TNAZ) is a high density, melt-castable explosive with the potential to replace TNT in melt-cast systems. The purpose of this review is to examine work performed to date and to identify technology gaps AMRL needs to address to permit its use in Australian Defence Force applications.

Synthetic work is well advanced, with pilot-plant scale operations in use. Chemical and physical characterisation has been extensively performed, as has hazard assessment; however, certain sensitiveness results vary and will require further evaluation.

Three studies of thermal decomposition have been performed and show similar trends with decomposition occurring *via* consecutive NO_2 losses. The decomposition gases have largely been identified.

Calculated and experimentally measured explosive properties show TNAZ to have an explosive performance similar to HMX and substantially improved over that of TNT. High quality pressed charges can be consistently produced, but melt-casting of TNAZ has not yet been perfected. Identified AMRL research directions include addressing melt-cast technology and examining TNAZ as a TNT-replacement in TNT/nitramine melt-cast fillings.