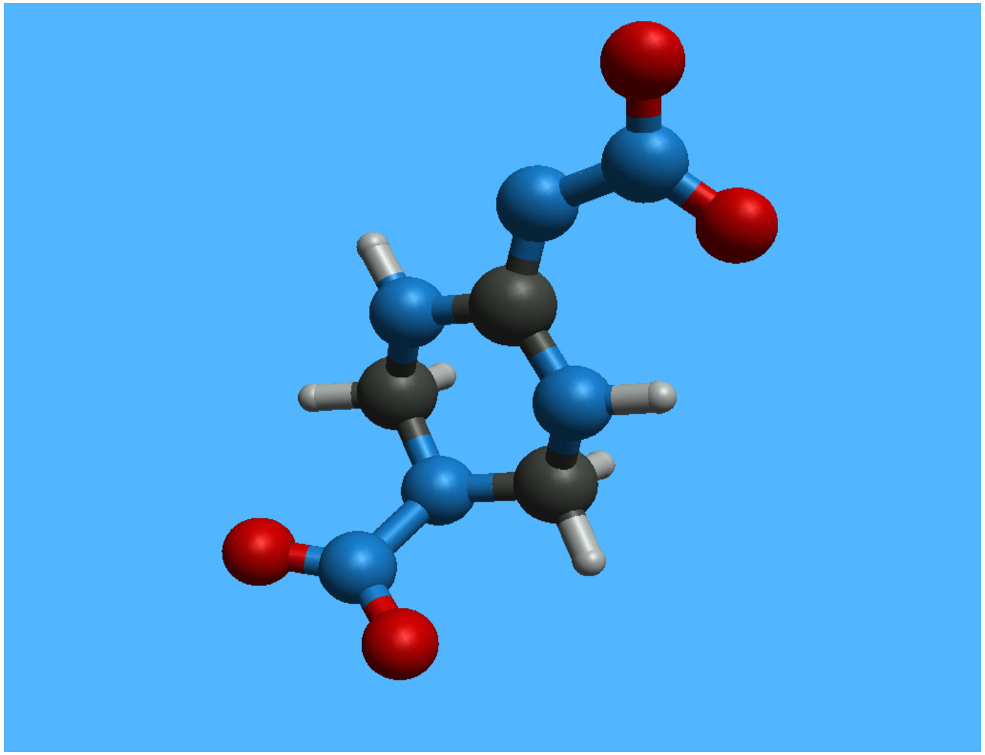
Synthesis and Characterization of NNHT (2-Nitrimino-5-nitro-hexahydro-1,3,5-triazine)



Dr Eamon Colclough

2009 Insensitive Munitions & Energetic Materials Technology Symposium

13th May 2009

Contents

01 Objectives

To examine a number of new energetic materials to determine the feasibility of scaling up from a few grammes to kilogramme quantities.

This was to involve two aspects:

- looking at improving procedures for synthesis of materials which are commercially available;
- looking at new cost effective synthesis routes to materials which are novel or less well developed.

The programme therefore addresses factors such as

- availability of raw materials,
- cost of raw materials
- synthetic routes
- practicality and safety of scale up

02 Downselection

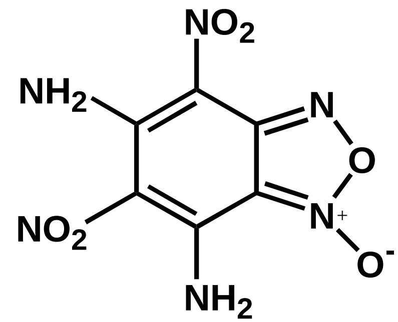
44 Heterocyclic explosive compounds added to database

Selection (initial) of ~10 candidates:

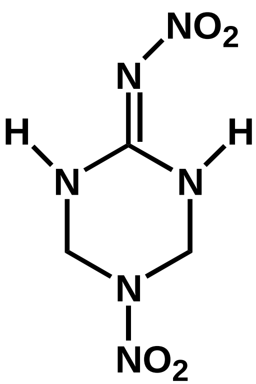
- Criteria included: Explosive output; Thermal stability (>200°C); Compatibility; Ease of synthesis; Available starting materials; Not yet commercialised

Initial selection refined to 5, subsequently 3 candidates:

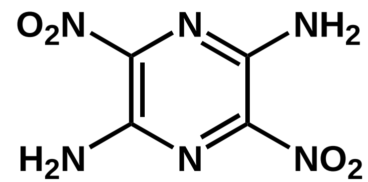
- Oxadiazole (CL-14); hexahydro-*s*-triazine (NNHT); pyrazine (ANPZ-i)
- Further selection criteria:
  - Effluent analysis
  - Handlability
  - Scalability



CL-14

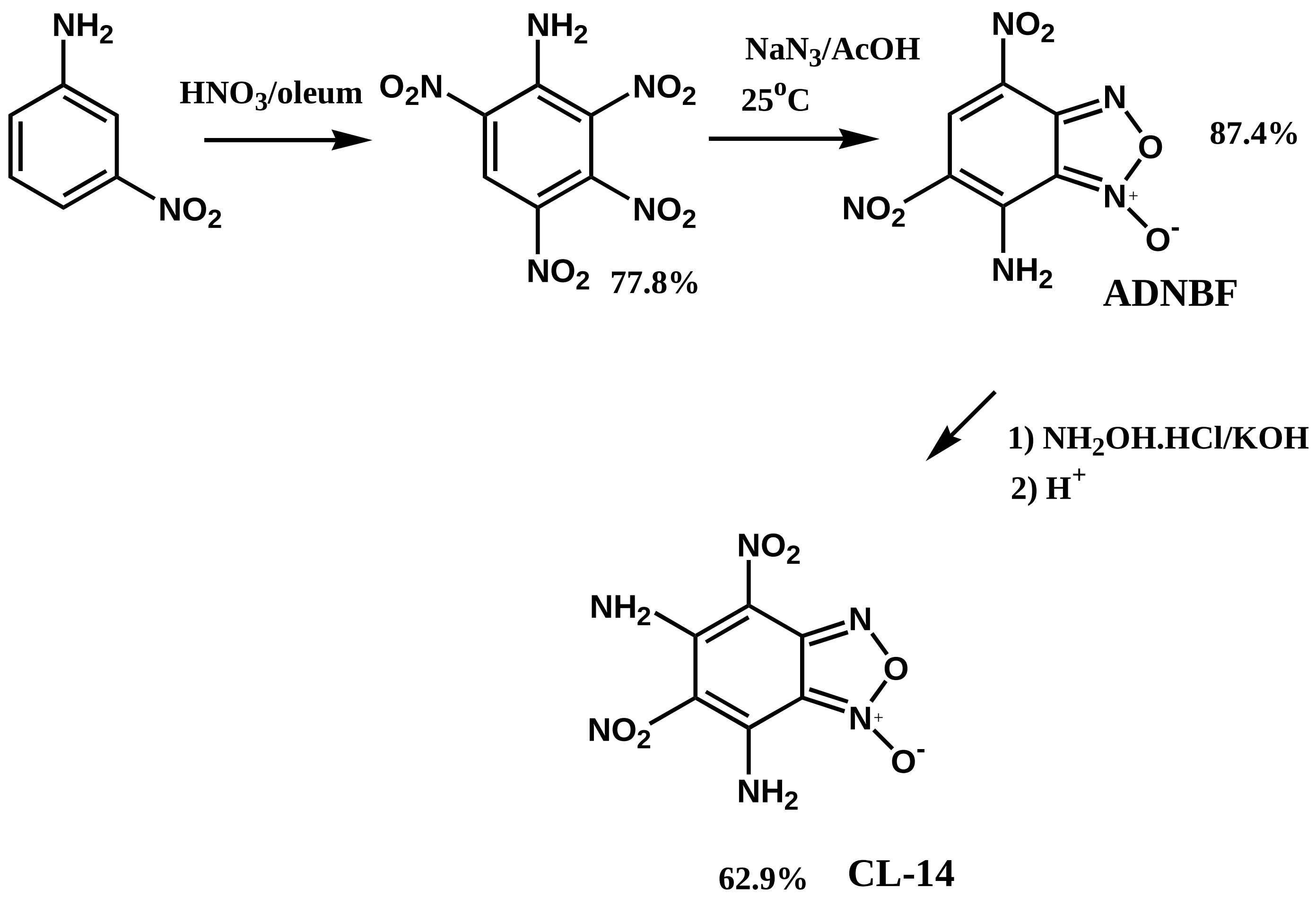


NNHT

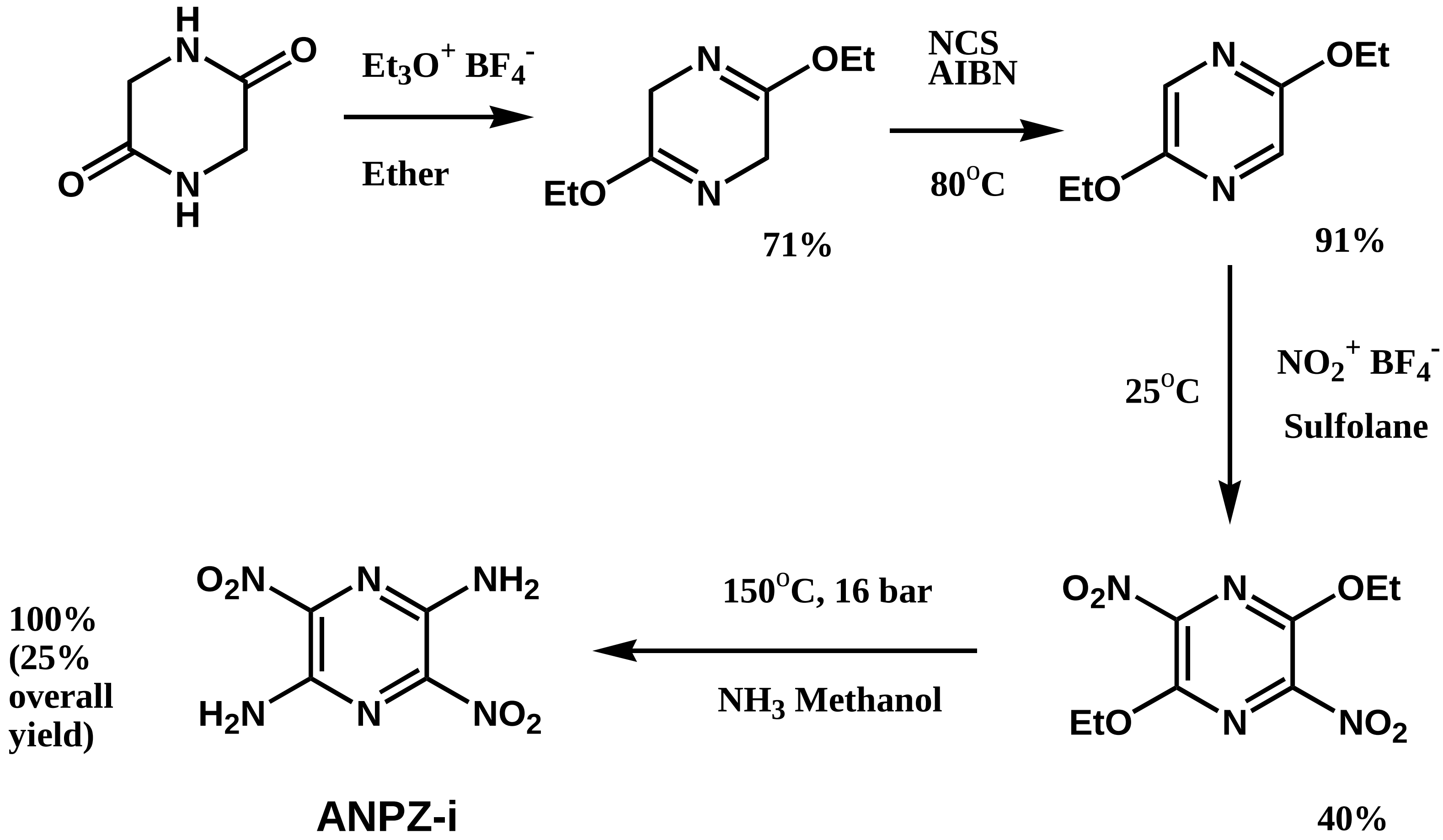


ANPZ-i

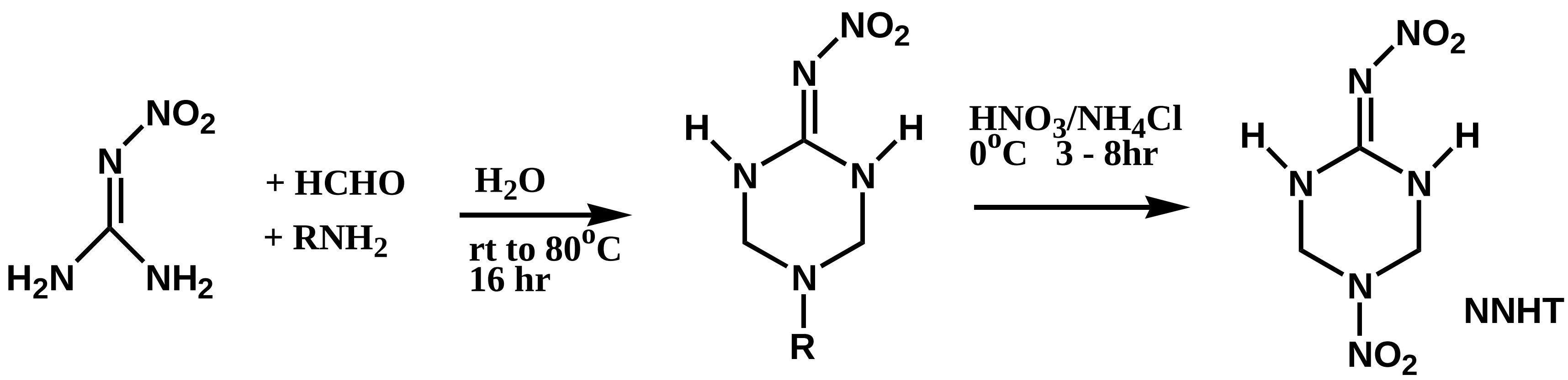
02 Downselection – CL-14 Synthesis



02 Downselection – ANPZ i Synthesis



02 Downselection – NNHT Synthesis



R	Yield
t-Bu	87

R	Yield
t-Bu	89

02 Downselection

CL14

3-step route (more complicated)

Energizing groups introduced at start of process

- requires HAZOP to be carried out earlier (stage 1/2)

Reaction control:

- precise temperature control required, particularly step 1
- efficient stirring required (all steps)

Efficient filtration of product & penultimate compound required

Safe handling of product & penultimate compound problematical

Automation not possible (stage 2/3 and beyond)

Waste disposal problem (azides, explosives)

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02 Downselection

ANPZ-i

4-step route (more complicated)

Reproducibility problems

Intermediates unstable to heat/air

One step (amination) requires autoclave (confinement problem)

Large amounts of by-products (cf. pharma processes)

Automation not possible

Waste disposal problem

Difficult and probably uneconomic to progress beyond stage 2

Alternative route required to ANPZ-i

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02 Downselection

NNHT

Reaction time should be <8 hr.

Recent results suggest:

- 3 hr. feasible
- yield not reduced appreciably

“Standard” equipment satisfactory

Few other problems anticipated on scale-up to stage 3 and beyond

Automation possible

02 Downselection

Comparative data for three candidate compounds:

	CL-14	NNHT	ANPZ-i
Pcj (GPa), predicted	33.3	29.3	34.9
Temp. of ignition ^{o}C	307	217	n/a
Impact sens. (BAM)	Insens.	Insens.	n/a
Friction sens. (BAM)	Insens.	Insens.	n/a
Ease of synthesis*	-	++	--
Effluent*	--	+	--
Handlability*	-	+	n/a
Scalability*	-	+	n/a

*Key: ++ (best) ←→ -- (worst)

Result: NNHT is preferred candidate

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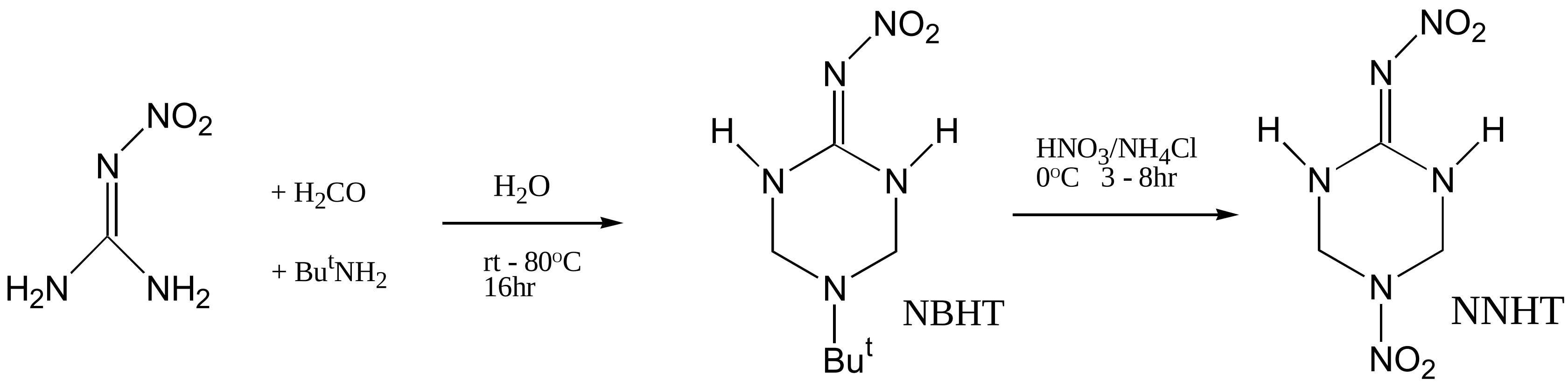
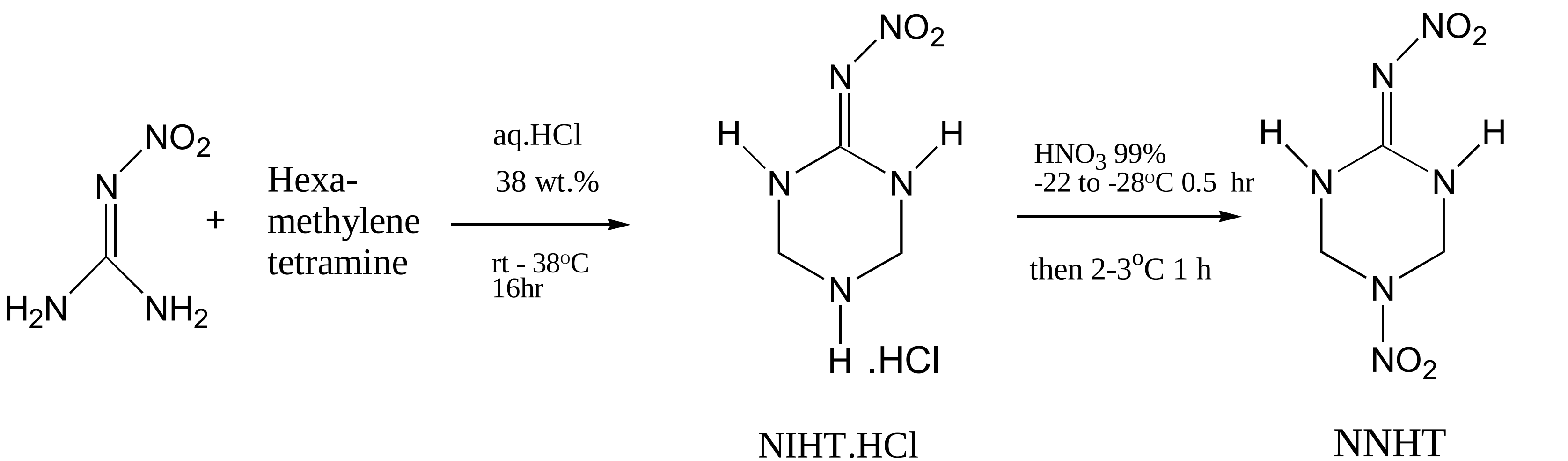
03
NNHT

03 NNHT – Synthesis routes





03 NNHT – Synthesis routes

Summary of status of respective routes:

t-Butylamine (NBHT) route:

- Reaction time of 1st step shortened from 16 hr to 3 hr without loss of yield or purity
- Mild exotherms during nitration reaction investigated

Hexamine (NIHT) route:

- Optimisation of 1st step completed (HCl concn. crucially affects yield)
- Nitration (2nd step) problematical:
  - NNHT isolated but yield strongly dependent on reaction conditions, esp. temperature
  - Products other than NNHT isolated (trinitro compound?)
  - Severe exotherm problem

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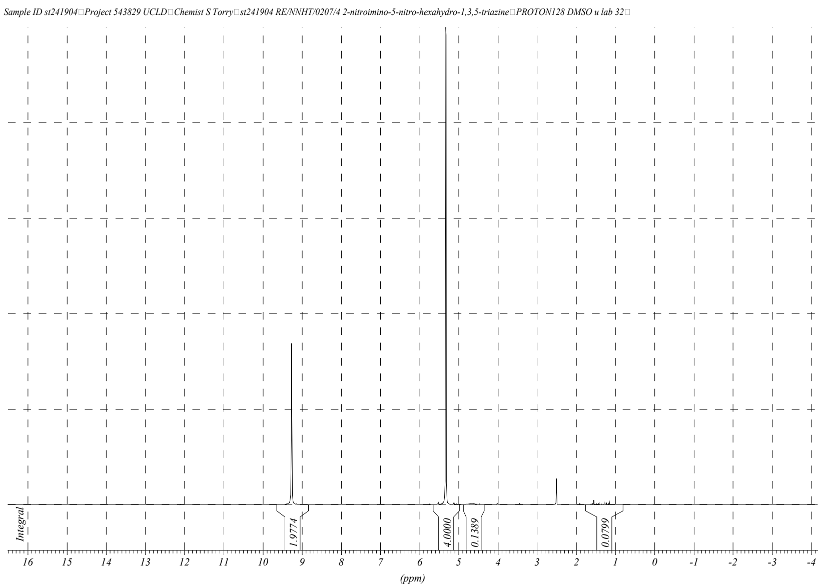
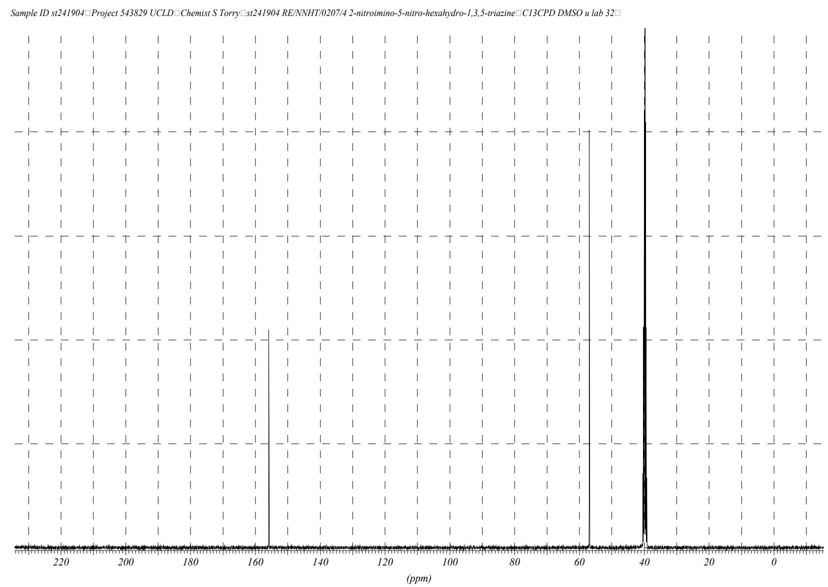
03 NNHT – Characterisation

NMR spectra for NNHT - shift values matched those reported in the literature





<u>^{1}H NMR of NNHT</u>

<u>^{13}C NMR of NNHT</u>

03 NNHT – Characterisation

Hazard tests showed that:

- Slight differences between crude NNHT (prepared via NBHT) and the recrystallised material are manifested
- These were judged to be insufficient to require a reassessment of the handling precautions for this material.

03 NNHT – Characterisation

Lit. impact sensitiveness of NNHT appears to be influenced by the recrystallisation solvent used:

- Australian work (for NNHT recryst. from acetone Dagley et al. *J. Energetic Materials* 1995, 13, 35)
  - Rotter figure of insensitiveness (F of I): 55 (cf ours 83)
  - Relative explosiveness low (from gas volumes)
  - Hazard ranking: NQ < NTO < NNHT < RDX
- Russian work (for NNHT recryst. from water Astachov et al. *Proc. Symp. NTREM Pardubice* 2005, 430)
  - Sensitivity "comparable to PETN"

03 NNHT – Characterisation

These data, particularly Russian, conflict with our measurements

- Possible reasons:
  - Change of recrystallisation solvent
  - Methods of measurement (Russian)

03 NNHT – Characterisation

Precipitation of NNHT from NMP solution effects a partial purification

NNHT can be effectively purified by recrystallisation from cyclohexanone

Recrystallised NNHT passes the vacuum stability test

Particle sizes have been measured for recrystallised (38µm) and precipitated (11.8µm) NNHT

Density of NNHT is in accord with literature 1.75gcm^{-3}

03 NNHT – Cook off

Small-scale cook-off tests: preliminary results:

- Run 1 (slow): Cook-off temp. 174.5°C; behaviour Type IV
- Run 2 (slow): Cook-off temp. 173.2°C; behaviour Type III
- Further test results awaited

Conclusion:

- NNHT shows behaviour more benign than Debrix 18AS (RDX-based)
- Subject to further testing, NNHT formulations may be suitable for application in IM

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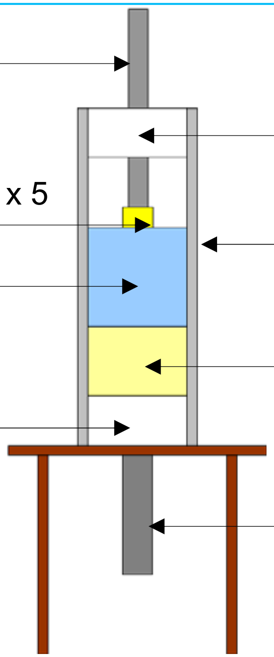
03 NNHT – Explosive cord testing

Small-scale cord Testing:

- The cord sustained detonation down to the smallest external diameter tested, 0.7 mm.
- Aluminium sheathed cords had a VOD of approximately 6.6 km/s which was sustained as the diameter was reduced.
- In contrast the lead sheathed cords showed lower VOD below 4 mm. The VOD in lead was much lower than in aluminium but this is as expected from previous results.
- The results indicate than NNHT can be used for applications in explosive train technology, even miniaturised systems at the scale of a few mm.

03 NNHT - Explosive Component Water Gap Testing:



ECWGT Apparatus

The ECWGT results for NNHT, compared to those for other IHEs tested (e.g. HNSIV, NONA), indicate that NNHT compares favourably with the all of the materials previously tested.

The potential of NNHT for use in initiator applications, such as laser-driven flyer or exploding foil initiators, is being examined.

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03 NNHT - Exploitation

Exploitation path

- The potential of NNHT for use as a gun propellant additive, in conjunction with varying amounts of RDX, plasticiser and energetic binder (polyNIMMO) was investigated by modelling. The cases of artillery and tank gun applications were investigated separately.

NNHT	polyNIMMO	RDX	K10	Tf (K)	Impetus (MJ/kg)	Mw (g/mol)	Co-volume (cc/g)	Gamma	CE (MJ/kg)
Artillery	***cf NQ***			***2830***	***1.051***				
35	**20**	**40**	**5**	**2797**	**1.143**	**20.341**	**1.193**	**1.2705**	**4.2255**
25	**30**	**40**	**5**	**2531**	**1.068**	**19.699**	**1.221**	**1.2773**	**3.8514**
Tank Gun	***cf FX***			***3420***	***1.168***				
25	**10**	**60**	**5**	**3322**	**1.271**	**21.735**	**1.132**	**1.2541**	**5.0020**
25	**20**	**50**	**5**	**2913**	**1.177**	**20.588**	**1.178**	**1.2664**	**4.4182**

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03 NNHT – Scale up assessment

Scale-up aspects – Summary

- Study of the first step (NHBT formation) indicated that:
  - The reaction was not strongly exothermic
  - The synthesis should work in a 20 L reactor (making ca. 1.2 kg NBHT)
  - No ‘show-stoppers’ were identified in the process

03 NNHT – Scale up assessment

Study of the second step (nitration of NBHT to NNHT) indicated that:

- The reaction shows a strong exotherm, occurring on addition of the catalyst
- The reaction is more exothermic (~2x) than typical aromatic nitrations
- The control of the exotherm could be problematic, possibly mitigated by:
  - Pre-mixing of the ammonium catalyst with the nitric acid, or
  - Use of a flow reactor configuration to improve heat transfer and reduce inventory
- A 20 L reactor, made of acid-resistant stainless steel, could be used at 1 kg per run

03 NNHT – Scale up assessment

Study of the recrystallisation step indicated that:

- A number of precautions would be necessary to ensure smooth and safe operation
- No ‘show-stoppers’ were identified in the process

04

Conclusions

04 Conclusions

Programme: carried out and delivered according to the plan

- One lower energy candidate (NNHT) has been synthesised successfully and has now been evaluated
- The most suitable route for scale-up of NNHT (via NBHT) has been evaluated
- Characterisation and purification studies are complete
- Initial scale-up studies are complete and show that scale-up is feasible
- NNHT has potential as a novel insensitive ingredient for propellant and explosive train applications

05 Acknowledgments

All partners in RTP14.10

QinetiQ

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