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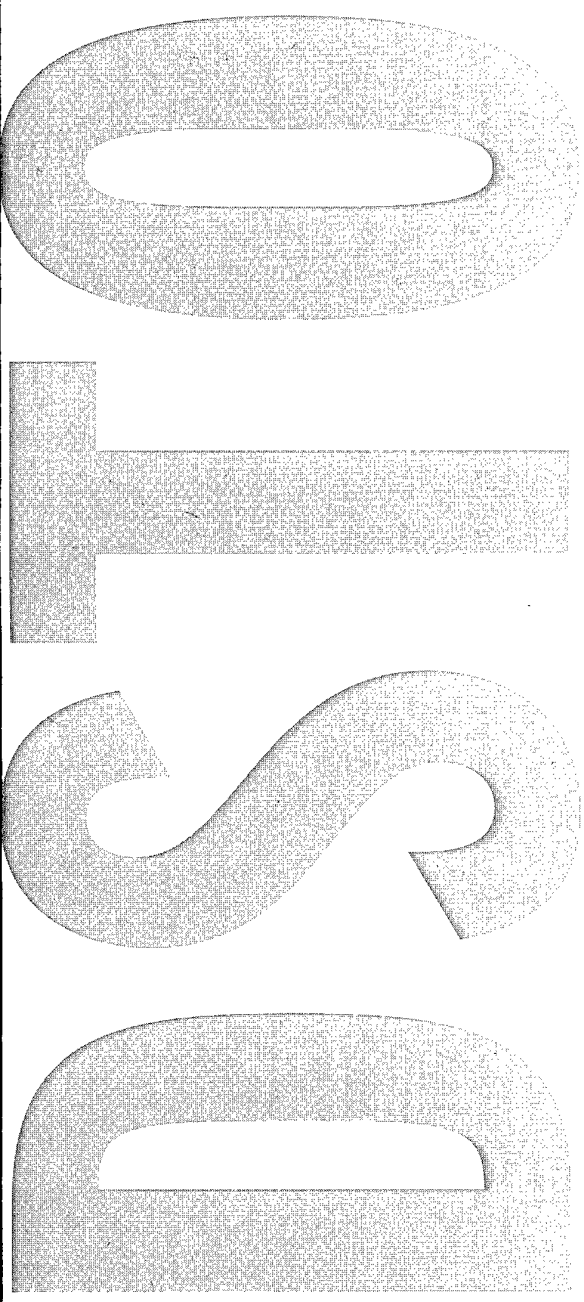

Evaluation of 1,3,3-Trinitroazetidine (TNAZ)-A High Performance Melt-Castable Explosive

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DSTO-TR-1000

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ABSTRACT

The melt-castable explosive 1,3,3-trinitroazetidine (TNAZ) has been assessed as a potential high energy replacement for TNT that could be processed in existing Australian industrial plant. TNAZ was produced using a five step synthetic route to give the target material in a maximum overall yield of 37%. The synthetic route chosen proved troublesome, with the Mitsunobu reaction employed to synthesize the azetidine ring non-reproducible and low yielding. Thermal analysis of neat and formulated TNAZ (60:40 RDX/TNAZ, designated ARX-4007) showed it to have high volatility and rapidly evaporated from the liquid phase (>101°C). Hazards assessment showed TNAZ to have an increased sensitiveness over TNT, while ARX-4007 showed sensitiveness levels similar to pentolite. TNAZ castings appeared to solidify from the melt to give layered plates and formed large numbers of shinkage voids. Shinkage problems were evident in both neat TNAZ and ARX-4007 castings, whilst mechanical properties were poor. Performance assessment of ARX-4007 as a general purpose metal accelerating explosive gave excellent VoD (8660 m/s) and P_{CJ} (33.0 GPa). It is concluded, however, that problems associated with synthesis, volatility, sensitiveness and casting make TNAZ unsuitable as a TNT replacement in melt-cast systems at this time.

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Evaluation of 1,3,3-Trinitroazetidine (TNAZ) - A High Performance Melt-Castable Explosive

Executive Summary

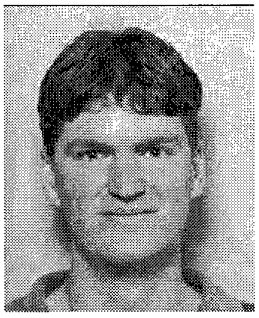
1,3,3-Trinitroazetidine (TNAZ) is a melt-castable explosive that has been proposed as a potential replacement for TNT. TNAZ has approximately 30% more energy than TNT and could be processed in existing Australian industrial facilities.

Experimental quantities were synthesised in 37% overall yield using a five step synthetic route, however, the synthesis was problematic and gave non-reproducible results. Thermal assessment of neat and formulated TNAZ (60:40 RDX/TNAZ, designated ARX-4007) showed it to have high volatility and rapidly evaporated from the liquid phase (>101°C). Hazards assessment showed TNAZ to have an increased sensitiveness over TNT, while ARX-4007 showed sensitiveness levels similar to pentolite and significantly greater than Composition B. It is unlikely that ARX-4007 type formulations would meet IM criteria.

ARX-4007 showed excellent explosive performance when testing for simple detonation parameters. Detonation velocity and pressure were measured at 8660 m/s and 33.0 GPa respectively and represent substantial improvements over Composition B (7860 m/s and 29.5 GPa).

Despite excellent explosive performance, it is concluded that TNAZ is not suitable as a TNT replacement at this time. Synthesis, processing and sensitivity issues represent serious problems and are unlikely to be overcome in the immediate future.

Authors



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Contents

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 pressed PBXs with high solid loadings of RDX or HMX. Such warheads, however, are typically only used 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 systems, melt-cast explosives or cast-cured PBXs are more suitable.

Australia's ordnance filling capability is based on melt-castable TNT-based compositions, with significant investment in new and upgraded plant having been made during the 1990s. Improved explosives that could be processed on existing plant are thus desirable for Australia. 1,3,3-Trinitroazetidine (TNAZ) is a high performance, melt-castable explosive that has been proposed as a potential replacement for TNT [1]. The low melting point of TNAZ (101°C *cf.* 81°C for TNT) would enable processing of formulations on modified ADI production lines, whilst its performance is approximately 30% greater than TNT. Successful formulation would enable a more powerful general purpose explosive to be developed.

TNAZ, however, is not without its problems. The synthetic route is lengthy and more expensive than for TNT. Problems associated with the high volatility of molten TNAZ are also well documented and formulated charges experience cavitation due to the high shrinkage levels of solidifying TNAZ. A significant body of work has been directed at these issues, however, no simple solution is available.

The aim of this study was to investigate the synthesis, sensitiveness, formulation and performance of TNAZ-based compositions and determine its suitability to provide the ADF with a more powerful melt-castable explosive, processable in Australian facilities.

2. Experimental

2.1 Materials and Instrumental Analysis

Chemical reagents for the synthesis of TNAZ were obtained from the Aldrich Chemical Company and used as received. Diisopropylazodicarboxylate (DIAD) for the Mitsunobu reaction was distilled prior to use.

Grade A Woolwich RDX [2] was obtained from ADI, washed with distilled water and oven dried at 60°C for use in formulations.

Nmr spectra were obtained on a Varian Gemini 200 spectrophotometer using a Solarius VNMR operating platform. ^{1}H and ^{13}C nmr spectra were measured at 200 and 50.3 MHz respectively. Chemical shifts are reported as δ values and are relative to internal tetramethylsilane ($CDCl_3$, DMSO-d_6) and sodium 3-(trimethylsilyl)-1-propane sulphonate (for D_2O). Mass spectra were run on a Micromass Platform II Single Quadrupole mass spectrometer operating in the electrospray mode. Melting

points were run at 3°C/min on a Mettler FP61 automatic melting point apparatus and are uncorrected. Infrared spectra were obtained on a Perkin Elmer 683 IR spectrophotometer using KBr disks.

Scanning Electron Microscopy (SEM) was run on a Phillips XL30 FEG instrument coupled to a EDAX DX4 integrated energy dispersive X-ray analyser operated at 2-20 kV beam energy. Samples were sputter coated with gold to reduce charging prior to analysis. TNAZ densities were determined on a calibrated Quantachrome Ultrapycnometer 1000.

2.2 Differential Scanning Calorimetry (DSC)

DSC experiments were performed on a Perkin Elmer DSC-7 using crimped aluminium sample pans. The instrument was calibrated daily using indium and zinc standards, or upon a change in run conditions. Traces were recorded at ramp rates of 2-20°C/min between 25 to 250°C under a flowing N_2 gas atmosphere (25 ml/min).

2.3 Thermal Gravimetric Analysis (TGA)

TGAs were performed using open aluminium pans under a flowing stream (25 ml/min) of N_2 gas. Temperature ramp rates of 5 and 10°C/min were used from ambient to 275°C. Alumina powder was used as the reference standard.

2.4 Vacuum Stability Testing

Vacuum stability testing was conducted on duplicate 1.0 g samples and the average evolved gas volume reported. Samples were run at 100 and 120°C for 48 hours.

2.5 Rotter Impact Sensitiveness

Impact sensitiveness was determined using a Rotter Impact apparatus [3a]. The test material was ground and passed through a 500 µm sieve prior to testing. A sample of about 30 mg was confined in a brass cap fitted over a polished steel anvil and impacted by a 5 kg weight falling from a preset height. Go / no-go was delineated by >1 ml gas evolution from the sample for a positive result. Impact heights were varied using a Bruceton Staircase procedure [4] with a total of 30 caps tested. The resulting Figure of Insensitiveness (F of I) is quoted relative to an RDX Standard (F of I = 80) and rounded to the nearest 5 units. Reported gas evolution represents the average of all positive results.

2.6 Friction Sensitiveness

Friction sensitiveness was determined using a Julius Peters BAM friction apparatus [5]. The BAM test employs a fixed porcelain peg and a sliding porcelain plate that is moved, once only, back and forth a total distance of 20 mm. The powdered explosive under test was placed between the tile and peg. The peg is fitted to a loading arm on which a weight is hung at set distances from the axis of the peg. The use of different weights at different distances results in a range of loads between 5 and 360 N being exerted on the sample. The limiting load, characterising the friction sensitiveness of a substance, is defined as the lowest load at which an event is seen from at least one

out of a minimum of six trials. A substance is considered too sensitive for transport if it exhibits a positive event with a limiting load of less than 80 N.

2.7 Temperature of Ignition

Temperature of Ignition (T of I) was determined using an instrument built to the specification for the ERDE test [3b]. Powdered samples of 200 mg were heated in glass test tubes at 5°C/min until an event occurred. An event was defined as the occurrence of either smoke/flame or an audible hiss/bang. The T of I reported is the lowest temperature at which an event occurred in duplicate samples.

2.8 Electrostatic Discharge Sensitiveness

The test procedure [3c] is designed to gauge the level of sensitiveness of a sample to ignition by electrostatic discharge. Three discharge levels (4.5, 0.45, 0.045 J) are trialed for the sample, with a total of 50 discharges per level. The reported result is the lowest level at which an event is observed.

3. Synthesis of TNAZ

A number of synthetic routes to TNAZ have been devised by Archibald [6, 7] and other workers [8-11]. The route used in this laboratory was that developed by Coburn *et al.* [12, 13] as shown in Figure 1. Analysis of the available literature indicated that this route offered the highest overall yield from readily available starting materials.

Nitromethane was reacted in a Mannich condensation with excess formaldehyde in aqueous solution to give the triol **1**. *Tert*-butylamine was added slowly to effect ring closure in a second condensation to give the oxazine **2** (98%). Nmr analysis showed the oxazine was isolated in sufficient purity (>95%) to use directly in the following reaction. Acidification with HCl followed by ring opening with hydrogen peroxide gave the diol **3** in 82%.

Formation of the azetidine **4** was highly problematic and non-reproducible in our hands. University contractors were unable to determine the source of this problem and had difficulty in producing large quantities of the azetidine. The purity of the starting material was suspected to be the cause, however, extensive recrystallisation of **3** and purification of reagents failed to improve yields. Formation of **4** *via* a Mitsunobu reaction gave a maximum yield of 67%, with most reaction attempts returning only small quantities of starting material and decomposition products.

Deformylation of **4** with aqueous sodium hydroxide followed by nitration with sodium nitrite gave the amine **5** in 85%. Nitrolysis of **5** with ammonium nitrate/acetic anhydride gave crude TNAZ. Crash recrystallisation from ethanol/water/ice gave the target molecule as short needles in 80% yield from **5**.

Recrystallised TNAZ had a measured density of 1.84 g/cm^3 by gas pycnometry (literature value 1.83 g/cm^3 [6]) with a particle size distribution of 10-300 μm by

SEM. The IR and MS spectra of TNAZ are shown in Figures 2 and 3 respectively. A detailed synthesis and spectral analysis is presented in Appendix A.

4. Hazard Assessment and Vacuum Stability

A summary of the hazard assessment and vacuum stability testing for TNAZ and a number of common secondary explosives is given in Table 1. Evolved Rotter impact gas volumes (ml) are given in parentheses.

Table 1. Sensitiveness Assessment for Synthesised TNAZ.

	TNAZ	TNT	RDX (Grade A)	NTO (200-400 μm)	PETN
F of I	110 (8.9)	> 150	80 (11.9)	120 (4.9)	50 (6.1)
BAM (N)	160	360	128	> 360	60**
ESD* (J)	4.5		0.45	> 4.5	
T of I (°C)	238	299	223	265	181
Vac Stab (ml/g)	0.95†	0.10†	0.10†	0.10‡	0.12‡

* Lowest energy level (4.5, 0.45, 0.045 J) at which an event occurs. ** [5]. † 100°C/48hrs. ‡ 120°C/48hrs.

Rotter impact and BAM friction testing of recrystallised TNAZ showed the sample to be significantly more sensitive to mechanical stimuli than TNT. T of I results also show a reduction in event onset temperature of approximately 60°C to 238°C. ESD tests show low sensitiveness to electrostatic discharge. The results from Table 1 above show that TNAZ has a significantly greater sensitiveness to hazardous stimuli that the TNT it is proposed to replace.

Sensitiveness testing on melt-cast samples of TNAZ gave identical results to those obtained from recrystallised samples.

Vacuum stability testing showed significant gas evolution (0.95 ml/g) compared to results obtained from other common explosives, although it is still well below a commonly accepted upper limit of 2 ml/g [14]. Additionally, significant vaporisation of TNAZ was observed and considerable quantities of material were deposited at the pressure transducer at the top of the tube.

5. Thermal Analysis

DSC analysis of TNAZ showed a melting endotherm with an onset temperature of 99°C. Evaporation of the molten energetic, however, occurred at a rapid rate and no decomposition exotherm was observed due to loss of the sample. Use of crimped sample pans gave similar results and the exotherm was unable to be observed. TGA/DTA analysis provided a clearer picture of the thermal behaviour of TNAZ (Figure 4). The endothermic melt is seen peaking at 103°C accompanied by a steady

evaporative TGA weight loss. The DTA baseline decreases steadily between approximately 120 and 180°C, reflecting the endothermic nature of TNAZ evaporation. Residual sample is seen to undergo exothermic decomposition at 185°C for a short period prior to total loss of sample due to the evaporation/decomposition process.

The rapid rate of evaporation of TNAZ from the molten phase is of concern from an explosives safety and processing viewpoint. To investigate this behaviour further, five samples of TNAZ were heated rapidly to above the melting point and held at constant temperature between 110 and 150°C for 30 minutes (Figure 5). Samples held at 110 and 120°C lost approximately 20% of their original mass over the test period, while higher temperatures lead to greater depletion rates. The sample held at 150°C had completely evaporated by the 28 minute mark and, while unrealistic of kettle temperatures used to process TNT and potentially TNAZ, indicates significant problems.

A second TGA/DTA experiment was run cycling the temperature between 40 and 110°C at 5°C/min and the melting and solidification points for TNAZ recorded. The experiment totalled 5 heating and cooling cycles and ran for a period of 3 hours (Figure 6). Endothermic melting was observed between 97.7 and 98.5°C during the experiment. Exothermic crystallisation, however, occurred at between 53.3 and 54.3°C and showed significant undercooling for neat TNAZ prior to conversion to a crystalline phase. Cycle four failed to solidify with the subsequent fifth cycle showing no melting endotherm. Undercooling of TNT occurs in a manner similar to TNAZ. Liquid TNT can be readily undercooled in thin films to 20°C for extended periods of time, with subsequent recrystallisation and grain growth type highly dependent on the amount of undercooling achieved [15].

6. Formulation and Explosive Performance

Melt-casting of TNAZ into cylindrical charges was performed in a similar manner to that used for TNT. TNAZ was heated to 115°C and open-cast into preheated (80°C) cylindrical moulds of 14 mm diameter. The casting was allowed to cool to ambient temperature and removed from the mould. The initial appearance of TNAZ resembled that seen from clear-cast TNT, with long grain growths evident along the length of the casting (Figure 7). Density measurements of cast samples appeared promising and was found to be 1.78 g/cm^3 (96% TMD), however, samples possessed poor mechanical strength and were extremely brittle. Handling of the charge caused plate-like TNAZ crystals to flake from the exterior.

SEM analysis of cast TNAZ showed the presence of numerous shrinkage voids (Figures 8 and 9). Longitudinal and perpendicular sectioning of cast, cylindrical TNAZ charges gave samples which where unable to be mechanically polished due to the poor mechanical strength of TNAZ. Each surface appeared to consist of platelet-like crystals of TNAZ that had little adhesion to adjacent crystals and were readily removed upon handling. Molten samples cast directly into metal trays also resulted in similar crystallisation patterns. Despite these poor results, it should be noted that only a small number of castings of molten TNAZ were conducted. Casting

techniques and temperatures were far from optimised, with subsequent casting possibly improved by further experimentation.

6.1 Formulation

A Composition B analogue using TNAZ in place of TNT was formulated to assess the potential performance of TNAZ-based compositions. The composition, designated ARX-4007 [16], contained 60% Grade A RDX and 40% TNAZ by weight. ARX-4007 was formulated by the incremental addition of RDX to molten TNAZ at 115°C. The resultant slurry was then hand stirred until thorough wetting of the nitramine was achieved. Molten ARX-4007 had a viscosity comparable to Composition B and was open-cast into cylindrical moulds. The density of ARX-4007 castings was found to be 1.76 g/cm^3 by gas pycnometry (97% TMD).

SEM analysis of the polished surface of ARX-4007 showed RDX evenly distributed throughout the casting (Figure 10). Mechanical polishing was achieved using a method designed for Composition B [17], while bromoform was found to be a suitable etching medium and left RDX standing proud of the matrix. Analysis of a fracture surface of ARX-4007 showed the presence of shrinkage voids throughout the composition (Figure 11). TNAZ appears to be more prone to void formation than TNT, possible due to its tendency to super-cool to temperatures well below the melting point and then rapidly crystallise. This behaviour created difficulties in obtaining high quality castings and resulted in matrices of poor mechanical strength and reduced densities.

The TGA/DTA trace of ARX-4007 is shown in Figure 12. Endothermic melting was seen to commence at approximately 95°C and peak at 103°C. A two-part exotherm is observed with the decomposition of TNAZ appearing as a small peak at approximately 180°C, followed by a larger RDX decomposition (232°C). TGA weight loss for the sample occurs over two distinct regions. An approximate 18% loss is seen from the melt to the first exotherm (180°C) due to TNAZ evaporation. A second loss is then seen for the remaining sample, most probably due to a combination of evaporation and TNAZ/RDX decomposition.

6.2 Hazard Assessment and Vacuum Stability

Sensitiveness and vacuum stability test data for ARX-4007 and a number of TNT-based compositions is presented in Table 2. Evolved Rotter Impact gas volumes (ml) are given in parentheses.

Table 2. Hazards Assessment for ARX-4007 and TNT-Based Compositions.

	ARX-4007	Composition B*	H-6*	Pentolite
F of I	60 (7.6)	130 (4.2)	150 (2.4)	70
BAM (N)	72	112	120	
ESD (J)†	0.45			
T of I (°C)	210	212	203	190
Vac Stab (ml/g)	0.32**	0.15‡	0.50‡	1.53‡

* Grade A. † Lowest energy level (4.5, 0.45, 0.045 J) at which an event occurs. ** 100°C/48hrs. ‡ 120°C/48hrs.

A significant increase in sensitiveness to mechanical stimuli was observed for ARX-4007 in comparison to a number of TNT-based explosives. Rotter impact F of I is lower than that seen for 50:50 Pentolite, a known sensitive secondary high explosive. BAM friction of 72 N is significantly less than that of Composition B (112 N) and below the 80 N minimum threshold required for the transport of dangerous goods [5]. Mechanical sensitiveness results obtained for ARX-4007 show the composition to have an increased sensitiveness over its individual components (see Table 1). The low sensitiveness is possibly influenced by interactions of shrinkage voids around solid RDX particles, as hazards testing of recrystallised and melt-cast samples of TNAZ gave identical results. A void-free casting may well give figures that show reduced sensitiveness, however, melt-casting of TNAZ is known to result in charges containing shrinkage defects, thus these figures are most likely representative of all such castings.

The composition showed a moderate response to electrostatic discharge (0.45 J) and had a T of I similar to Composition B. Vacuum stability testing resulted in improved gas evolutions compared to neat TNAZ. This result is probably due to reduced quantities of TNAZ being present. No gross compatibility problems with RDX were evident.

7. Performance Assessment

The velocity of detonation (VoD) and detonation pressure (P_{CJ}) for ARX-4007 were determined using unconfined cylindrical charges (14 mm diameter, 100 mm length) open-cast to a density of 1.76 g/cm^3 (calculated from charge dimensions and mass). Shots were boosted with 50:50 pentolite cylinders (14 mm diameter) and initiated with Resi 501 EBW detonators. VoD was determined by high-speed streak photography and time-of-arrival piezoelectric pins spaced at 10.0 mm intervals along the charge axis (Figure 13). P_{CJ} was estimated *via* dent tests [18] into mild steel witness plates and referenced to Composition B charges of identical dimensions (Figure 14). A single witness plate (50 mm thick) was sufficient to record dent depths.

A summary of performance results is given in Table 3.

Table 3. Explosive Performance of ARX-4007 and Composition B.

Material	ρ (g/cm³)	%TMD	VoD (m/s)			Dent Depth (Ave, mm)
			Cheetah*	Streak	Piezo Pins	
ARX-4007	1.76	97	8770	8890	8660	3.44
Composition B	1.67	96	7810	7870	7440	2.50

* Cheetah program, version 2.0.

ARX-4007 detonation velocities were measured at 8890 and 8660 m/s from streak and piezoelectric pins respectively. Inherent difficulties in obtaining true recording points from a streak record have possibly given this result an artificially high velocity as the recorded result is significantly greater than that calculated using the Cheetah program. A velocity of 8660 m/s for ARX-4007, determined from time-of-arrival probes, is most probably a more accurate measurement for the composition.

Average dent depths for ARX-4007 and Composition B were 3.44 and 2.50 mm respectively. Using a P_{CJ} of 29.5 GPa for Composition B [19], the detonation pressure for ARX-4007 was estimated at 40.8 GPa.

Such a high value of P_{CJ} is clearly incorrect, with the calculated performance of ARX-4007 expected to be close to that of neat RDX (Cheetah, P_{CJ} = 32.98 GPa). Inspection of the results obtained for Composition B (piezoelectric pins) showed a VoD well below the limiting velocity. This has probably resulted from small charge diameters being used during the experiment, with the resulting performance less than that achievable with greater diameters. The dent depth recorded for Composition B would hence be shallower than expected and an overestimation of P_{CJ} made for ARX-4007.

Use of the relationship

$$P_{CJ} = \frac{\rho D^2}{\gamma + 1}$$

where ρ = density (g/cm³).
D = limiting velocity of detonation (km/s).
γ = ratio of the specific heats of the detonation product gases.

derived by Fickett and Davis from simple one-dimensional detonation theory can be used to approximate the detonation pressure (GPa) from experimentally derived VoD and charge densities [20]. Allowing γ to be equal to 3 (a good approximation for most high explosives close to TMD), then P_{CJ} = 33.0 GPa at a VoD of 8660 m/s. This figure closely matches that calculated from Cheetah and gives a better estimate of the detonation pressure.

Experimentally derived estimates of VoD and P_{CJ} for ARX-4007 were thus 8660 m/s and 33.0 GPa respectively.

8. Conclusion

This study has examined the use of TNAZ as a potential high-energy, melt-castable replacement for TNT that could be processed on Australian industrial plant. The explosive performance of TNAZ in the composition ARX-4007 (60:40 RDX/TNAZ) was shown to be excellent and gave performance improvements of approximately 11% over Composition B. The composition (and other similar formulations) would probably be processable in ADI plant, with alterations to kettle and processing temperatures required.

A number of serious drawbacks, however, are noted.

1. The synthetic route trialed was long and in our hands, problematic. Overall yields were low and the cost per kilogram on an industrial scale would be significantly more than for TNT.
2. TNAZ was shown to be highly volatile and resulted in significant losses of material at temperatures above the melting point. A large body of work looking at methyl nitroaniline eutectic mixtures has been performed in the US to lower the melting point and processing temperatures and minimise TNAZ losses [21]. Although quite successful, performance degradations were observed to a level comparable with TNT, while the problem of high sensitivity was not resolved.
3. Highly porous and cracked castings are produced due to TNAZ shrinkage.
4. Hazards testing of both TNAZ and ARX-4007 showed a large increase in sensitiveness compared to TNT. Such compositions would probably have little chance in achieving IM compliance.

It is concluded that TNAZ is not suitable as a TNT replacement for Australia at this time. It is recommended that no further examination of this material be conducted, however, a watching brief should be maintained to monitor any advances that may make TNAZ useable on an industrial scale.

9. Acknowledgments

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11. Figures

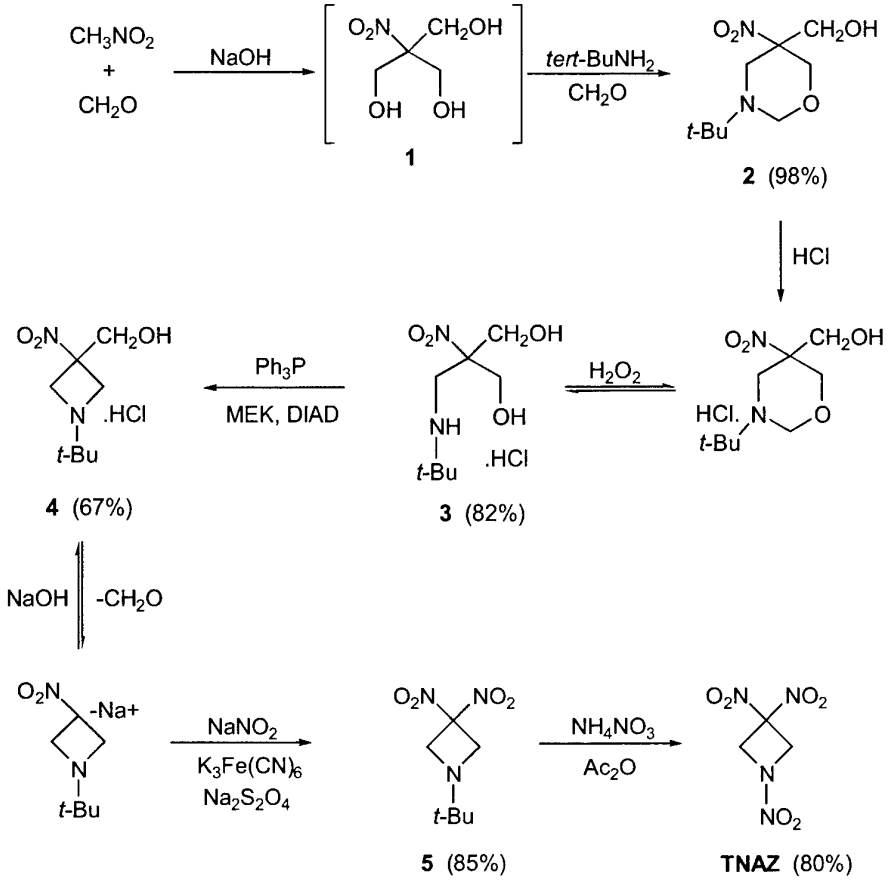

Figure 1. Synthetic route for TNAZ. Yields refer to maximum quantities achived during this study.

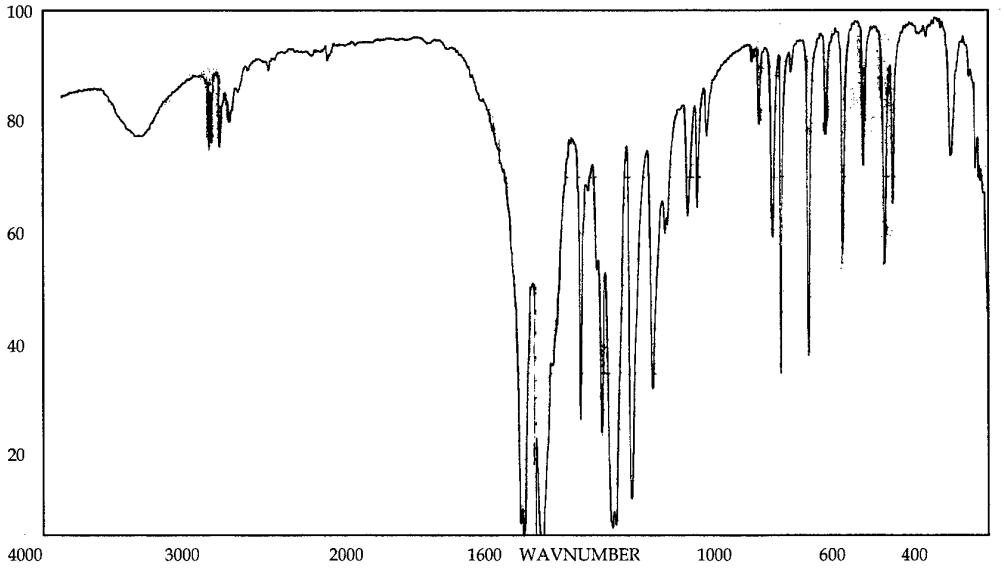

Figure 2. IR spectrum of recrystallised TNAZ (KBr pellet).

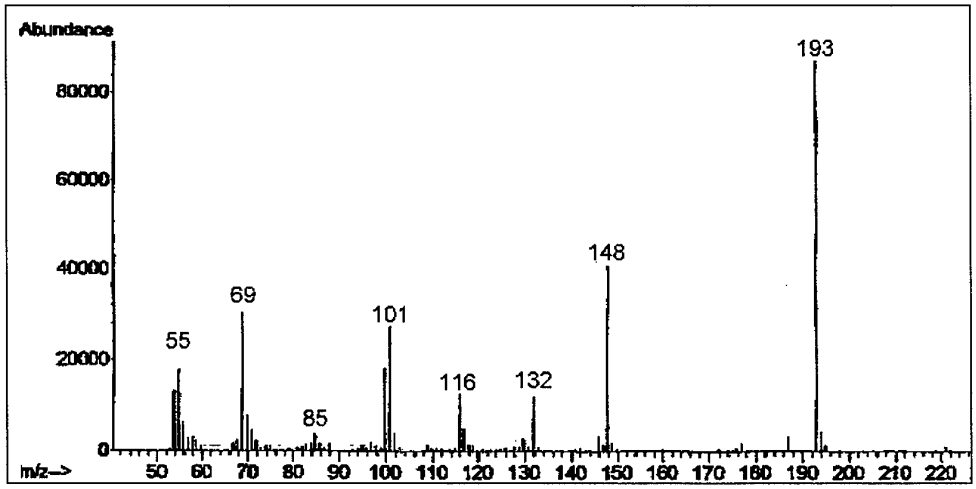

Figure 3. Mass Spectrum (ES+ve) of TNAZ.

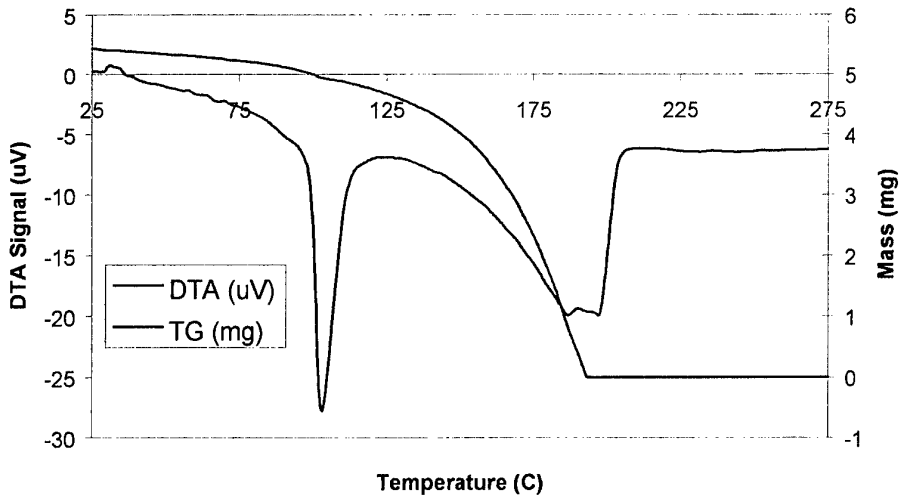

Figure 4. TGA/DTA traces of recrystallised TNAZ.

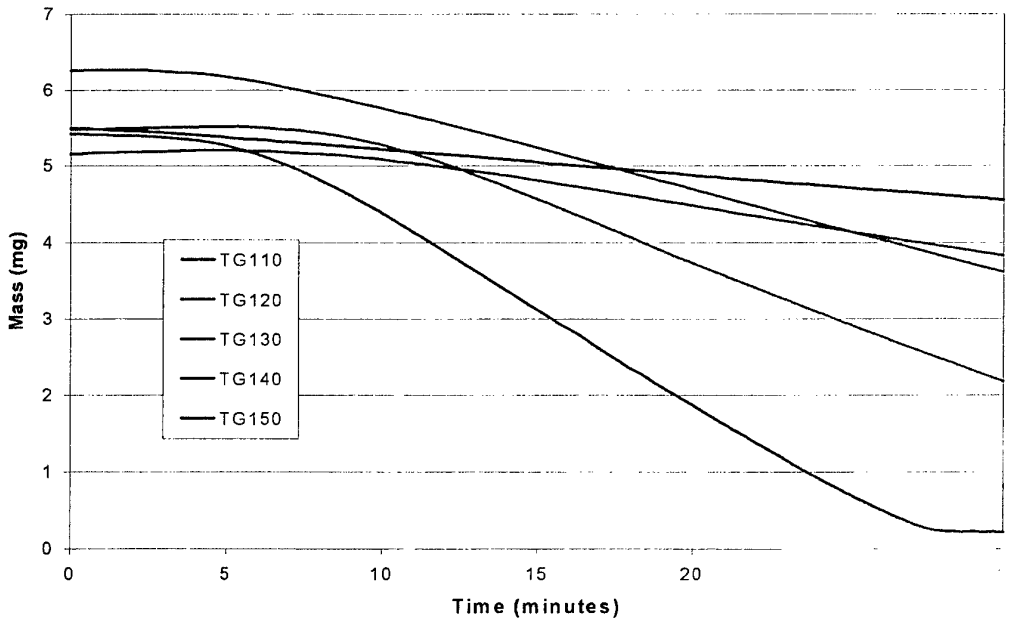

Figure 5. TGA traces of TNAZ held at 110-150°C for 30 minutes.

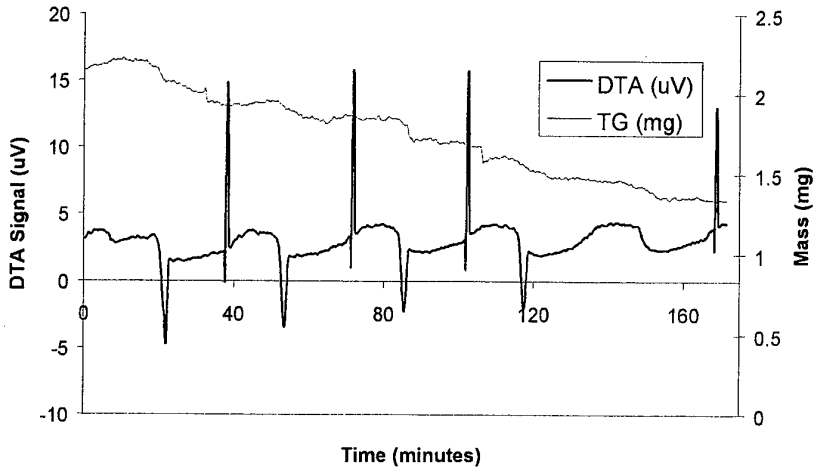

Figure 6. TGA/DTA of TNAZ cycled between 40 and 110°C.

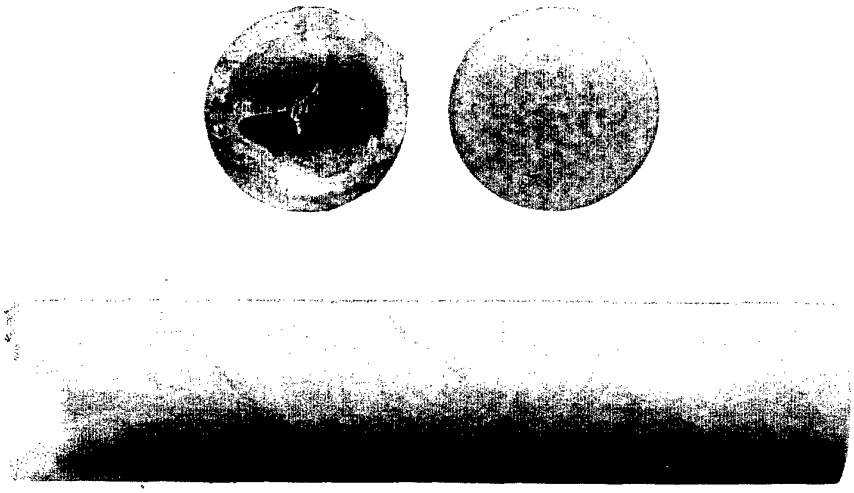

Figure 7. Melt-cast TNAZ charge. Top of casting (top left), base of casting (top right).

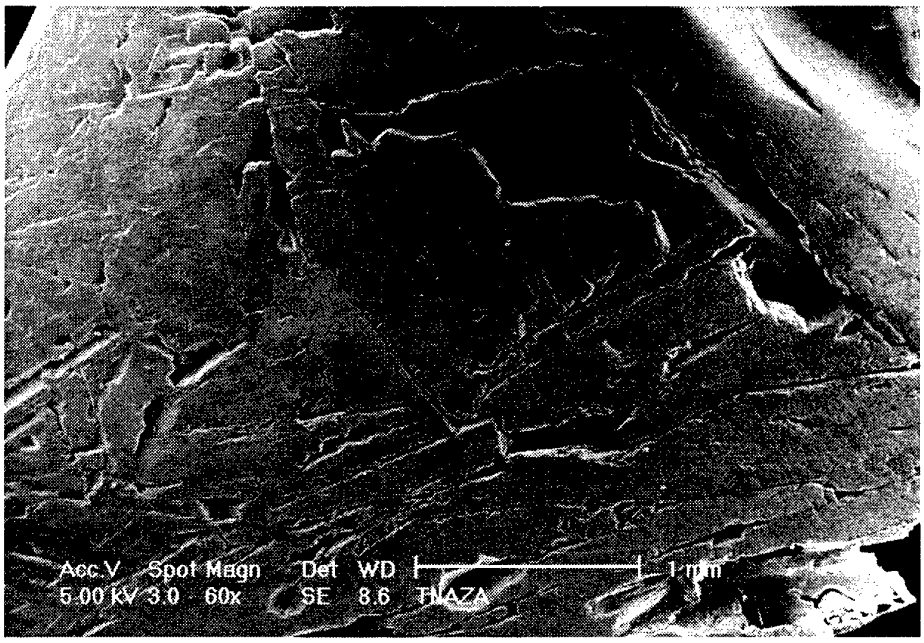

Figure 8. SEM analysis of unpolished melt-cast TNAZ. Numerous shrinkage cracks and voids evident throughout the casting. TNAZ solidified in a layered manner.

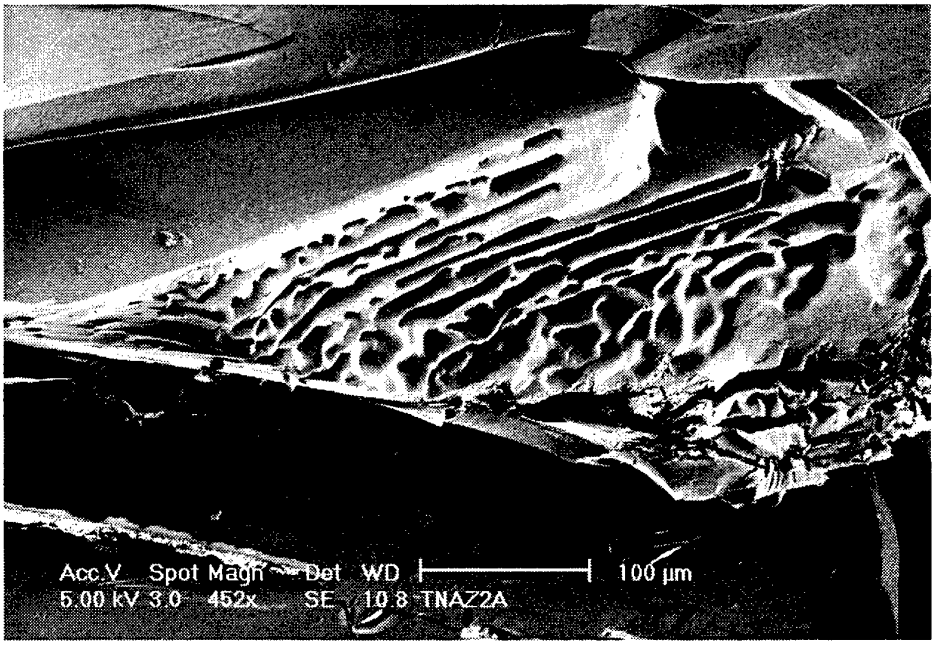

Figure 9. High resolution SEM of cracks within the TNAZ casting.

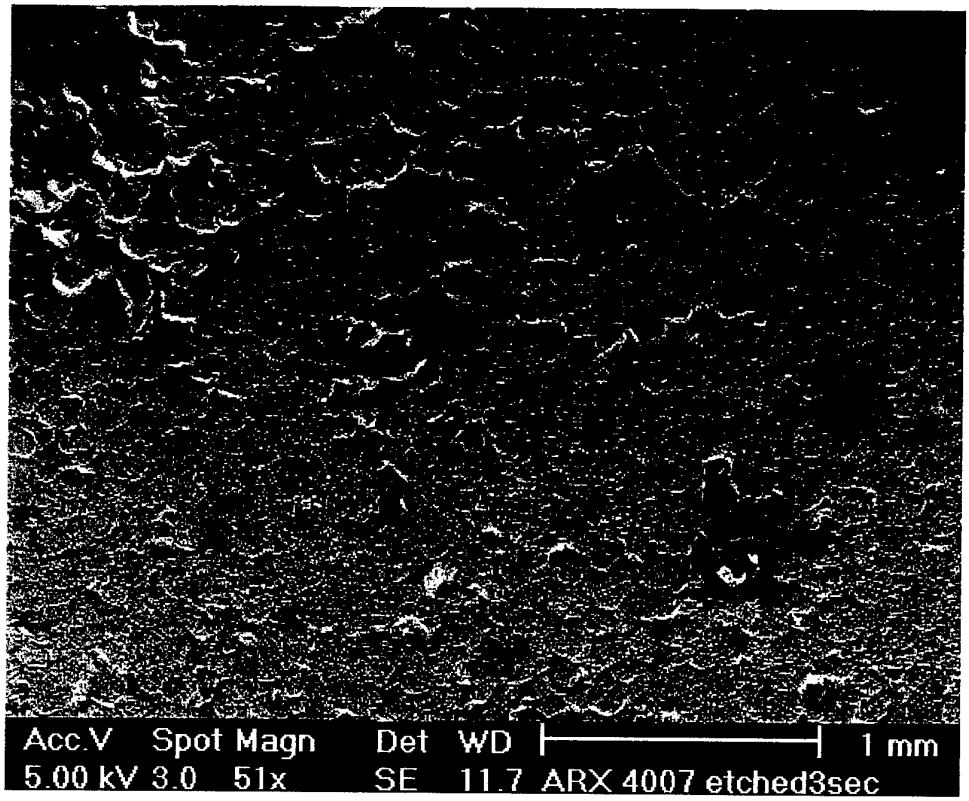

Figure 10. Micrograph of polished and etched ARX-4007 sample.

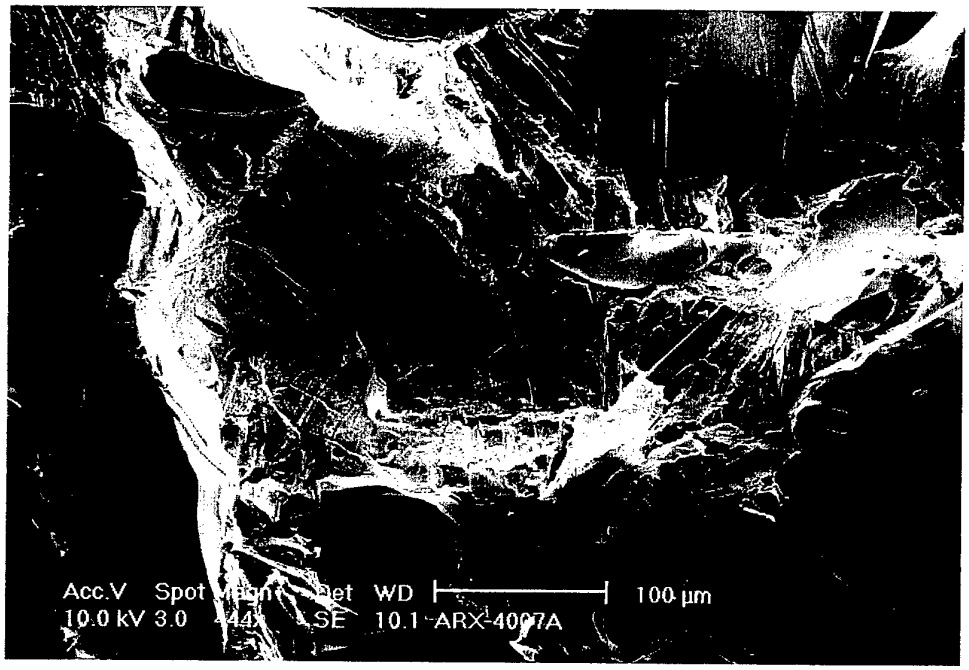

Figure 11. SEM micrograph of a fracture surface of ARX-4007 shows long shrinkage cracks within the TNAZ matrix. RDX particles (smooth areas) are seen on the peripheral of the micrograph.

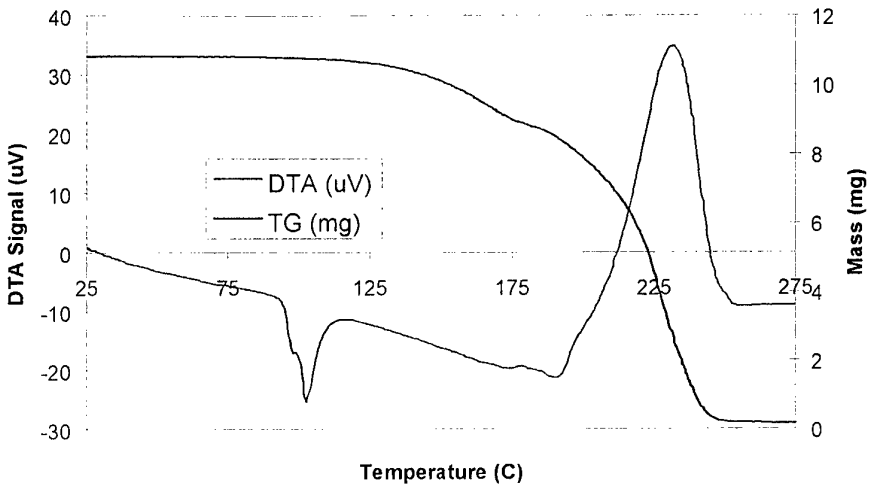

Figure 12. TGA/DTA of ARX-4007.

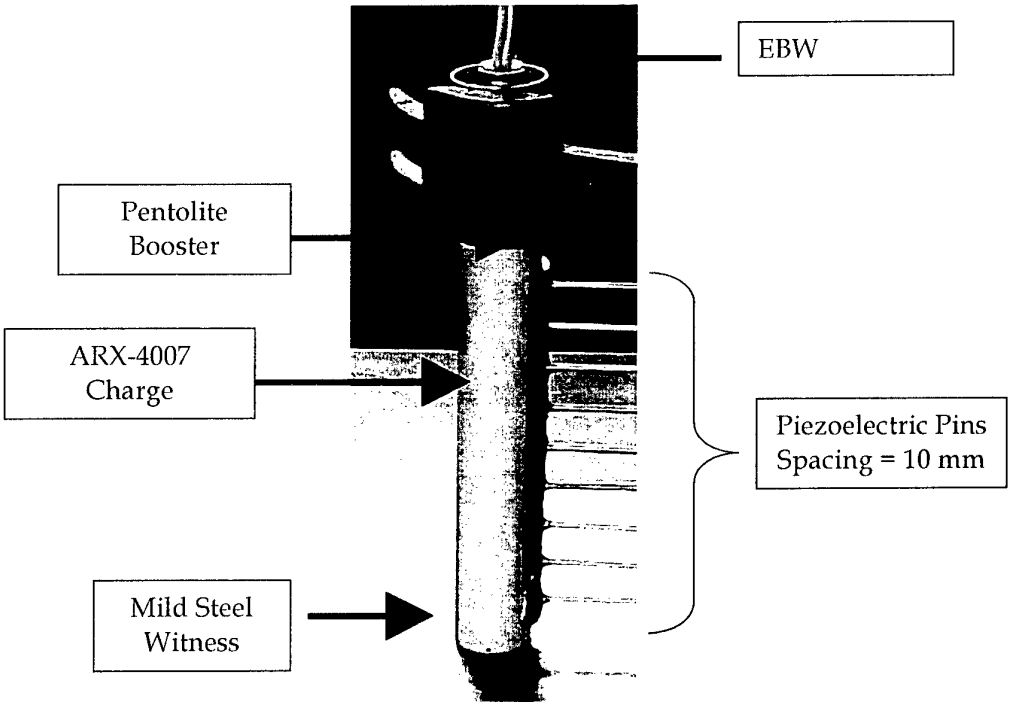

Figure 13. Experimental set-up for VoD and dent test assessment.

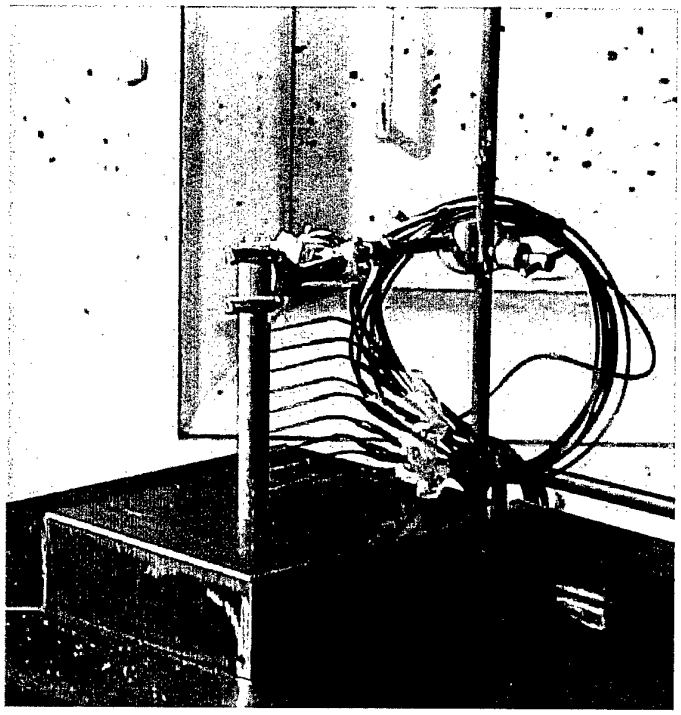

Figure 14. Experimental set-up for dent tests. ARX-4007 and Composition B charges are held flush to the witness plate to record dent depths.

Appendix A: Synthesis of 1,3,3-Trinitroazetidine

3-*Tert*-butyl-5-hydroxymethyl-5-nitrotetrahydro-1,3-oxazine (2)

To a solution of paraformaldehyde (405.3 g, 13.51 mol) and NaOH (cat.) in water (1500 ml) at 40°C was slowly added nitromethane (162 ml, 3.75 mol) over a 1 hour period. The solution was heated to 60°C and *tert*-butylamine (318 ml, 3.18 mol) added dropwise over 1 hour. The mixture was then stirred for a further hour, cooled (ambient temperature) and stirred for 16 hours. The precipitate was collected *via* vacuum filtration and freeze dried to constant mass to give **2** (682.2 g, 98%) as a white powder, mp 133-138°C.
^{1}H NMR (DMSO-d_6) δ 1.0 (s, 9H), 2.64 (d, 1H), 3.62 (m, 4H), 3.86 (d, 2H), 4.49 (dd, 2H), 4.54 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 26.4, 48.8, 52.4, 64.1, 68.1, 80.8, 89.4; IR (KBr) 3300 (OH), 2900 (NCH_2), 1550 (NO_2), 1370 (OH), 1100 (COC), 900 cm^{-1}; MS (ES+ve) *m/z* 219 ($M+H^+$), 204, 83, 42.

2-*Tert*-butylaminomethyl-2-nitro-1,3-propanediol hydrochloride (3)

To an aqueous solution of conc. HCl (83.4 ml) in water (500 ml) was added **2** (281.0 g, 1.0 mol) and the mixture heated to 40°C to effect dissolution. Aqueous H_2O_2 solution (30%, 110 ml) was added and the mixture stirred at 60°C for 1 hour followed by 16 hours at ambient temperature. The solvent was removed *in vacuo*, the residue dried azeotropically with isopropanol, filtered, washed with cold propanol and dried to give **3** as off-white powder (198.9 g, 82%), mp 172-175°C.
^{1}H NMR (D_2O) δ 1.45 (s, 9H), 3.85 (s, 2H), 3.97 (asy.d, 2H), 4.21 (asy.d, 2H), 4.78 (s, 4H); ^{13}C NMR (D_2O) δ 23.8, 43.0, 58.7, 62.1, 91.7; IR (KBr) 1560 (NO_2), 1405, 1110, 1025, 850 cm^{-1}; MS (ES+ve) *m/z* 207 (M^+), 151 (M-*t*Bu$^+$).

1-*Tert*-butyl-3-hydroxymethyl-3-nitroazetidine hydrochloride (4)

To a vigorously stirred mixture of diol **3** (50.0 g, 210 mmol) and diisopropylazodicarboxylate (45.56 g, 230 mmol) in butanone (80 ml) at 50°C was added dropwise a solution of triphenylphosphine (59.0 g, 260 mmol) in minimum butanone over 1 hour maintaining a solution temperature of 50-55°C. The mixture stirred at 50°C for 3 hours, filtered, washed with cold butanone (30 ml) and dried to give **4** (31.1 g, 67%) as an off-white solid, mp 158-161°C.
^{1}H NMR (D_2O) δ 1.07 (bs, 9H), 3.97 (bs, 2H), 4.50 (bs, 6H); ^{13}C NMR (D_2O) δ 22.0, 53.0, 60.7, 61.9, 80.9; IR (KBr) 1558, 1355, 1195, 1080, 995, 865 cm^{-1}.

1-*Tert*-butyl-3,3-dinitroazetidine (5)

To a solution of **4** (11.28 g, 50 mmol) in water (50 ml) was added aqueous NaOH (6.0 g, 150 mmol) in 25 ml of water and the resulting light yellow solution stirred at ambient temperature for 3 hours. The reaction was cooled to 10°C and a chilled solution of sodium nitrite (13.8 g, 200 mmol) and potassium ferricyanide (0.165 g, 5.0 mmol) in water (38 ml) slowly added. Solid sodium persulfate (14.9 g, 63 mmol) was added in a single portion and the yellow solution warmed to ambient temperature for 1 hour and extracted with dichloromethane (3 x 40 ml). The organic phase was dried ($MgSO_4$) and reduced *in vacuo* to give **5** (8.65 g, 85%) as a yellow oil which solidified on standing, mp ≈16°C.
^{1}H NMR ($CDCl_3$) δ 1.0 (s, 9H), 4.1 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 23.6, 52.5, 55.0; IR (KBr) 2995, 1575, 1370, 1340, 1240, 1075, 840 cm^{-1}; MS (ES+ve) *m/z* 204 ($M+H^+$), 188, 157, 148.

1,3,3-Trinitroazetidine (TNAZ)

To a vigorously stirred solution of **5** (8.65 g, 43 mol) in acetic anhydride (35.7 ml) was added NH_4NO_3 (5.14 g, 64.3 mmol) over a 5 minute period. The suspension was heated to 75°C to complete dissolution, stirred for 4 hours, cooled (ambient temperature) and stirred for a further 16 hours. The resulting mixture was then vacuum filtered to give crude TNAZ (7.11 g, 87%). The solid was dissolved in hot ethanol and poured into water/ice to give pure TNAZ (6.54, 80%) as off-white needles, mp 99-100°C.
^{1}H NMR ($CDCl_3$) δ 5.20 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 63.4, 103.5; IR (KBr) 1600, 1550, 1340, 1280, 1220, 845, 765, 665 cm^{-1}; MS (ES+ve) *m/z* 193 ($M+H^+$), 148, 116, 101, 69, 55.

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19. ABSTRACT

The melt-castable explosive 1,3,3-trinitroazetidine (TNAZ) has been assessed as a potential high energy replacement for TNT that could be processed in existing Australian industrial plant. TNAZ was produced using a five step synthetic route to give the target material in a maximum overall yield of 37%. The synthetic route chosen proved troublesome, with the Mitsunobu reaction employed to synthesize the azetidine ring non-reproducible and low yielding. Thermal analysis of neat and formulated TNAZ (60:40 RDX/TNAZ, designated ARX-4007) showed it to have high volatility and rapidly evaporated from the liquid phase (>101°C). Hazards assessment showed TNAZ to have an increased sensitiveness over TNT, while ARX-4007 showed sensitiveness levels similar to pentolite. TNAZ castings appeared to solidify from the melt to give layered plates and formed large numbers of shinkage voids. Shinkage problems were evident in both neat TNAZ and ARX-4007 castings, whilst mechanical properties were poor. Performance assessment of ARX-4007 as a general purpose metal accelerating explosive gave excellent VoD (8660 m/s) and P_{CJ} (33.0 GPa). It is concluded, however, that problems associated with synthesis, volatility, sensitiveness and casting make TNAZ unsuitable as a TNT replacement in melt-cast systems at this time.