# Synthesis and Small-scale Performance Characterization of "New" Insensitive Energetic Compounds

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LDRD

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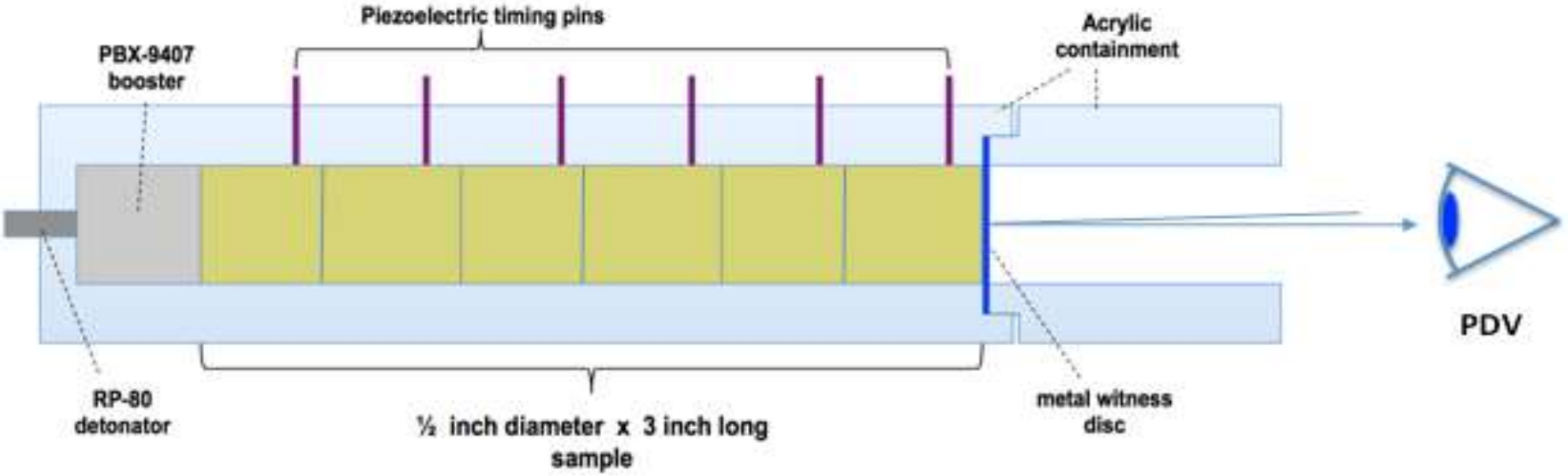
# LLNL Energetic Materials Synthesis Group

- **Our goal is to discover and develop energetics that exceed the performance of existing materials in a variety of different areas.**

- **The end state of the group's work is to fully characterize new energetic compounds so that they are essentially put "on the shelf" for consideration as ingredients in future systems.**

- **For each promising compound we strive to characterize it with respect to heat of formation, density, detonation velocity and CJ pressure using the Disc Acceleration eXperiment (DAX), as well as thermal stability (DSC, CRT, ODTX) and small-scale safety tests.**

# Disc Acceleration eXperiment




- **Front plate push experiment with timing pins**
- **Envisioned as a low-cost , rapid assessment tool for HE performance characterization, ~$5k**
- **Test allows us to acquire performance data, w/ 1-2% precision -help to decide on further development and testing of materials**

Lorenz, K. T.; Lee, E. L.; Chambers, R. *Propellants, Explosives, Pyrotechnics* **2015**, *40*, 95.

# Data can be used to extract EOS

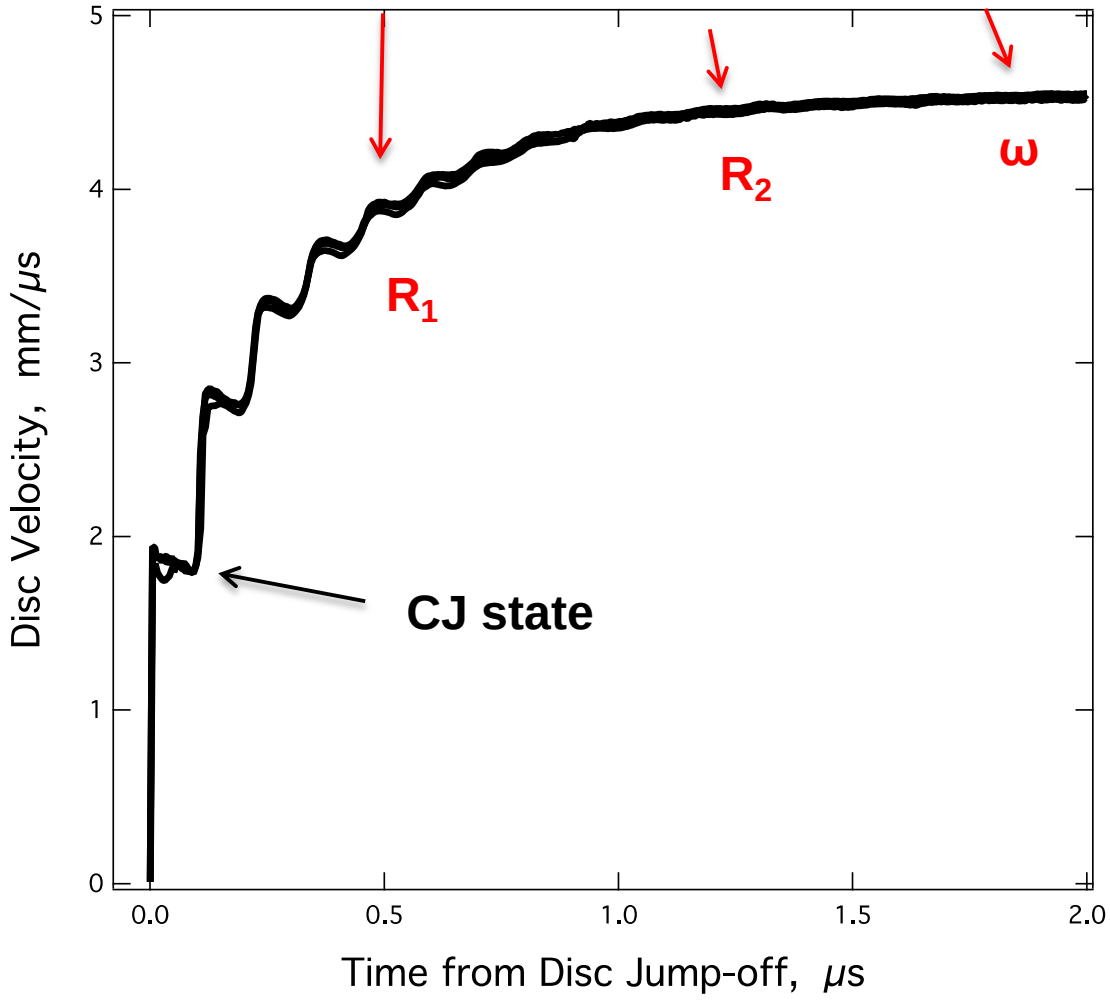
**Independent metrics can be extracted**

- **CJ pressure: ± 2%**
- **Detonation Velocity: ± 0.25%**
- **Time-dependent disc energy: ± 1%**

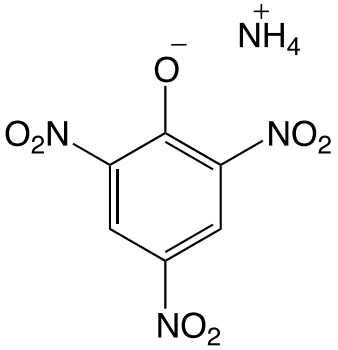
**The velocity-time data of the witness plate is a sensitive metric for the product-gas EOS.**

- **Expansion volumes to ~3**
- **Burn rate may be modeled, or taken from other additional data**

$$P_{rx} = A\left(1 - \frac{w}{R_1 V}\right)e^{-R_1 V} + B\left(1 - \frac{w}{R_2 V}\right)e^{-R_2 V} + \frac{wE_s}{V}$$

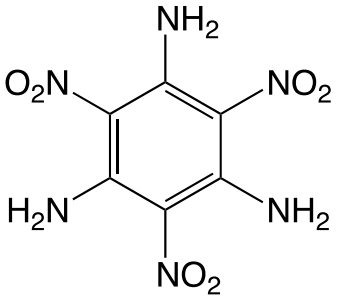


# Insensitive Explosives



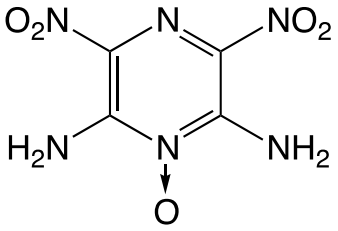

**Explosive D**

- **A strong relationship exists between explosive performance and sensitivity. Want to understand the relationship and find materials which deviate from it.**




**TATB**

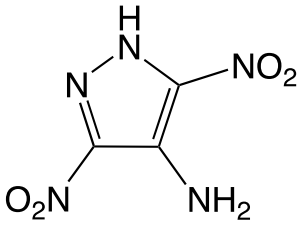
- **Ammonium picrate was the insensitive explosive a hundred years ago. TATB is the ultimate insensitive explosive. LLM-105 developed in last decades as a higher performing alternative.**




**LLM-105**

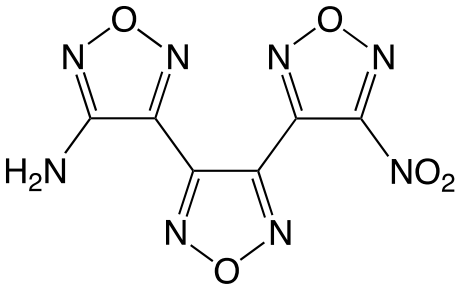
- **Commonality is the presence of nitro groups bound to $sp^2$ carbon atoms and amino groups. TATB and LLM-105 have especially high densities**

# “New” Insensitive Ingredients



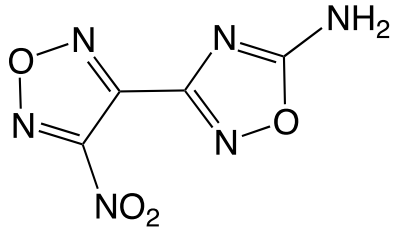
**ADNP**

- **High density, good predicted performance**



**LLM-175**

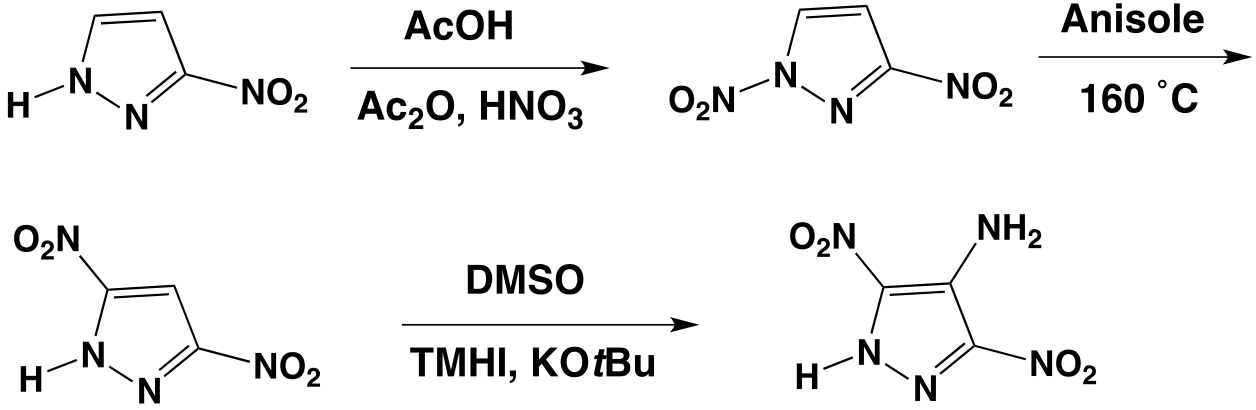
- **High heat of formation, melts at 100˚C**

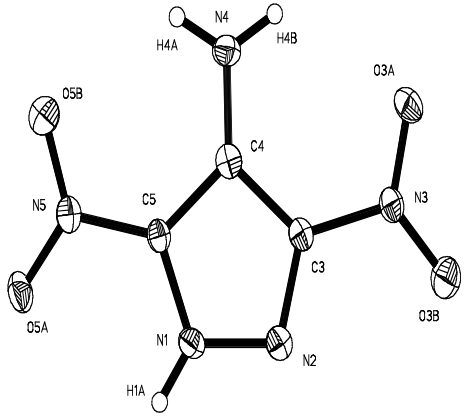


**LLM-201**

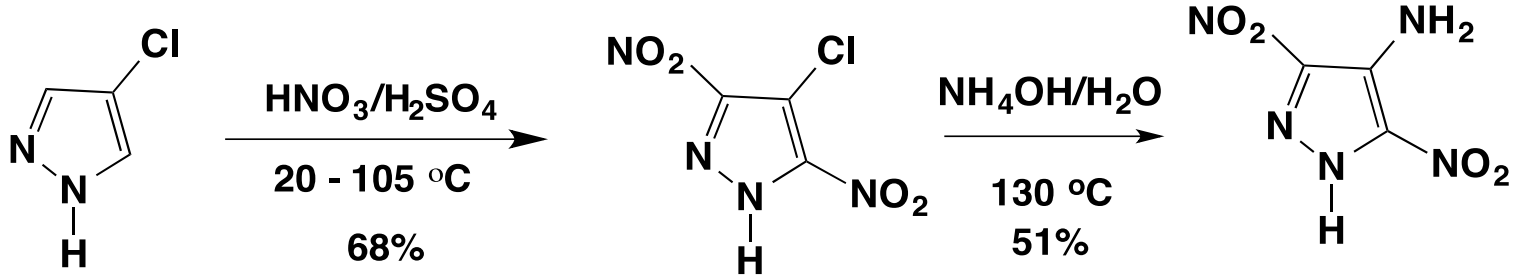
- **Insensitive in SSST, melts at 100 ˚C, lowest performing**

# 4-amino-3,5-dinitropyrazole (ADNP/LLM-116)




Schmidt, R. D.; Lee, G. S.; Pagoria, P. F.; Mitchell, A. R.; Gilardi, R. *J. Heterocycl. Chem.* **2001**, *38*, 1227.

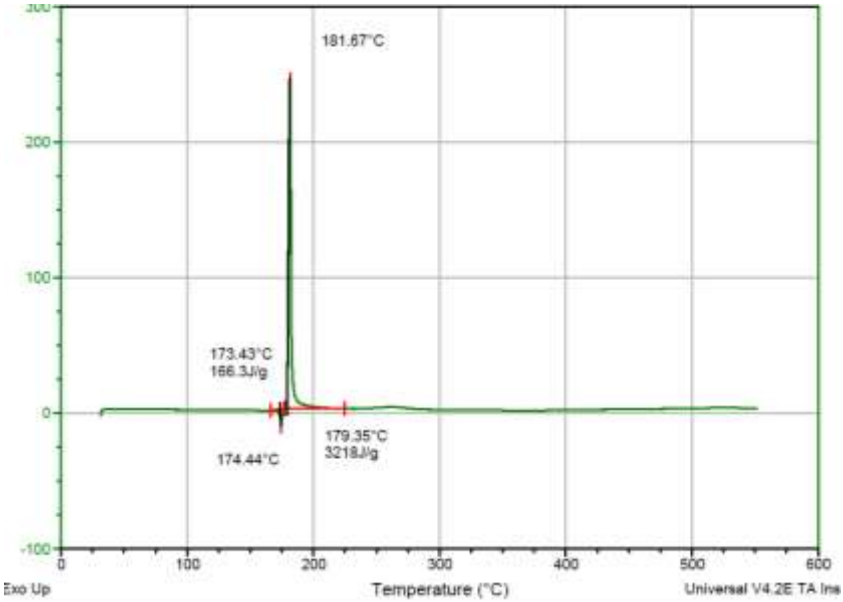


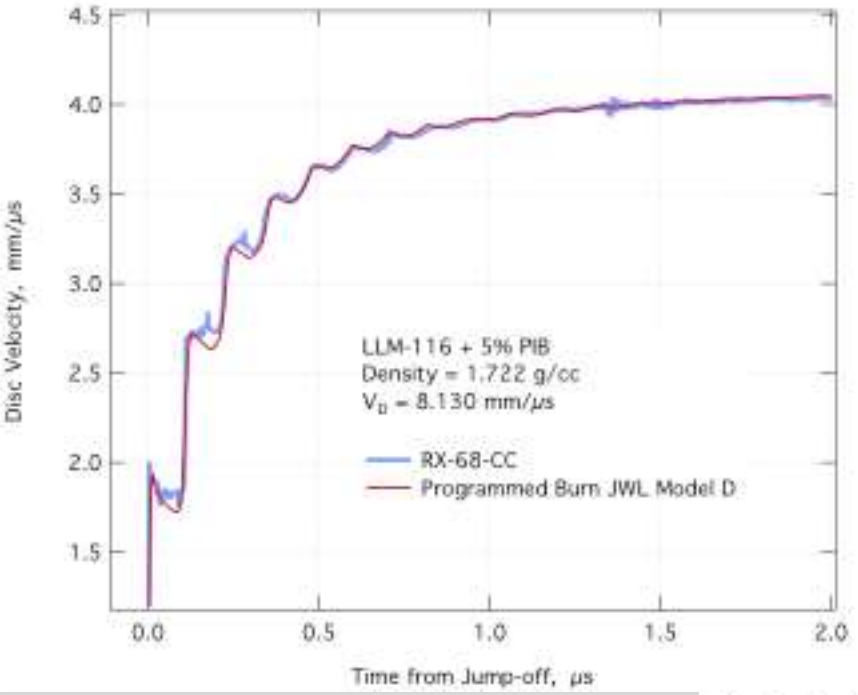

Dalinger, I. L.; Vatsadze, I. A.; Shkineva, T. K.; Popova, G. P.; Shevelev, S. A. *Synthesis* **2012**, *44*, 2058.

**Dalinger synthesis currently used. Amination under pressure is a drawback.**

# ADNP/LLM-116

- Density: 1.900 g/cc
- $Dh_{50}$: 168 cm (32 cm for HMX)
- Spark Sensitivity: Insensitive (1J 510 ohm)
- Friction: 0/10@ 36kg (BAM)
- Heat of formation: -0.2 kcal/mole*
- CRT: 0.03 cc/ 0.25g @ 80 ˚C



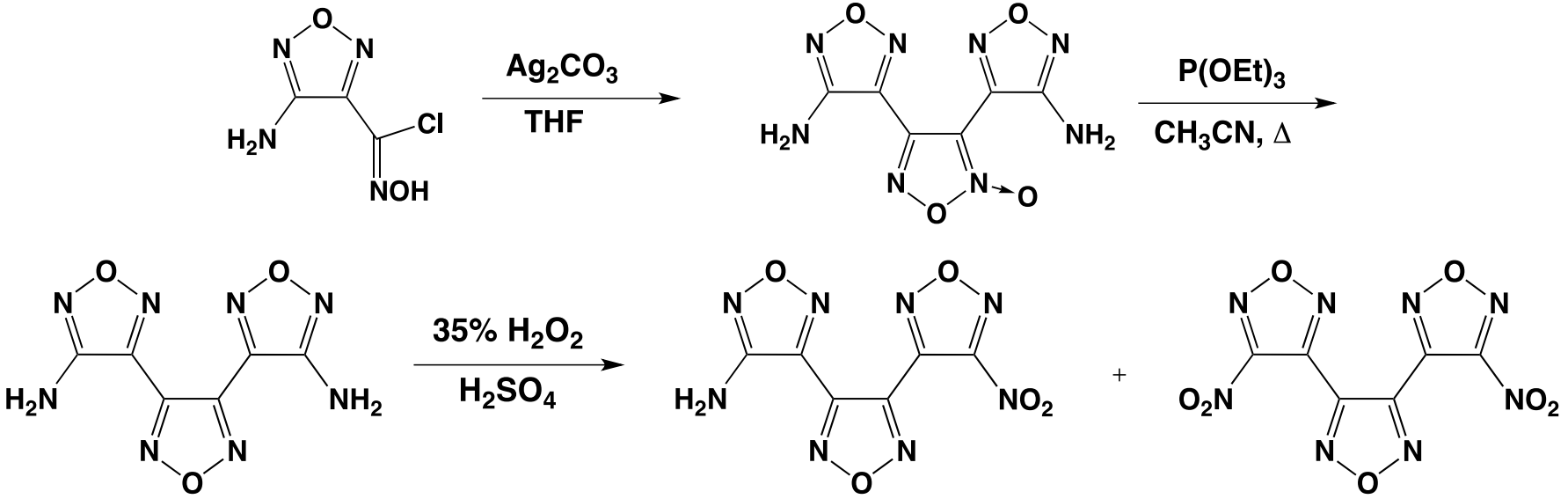




| Formulation | Density (%TMD) | VOD km/s | CJ GPa | $E_3$ kJ/cc |
|---|---|---|---|---|
| ADNP | 1.900 (100) | 8.68 | 32.8 | 6.85 |
| w/ 5% PIB | 1.722 (95.6) | 7.74 | 23.5 | 5.48 |
| w/ 5% PIB from DAX | 1.722 (95.6) | 8.130 | 31.4 | 4.84 |

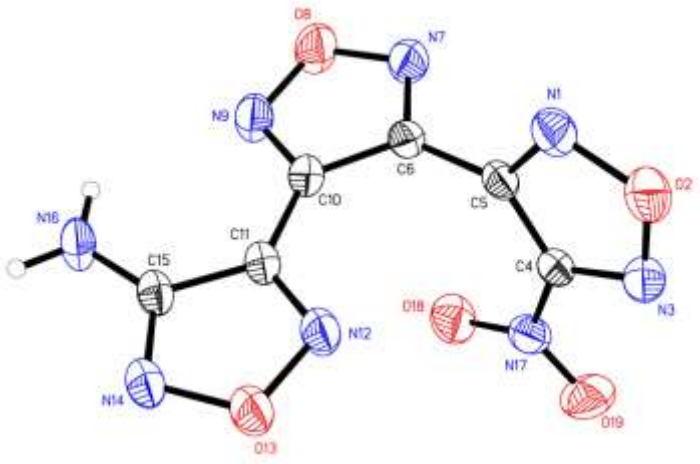


*Lebedev, V. P.; Matyushin, Y. N.; Inozemtcev, Y. O.; Dalinger, I. L.; Shevelev, S. A.; Fomenkov, I. V. *Int. Annu. Conf. ICT* **1998**, *29th*, 180.1

# 3-(4-nitro-1,2,5-oxadiazol-3-yl)-4-(4-amino-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole (LLM-175)




**LLM-175** **LLM-172**

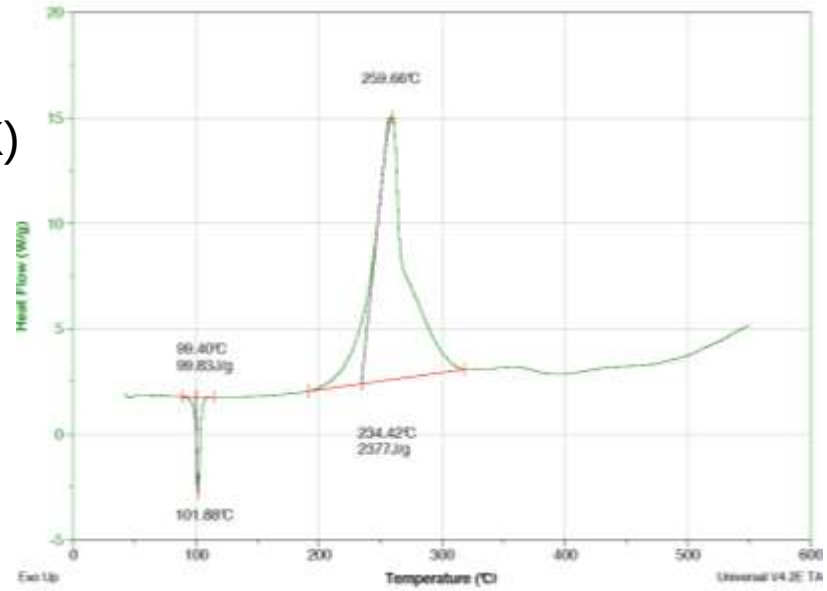


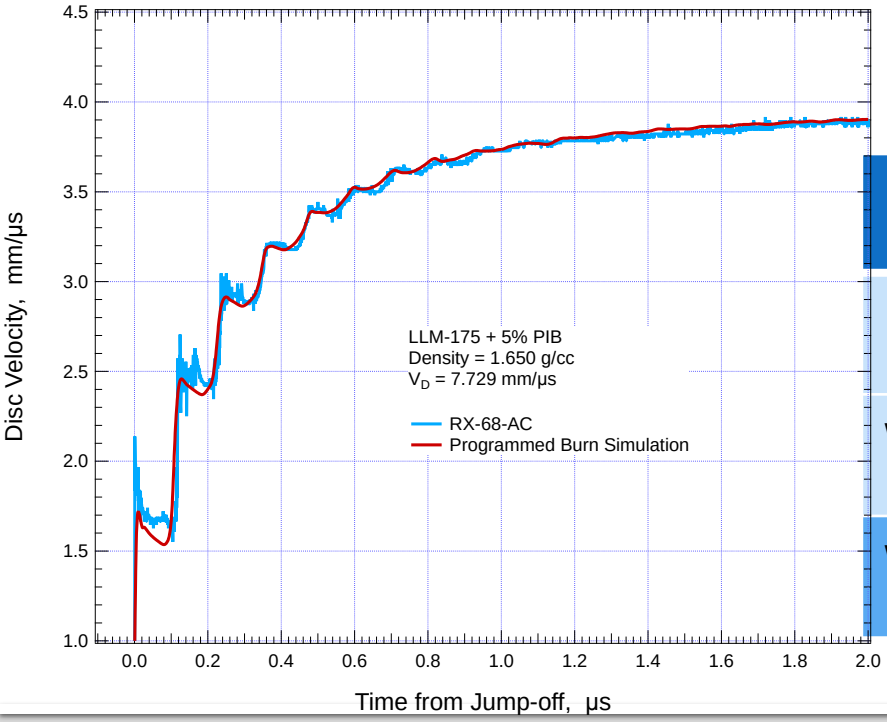
**Yields a ~1:1 mixture. The dinitro compound precipitates from the reaction and is filtered before quenching.**

**LLM-172 melts at 84 ˚C**
**LLM-175 melts at 100 ˚C**

# LLM-175

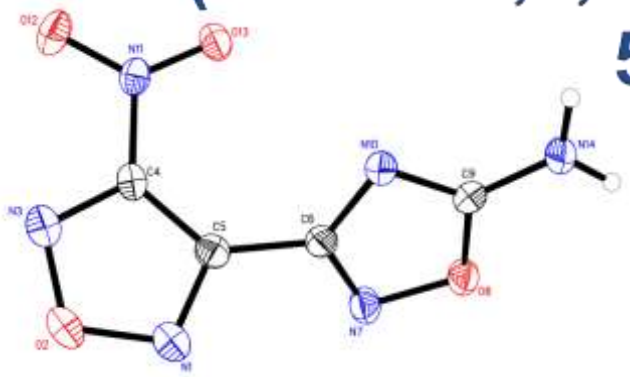
- Density: 1.782 g/cc
- $Dh_{50}$: >177 cm (32 cm for HMX)
- Spark Sensitivity: Insensitive (1J 510 ohm)
- Friction: 1/10@ 24kg (BAM)
- Heat of formation: +159.5 kcal/mole
- CRT: 0.9 cc/g @ 120 ˚C

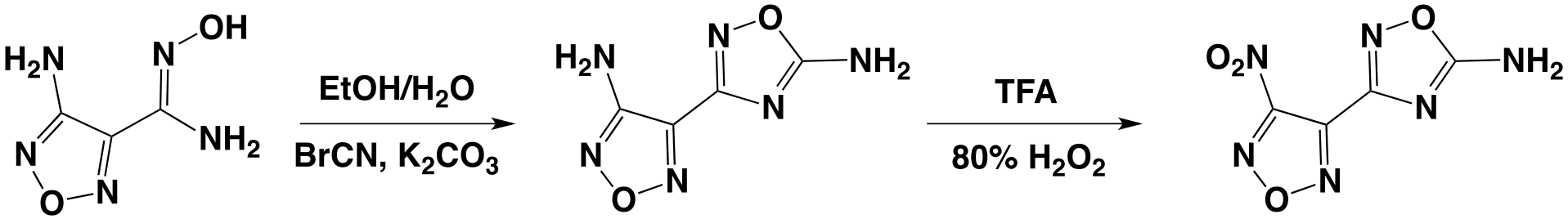



| Formulation | Density (%TMD) | VOD km/s | CJ GPa | $E_3$ kJ/cc |
|---|---|---|---|---|
| LLM-175 | 1.782 (100) | 8.10 | 27.0 | 6.94 |
| w/ 5% PIB | 1.650 (97.0) | 7.41 | 25.1 | 5.78 |
| w/ 5% PIB from DAX | 1.650 (97.0) | 7.729 | 31.4 | 5.01 |

# 3-(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5-amine (LLM-201)





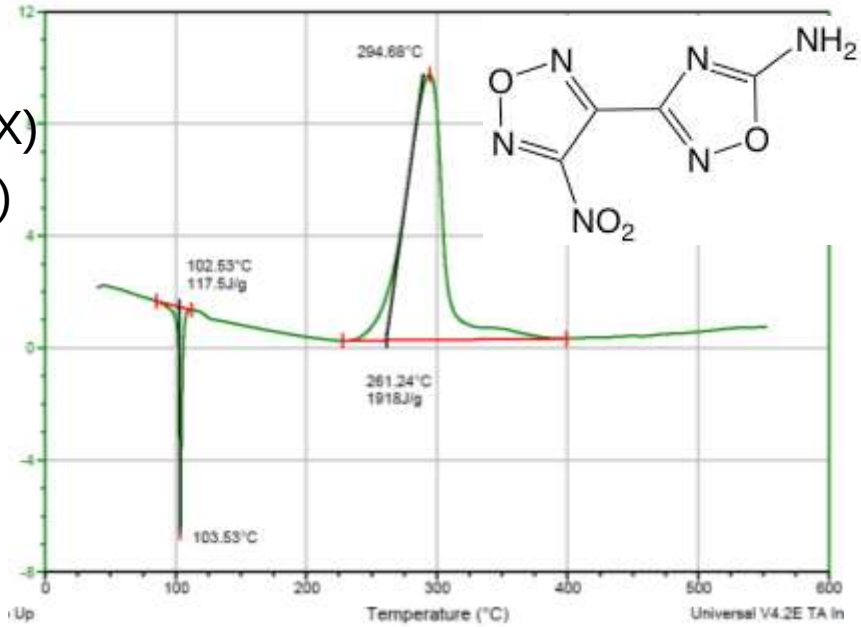

**LLM-201 melts at 100 ˚C**

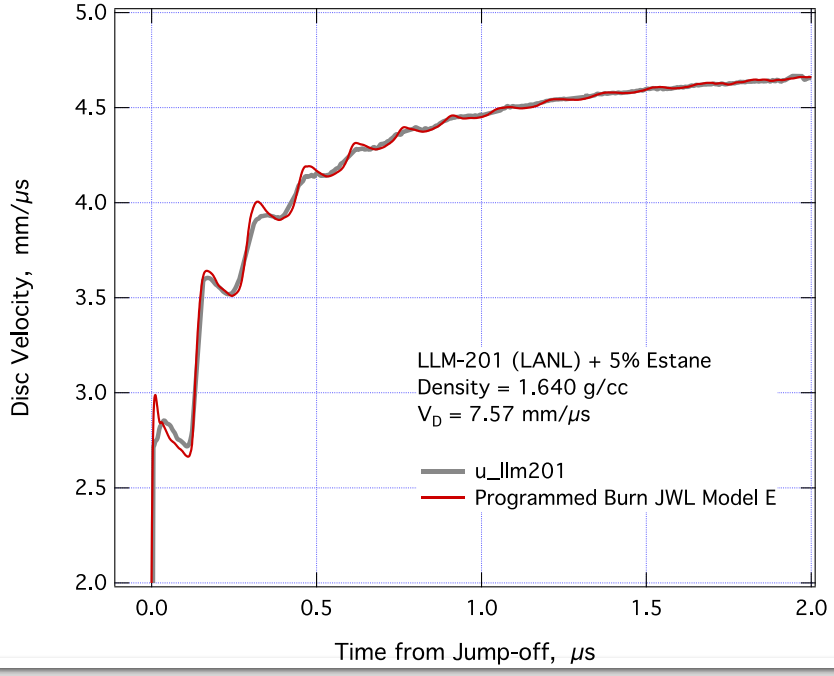
**So far, need to use TFA for oxidation. Decomposes in aqueous sulfuric acid.**

Diamino precursor: Shaposhnikov, S. D.; Korobov, N. V.; Sergievskii, A. V.; Pirogov, S. V.; Mel'nikova, S. F.; Tselinskii, I. V. *Russ. J. Org. Chem.* **2002**, *38*, 1351.

# LLM-201

- Density: 1.736 g/cc
- $Dh_{50}$: >177 cm (32 cm for HMX)
- Spark Sensitivity: Insensitive (1J 510 ohm)
- Friction: 0/10@ 36kg (BAM)
- Heat of formation: +46.3 kcal/mole
- CRT: 0.1 cc/g @ 80 ˚C




| Formulation | Density (%TMD) | VOD km/s | CJ GPa | $E_3$ kJ/cc |
|---|---|---|---|---|
| LLM-201 | 1.736 (100) | 7.80 | 24.5 | 5.75 |
| w/ 5% estane | 1.64 (96.7) | 7.52 | 22.1 | 4.87 |
| w/ estane from DAX | 1.64 (96.7) | 7.757 | 31.4 | 4.46 |

# Conclusions

- **3 promising insensitive energetic materials have been synthesized at >25g and subjected to the DAX performance test**

- **Each material has drawbacks:**
  **-ADNP decomposes at relatively low T**
  **-LLM-175 is produced as a mixture, need to find use for side product**
  **-LLM-201 requires TFA for oxidation**

- **Does measured performance and SSST warrant further development?**

# Acknowledgements


- LLNL Energetic materials synthesis group
- Elizabeth Francois (LANL) for DAX experiment of LLM-201
- LLNL HEAF technical staff
- Octavio Cervantes for combustion calorimetry
- The Joint DoD / DOE Munitions Technology Development Program (JMP)
- LLNL LDRD 12-ERD-066

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