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March 7, 2013

New Trends in Research of Energetic Materials
Pardubice, Czech Republic
April 10, 2013 through April 12, 2013

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New Polynitro Alkylamino Furazans

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Abstract:

New energetic compounds have been synthesized which consist of 1,2,5-oxadiazoles substituted with poly-nitro alkyl amines. The 2,2,2-trinitroethylamino- containing compounds are 3-(4-((2,2,2-trinitroethyl)amino)-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5-amine (LLM-199), $N^4,N^{4''}$ -bis(2,2,2-trinitroethyl)-[3,3':4',3''-ter(1,2,5-oxadiazole)]-4,4''-diamine (LLM-204), and 4''-nitro- N -(2,2,2-trinitroethyl)-[3,3':4',3''-ter(1',2',5'-oxadiazol)]-4-amine (LLM-206). N^3,N^4 -bis(2-fluoro-2,2-dinitroethyl)-1,2,5-oxadiazole-3,4-diamine (LLM-208) replaces a nitro group with a fluorine atom. These new materials have been treated with acetyl nitrate to afford the acyclic nitramines N,N' -([3,3':4',3''-ter(1,2,5-oxadiazole)]-4,4''-diyl)bis(N -(2,2,2-trinitroethyl)nitramide) (LLM-211) and N,N' -(1,2,5-oxadiazole-3,4-diyl)bis(N -(2-fluoro-2,2-dinitroethyl)nitramide) (LLM-209). New materials have been subjected to small-scale safety testing and their responses to impact, friction, and electrostatic discharge have been measured along with thermal stability testing (CRT). Chemical structures have been determined by spectroscopy and single crystal x-ray diffraction. Syntheses up to the 10 gram scale have been carried out and material detonation properties and I_{sp} have been predicted relative to HMX. The syntheses, reactivity and relative thermal stability of these new compounds are discussed.

Keywords: EM synthesis; heterocycles; 2,2,2-trinitroethyl; 2-fluoro-2,2-dinitroethyl

1 Introduction

The goal of the energetic materials synthesis group at LLNL is to synthesize and scale-up new energetic compounds in search of performance and safety that improves upon currently deployed energetic materials. We must be cognizant of the ease and cost of synthesis so our interests also lie in the improvement of the preparative routes of known materials. Much of our efforts in new material synthesis has been on the preparation of unsaturated heterocycles with energetic functional groups such as LLM-105 [1] and BNFF-1 (LLM-172) [2]. By modulating the functional groups we seek to tune material properties such as melting point, thermal stability, and increase the density while improving on material sensitivities to mechanical insult. The current work details the incorporation of polynitro alkylamino functional groups into 1,2,5-oxadiazoles (furazans) in an effort to prepare dense, thermally stable energetic materials.

2 Experimental

2.1 LLM-199: 3-(4-((2,2,2-trinitroethyl)amino)-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5-amine

The synthesis of 3-(4-amino-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5-amine was reported in 2002 [3] via reaction of cyanogen bromide with 3-amino-1,2,5-oxadiazole-4-carbamidoxime. The bi-cycle was dissolved in a 3:1 mixture of methanol and DMF and refluxed in the presence of trinitroethanol (Figure 1). Evaporation of the solvent and washing with hot water afforded a white solid that melted with decomposition at 157 °C (DSC 10 °C min⁻¹). ¹H NMR (90 MHz, DMSO-d₆) δ 7.90 (s, 2H), 6.71 (br, 1H), 5.51 (d, *J* = 7 Hz, 2H); ¹³C NMR (150 MHz, acetone-d₆) δ 172.16, 158.78, 154.73, 136.45, 48.04. Different solvent systems were investigated to obtain single crystals suitable for x-ray diffraction but in all cases high aspect ratio needles were obtained. Material response to impact, spark, friction, and thermal aging are listed in Table 1.

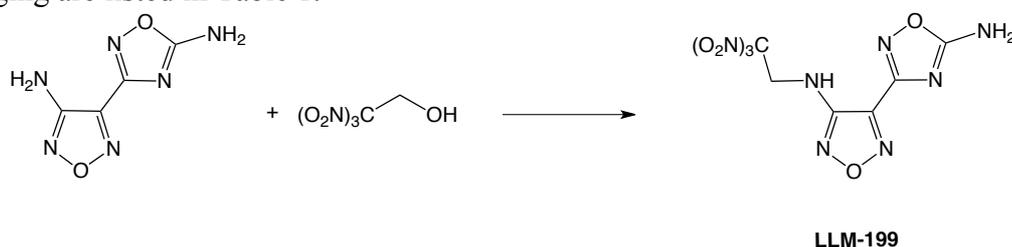


Figure 1: Synthesis of LLM-199

2.2 LLM-204: *N*⁴,*N*^{4''}-bis(2,2,2-trinitroethyl)-[3,3':4',3''-ter(1,2,5-oxadiazole)]-4,4''-diamine

3,4-bis(4-amino-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole [2] was generated by reduction of 3,4-bis(4-amino-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole-1-oxide [4] with triethylphosphite [5] and subsequently reacted with formalin and nitroform in methanol at 70 °C in a closed vessel (Figure 2). LLM-204 was isolated by filtration, the colorless crystalline solid melting at 183 °C with decomposition (DSC 10 °C min⁻¹). ¹H NMR (600 MHz, acetone-d₆) δ 6.873 (t, *J* = 7 Hz, 2H), 5.562 (d, *J* = 7 Hz, 4H); ¹³C NMR (150 MHz, acetone-d₆) δ ¹³C NMR (150 MHz, acetone-d₆) δ 155.83, 143.68, 135.43, 125.90 (br), 48.26.

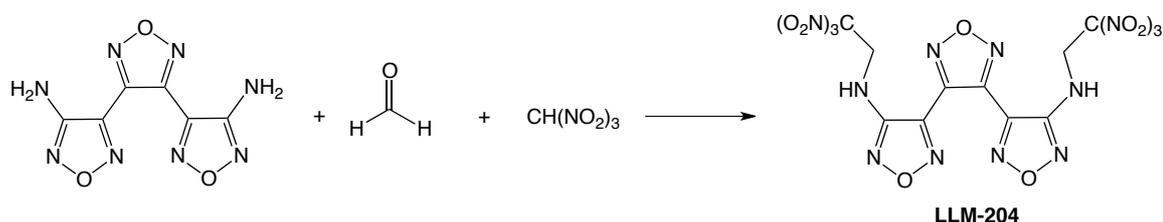


Figure 2: Synthesis of LLM-204

The structure of LLM-204 was unambiguously determined by an x-ray crystallographic study and is shown in Figure 3. LLM-204 is orthorhombic and crystallizes in the *Pbcn* space group with a measured density of 1.755 g cm⁻³ at 20 °C. The material has small-scale safety test results for impact and friction that lie between HMX and PETN, the results of which are shown in Table 1 and has been prepared in 10 gram batches at LLNL. The heat of combustion was measured on a Parr model 6300 calorimeter and found to be -5364 kJ mol⁻¹. The heat of formation of LLM-204 was calculated as 571 kJ mol⁻¹ using the method of Rouse [6].

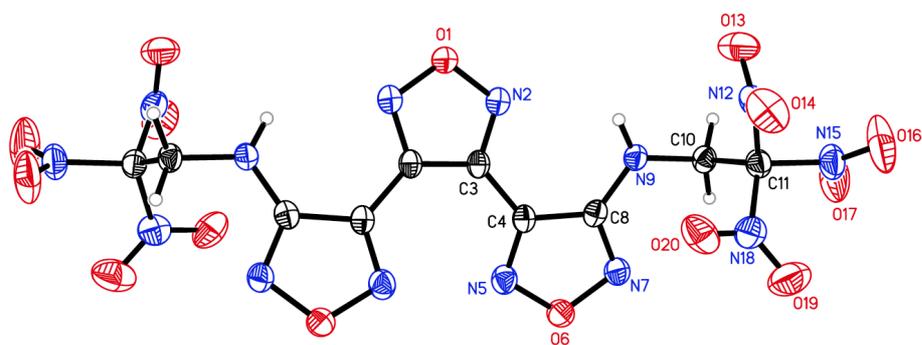


Figure 3: X-ray structure of LLM-204. Thermal ellipsoids are drawn at the 50% level of probability. Selected bond lengths [Å] and torsion angles [°]: C8-N9 = 1.364, N9-C10 = 1.435, C11-N12 = 1.528, C11-N15 = 1.518, C11-N18 = 1.537; C3'-C3-C4-N5 = 19.8, C8-N9-C10-C11 = -103.7, N7-C8-N9-C10 = 6.8.

2.3 LLM-206: 4''-nitro-*N*-(2,2,2-trinitroethyl)-[3,3':4',3''-ter(1',2',5'-oxadiazol)]-4-amine

LLM-206 is prepared by addition of formaldehyde to the amino group of 3-(4-nitro-1,2,5-oxadiazol-3-yl)-4-(4-amino-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole (LLM-175) followed by condensation with nitroform (Figure 4). ^1H NMR (600 MHz, acetone- d_6) δ 6.875 (t, J = 7 Hz, 1H), 5.612 (d, J = 7 Hz, 2H); ^{13}C NMR (150 MHz, acetone- d_6) δ 161.18 (br), 156.45, 145.20, 141.93, 140.13, 136.76, 126.74 (br), 49.17. Small-scale safety tests have yet to be performed on LLM-206.

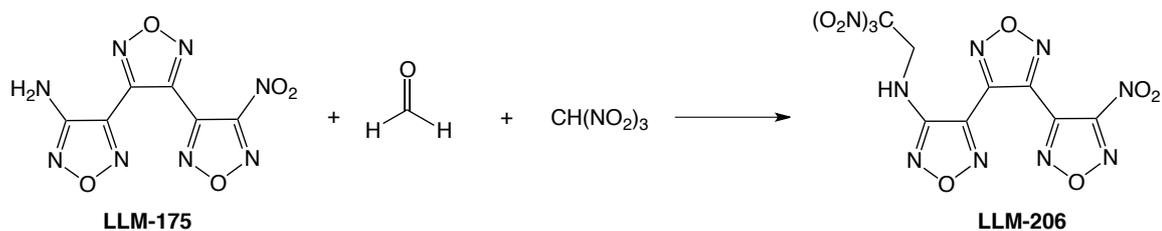


Figure 4: Synthesis of LLM-206 from LLM-175

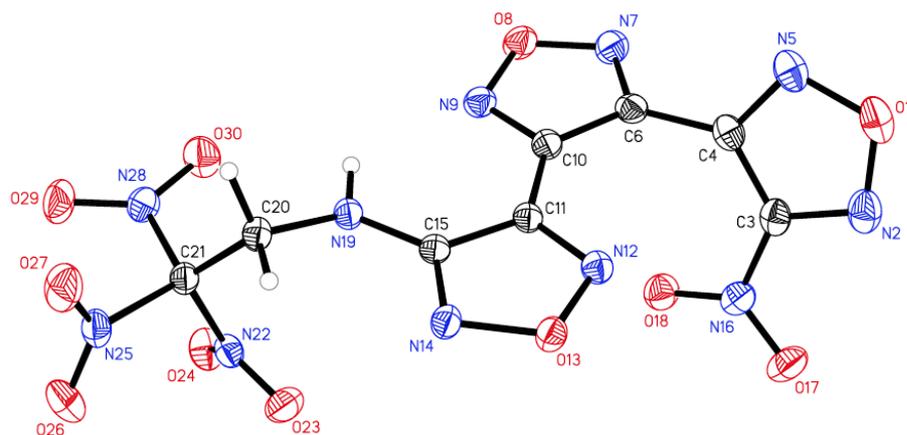


Figure 5: X-ray structure of LLM-206. Thermal ellipsoids are drawn at the 50% level. Selected bond lengths [Å] and torsion angles [°]: C21-N22 = 1.518, C21-N25 = 1.524, C21-N28 = 1.525, C20-N11 = 1.447, N19-C15 = 1.363, C10-C11 = 1.455, C4-C6 = 1.472, C3-N16 = 1.541; N14-C15-N19-C20 = 16.3, C6-C10-C11-C15 = 175.1, C3-C4-C6-C10 = 59.9.

The structure of LLM-206 was confirmed by x-ray crystallography (Figure 5). LLM-206 is triclinic and crystallizes in the P-1 space group with a density of 1.845 g cm⁻³ measured at 20 °C. Some material performance parameters, relative to HMX, were estimated using Cheetah 7.0 (Table 2).

2.4 LLM-208: N³,N⁴-bis(2-fluoro-2,2-dinitroethyl)-1,2,5-oxadiazole-3,4-diamine

Diaminofurazan [7] was heated at 50 °C with 2-fluoro-2,2-dinitroethanol in the presence of potassium carbonate in water to afford N³,N⁴-bis(2-fluoro-2,2-dinitroethyl)-1,2,5-oxadiazole-3,4-diamine (LLM-208, Figure 6). The material melts at 157 °C with a peak exotherm at 197 °C (DSC 10 °C min⁻¹). ¹H NMR (600 MHz, acetone-d₆) δ 6.448 (br, 2H), 4.972 (d, *J* = 7 Hz, 2H), 4.944 (d, *J* = 7 Hz, 2H); ¹³C NMR (150 MHz, acetone-d₆) δ 149.19, 122.54, 120.61, 46.42, 46.29. The density of LLM-208 was measured by gas pycnometry to be 1.8396 g cm⁻³ at room temperature. Assuming a 1% fraction of closed crystal voids results in a theoretical maximum density of 1.8582 g cm⁻³. The material has been synthesized at the 10-gram scale at LLNL and small-scale safety test results are listed in Table 1. Performance estimates were calculated using Cheetah and are shown in Table 2.

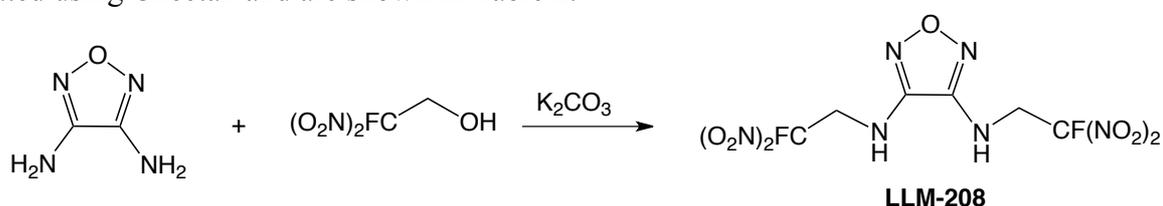


Figure 6: Synthesis of LLM-208 via condensation of DAF and FDNE

2.5 Nitramines: LLM-209 and LLM-211

LLM-204 and LLM-208 were dissolved in 0 °C 100% nitric acid and acetic anhydride was dropped into the solution. The nitration mixtures were quenched with crushed ice and the nitramines were isolated by filtration and washed with water to afford white solids (Figure 7). LLM-209 melts at 92 °C and decomposes while LLM-211 melts at 100 °C with resulting decomposition. The response of LLM-209 to impact, friction, and spark was measured and the results are listed in Table 1. LLM-209: ¹H NMR (90 MHz, acetone-d₆) δ 6.310 (s, 2H), 6.168 (s, 2H). LLM-211: ¹H NMR (90 MHz, acetone-d₆) δ 6.676 (s).

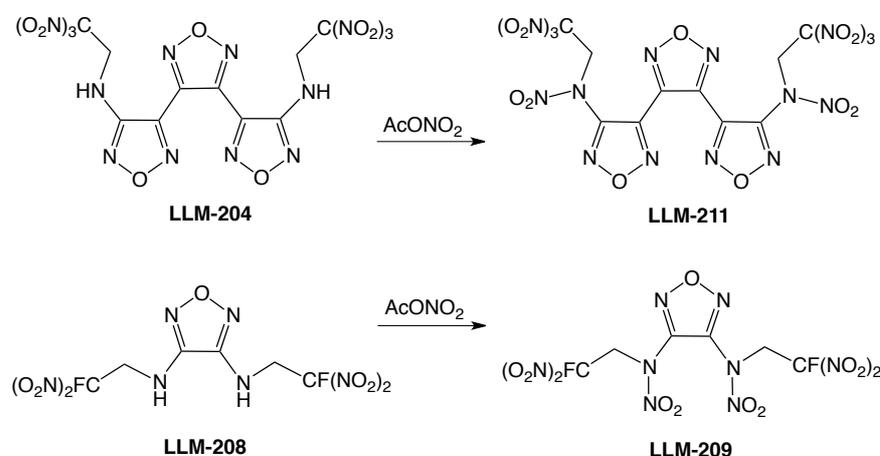


Figure 7: N-nitration of polynitro alkylaminofurazans

3 Results and Discussion

LLM-204 is the most sensitive and least thermally stable compound studied. It is postulated that the mechanical sensitivity and thermal instability of the trinitromethyl functional group derives from the steric crowding induced by the three NO₂ groups around the carbon atom [8]. Indeed, elongated sp³ carbon-nitrogen bonds are observed in the x-ray crystal structures of both LLM-204 and LLM-206 (Figures 3 and 5). The three furazan rings of LLM-206 are 20° out of plane with the trinitromethyl groups on opposite faces of the ring system. While LLM-206 has two furazan rings nearly coplanar (2.5° out of plane) and the 4-nitro substituted furazan ring twisted out of plane with a torsion angle of 60° between the four carbon atoms of the heterocycles (Figure 5). This arrangement places the nitro group and the trinitromethyl group on the same face of the molecule and contributes to a density that is 5% higher than LLM-204.

Table 1: Results of small-scale safety tests

Compound	Dh ₅₀ (cm)	CRT (cm ³ /g @ 80 °C)	Spark	Friction (BAM) (kg)	DSC peak ex- otherm (°C)
LLM-199	64	0.18	No	1/10 @ 32.4	187
LLM-204	24	0.99	No	1/10 @ 16.0	207
LLM-208	119	0.28	No	1/10 @ 32.4	197
LLM-209	37	TBD	No	1/10 @ 16.8	101
HMX	30-32	0.05	No	1/10 @ 16.0	279

The inclusion of amino groups in energetic compounds, while decreasing performance, can lead insensitive materials such as TATB, FOX-7 [9], and LLM-105. LLM-199 is an energetic material with a 3:2 ratio of nitro to amino groups. It is less sensitive than LLM-204, though both materials contain the trinitroethylamino substituted 1,2,5-oxadiazole ring. And somewhat surprisingly, the thermal aging test at LLNL, the CRT, shows LLM-199 to be much more thermally stable than LLM-204 with approximately 80% less off-gassing measured after 22 hours at 80 °C. This is in spite of the fact that LLM-204 has higher exothermic onset and peak exothermic temperatures than LLM-199, as measured by differential scanning calorimetry. Attempts to oxidize the amino group appended to the 1,2,4-oxadiazole ring, even with 80% H₂O₂, were unsuccessful and various conditions were explored to condense another trinitroethanol molecule, all without success. Indeed, we are unaware of any examples of the oxidation of a 5-amino substituted 1,2,4-oxadiazole to a nitro group.

By substituting the trinitroethyl functionality by fluorodinitroethyl more thermally stable materials are obtained, but with a sacrifice in energy [10, 11]. We obtained a less sensitive and thermally stable material, LLM-208, following this rationale. There are advantages to the inclusion of fluorine for certain energetic materials applications due to its oxidizing properties [12].

The nitramine LLM-209 is CO₂ balanced and LLM-211 is -7.4% oxygen deficient, but the low phase stability and decomposition during the melt will hamper their utility in most applications. While alkyl amines substituted with the trinitroethyl group can be stabilized by N-nitration [13], the same effect is not observed with the amino furazans prepared. Thermal aging tests (CRT) have not been run on these nitramines to date. LLM-209 has small-scale safety test results similar to HMX for friction and impact.

Table 2: Estimation of performance properties and I_{sp} (Cheetah)

Material	% HMX @ 2.2 V/V ₀	Energy (kJ/cc)	Shock Velocity	C _j Pressure	Specific Impulse
LLM-204	84 %	-9.75	8.37 km/s	30.24 GPa	268 s
LLM-206	94 %	-10.53	8.76 km/s	33.98 GPa	269 s
LLM-208	94 %	-10.50	8.32 km/s	32.94 GPa	269 s
HMX	102 %	-11.00	9.25 km/s	37.188 GPa	265 s

4 Conclusion

New 1,2,5-oxadiazole compounds have been synthesized which possess polynitro ethylamino functionalities. The sensitivity characteristics of some of these materials have been measured and some performance properties have been estimated. LLM-208 and LLM-204 have been prepared at the 10-gram scale in our laboratories. Further investigations into the properties of these materials and their derivatives are on going.

Acknowledgments

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-CONF-624954. We are grateful for funding of this work from LDRD 12-ERD-066.

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