Process Improvement of Melt Pour Explosive 3,4-Dinitropyrazole (DNP)

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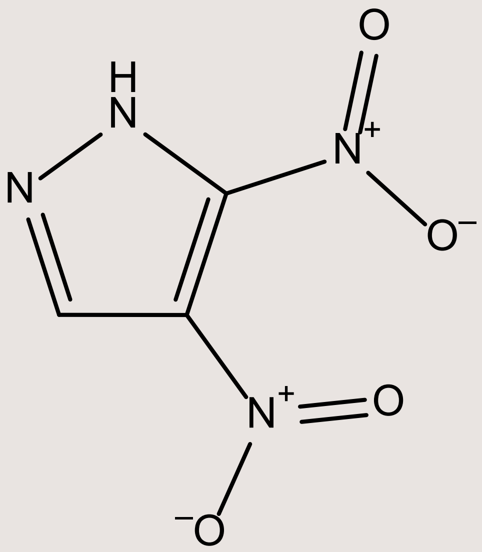
BAE SYSTEMS

Background

- Recent shift towards IM explosives resulted in a need for a less sensitive replacement for TNT (classic melt pour explosive filler)
- Material required to have similar melting profile and explosive performance
- 3,4-dinitropyrazole (DNP) identified as a highly promising candidate
  - Commercially available starting material
  - Easily nitrated to final product
  - Similar melt temperature



DNP

DNP Performance

- Better explosive performance than Comp-B
- Higher density than both Comp-B and TNT
- Increased stability towards external stimuli

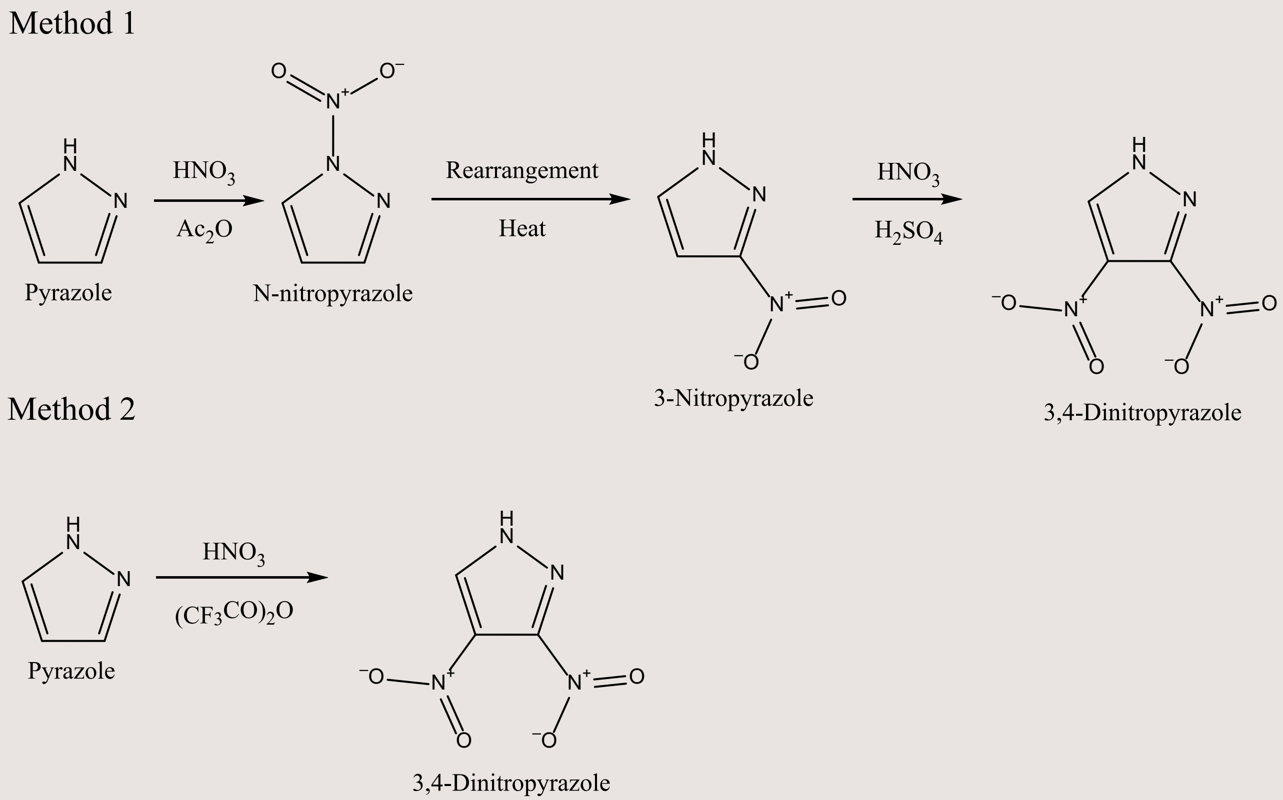
Property	TNT	MIL-C-401E Comp-B	DNP
DSC Exotherm (°C)	288	214	276
P_{CJ} (GPa)	18.91	29.22	30.2
Density (g/cc)	1.63	1.71	1.87
VOD (km/s)	6.63	8.02	8.25
√2E (mm/μs)	6.94	7.91	
BAM Friction (N)			246 (164[1])
Naval Impact (cm)	157 (27[1])	59	55 (39[1])
ESD (J)	0.19		0.2625
DSC Melt (°C)	80.9	79.0	87

[1]RDX Class 5 Standard

DNP Legacy Synthesis

- Two primary synthetic routes

1. Mixes Sulfuric / Nitric acid
   - Not scalable at HSAAP due to limited ability to recover spent sulfuric acid
2. Trifluoroacetic anhydride
   - Not scalable at HSAAP due to inability to recover trifluoroacetic anhydride / trifluoroacetic acid

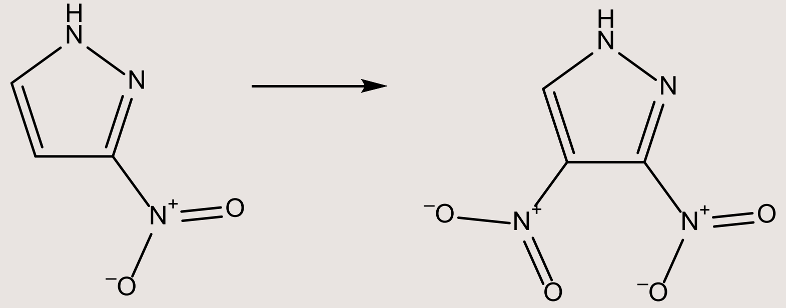


Project Goals

1. Simplify DNP synthesis to:
   1. Allow it to be manufactured at HSAAP
   2. Limit operator exposure
   3. Reduce overall labor cost
2. Decrease / Eliminate waste streams
   1. Eliminate need for off-site disposal
   2. Decrease final cost of DNP

Initial Exploration of Alternative Nitration Protocol

- Initial trials (-43, -44, -45) were sampled at end of reaction, not fully worked up
  - New chemistry showed promise
  - Inconsistent nitration
- Second set (-48, -50, -52) showed increased efficacy
  - 2-step single-pot process
    - nitration and sample workup/purification
  - No organic solvents required
  - More reliable conversion
  - High nitrate content of final product
- Required a modification to final product to eliminate remaining nitric acid in the solid material



3-Nitropyrazole → 3,4-Dinitropyrazole

Trial	Yield (%)	Purity (%)	Nitrate Content (wt%)
1190-43	NA	2.5	NA
1190-44	NA	100 (oil)	NA
1190-45	NA	12.4	NA
1190-48	78.4	99.9	0.24
1190-50	51.2	100.0	0.25
1190-52	100.0	96.8	0.33

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Optimization of New Protocol

- DOE process optimization (17 trials)
  - Variation of 5 reaction parameters
- System showed dependence on only one 1 parameter, with remaining 4 providing minor/no influence
- Optimal reaction parameters: Trial 17
  - Highest yield and purity
  - Acceptable nitrate concentration

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Yield (%)	12.6	40.0	62.5	62.8	0.12	62.5	0.33	0.09	22.7	30.9	2.45	63.2	0.14	62.62	65.4	1.98	**67.9**
Purity (%)	0.66	99.8	99.9	99.9	0.29	99.9	3.36	0.27	67.5	65.4	16.0	98.8	0.37	99.8	98.5	5.36	**99.9**
Nitrate (wt%)	0.02	0.00	0.11	0.12	0.01	0.00	0.01	0.02	0.01	1.28	0.01	0.01	0.02	0.02	0.02	0.01	**0.03**
DSC Melt (°C)	175.6	85.9	87.3	87.9	176.3	87.5	172.8	175.0	67.9	oil	64.8 156.6	87.3	175.2	86.5	83.8	171.1	**86.5**

Effects on Explosive Sensitivity

- All trials which formed DNP showed similar explosive sensitivity
- No discernable difference between samples
- Samples which showed poor/no conversion were not tested

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Purity (%)	0.66	99.8	99.9	99.9	0.29	99.9	3.36	0.27	67.5	65.4	16.0	98.8	0.37	99.8	98.5	5.36	99.9
Nitrate (wt%)	0.02	0.00	0.11	0.12	0.01	0.00	0.01	0.02	0.01	1.28	0.01	0.01	0.02	0.02	0.02	0.01	0.03
Holston Impact (cm)	NA	>85 (45.8)	>85 (45.8)	>85 (45.8)	NA	>85 (45.8)	NA	NA	>85 (47.5)	NA	NA	>85 (47.5)	NA	>85 (50.8)	>85 (47.5)	NA	>85 (50.8)
BAM Friction (N)	NA	>221 (221)	>221 (221)	>221 (221)	NA	>221 (221)	NA	NA	>247 (247)	NA	NA	>247 (247)	NA	>234 (234)	>221 (221)	NA	>234 (234)
ESD (J)	NA	0.138 (0.074)	0.138 (0.089)	0.101 (0.089)	NA	0.138 (0.074)	NA	NA	0.138 (0.074)	NA	NA	0.165 (0.074)	NA	1.165 (0.089)	0.138 (0.089)	NA	0.138 (0.089)

Initial Scaleup: RC1e

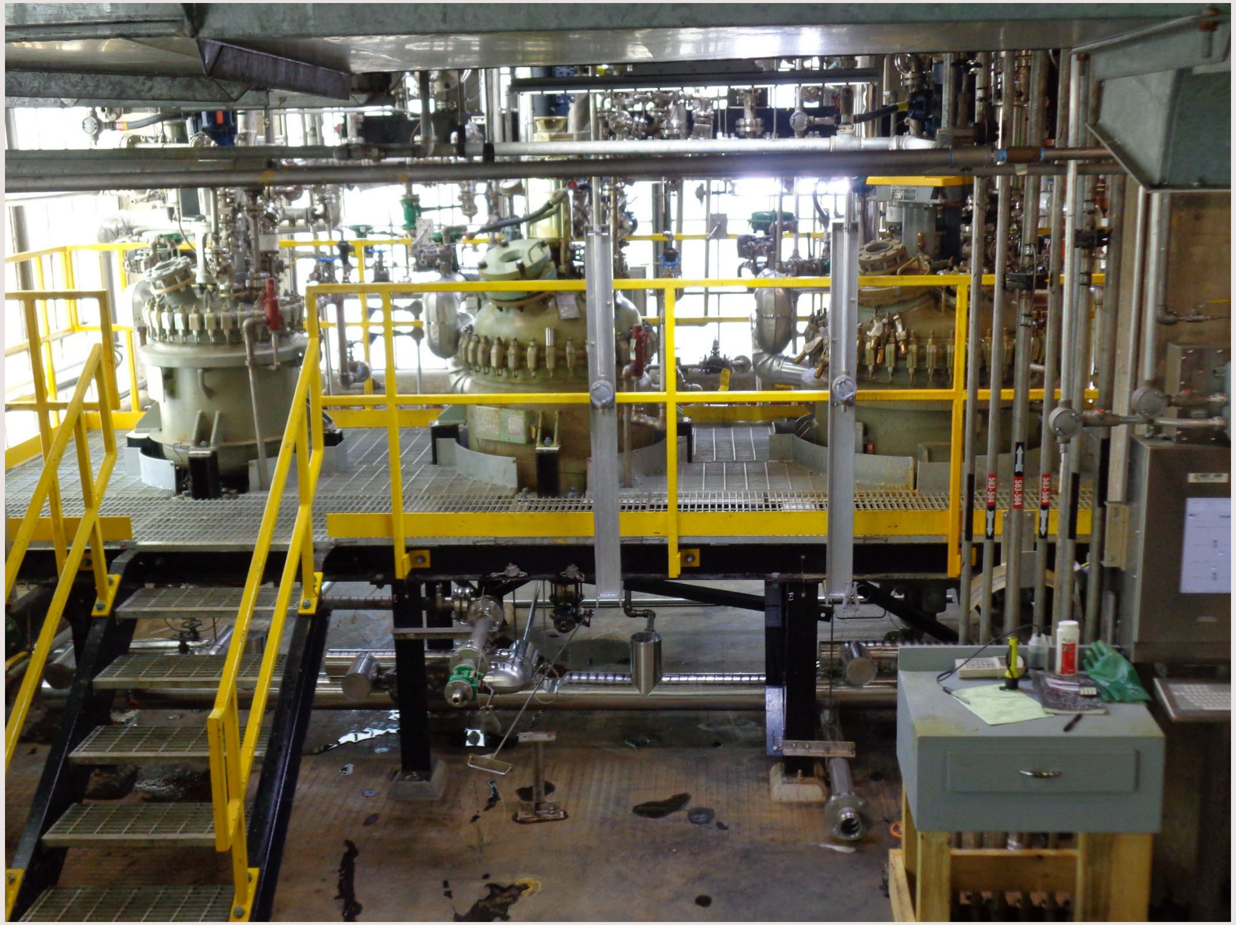
- Procedure scaled up to run in Mettler Toledo RC1e unit
  - 2L primary reaction vessel
  - Completely computer controlled
  - Provides continual monitoring of reaction parameters and calculation of heats of reaction
- Two trials
- Good reproducibility
- 100% yield when accounted for DNP remaining in final waste stream

Sample	Yield (%)	Purity (%)	Nitrate (wt%)	T_{melt} (°C)	ESD (J)	BAM Friction (N)	Holston Impact (cm)
1203-30	73	99.70	≤0.02	87.3	0.165 (0.074)[1]	278 (212)[1]	>85 (53)[1]
1203-32	73	99.87	≤0.02	85.3	0.138 (0.074)[1]	268 (212)[1]	>85 (53)[1]

[1]RDX Class 5 Standard

Upcoming Effort: Pilot Plant

- Transitioning new manufacturing process to HSAAP Pilot Plant facility
  - Multiple batches will be produced
  - Process challenges will be fully addressed
  - Final material provided to customer for evaluation



Summary

- DNP is a leading candidate for next-generation melt pour IM explosive
  - Legacy synthesis routes not scalable at HSAAP
- New synthesis process developed
  - Fully proved out on lab scale and able to be scaled based on HSAAP infrastructure
  - Waste streams easily managed on site
- Process to be scaled up to HSAAP pilot plant facility
  - Allow for final process challenges to be addressed
- Ready for full scale production at HSAAP