

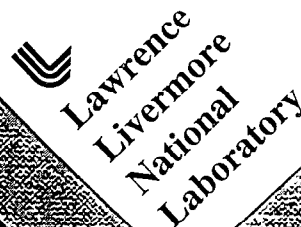
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PREPRINT

**Synthesis, Scale-up and Characterization of
2,6-Diamino-3,5-dinitropyrazine-1-oxide
(LLM-105)**

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Synthesis, Scale-up and Characterization of 2,6-Diamino-3,5-dinitropyrazine-1-oxide (LLM-105)

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Abstract

We have synthesized 400g of the new, insensitive, energetic heterocycle, 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) with 81% the energy of HMX and excellent thermal stability. The synthesis is a three step reaction sequence from the commercially available starting material, 2,6-dichloropyrazine, with an overall yield of 36%. In this paper we will describe the scale-up of the synthesis of LLM-105 and report on performance and shock sensitivity experiments performed on this material.

Results

The synthesis of LLM-105 through the oxidation of 2,6-diamino-3,5-dinitropyrazine with trifluoroaceticperacid at room temperature was first reported by us in 1995¹. The synthesis of the immediate precursor to LLM-105, 2,6-diamino-3,5-dinitropyrazine (ANPZ), was first reported by D.S. Donald at DuPont² and repeated in our laboratories in the initial synthesis of LLM-105. This involved the condensation of diaminomaleonitrile with diiminosuccinonitrile in trifluoroacetic acid to give tetracyanopyrazine, which when reacted with ammonia gives 2,6-diamino-3,5-dicyanopyrazine. This was hydrolyzed to the dicarboxylic acid and then nitratively decarboxylated with a nitric/sulfuric acid mixture to give 2,6-diamino-3,5-dinitropyrazine (ANPZ).² This first synthesis provided enough material to perform small scale safety tests and characterization of the physical properties of LLM-105. It was found to be a thermally stable (DSC = 342 °C), relatively insensitive energetic material (Dh₅₀ = 117cm) with 81% the energy of HMX. The energy content and thermal stability of this material make it very interesting for several applications, including insensitive boosters and detonators. In FY96 we scaled-up the synthesis of LLM-105 to the 20g scale which allowed preliminary safety and performance testing to determine if further scale-up was warranted. Small scale performance confirmed the predicted performance of LLM-105 and scale-up to the 0.5 kg scale was initiated. The original synthesis of the precursor to LLM-105, 2,6-diamino-3,5-dinitropyrazine (ANPZ)¹ was determined to be too difficult for scale-up to the 0.5

kg scale so two new approaches were investigated. These two new approaches are more environmentally friendly and have a shorter reaction sequence than the original method. The first method involved the condensation of commercially available alloxan monohydrate and 5,6-diaminouracil in water to yield 2,4,5,7-tetrahydroxy[5,4-g]pyrimidopteridine³ which was treated with aqueous sodium hydroxide at 170 °C in a Parr pressure vessel to yield 2,6-diamino-3,5-dicarboxypyrazine⁴ (Fig. 1). We have attempted to nitratively decarboxylate this material to ANPZ, in a manner similar to that used in the original synthesis, but have thus far been unsuccessful. Because of this difficulty this synthesis was abandoned in favor of a more viable method reported in a recent Russian Patent⁵ and shown in Figure 2.

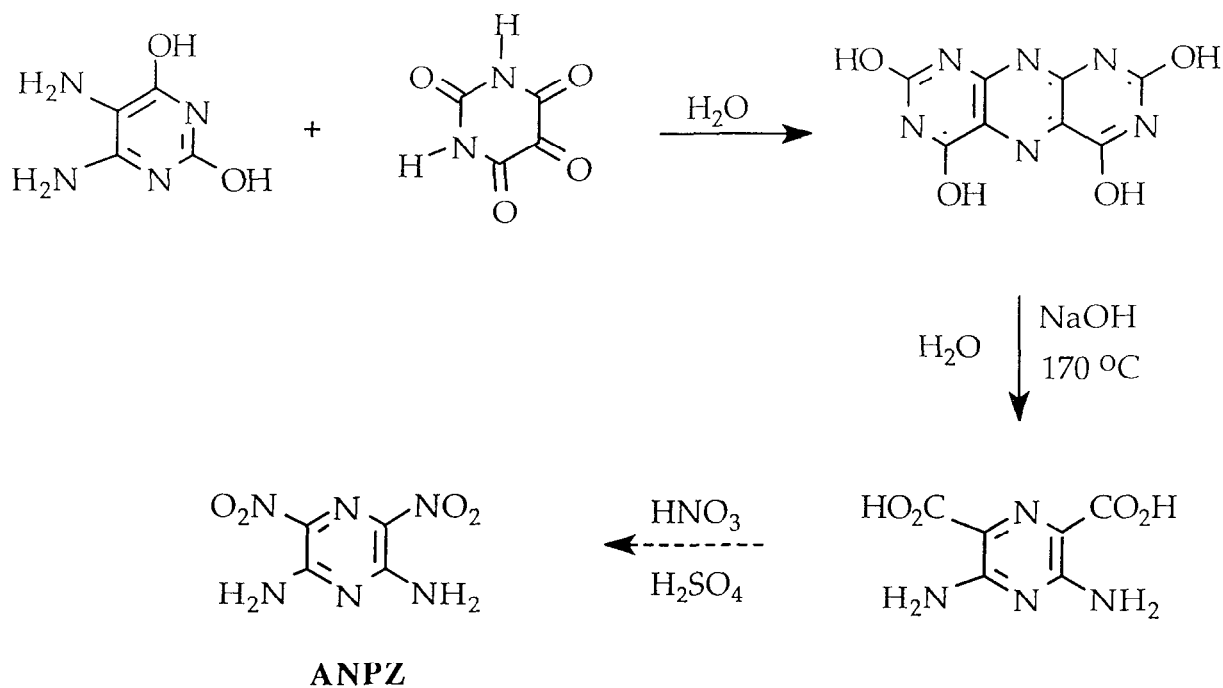


Fig. 1. Alternative approach to the synthesis of ANPZ and LLM-105.

This new synthesis was performed initially at the 10g scale to confirm its viability and was then scaled up to the 0.5 kg scale. The scale-up was performed in a batch process with energetic intermediates synthesized at the 100g or less scale. The synthesis of 2-chloro-6-methoxypyrazine involved reacting sodium methoxide with 2,6-dichloropyrazine in stoichiometric amounts in refluxing methanol for 6h. The reaction mixture was allowed to cool and poured into excess ice water and the resulting precipitate was collected immediately by suction filtration and stored cold. We found the product has a melting point very close to room temperature and upon standing turns into a white oil which was difficult to use in further synthetic reactions. In addition 2-chloro-6-methoxypyrazine has a high vapor pressure and will sublime at room temperature upon sitting. The product may be dried before using by dissolving in a minimum amount of ether, drying over anhydrous magnesium sulfate, and

removing the ether under vacuum. This material is >95% pure and may be used directly in the next step.

The synthesis of 2-chloro-6-methoxy-3,5-dinitropyrazine involved the reaction of 2-chloro-6-methoxypyrazine with a mixture of 20% fuming sulfuric acid and 98-100% nitric acid. The reaction was initially heated at 35-40 °C for 1h and then at 75-80 °C for 3h. Careful control of the reaction temperature is important in this step because at the elevated temperatures the reaction becomes self-heating. The reaction was quenched by cooling and pouring into ice water and the precipitate collected by suction filtration and washed with cold water. This gave a yellow powder in 48-55% yield which was used directly in the next step. The yield may be increased by extraction of the product from the aqueous solution with ethyl acetate but we chose not to add this extraction step to the scale-up.

The treatment of 2-chloro-6-methoxy-3,5-dinitropyrazine with aqueous ammonia in acetonitrile at 60 °C for 1h gave 2,6-diamino-3,5-dinitropyrazine in 80% yield as a yellow precipitate which also may be used directly in the next step. The oxidation of 2,6-diamino-3,5-dinitropyrazine involved treatment with a mixture of trifluoroacetic acid and 30% hydrogen peroxide at room temperature overnight. This is a heterogeneous reaction and the product is easily filtered from the reaction mixture and washed with water to give LLM-105 as a brilliant yellow powder in 95% yield. Recrystallization of LLM-105 to remove acid impurities was accomplished by dissolving LLM-105 in a hot DMF/DMSO mixture and adding an equivalent amount of hot water to yield LLM-105 as fine needles. A total of 400g of LLM-105 was synthesized. This material was formulated with Kel-F and used in a series of shock sensitivity experiments. The poor rheology of the LLM-105 crystals allowed us to press the parts for these measurements to only 92.4% TMD but still encouraging results were obtained. Three experiments were performed at 30, 42 and 58 Kbar shock loading pressures, respectively. At 30 Kbar pressure no reaction was observed while at 42 Kbar a reaction occurred but transition to full detonation did not occur at the maximum measured 19.7 mm travel distance. At 58 Kbar LLM-105 rapidly transitioned to full detonation. These are quite encouraging results for a material with 7.5% porosity and comparisons to other materials (including TATB) with similar pressing densities showed LLM-105 approaches TATB in shock sensitivity and is superior to HMX and HNS. ODTX (One dimensional-time -to-explosion) experiments were also performed on LLM-105 and the results indicate LLM-105 has essentially the same thermal stability as TNT, and is intermediate between HMX and TATB. These experiments placed the critical temperature of LLM-105 at 190-214 °C.

We are currently investigating other recrystallization solvents in order to improve the rheology of the product and its formulations.

We also performed some process and development work in the hope of decreasing the cost of synthesis of LLM-105. We investigated the use of commercially available 90% HNO₃ to replace the anhydrous HNO₃ in the nitration step and the use of oxone in water as the oxidizing reagent instead of

the more expensive trifluoroacetic acid/ hydrogen peroxide mixture in the final oxidation step. 90% HNO₃ was found to give the desired product in a total yield comparable to anhydrous HNO₃ but the product contains approximately 25% of an unknown impurity which may be removed after the amination step by refluxing in water. The use of oxone in a four fold excess in refluxing water for 4h resulted in the oxidation of ANPZ LLM-105 in 50% yield. The use of more oxidizing reagent or longer reaction times led to a reduced yield while lower temperatures and a lesser amount of oxone yielded incomplete oxidation. The use of sodium bicarbonate as a buffer for the oxidation resulted in complete decomposition of the starting material. The combination of acetone or 2-butanone and oxone at room temperature as the oxidizing agent resulted only in recovered starting material. Because of these difficulties the original synthetic method was used in our scale-up with some minor improvements in yields and isolation procedures.

Summary

We have synthesized 400g of LLM-105, an interesting insensitive energetic material with 81% the energy of HMX. This material is a thermally stable, shock insensitive explosive which may have applications in both insensitive booster and main charge applications.

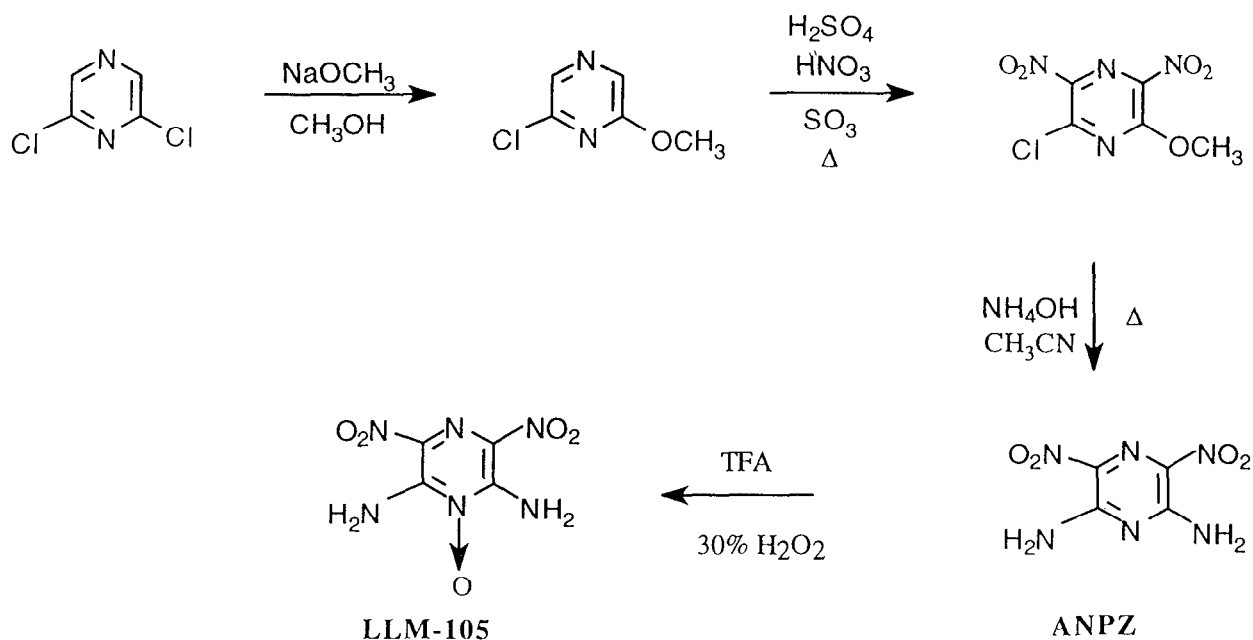


Fig. 2. Recently reported synthesis of ANPZ.⁵

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