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Formation, Preparation, and Characterization of
4-Diazo-3,5-bis(4-amino-3,5-dinitropyrazol-1-yl)pyrazole
(LLM-226)

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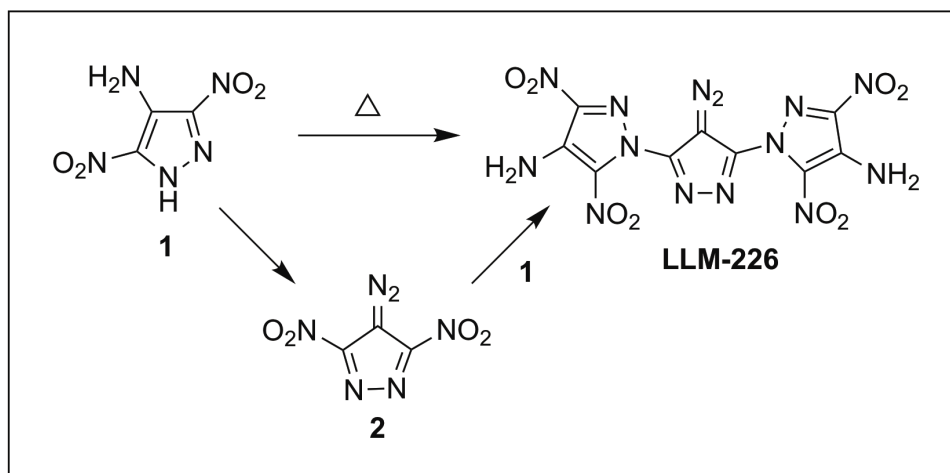
Trimerization of 4-Amino-3,5-dinitropyrazole: Formation, Preparation, and Characterization of 4-Diazo-3,5-bis(4-amino-3,5-dinitropyrazol-1-yl)pyrazole (LLM-226)

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4-Amino-3,5-dinitropyrazole (LLM-116, **1**) undergoes trimerization to 4-diazo-3,5-bis(4-amino-3,5-dinitropyrazol-1-yl)pyrazole (LLM-226) upon heating. A mechanism is proposed and discussed. LLM-226 is a new diazo-based energetic material, thermally stable, and insensitive to impact, friction and spark. The material may be prepared by heating **1** and 4-diazo-3,5-dinitropyrazole (**2**) in a mixture of toluene and butyl acetate at 110 °C or heating **1** alone in dichlorobenzene at 160 °C. The characterization of LLM-226 including X-ray crystallographic analysis is included, along with a proposed mechanism of formation.

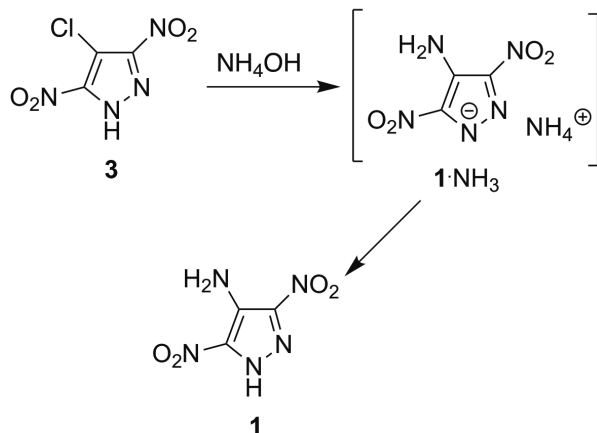
INTRODUCTION

4-Amino-3,5-dinitropyrazole (LLM-116, **1**) is an insensitive energetic material [1-2] and a starting material for many new explosives and propellants [3-10]. Several methods have been reported in the literature for the preparation of the material [11], but the amination of 4-chloro-3,5-dinitropyrazole (**3**) via nitration of commercially available 4-chloropyrazole has become the most popular approach [12]. In 2001, we reported the first

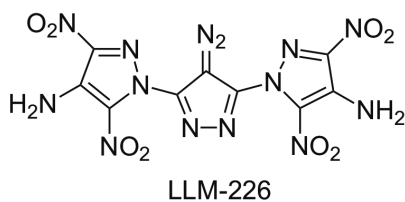
synthesis of **1** by direct amination of 3,5-dinitropyrazole with 1,1,1-trimethylhydrazinun iodide (TMHI), revealing that **1** is a thermally stable compound, exothermically decomposing at 183 °C by Differential Scanning Calorimetry (DSC) [2]. Recently, Shevelev, et al. reported that the amination of **3** with 28% aqueous NH_4OH solution gave **1** in high yield (Scheme 1) [12].

The NH_4OH amination process does not give the final product, but an ammonium salt, $\mathbf{1}\cdot\text{NH}_3$. To obtain pure **1**, the salt is acidified

Scheme 1



with aqueous H₂SO₄ to pH=1 and the product is extracted into ethyl acetate and recrystallized from water. This recrystallization yields a mono-hydrate of 4-amino-3,5-dinitro-1H-pyrazole (**1**) [2]. When the hydrated **1** was dissolved in refluxing toluene in an attempt to azeotrope the water, a small amount of brown solid was found suggesting that some decomposition of **1** occurred during the processing. The brown solid, unlike molecule **1**, was insoluble in water and poorly soluble in acetonitrile and acetone, but soluble in *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). Isolation and purification of the brown solid gave a pale yellow solid which was identified as 4-diazo-3,5-bis(4-amino-3,5-dinitro-1H-pyrazol-1-yl)pyrazole (LLM-226), a new energetic compound containing a stable diazo group.



In this paper, we report the formation, preparation and characterization of LLM-226, along with a discussion of the reaction mechanism, the X-ray crystallographic analysis and the small-scale safety properties.

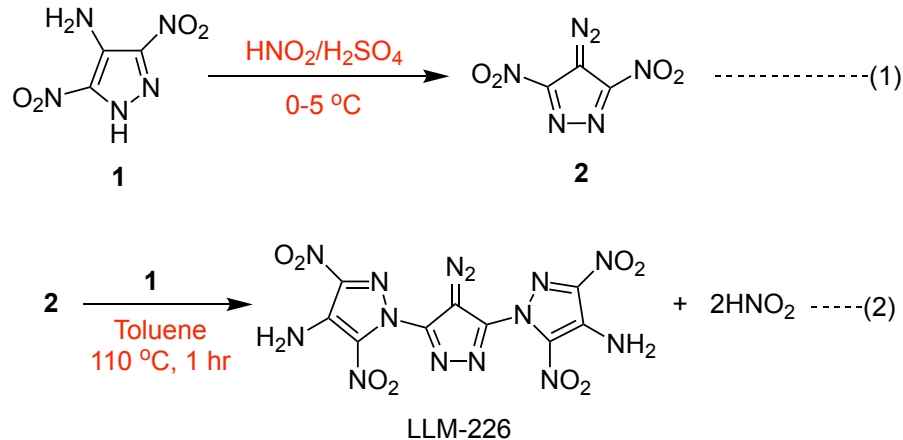
RESULTS AND DISCUSSION

Formation of LLM-226

As mentioned above, LLM-226 was found during the dehydration of hydrated 4-amino-3,5-dinitro-1H-pyrazole (**1**) in toluene at 110 °C. The molecule is a trimer of **1** composed of a central 4-diazopyrazole with two appending 4-amino-3,5-dinitro-1H-pyrazole units. We suggest that LLM-226 is formed by the nucleophilic substitution of the two nitro groups of 4-diazo-3,5-dinitro-1H-pyrazole (**2**) with **1** as described in Scheme 2. It is believed that the intermediate **2** is formed by diazotization of **1** with nitrogen oxides or HONO, which is generated through an initial decomposition of **1** or other sources such as from the decomposition of impurities (*vide infra*).

4-Diazo-3,5-dinitro-1H-pyrazole (**2**) is known. Shevelev, et al. reported that the amino group in 4-amino-3,5-dinitro-1H-pyrazole (**1**) could be diazotized to **2** with NaNO₂ in aqueous H₂SO₄ at 0-5 °C and found that the nitro groups of **2**, due to lack of hydrogen bonding, are readily replaced by weak nucleophiles, such as Br⁻ and N₃⁻ to give 4-diazo-bromonitro- and 4-diazo-azidonitro-1H-pyrazole, respectively [13]. **1** is a weak nucleophile, but the anion of **1** shows reasonable reactivity toward the electrophiles, such as bromonitromethane or diiodomethane at elevated temperature to give corresponding *N*-substituted compounds [3-4]. The nucleophilic substitutions of **1** to **2** has not been previously reported as our knowledge. To verify our hypothesis, we mixed 1.5 mmol of **2**, prepared according to Shevelev's procedure [13], and 5.8 mmol of purified **1** in 30 ml of anhydrous toluene and heated the mixture at 110 °C for 1.0 hour. LLM-226 was found in the reaction mixture and isolated in the yield of 16%, suggesting that **2** is a possible intermediate in the formation of LLM-226.

Scheme 2



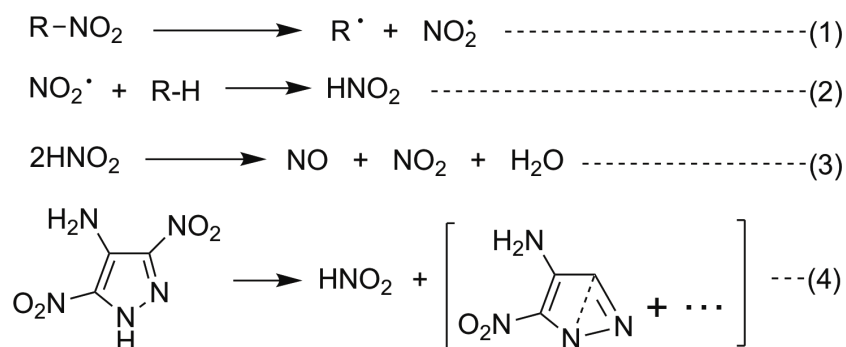
The diazotization of amines to diazo compounds is a general synthetic method in organic chemistry. The active species in the diazotization is nitrous acid, HNO_2 , or its cation NO^+ when the reaction is carried out under acidic conditions. While the sources of nitrous acid vary [14], one of the sources less mentioned in organic chemistry is in the byproducts from the decomposition of nitro-based energetic materials. In general, nitro-based energetic materials decompose to form various nitrogen oxides such as nitrogen dioxide and nitrogen oxide. For example, 2,4,6-trinitrotoluene (TNT) undergoes thermal decomposition to release the nitrogen dioxide radical, which may abstract a hydrogen from solvent or from TNT itself to give HNO_2 (Scheme 3, eq. 1-2) [15-16]. This behavior may also be true for the nitro-based heterocyclic energetic materials such as 4-amino-3,5-dinitro-1H-pyrazole (**1**). Wang, et al. reported that the thermal decomposition of **1** at 173 °C would generate nitrogen monoxide (NO), nitrogen dioxide (NO_2) and water as determined by thermogravimetry-mass spectrometer (TG-MS) and

infrared spectroscopy (IR) [17]. These gas products may be the secondary decomposition products of initially formed nitrous acid as shown in Scheme 3. Therefore, it is believed that HNO_2 could be one of the byproducts in the thermal decomposition of **1** (Scheme 3, eq. 4).

To further establish the mechanism, we mixed 4.7 mmol of purified **1** in 15 ml of 1,3-dichlorobenzene and heated the mixture at 160 °C for 10 min. giving LLM-226 in 39% isolated yield. It is suggested that the first molecule of **1** decomposes at the reaction temperature to give HNO_2 (Scheme 3, eq. 4) which reacts with a second molecule of **1** to give **2** (Scheme 2, eq. 1). The nucleophilic substitution of the nitro groups of **2** with **1** facilitates the formation of LLM-226. With each nucleophilic displacement step, another molecule of HNO_2 is formed, which may react with another molecule of **1**, leading to further conversion of **1** to LLM-226.

During the course of our studies, there was some evidence that the impurities found in the crude product from the synthesis of 4-amino-3,5-dinitro-1H-pyrazole (**1**) may catalyze the decomposition of **1**. As mentioned above, LLM-226 was found in the dehydration of

Scheme 3



crude **1** at refluxing toluene temperature (~110 °C). However, pure **1** is thermally and chemically stable in the solvent at the temperature. This suggests that the formation of LLM-226 in refluxing toluene solvent may be initiated by the impurities found in crude **1**. To elucidate the reaction mechanism and identify the impurities that may be catalyzing the decomposition of **1**, an analysis of the products formed during each stage of the synthetic process was investigated. The amination of **3** initially produces the ammonium salt (**1**•NH₃) (Scheme 1), which is thermally stable, exothermal decomposing at 262 °C (DSC). Acidification of the salt with aqueous H₂SO₄ and extraction with ethyl acetate gave crude **1**. This crude product was subjected to Thin Layer Chromatography (TLC) analysis. It indicated that the product did not contain 4-diazo-3,5-dinitropyrazole (**2**) (CH₂Cl₂/ethyl acetate, 10:1, R_f = 0.49) but did contain small amounts of impurities (ethyl acetate/acetic acid, 50:1, R_f = 0.63 and 0.95; **1**: R_f = 0.37). The impurities could not be completely removed from **1** by the recrystallization from water, toluene, diethyl ether, benzene/diethyl ether, benzene/acetic acid, or 1,2-dichloroethane, but were completely removed by a recrystallization from a mixture of propionic acid, benzene and acetic acid (3.2:5:1) (see experimental section). **1** purified by this method produces a product with good thermal stability at 110 °C in toluene, showing no decomposition to LLM-226 nor other products, as determined by ¹H-NMR spectroscopy and TLC analysis. This suggests that these impurities somehow catalyze the decomposition of **1** to LLM-226. Unfortunately, all attempts at isolating and identifying these impurities thus far have been unsuccessful.

Preparation of LLM-226

Several synthetic methods were investigated in an effort to both synthesize larger quantities of LLM-226 for characterization as an energetic material and in an attempt to understand the mechanism of formation. Surprisingly, simple treatment of 4-amino-3,5-dinitropyrazole (**1**) with a small amount of NaNO₂ and aqueous H₂SO₄ in toluene or butyl acetate did not produce LLM-226. Two other methods investigated were: 1) a nucleophilic substitution of **1** to **2**; and 2) a thermal decomposition of **1** in polar, aprotic high-boiling solvents that are relatively inert to nitrosation.

In the first method, a mixture of 5.2 mmol of **2**, prepared from the diazotization of **1** with NaNO₂ in aqueous H₂SO₄ solution [13], and 15.0 mmol of **1** in 15 ml of butyl acetate and 25 ml of toluene was heated at 110 °C for 1.0 hour. The precipitate was collected by filtration at 50-60 °C and washed with acetonitrile. This gave pure LLM-226 in 51% yield. If the reaction mixture is cooled to room temperature, the filtration and wash procedure does not give a pure LLM-226. Therefore, a further purification step is needed (see experimental section).

Some interesting solvent effects on the substitution of **1** to **2** were noted. When the reaction was carried out in toluene, the yield of LLM-226 was 16%. This may be attributed to the poor solubility of **1** in toluene. However, when butyl acetate was used alone as the solvent, while the solubility is good, the yield did not increase significantly (26%). The best yield was obtained by using a mixture of toluene and butyl acetate as mentioned above. A higher yield may be possible by modifying and optimizing the reaction conditions with regarding to solvent, time, and temperature.

Table 1. Thermal stability and sensitivity of LLM-226, **1** and **2**

Compound	Density (g/cm ³)	mp. (°C)	T _d ^b (°C)	Dh ₅₀ ^c (cm)	Friction (BAM)	Spark J @ 0 Ohms ^e
LLM-226	1.83	-	278	31	1/10 @32.4kg	0.014
2	1.81 ^a	156	212	10	2/6 @ 0.5kg	0.00063
1	1.90 ^f	176	182	177	0/10 @ 36kg	0.038

^a Ref. [18]; ^b DSC peak exotherm; ^c 2.5kg weight, up-down Bruce-ton method; ^d friction sensitive; ^e Spark sensitive. ^f Ref. [2]

Direct thermal decomposition of **1** in organic solvent is also a convenient method for the preparation of LLM-226. As we have already discussed earlier, the best yield we received by this method was 39%. The reaction temperature is critical to the conversion. When **1** was heated in chlorobenzene at refluxing temperature (~135 °C) for 1.0 hour, no reaction was observed. However, at 160 °C in dichlorobenzene, **1** melts and decomposes fairly fast to give LLM-226. Heating for 10 min. at 160 °C was the optimal conditions, in which about 80-90% of **1** was decomposed. A longer heating period generates tar-like byproducts and make the isolation of LLM-226 more difficult.

These two methods both have advantages and disadvantages. The first method gives the product in a high yield and uses lower reaction temperatures, but the drawback is that 4-diazo-3,5-dinitropyrazole (**2**) is very sensitive and needs to be handled with care. The second method is easy to handle, but the yield is low, and the exothermal decomposition is difficult to control for large scale preparation.

Characterization of LLM-226

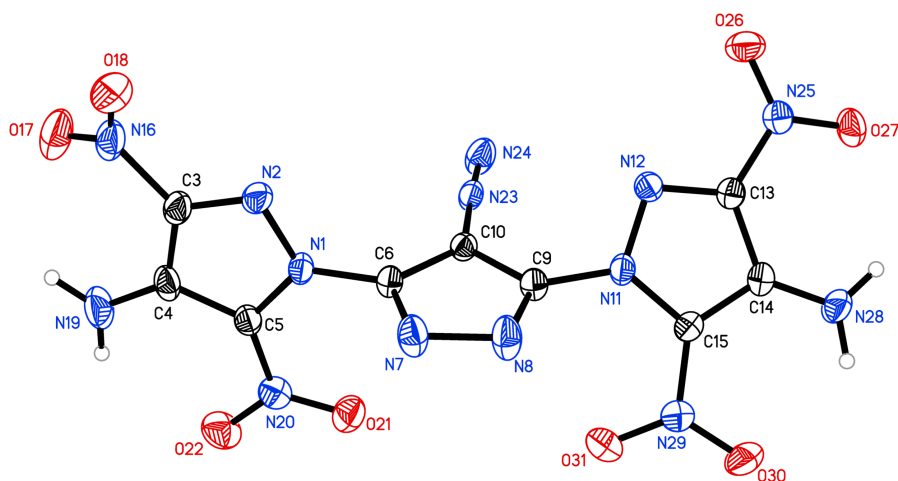
The molecular structure of LLM-226 has been fully characterized by NMR, IR, and MS.

and confirmed by X-ray crystallographic analysis. In LLM-226, the diazo group characteristics appear similar to those diazo compounds reported in the literature. The carbon connected to the diazo group appears at 77.9 ppm in the ¹³C NMR spectrum, similar to that of the carbon in 4-diazo-3,5-dinitropyrazole (**2**) at 80.00 ppm reported by Shevelev et al. [13] and 76.6 ppm by Li, et al [18]. In the infrared (IR) spectrum, LLM-226 has typical diazo absorption at 2188 cm⁻¹ (thin film), compared to that of 4-diazo-3-methyl-5-carboxamidopyrazole ($\nu=2180$ cm⁻¹, KBr pellet) [19], 4-diazo-2-nitrophenol ($\nu=2190$ cm⁻¹, KBr pellet) [20] and **2** ($\nu=2240$ cm⁻¹, KBr pellet) [18]. Details of the analysis can be found in the Experimental Section.

Different than **2**, LLM-226 is thermally stable and relatively insensitive to impact, friction and spark. Differential Scanning Calorimetry (DSC) showed that LLM-226 had a peak exotherm at 278 °C with no melting point. The drop hammer impact sensitivity (Dh₅₀) of LLM-226 is 31 cm (HMX=32 cm), compared to **2** (Dh₅₀=10 cm) and **1** (Dh₅₀=177 cm), where **1** does not contain diazo group (Table 1).

Generally, many diazo energetic materials were found to be sensitive, for example, **2** [17] and 2-diazo-3,5-dinitrophenol [21]. Interestingly, LLM-226 has about the same

Table 2. Hydrogen bonds for LLM-226 [\AA and $^\circ$]



D-H...A	D(D-H)	D(H...A)	D(D...A)	< (DHA)
N(19)-H(19A)...O(22)	0.88	2.31	2.841(3)	119.1
N(19)-H(19B)...O(17)	0.88	2.38	2.906(3)	118.5
N(28)-H(28A)...O(17)#1	0.88	2.34	3.174(3)	157.1
N(28)-H(28A)...O(30)	0.88	2.28	2.827(3)	119.7
N(28)-H(28B)...O(27)	0.88	2.27	2.821(3)	120.9

Symmetry transformations used to generate equivalent atoms: #1 $x+1/2, -y+1/2, z-1/$

impact sensitivity as 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) and is insensitive to friction and spark.

The weakest bond in a molecule usually contributes to the thermal stability and the sensitivity of the material. A well-arranged molecular structure and solid-state packing ensure LLM-226 to be relatively thermal stable and less sensitive to impact than most of compounds containing a diazo group. LLM-226 is composed of two amino-dinitropyrazole moieties and one diazopyrazole, in which the nitro- group and diazo- are attached to different pyrazole rings. The arrangement of the amino and nitro group on the pyrazole rings are expected to provide additional stabilization through a strong inter- and intra-molecular hydrogen bonding, similar to those found in known thermally stable and insensitive

compounds such as 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) [22]. Indeed, X-ray analysis indicates that the molecule of LLM-226 has four pairs of intramolecular hydrogen bonds and one strong intermolecular bonding between amino and nitro groups (Table 2).

Of course, many factors could affect the sensitivity of an energetic material. In solid state, the manner of a molecular packing may make a great contribution to sensitivity of the material [22]. As expected, there is no hydrogen bonding between the diazo and the amino group, but there are existing strong short contacts between the diazo and the nitro groups. In the solid state, eight molecules of LLM-226 are packed in a monoclinic crystal system with the space group $C2/c$ and cell

parameters $a = 17.869 \text{ \AA}$, $b = 10.7483 \text{ \AA}$, $c = 17.307(3) \text{ \AA}$, and $\beta = 111.099^\circ$. The unit cell volume is 3101.2 \AA^3 and density (20°C) is 1.833 g/cm^3 . LLM-226 has a nonplanar structure with torsion angles of -85.57° for N2-N1-C6-C10 and 51.11° for N12-N11-C9-C10. Therefore, there is no intramolecular diazo-oxygen short contact, but there are three close intermolecular contacts shorter than the sum of the van der Waals radii (3.07 \AA for O and N). Two of the three are significantly shorter (2.77 \AA and 2.80 \AA). Each contact involves the diazo group and a nitro group on another molecule of LLM-226 (Fig. 1). These short contacts may provide extra stabilization to the diazo functional group.

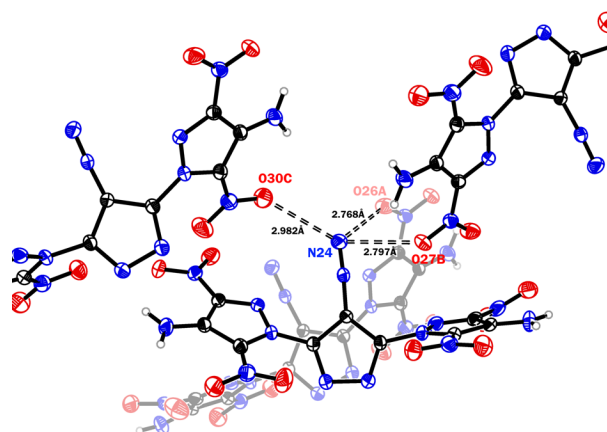


Fig. 1. A thermal ellipsoid plot of LLM-226 showing the intermolecular short contacts of diazo-nitro group in the solid state

In conclusion, evidence was provided that 4-diazo-3,5-dinitropyrazole (**2**) is an intermediate in the formation of the new energetic material, 4-diazo-bis(4-amino-3,5-dinitropyrazol-1-yl)pyrazole (LLM-226). The formation may involve diazotization of 4-amino-3,5-dinitropyrazole (**1**) with a diazotization reagent, such as HNO_2 and/or NO^+ , which are generated from the thermal decomposition of **1** or from the impurities that exist in the crude **1**. The preparation of significant quantities of LLM-226 is possible either by the reaction of **1** and **2** in the mixture

of toluene and butyl acetate solution at 110°C or by heating **1** alone in dichlorobenzene at 160°C for 10 min. LLM-226 is a new diazo compound, thermally stable and relatively insensitive to impact, friction and spark. This enhanced stability is attributed to the considerable hydrogen bonding between the amino and the nitro groups and from the short contact between the diazo group and the nitro groups through the intermolecular interactions.

EXPERIMENTAL

Warning! The compounds described herein are explosives and should be handled only by experienced explosives handlers. They may be sensitive to shock, friction or spark initiation and may transition to detonation upon heating. Special precaution must be paid to 4-diazo-3,5-dinitropyrazole (**2**) since the material has been classified as primary explosive.

Infrared spectrum was collected using a Bruker Alpha ZnSe ATR FTIR as thin films. ^1H and ^{13}C NMR spectra were acquired on either a Bruker 600 MHz spectrometer (600 and 150 MHz, respectively) or an Anasazi Instruments Eft-90 MHz spectrometer with Varian magnet (90 and 22.5 MHz, respectively). ^1H and ^{13}C NMR chemical shifts were reported relative to the residual solvent protons as internal standard, such as, $\text{DMSO-}d_6$ (2.5 ppm) and $\text{acetone-}d_6$ (2.05 ppm). Differential scanning calorimetry (DSC) measurements were recorded using a TA Instruments DSC Q2000. LC-MS was performed on Thermo Scientific equipped with Ultimate 30000 system monitored by Chromeleon 7 and MSQ Plus Mass detector controlled by MSQ 2.0.

X-ray crystallography: Colorless crystals were mounted on a MiteGen MicroMesh by using a small amount of Cargille Immersion oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a

SMART APEX II CCD detector. The crystals were irradiated by using graphite monochromated MoK α radiation ($\lambda = 0.71073$). An Oxford Cobra low-temperature device was used to maintain the crystals at a constant 150(2) K during data collection. Data collection was performed, and the unit cell was initially refined by using APEX2 [v2010.3-0]. Data reduction was performed using SAINT [v7.68 A] and XPREP [v2008/2]. Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS [v2008/1]. The structure was solved and refined with the aid of the programs in the SHELXTL-plus [v2008/4] system of programs. The full-matrix least-squares refinement on F² included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were included by using a riding model.

All reagents and solvents were purchased from commercial suppliers and used without further purification.

Preparation and purification of 4-amino-3,5-dinitropyrazole (LLM-116, 1)

Compound **1** was prepared and purified by a modification of literature procedures [11-12]. A mixture of 4-chloro-3,5-dinitropyrazole (15.0 g, 77.9 mmol) and 150 ml of aqueous NH₄OH (28-30%) was sealed in a high-pressure vessel. The mixture was heated in an oil bath at 130 °C for 16 hours with gentle stirring. The precipitate formed after cooling to room temperature was collected by filtration and washed with cold water (2x20 ml). This gave ammonium 4-amino-3,5-dinitropyrazolate salt (**1**•NH₃). The salt is a thermally stable compound, decomposing at 262 °C (DSC).

The ammonium salt was suspended in 170 ml of ethyl acetate and 40 g of ice. With vigorously stirring, 21 ml of 20% of aqueous sulfuric acid (prepared from 20 ml of concentrated sulfuric acid and 80 g of ice) was

added. The mixture was stirred at room temperature for 20 min. to give a clear solution. The organic phase was separated, and the aqueous phase was extracted with ethyl acetate (2x20 ml). The combined organic phase was washed with brine (2x40 ml) and dried over MgSO₄. After evaporation of the solvent on a Rotary Evaporator at 50 °C, the residue was triturated with a mixture of benzene (50 ml) and propionic acid (50 ml) and filtered. The solid was then refluxed in a mixture of 80 ml of propionic acid, 125 ml of benzene and 25 ml of acetic acid in an oil bath (100 °C) for 1.5 hours while collecting azeotropic solution (~35 ml). The clear solution was allowed to cool to room temperature with gentle stirring. The precipitate was collected by filtration and washed with a mixture of propionic acid and benzene (1:1, 30 ml), dried under suction for 1 hr and further dried at 20 °C/0.01 torr for 20 hrs to give 12.0g (89%) of 4-amino-3,5-dinitropyrazole (**1**). The purity of the material was determined by thin layer chromatography (TLC) (ethyl acetate/acetic acid, 50:1, R_f = 0.37) and ¹H NMR spectroscopy. Differential Scanning Calorimetry (DSC) (10 °C/min); endotherm peak at 175.5.0 °C, exotherm peak at 182.1 °C [lit [2] DSC (10 °C/min) endotherm peak at 175.7 °C; exotherm peak at 183.6 °C]. ¹H NMR (acetone-d₆): δ 12.20 (sb, 1H), 6.76 (s, 2H); ¹³C NMR (acetone-d₆): δ 139.0, 129.0.

Formation of 4-diazo-bis(4-amino-3,5-dinitropyrazol-1-yl)pyrazole (LLM-226) from the dehydration of hydrated (1**) in toluene**

Compound **1** was prepared using a reported literature with slightly modifications [11-12]. A mixture of 4-chloro-3,5-dinitropyrazole (10.0g, 51.9 mmol) and 100 ml of aqueous NH₄OH (28-30%) was sealed in a high-pressure vessel and heated for 16 hours as described above. The ammonium salt was

suspended in 100 ml of ethyl acetate and 30 g of ice. With vigorously stirring, 15 ml of 20% of aqueous sulfuric acid (prepared from 20 ml of concentrated sulfuric acid and 80 g of ice) was added and the clear mixture was stirred at room temperature for further 20 min. The organic phase was removed, and the aqueous phase was extracted with ethyl acetate (2x15 ml). The combined organic phase was washed with brine (2x10ml), dried with MgSO₄. After evaporation of the solvent on a Rotary Evaporator at 50 °C, the residue was refluxed with 30 ml of water, and allowed to cool to room temperature. The precipitate was collected by filtration and washed with small amount of cool water and dried under suction to give hydrated 4-amino-3,5-dinitropyrazole, **1**•H₂O [2].

1•H₂O (6.7g, 35 mmol) was suspended in 60 ml of toluene. The mixture was heated in an oil bath (130 °C, refluxing temperature ~110 °C) while collecting azeotropic solution (~10 ml). During the heating, the solid of **1**•H₂O dissolved slowly while a brown precipitate formed and gradually deposited on the wall of the flask. The clear, hot solution was decanted into another flask, and the remaining solid was dissolved in 5 ml of DMF and the solution was titrated with 20 ml of acetonitrile with stirring. The precipitate was collected by filtration, washed with acetonitrile, and dried under suction to give LLM-226 as a pale-yellow solid, 0.28g. The purity of the material was determined by TLC (ethyl acetate/toluene, 1:1, R_f = 0.58) and ¹H NMR spectroscopy. Differential Scanning Calorimetry (DSC) (10 °C/min); exotherm peak at 278.3 °C; ¹H NMR (DMSO-d₆): δ 7.69 (s, 4H); ¹³C NMR (DMSO-d₆): δ 147.1, 144.0, 131.8, 130.8, 77.9; IR (thin film) 3478.4, 3364.3, 2188.2 (diazo), 1642.8, 1531.6, 1475.6, 1313.6, 860.5, 827.1 cm⁻¹; MS (-75 V, EI) m/z 436.94 (M⁺+H, 100%), calculated C₉H₄N₁₄O₈ (M, 436.03). The x-ray quality single crystal was prepared in acetone.

Preparation of 4-diazo-bis(4-amino-3,5-dinitropyrazol-1-yl)pyrazole (LLM-226) from the reaction of **1 and **2****

*The reaction of **1** and **2** in toluene and butyl acetate mixture:* To a 100 ml three-necked round bottom flask equipped with thermometer, stir bar, and Dean-Stark trap were added **1** (2.6 g, 15.0 mmol), **2** (0.95g, 5.16 mmol), butyl acetate (15 ml), and toluene (25 ml). The mixture was stirred and heated at 110 °C. After heating for about 10 min., the clear solution turned cloudy and a precipitate formed. The heating was continued for 1.0 hr. and allowed to cool to 50 °C. The precipitated was filtered off when hot and washed with butyl acetate (2x2 ml), acetonitrile (1.0 ml), and dried under suction to give LLM-226, 1.15g (51%). The purity of the material was determined by NMR and TLC.

*The reaction of **1** and **2** in toluene:* The procedure used is the same as that described above. **1** (1.0 g, 5.8 mmol), **2** (0.27 g, 1.5 mmol), and anhydrous toluene (30 ml) were heated at 110 °C for 1.0 hr. LLM-226 was isolated in 0.10g (16%).

*The reaction of **1** and **2** in butyl acetate:* The procedure used is the same as that described above. **1** (0.33g, 1.9 mmol), **2** (0.061g, 0.33 mmol), and butyl acetate (5.0 ml) were heated at 110 °C for 1.0 hour. LLM-226 was isolated in 0.038g (26%).

Trying to preparation of LLM-226 from the reaction of 4-amino-3,5-dinitropyrazole (1**) with NaNO₂ and aqueous H₂SO₄**

*The reaction of **1** and NaNO₂ in aq. H₂SO₄ in toluene and butyl acetate:* **1** (0.10g, 0.58 mmol), NaNO₂ (0.020g, 0.29 mmol), 20% aqueous H₂SO₄ (0.2 ml), toluene (5.0 ml), and butyl acetate (2.0 ml) were heated at 110 °C for 1.0 hour. Some brown solid was formed, but no LLM-226 was identified.

*The reaction of **1** and NaNO₂ in aq. H₂SO₄ in toluene:* **1** (0.10g, 0.58 mmol), NaNO₂ (0.008g, 0.11 mmol), 20% aqueous H₂SO₄ (0.2

ml), toluene (5.0 ml), were heated at 110 °C for 1.0 hour. Some yellow sticky precipitate was formed, but no LLM-226 was identified.

Thermal decomposition of 4-amino-3,5-dinitropyrazole (1) in 1,3-dichlorobenzene to LLM-226

Into a 50 ml of round-bottom flask equipped with thermometer and stir bar were added pure **1** (0.81g, 4.7 mmol) and 1,3-dichlorobenzene (15 ml). The mixture was stirred in an oil bath as the bath temperature was increased to 160 °C over a period of 30 min. The mixture was then stirred at 160 °C for 10 min., the dark brown mixture was allowed to cool to room temperature, and the precipitate was collected by filtration and washed with acetonitrile (1.0 ml). The solid was dissolved in 0.5 ml of DMF and warmed to 50 °C to give a dark, clear solution. Acetonitrile (5 ml) was added with stirring, and the clear mixture was stirred at room temperature overnight. The resulting yellow precipitated was collected by filtration, washed with acetonitrile (0.5 ml) and dried under suction to give LLM-226, 0.27g (39%).

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Supporting Information

Proton and carbon-13 NMR are available. X-ray data is available at The Cambridge Crystallographic Data Center with code: CCDC1834767

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