

Lithium Nitropyrazolates as Potential Red Pyrotechnic Colorants

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Dedicated to Professor Dr. Wolfgang Beck on the occasion of his 90th Birthday.

Strontium-based red pyrotechnic colorants have fallen into disrepute due to the harmful influence of this alkaline earth metal on adolescents. In this context, the energetic character, safety, and combustion to benign nitrogen gas of nitropyrazoles are used for the design of the corresponding lithiated materials, which are investigated as potential replacements in the current work. For this purpose, the lithium salts of 3,4-dinitro-1*H*-pyrazole, 3,5-dinitro-1*H*-pyrazole, 4-amino-3,5-dinitro-1*H*-

pyrazole, 3,4,5-trinitro-1*H*-pyrazole, and 4-hydroxy-3,5-dinitro-1*H*-pyrazole were extensively characterized by standard analytical methods, low-temperature single-crystal X-ray diffraction, studies of the thermo-chemical behavior, and sensitivity assessments. Our assumption that the high nitrogen contents and the low oxygen balances of these compounds would adjust a cool, reductive flame atmosphere essential for red emissions by lithium was put to the test.

Introduction

Nitropyrazoles have already found application in a wide range of pharmaceuticals and optics.^[1] Lately, these compounds have also attracted interest among the energetic materials research community due to their balance between explosive performance and safety, while compared to high-energy density materials with a carbon backbone combusting to high volumes of environmentally benign nitrogen gas (see Figure 1).^[2] The combustion of their numerous nitrogen atoms, especially that of neighboring ones, to triple-bonded dinitrogen leads to high heats of formation,^[2,3] whereas the introduction of the explosophores forming dipolar interactions increases the density^[4] (3,4-dinitro-1*H*-pyrazole (**3**):^[5] $\rho = 1.79 \text{ g cm}^{-3}$ at 298 K; 3,5-dinitro-1*H*-pyrazole (**5**):^[5] $\rho = 1.78 \text{ g cm}^{-3}$ at 298 K; 3,4,5-trinitro-1*H*-pyrazole (**9**):^[6] $\rho = 1.87 \text{ g cm}^{-3}$ at 293 K) and in combination with the substitution of carbon atoms in the ring by nitrogen contributes to positive oxygen balances (**3/5**: $\Omega_{\text{CO}} = 0\%$; **9**: $\Omega_{\text{CO}} = 20\%$). The aromaticity accounts for their thermal stabilities^[7] (**3**):^[5] $T_{\text{dec}}(\text{onset}) = 285^\circ\text{C}$; **5**):^[5] $T_{\text{dec}}(\text{onset}) = 299^\circ\text{C}$; **9**):^[6] $T_{\text{dec}}(\text{onset}) = 264^\circ\text{C}$) and their low sensitivities toward destructive stimuli further guarantee safe handling (**3**):^[5] FS = 360 N, ESD = 1.5 J; **5**):^[5] FS = 360 N, ESD = 1.0 J; **9**):^[6] FS = 92 N, ESD >

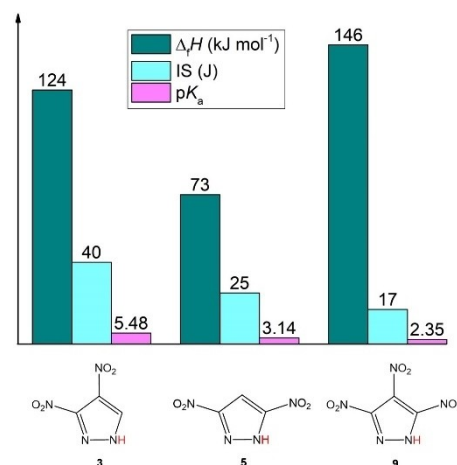


Figure 1. The combination of large energy content and low vulnerability in nitropyrazoles along with high acidity.

0.8 J). However, one decisive drawback of nitropyrazoles is the considerable acidity of the *N*-bonded proton resulting in a lack of compatibility and storage problems. There are three different possibilities to stabilize the nitropyrazole backbone: *N*-functionalization, amination or salt formation. While deprotonation by a base partially lowers the sensitivities toward ignition stimuli,^[8] hydrogen bonding between proton-donating amino groups and neighboring proton-accepting nitro functionalities^[9] additionally raises the density^[10] (4-amino-3,5-dinitro-1*H*-pyrazole (**8**): $pK_a = 3.42$,^[11] $\rho = 1.90 \text{ g cm}^{-3}$ at 294 K,^[12] $T_{\text{dec}}(\text{onset}) = 176^\circ\text{C}$,^[12] FS > 360 N,^[13] IS = 12 J^[13]). The same effect is expected for hydroxylation of nitropyrazoles since the hydroxyl group also acts as proton donor (4-hydroxy-3,5-dinitro-1*H*-pyrazole (**10**): $2/3 \text{ H}_2\text{O}$:^[6] $\rho = 1.81 \text{ g cm}^{-3}$ at 293 K, $T_{\text{dec}}(\text{peak}) = 194^\circ\text{C}$).

Although pyrotechnic colorants should also contribute to the energetic character of a formulation, have low sensitivities

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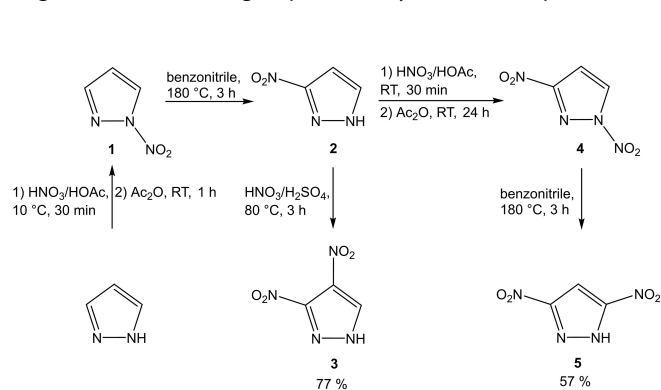
toward destructive stimuli, and form environmentally acceptable combustion products, the literature provides hardly any information on the application of metal nitropyrazolates in this area.^[14] Especially in the case of red light-producing pyrotechnics based on lithium, which was recently proposed as strontium replacement after its proven adverse effect on the skeletal development,^[15,16] the high nitrogen content of the nitropyrazoles should be advantageous. Lithium is bioactive, however, a total daily dose of roughly 200 to 1000 mg is required for the treatment of depression or bipolar disorder^[17] as opposed to the oral reference dose of 0.3 mg/kg/day for strontium.^[18] The red flame color of lithiated materials originates from the emissions of the metastable atomic species at 671 and 610 nm,^[15,19] but high flame temperatures promote higher energetic electron transitions yielding orange light.^[20] As a consequence, the flame needs to be cooled,^[20] e.g. via the release of nitrogen gas.^[21] Another requirement for a red signature by lithium is a reductive flame atmosphere,^[15] since otherwise incandescent reaction products are present covering the useful emission lines.^[22]

We herein present the lithium salts derived from 3,4-dinitro-1*H*-pyrazole, 3,5-dinitro-1*H*-pyrazole, 4-amino-3,5-dinitro-1*H*-pyrazole, 3,4,5-trinitro-1*H*-pyrazole, and 4-hydroxy-3,5-dinitro-1*H*-pyrazole that were extensively characterized by infrared spectroscopy, multinuclear magnetic resonance, elemental analysis, low-temperature single-crystal X-ray diffraction, differential thermal analysis, thermogravimetric analysis, and assessments of their sensitivities to friction, impact, and electrostatic discharge. Furthermore, their capability to serve as red coloring agents is evaluated.

Results and Discussion

Synthesis

Nitration of 1*H*-pyrazole using mixed acid takes place in 4-position.^[23] In order to introduce a nitro group in the 3-position, an indirect route over *N*-functionalization with the use of nitric acid/acetic anhydride^[24] and subsequent thermal rearrangement^[25] needs to be taken (see Scheme 1). The migration of the nitro group is thereby assumed to proceed via

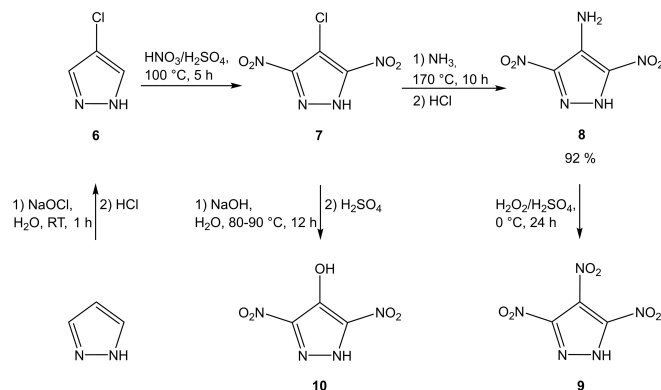


Scheme 1. Synthesis of 3,4-dinitro-1*H*-pyrazole (3) and 3,5-dinitro-1*H*-pyrazole (5).

a [1,5] sigmatropic shift and tautomerization of 3*H*-pyrazole.^[26] *N*-nitropyrazoles are less stable than the *C*-substituted analogues^[26] and their isomerization is sometimes accompanied by partial denitration.^[23] Although a lot of effort has been put into finding synthesis strategies circumventing the unstable intermediate 1-*N*-nitropyrazole (1) and into establishing milder and more environmentally benign nitration systems,^[27] the conventional method has been studied more comprehensively.^[23,26] When 1 was rearranged according to our optimized procedure,^[28] we did not encounter any problems concerning the isolation of the desired product, but with that of 1,3-dinitropyrazole (4). Commonly, after thermolysis 5 is separated from 3-nitro-1*H*-pyrazole (2) impurities by precipitation of a corresponding salt and subsequent neutralization^[5,29] or by recrystallization from benzene.^[23] This solvent is toxic, however, the high solubility of sodium 3,5-dinitropyrazolate in aqueous media makes its precipitation problematic, especially when working on a small scale. We found out that the use of a saturated sodium hydroxide solution ensures the formation of a solid.

The literature provides three different synthetic pathways towards 8: a) amination of 5 via vicarious nucleophilic substitution of hydrogen by 1,1,1-trimethylhydrazinium iodide or 4-amino-1*H*-1,2,4-triazole in the presence of potassium *tert*-butoxide,^[12,30] b) aromatic nucleophilic substitution of 4-chloro-3,5-dinitro-1*H*-pyrazole (7) or 9 by ammonia,^[6,11,30b] c) alkaline or acidic hydrolysis of the protective carbamate group of 4-carbomethoxyamino-3,5-dinitro-1*H*-pyrazole or 4-carbethoxyamino-3,5-dinitro-1*H*-pyrazole, respectively.^[11,30b] Since among these synthetic routes the one starting from 7 is the most efficient and environmentally benign and can even be scaled up to small pilot plant scale,^[6,11,12,30] it was chosen for synthesis of 8 (see Scheme 2). While 8 is readily oxidized to 9 by peroxydisulfuric acid,^[6] nucleophilic substitution of 7 by sodium hydroxide leads to 10.^[31]

Apart from 9, which hydrolyses in alkaline water^[6] and was thus treated with lithium carbonate in ethanol, all other neutral compounds were reacted with stoichiometric amounts of lithium hydroxide in aqueous solution for at least one hour at room temperature or within a shorter period of time at elevated

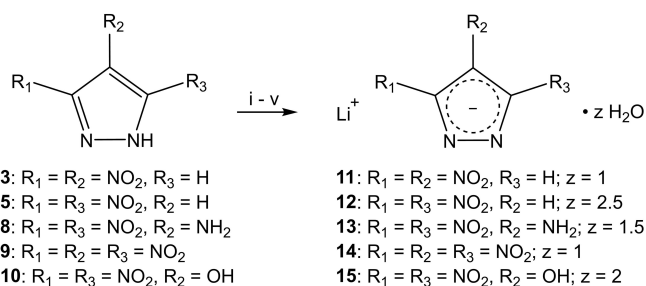


Scheme 2. Synthesis of 4-amino-3,5-dinitro-1*H*-pyrazole (8), 3,4,5-trinitro-1*H*-pyrazole (9), and 4-hydroxy-3,5-dinitro-1*H*-pyrazole (10).

temperature to give the corresponding lithium salts (see Scheme 3). While lithium 4-oxo-3,5-dinitroprazolates · 2 H₂O (**15**) precipitated from the mother liquor upon reducing its volume, the other crude products were recrystallized from different solvents.

Crystal Structures

While *Drukenmüller* et al. already refer to the difficulty of obtaining single crystals of 3,5-dinitroprazolates, even fewer crystal structures of salts of **3** and **8** are deposited in The Cambridge Crystallographic Data Centre.^[5,14,32] The search for 4-oxo-3,5-dinitroprazolates did not even return one hit. However, all salts included in this study were successfully crystallized from *iso*-propanol, ethyl acetate, ethanol, and a 1:1-mixture of water and methanol, respectively, before single-crystals were prepared and X-ray diffraction was conducted at temperatures ranging from 107 to 123 K. In contrast to elemental analysis, this analytical method indicates that **12** crystallizes as trihydrate. Furthermore, in **15** instead of the ring nitrogen atom the hydroxyl group is deprotonated due to the higher acidity of the latter functionality. **11**, **12** · 3 H₂O, and **14** crystallize in monoclinic space groups (**11**: *P*₂₁/*c*; **12** · 3 H₂O/**14**: *P*₂₁/*n*), whereas **13** and **15** both crystallize in the triclinic space group *P*–1. Comparing the densities of the corresponding neutral compounds **3**, **5**, and **9**, those of **11** and **12** · 3 H₂O would be expected to be very similar and **14** should be packed closest, but **12** · 3 H₂O contains the most units of crystal water of all investigated lithiated materials and thus has the lowest density of 1.76 g cm^{–3}. The loose packing in **12** · 3 H₂O is also reflected by the remarkably low degree of cross-linking of this polymer. While in all other structures adjacent anions are connected by lithium cations and the latter mostly share water molecules, only the second motif is to be found in **12** · 3 H₂O. The densities of **13** and **15** should both significantly exceed those of the afore-mentioned lithium pyrazolates as on the one hand extensive hydrogen bonding is formed and on the other hand ring nitrogen atoms, nitro groups as well as the oxo group should act as electron donors to the lithium cation. Astonish-



Scheme 3. Synthesis of lithium 3,4-dinitroprazolates · H₂O (**11**), lithium 3,5-dinitroprazolates (12) · 2.5 H₂O, lithium 4-amino-3,5-dinitroprazolates · 1.5 H₂O (**13**), lithium 3,4,5-trinitroprazolates · H₂O (**14**), and lithium 4-oxo-3,5-dinitroprazolates · 2 H₂O (**15**). Reagents and conditions: (i) 1) LiOH, H₂O, RT, 1 h; 2) *i*PrOH, 76%; (ii) 1) LiOH, H₂O, RT, 1 h; 2) EtOAc, 74%; (iii) 1) LiOH, H₂O, RT, 1 h; 2) EtOH, 53%; (iv) 1) Li₂CO₃, EtOH, RT, 1 d; 2) EtOH; (v) LiOH, H₂O/MeOH (1:1), 80 °C, 15 min, 86%.

ingly, the density of **13** with a value of 1.78 g cm^{–3} is the second lowest, which might originate from a disordered water molecule.

In all investigated moieties, the pyrazole ring is planar and the intracyclic bonds match those of the parent compound (1.33–1.38 Å^[33]) taking into account that the bonds in anions are in general slightly elongated.^[6] The substituents are essentially coplanar, however, the nitro groups on C1 in **11** and on C2 in **14** with torsion angles of –23° and –79 to –86°, respectively, bend out of the ring plane due to steric hindrance. Additionally to the ubiquitous classical O–H...N/O hydrogen bonds as well as the N–H...O contacts in **13** and **15** with lengths between 2.88 and 3.11 Å, non-classical C–H...O interactions with bond lengths in the range of 3.04–3.39 Å can be found in the structures of **11** and **12** · 3 H₂O. While the classical hydrogen bonds in **12** · 3 H₂O, **13**, and **15** are partially slightly shortened, those in **14** are elongated. Furthermore, the number of different donor-acceptor combinations and the total of all contacts are the lowest for **11** and **14**.

None of the coordination spheres of lithium discussed herein match regular polyhedra. In **11**, each lithium atom is tetrahedrally coordinated by one ring nitrogen each of two 3,4-dinitroprazolates units and by two water molecules, whereby the angle O5ⁱⁱ–Li1–N2ⁱ is considerably widened (see Figure 2).

In contrast to that, the lithium cations in **12** · 3 H₂O have an octahedral coordination sphere consisting of the nitro group of a 3,5-dinitroprazolates anion and five units of crystal water (see Figure 3). However, the remarkably long distances between Li1 and the nitro group O1 of 2.53 Å and especially between Li1 and the shared water molecule O6ⁱ of 2.61 Å should be noticed. The latter irregularities might also explain the fact that the crystal water content of the same sample determined by elemental analysis was only 2.5. The bridging aqua ligand might be slowly split off to reduce the amount of water included per unit cell. Even if repeated X-ray diffraction still gave the

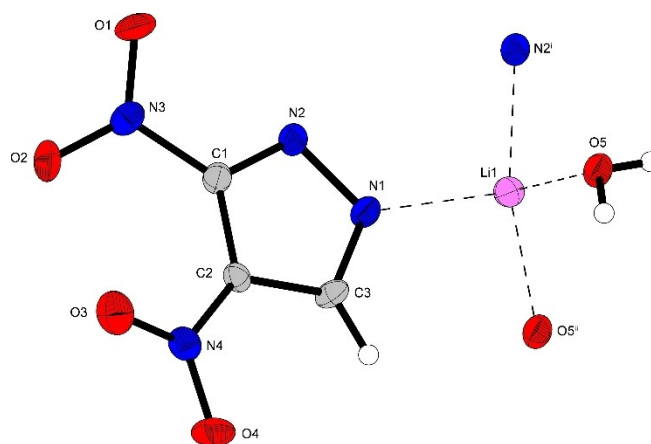


Figure 2. Advanced molecular unit of lithium 3,4-dinitroprazolates · H₂O (**11**). Selected bond lengths (Å): N1–Li1 2.044(9), N2ⁱ–Li1 2.056(9), O5–Li1 2.101(11), O5ⁱⁱ–Li1 2.098(10); selected bond angles (°): N1–Li1–N2ⁱ 106.6(4), O5ⁱⁱ–Li1–N2ⁱ 130.8(5), O5–Li1–N2ⁱ 99.3(4), O5ⁱⁱ–Li1–N1 101.0(4), O5–Li1–O5ⁱⁱ 111.2(4), O5–Li1–N1 106.0(4); symmetry codes: (i) –x, 2–y, –z; (ii) 1+x, y, z.

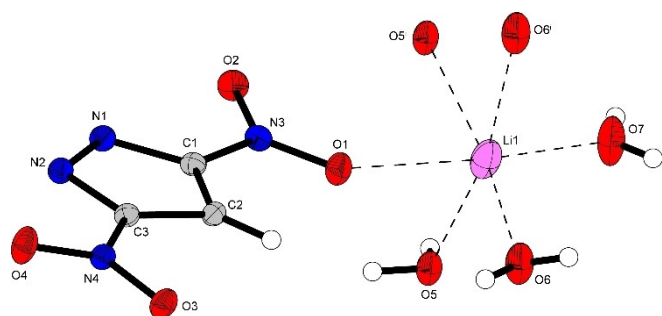


Figure 3. Advanced molecular unit of lithium 3,5-dinitropyrazolate (**12**) · 3 H₂O. Selected bond lengths (Å): O5¹–Li1 2.064(3), O7–Li1 1.961(3), O6–Li1 2.005(3), O5¹–Li1 2.184(3); selected bond angles (°): O5¹–Li1–O6 85.35(11), O5¹–Li1–O5¹ 104.35(11), O5¹–Li1–O7 98.25(11), O6–Li1–O7 96.64(12), O5¹–Li1–O7 102.36(11); symmetry code: (i) –1 + x, y, z.

trihydrate, this analytical method is less representative of the statistical distribution within the sample.

In **13**, the coordination sphere of lithium is trigonal bipyramidal and it is built by one ring nitrogen atom each of two 4-amino-3,5-dinitropyrazolate anions, one nitro functionality, and two units of bridging crystal water (see Figure 4). The channels between the resulting chains of dimers are filled with an additional half-occupied water (see Figure 5).

Interestingly, in **14** two different coordination spheres of lithium can be found: an octahedral structure motif with one ring nitrogen atom and one nitro group each of two 3,4,5-trinitropyrazolate moieties, one nitrogen of an additional anion, and an aqua ligand as well as a tetrahedral environment by one nitrogen and one nitro substituent of a nitropyrazolate unit and by two water molecules (see Figure 6). Nevertheless, similarly as with **12** · 3 H₂O the dative bonds of two of the ligands to the octahedrally coordinated lithium atom are highly elongated,

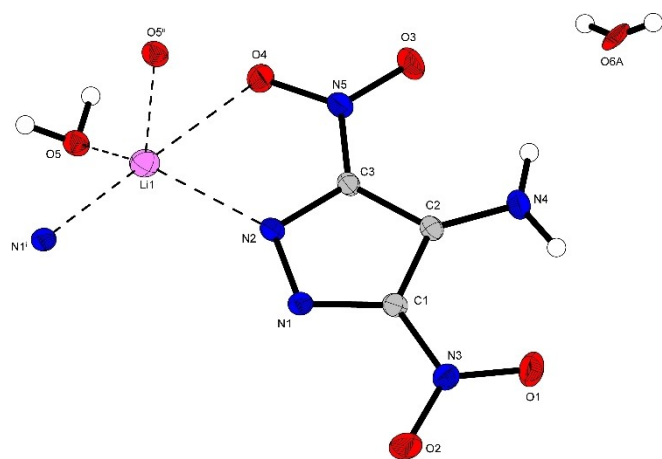


Figure 4. Advanced molecular unit of lithium 4-amino-3,5-dinitropyrazolate · 1.5 H₂O (**13**). Selected bond lengths (Å): O5¹–Li1 2.014(4), O5¹¹–Li1 1.997(4), O4–Li1 2.441(4), N2–Li1 2.100(4), N1¹–Li1 2.116(4); selected bond angles (°): O4–Li1–O5 79.37(13), O4–Li1–O5¹¹ 82.08(13), O4–Li1–N2 72.01(12), O5¹–Li1–O5¹¹ 116.23(19), O5¹¹–Li1–N2 102.99(15), O5¹–Li1–N2 127.01(18), O5¹–Li1–N1¹ 99.49(16), O5¹¹–Li1–N1¹ 99.73(16), N1¹–Li1–N2 107.76(17), O4–Li1–N1¹ 178.17(17); symmetry codes: (i) 1–x, 2–y, 1–z; (ii) –1 + x, y, z.

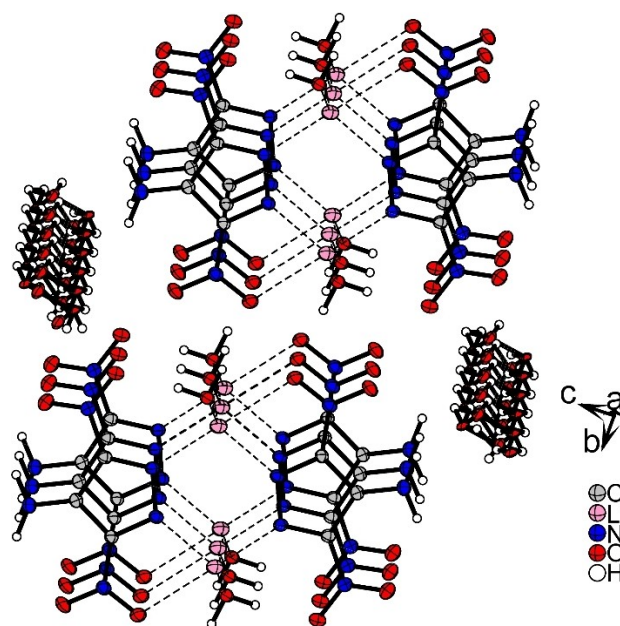


Figure 5. Macroscopic structure of lithium 4-amino-3,5-dinitropyrazolate · 1.5 H₂O (**13**).

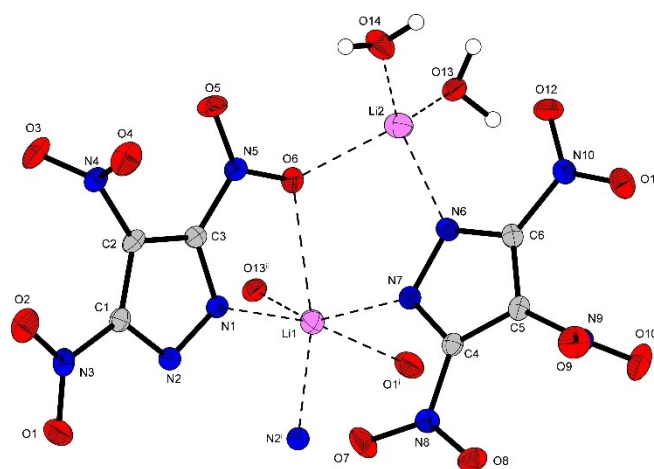


Figure 6. Advanced dimer of lithium 3,4,5-trinitropyrazolate · H₂O (**14**). Selected bond lengths (Å): N1–Li1 2.062(3), O13¹–Li1 2.172(3), N7–Li1 2.169(3), N2–Li1 2.095(3), O14–Li2 1.875(3), O13–Li2 1.965(3), N6–Li2 2.083(3), O6–Li2 2.066(3); selected bond angles (°): O13¹–Li1–N1 96.58(11), N1–Li1–N7 103.63(11), N1–Li1–N2¹ 100.19(14), O13¹–Li1–N2¹ 88.77(10), N2¹–Li1–N7 114.98(13), O6–Li2–O14 103.27(13), O14–Li2–N6 120.65(14), O13–Li2–O14 111.95(16), O6–Li2–N6 89.14(13), O13–Li2–N6 109.02(13), O6–Li2–O13 121.75(13); symmetry codes: (i) 1–x, 1–y, 1–z; (ii) –x, 1–y, 1–z.

but here it is the nitro groups (O6–Li1 2.51 Å, O1¹–Li1 2.61 Å). Additionally, N1 and O6 as well as O1¹ and N2¹ are close together, since these ligands are bound to the same pyrazole ring, respectively. The angle N2¹–Li1–N7 is remarkably widened. The tetrahedral coordination sphere is distorted in a way that the angle O6–Li2–N6 is very narrow. This is the only of the studied crystal structures in which adjacent lithium cations are not only connected by water bridges, but also by a nitro group.

The lithium cation in **15** is octahedrally coordinated by the oxo group and one nitro functionality of a 4-oxo-3,5-dinitropyrazolate unit, by one ring nitrogen atom and one nitro substituent of another anion, and by two aqua ligands (see Figure 7). The difference between the lengths of the bonds of the lithium atom to the two water molecules is the second greatest here. The coordination geometry is the most symmetric in this row and is only disturbed by the fact that the angle $O1^1-Li1-N2^1$ is narrow due to the common pyrazole ring of the ligands. The crystal structure of **15** is the only one lacking water bridges between the lithium cations.

Physico-Chemical Properties

Even if next-generation pyrotechnic formulations should have a lower impact on health and environment, they must be at least as safe as current systems.^[34] In order to evaluate the suitability of **11–15** as red colorants from this point of view, the thermal stabilities of these compounds were determined by DTA using a heating rate of 5°C min^{-1} . In the case of **11**, DTA of a sample after storage at ambient conditions for one day revealed its hygroscopicity, whereas **14** already deliquesces within a shorter period of time (see Supporting Information). This behaviour matches our findings that in the crystal structures of **11** and **14** the angles deviate the most from the expected values for the respective coordination spheres of lithium and that only weak hydrogen bonding is formed.

The large difference between the dehydration and the decomposition temperature of hydrated **12** allowed us to approach the problem of a non-homogeneous crystal water content by heating this material at 100°C overnight. Indeed, we obtained the water-free lithium salt in this way, but after

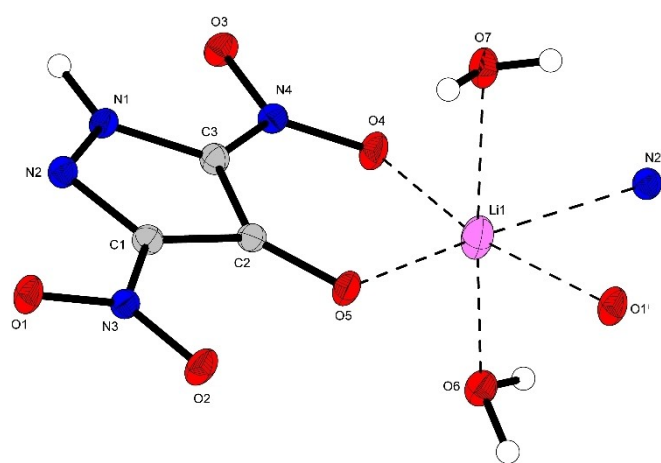


Figure 7. Advanced molecular unit of lithium-4-oxo-3,5-dinitropyrazolate-2 H_2O (**15**). Selected bond lengths (Å): O4–Li1 2.051(3), O7–Li1 2.345(3), N2¹–Li1 2.290(3), O1¹–Li1 2.102(3), O6–Li1 2.136(3), O5–Li1 1.981(3); selected bond angles ($^\circ$): O4–Li1–O7 87.77(11), O7–Li1–N2¹ 89.06(11), O1¹–Li1–O7 89.65(12), O5–Li1–O7 87.74(12), O4–Li1–N2¹ 94.82(11), O1¹–Li1–N2¹ 72.95(10), O1¹–Li1–O5 97.92(12), O4–Li1–O5 94.15(13), O4–Li1–O6 92.23(13), O6–Li1–N2¹ 87.30(11), O1¹–Li1–O6 89.58(12), O5–Li1–O6 95.90(13), O6–Li1–O7 176.35(15); symmetry code: (i) x, 1 + y, z.

exposure to air for one day the 2.5-hydrate was recovered as apparent from the reappearing endothermic signal at roughly 60°C as well as from elemental analysis (see Figure 8).

Compounds **13** and **15**, which did not show any irregularities concerning hydration, were additionally studied by TGA. While in the case of **13** the weight reduction by 4% at already 93°C indicates the loss of the disordered hemihydrate followed by the splitting of another unit of crystal water at elevated temperature (see Figure 9), the weight decrease of **15** by almost 8% at roughly 110°C correlates well with the separation of the weakly bound water molecule O7 (see Figure 10). Interestingly, the leaving of the second aqua ligand takes place at remarkably high temperature and even releases heat. Our theory to explain this phenomenon is that after the loss of the second crystal water a rearrangement to an energetically more favorable lattice takes place.

However, $12 \cdot 2.5 \text{ H}_2\text{O}$ is the most thermally stable among the investigated lithiated materials followed by **15** (see Table 1). The fact that **13** decomposes at significantly lower temperature coincides with the smaller coordination number of lithium in the respective structure. On the other hand, the latter

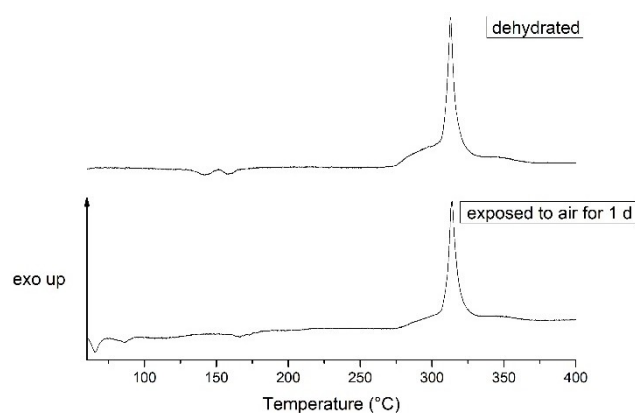


Figure 8. DTA plots of water-free lithium 3,5-dinitropyrazolate (**12**) from top to bottom after synthesis and exposure to air for one day.

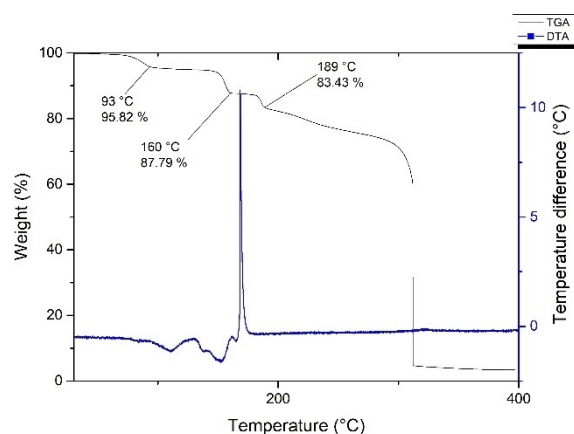


Figure 9. Combined DTA and TGA plots of lithium 4-amino-3,5-dinitropyrazolate $\cdot 1.5 \text{ H}_2\text{O}$ (**13**).

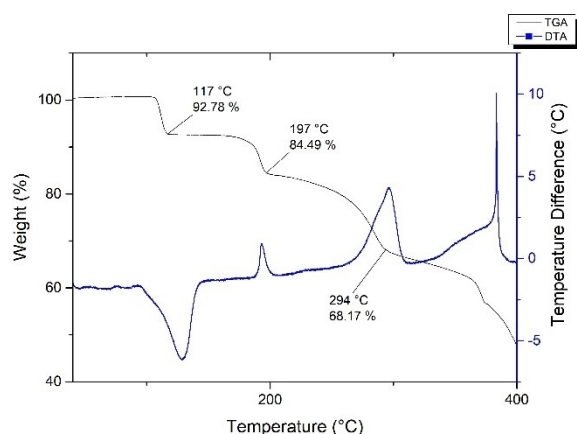


Figure 10. Combined DTA and TGA plots of lithium 4-oxo-3,5-dinitroprazole · 2 H₂O (15).

compound is only less sensitive to friction, whereas 12 · 2.5 H₂O is sensitive to impact and like 15 also responds to electrostatic discharge. Regarding all determined sensitivity parameters, 13 seems to have the highest potential as pyrotechnic ingredient at this point and will function as both color imparter and fuel in a mixture due to its negative oxygen balance.

Pyrotechnic Performance

A chlorine-free strontium-based composition^[21] was chosen as pyrotechnic matrix in order to test 13 for a red flame coloration. In the “drop-in” formulation, strontium nitrate was replaced by the ammonium oxidizer and 5-amino-1*H*-tetrazole serving as reducing agent was substituted by the new lithium salt (see Table 2). As metals unfavorably increase the flame temperature of such mixtures and the oxidation product of magnesium incandescences, the content of this fuel was reduced. The resistance of the resulting composition to moisture was attempted to be enhanced by using a higher amount of binder, still the test formulation is hygroscopic.

Figure 11 and Table 3 show that red light is emitted and the dominant wavelength almost reaches the minimum benchmark of 600 nm.^[21] While in comparison to the control the color

Table 2. Composition of a strontium-based chlorine-free reference and a test formulation containing lithium 4-amino-3,5-dinitroprazole · 1.5 H₂O (13).

	Reference	Test
Sr(NO ₃) ₂ [wt %]	48	
NH ₄ NO ₃ [wt %]		48
Mg [wt %] ^[a]	33	12
CH ₃ N ₅ [wt %]	12	
13 [wt %]		30
EPON 813/VERSAMID 140 [wt %] ^[b]	7	10

[a] Magnesium with a mesh size 50/100 (300 μm > grain size > 150 μm).
[b] EPON 813 and VERSAMID 140 in a weight percent ratio of 80:20.



Figure 11. Combustion of the test formulation.

Table 3. Physico-chemical properties of reference and test formulation.

	Reference	Test
T _{dec} (onset) [°C] ^[a]	244	173
FS [N] ^[b]	192	> 360
IS [J] ^[c]	10	10
ESD [J] ^[d]	1.0	1.4
BT [s] ^[e]	3	15
λ _d [nm] ^[f]	606	599
Σ [%] ^[g]	75	64
LI [cd] ^[h]	14083	481

[a] Onset decomposition temperature. [b] Friction sensitivity. [c] Impact sensitivity. [d] Electrostatic discharge sensitivity. [e] Burn time. [f] Dominant wavelength. [g] Spectral purity. [h] Luminous intensity.

Table 1. Physico-chemical properties of lithium 3,5-dinitroprazole (12) · 2.5 H₂O, lithium 4-amino-3,5-dinitroprazole · 1.5 H₂O (13), and lithium 4-oxo-3,5-dinitroprazole · 2 H₂O (15).

	11	12 · 2.5 H ₂ O	13	14	15
Ω _{CO₂} [%] ^[a]	-22	-19	-23	0	-11
T _{dehydr} (onset) [°C] ^[b]	141	61	93, 132	111	109, 189
T _{dec} (onset) [°C] ^[c]	141	321	168	253	269
g.s. [μm] ^[d]	> 1000	< 100	100–500		< 100
FS [N] ^[e]	288	> 360	360		> 360
IS [J] ^[f]	15	35	> 40		> 40
ESD [J] ^[g]	0.2	0.2 ^[h]	1.5		0.2

[a] Oxygen balance with respect to formation of CO₂ and Li₂O. [b] Onset dehydration temperature. [c] Onset decomposition temperature. [d] Grain size. [e] Friction sensitivity. [f] Impact sensitivity. [g] Electrostatic discharge sensitivity. [h] The electrostatic discharge sensitivity of lithium 3,5-dinitroprazole · 2.5 H₂O was measured using a grain size of 100–500 μm.

purity of the investigated pyrotechnic mixture is still acceptable, its luminosity is by far lower. Spectral purity and luminous intensity are well-known antagonists in lithium flame chemistry: if the light output is improved by generating more condensed magnesium oxide in the flame, the color purity will suffer from that.^[19] Elsewhere, the use of magnesium with a smaller particle size turned out to enhance the luminosity without significantly impairing the spectral purity.^[21] Regarding safety, the test composition is thermally stable up to 173 °C and less sensitive to friction and electrostatic discharge than the reference.

Conclusion

The hardly explored lithium salts of 3,4-dinitro-1*H*-pyrazole, 3,5-dinitro-1*H*-pyrazole, 4-amino-3,5-dinitro-1*H*-pyrazole, 3,4,5-trinitro-1*H*-pyrazole, and 4-hydroxy-3,5-dinitro-1*H*-pyrazole were investigated as potential replacements for strontium-based red pyrotechnic colorants. The neutral compounds were prepared applying common synthetic strategies, whereby the work-up of 3,5-dinitro-1*H*-pyrazole was improved, and were subsequently reacted with lithium bases. Thermal dehydration studies revealed lithium 3,4-dinitropyrazolate·H₂O and especially lithium 3,4,5-trinitropyrazolate·H₂O to be hygroscopic, whereas sensitivity assessments marked lithium 3,5-dinitropyrazolate·2.5 H₂O and lithium 4-oxo-3,5-dinitropyrazolate·2 H₂O as less useful for application in pyrotechnic items. Although the resistance of a test formulation containing lithium 4-amino-3,5-dinitropyrazolate·1.5 H₂O to moisture and its luminosity should be enhanced in the future, the capability of this lithiated material to impart red color to a flame was demonstrated.

Experimental Section

CAUTION! The reactions of pyrazole described herein, especially the multiple nitrations, are partly exothermic and the respective products, their lithium salts, and the investigated pyrotechnic formulations are potentially explosive energetic materials, which are sensitive to various environmental stimuli (e.g. heat, friction, impact or electrostatic discharge). Therefore, proper safety precautions (safety glasses, face shield, leather coat, earthed equipment and shoes, KEVLAR gloves, KEVLAR sleeves, and ear protectors) have to be taken when synthesizing and manipulating these compounds.

3,4-Dinitro-1*H*-pyrazole (3):^[23] A suspension of 3-nitro-1*H*-pyrazole (2.00 g, 18 mmol, 1 eq.) in concentrated sulfuric acid (96%, 3 mL, 56 mmol, 3 eq.) was cooled to approximately 0 °C and concentrated nitric acid (100%, 2 mL, 48 mmol, 3 eq.) was added dropwise at a rate so that the temperature was below 10 °C. After the addition of further sulfuric acid (96%, 7 mL, 131 mmol, 7 eq.), the nitration mixture was allowed to warm to room temperature and subsequently heated at 80 °C for three hours before it was quenched with ice/water (200 mL). The resulting solution was extracted with diethyl ether (3×50 mL) and the combined organic phases washed with bidistilled water (2×50 mL) and a saturated sodium chloride solution (50 mL). After the organic layers had been dried over magnesium sulfate, the solvent was evaporated to give a yellowish crystalline material (2.16 g, 14 mmol, 77%).

IR (ATR): $\tilde{\nu}$ = 3294 (m), 3260 (m), 3149 (m), 3135 (m), 2901 (w), 1768 (vw), 1541 (s), 1518 (vs), 1489 (s), 1477 (s), 1448 (m), 1426 (m), 1375 (s), 1341 (vs), 1273 (s), 1182 (w), 1154 (m), 1094 (s), 1065 (s), 935 (w), 888 (vw), 847 (m), 806 (vs), 796 (vs), 754 (s), 737 (vs), 608 (m), 575 (m), 470 (m), 445 (w) cm⁻¹. ¹⁴N{H} NMR (DMSO-*d*₆, 25 °C): δ = -25.5 (br s, NO₂) ppm. ¹³C{H} NMR (DMSO-*d*₆, 25 °C): δ = 148.1 (s, C-NO₂), 132.7 (s, CH), 126.3 (s, C-NO₂) ppm. ¹H{H} NMR (DMSO-*d*₆, 25 °C): δ = 14.90 (br s, 1H, NH), 9.13 (s, 1H, CH) ppm. EA (C₃H₂N₄O₄, 158.07): calcd. N 35.45, C 22.80, H 1.28%; found N 34.95, C 22.95, H 1.56%. DTA (5 °C min⁻¹): 72 (endothermic), 243 (exothermic) °C.

3,5-Dinitro-1*H*-pyrazole (5): 1,3-Dinitropyrazole (1.00 g, 6 mmol, 1 eq.) was thermally rearranged by heating a suspension in benzonitrile (28 mL) at 180 °C for roughly three hours. Upon addition of a saturated sodium hydroxide solution (22 mL) to the cool reaction mixture, sodium 3,5-dinitropyrazolate precipitated, which was filtered off, suspended in water (20 mL), and acidified to pH = 1 with hydrochloric acid. The resulting solution was extracted with diethyl ether (3×50 mL), dried over magnesium sulfate, and allowed to stand for crystallization. The title compound was obtained in the form of colorless crystals (0.57 g, 4 mmol, 57%).

IR (ATR): $\tilde{\nu}$ = 3202 (m), 3165 (m), 3148 (m), 1693 (vw), 1566 (m), 1527 (s), 1477 (m), 1446 (m), 1399 (m), 1365 (s), 1331 (vs), 1271 (m), 1202 (s), 1083 (m), 1054 (w), 1012 (m), 983 (s), 846 (s), 829 (vs), 815 (s), 758 (m), 742 (vs), 686 (s), 628 (m), 604 (m), 572 (m), 512 (s) cm⁻¹. ¹⁴N{H} NMR (DMSO-*d*₆, 25 °C): δ = -25.2 (br s, NO₂) ppm. ¹³C{H} NMR (DMSO-*d*₆, 25 °C): δ = 151.4 (s, C-NO₂), 99.8 (s, CH) ppm. ¹H{H} NMR (DMSO-*d*₆, 25 °C): δ = 13.57 (br s, 1H, NH), 7.94 (s, 1H, CH) ppm. EA (C₃H₂N₄O₄, 158.07): calcd. N 35.45, C 22.80, H 1.28%; found N 34.65, C 22.66, H 1.52%. DTA (5 °C min⁻¹): 167 (endothermic), 284 (exothermic) °C.

4-Amino-3,5-dinitro-1*H*-pyrazole (8):^[5] A steel autoclave containing a suspension of 4-chloro-3,5-dinitro-1*H*-pyrazole (27.00 g, 140 mmol, 1 eq.) in concentrated ammonia solution (250 mL) was heated at 170 °C for ten hours. After the reaction mixture had cooled to room temperature, it was brought to pH = 1 using concentrated hydrochloric acid. Subsequently, the solution was extracted with ethyl acetate (4×200 mL), the combined organic layers were dried over magnesium sulfate, and the solvent was removed on a rotary evaporator to yield a yellow powder (22.33 g, 129 mmol, 92%).

IR (ATR): $\tilde{\nu}$ = 3432 (m), 3319 (s), 3151 (m), 2999 (m), 2929 (m), 1634 (vs), 1578 (m), 1510 (s), 1470 (s), 1430 (s), 1392 (w), 1340 (s), 1319 (s), 1297 (s), 1230 (s), 1208 (s), 1089 (m), 991 (m), 941 (m), 925 (m), 846 (s), 827 (s), 735 (m), 721 (s), 665 (m), 640 (w), 591 (w), 517 (vs), 494 (vs) cm⁻¹. ¹⁴N{H} NMR (DMSO-*d*₆, 25 °C): δ = -23.8 (br s, NO₂) ppm. ¹³C{H} NMR (DMSO-*d*₆, 25 °C): δ = 137.7 (s, C-NO₂), 128.7 (s, C-NH₂) ppm. ¹H{H} NMR (DMSO-*d*₆, 25 °C): δ = 11.00 (br s, 1H, NH), 7.11 (br s, 2H, NH₂) ppm. EA (C₃H₃N₅O₄, 173.09): calcd. N 40.46, C 20.82, H 1.75%; found N 40.58, C 20.94, H 1.64%. DTA (5 °C min⁻¹): 159 (endothermic, followed by exothermic signal) °C.

Lithium 3,4-dinitropyrazolate·H₂O (11): The acid base reaction of 3,4-dinitro-1*H*-pyrazole (0.50 g, 3 mmol, 1 eq.) with lithium hydroxide (78 mg, 3 mmol, 1 eq.) in water (5 mL) was allowed to proceed at room temperature for one hour before the reaction mixture was filtered and the solvent was removed from the filtrate in vacuo. The residue was recrystallized from 2-propanol (70 mL) to give a light brown solid (0.44 g, 2 mmol, 76%).

IR (ATR): $\tilde{\nu}$ = 3615 (w), 3541 (m), 3416 (m), 3303 (w), 3140 (m), 1748 (vw), 1665 (m), 1531 (s), 1488 (vs), 1434 (s), 1396 (s), 1376 (s), 1337 (vs), 1286 (s), 1164 (s), 1118 (m), 1084 (s), 954 (m), 937 (w), 874 (w), 853 (s), 810 (s), 749 (s), 673 (w), 635 (m), 609 (m), 541 (s), 489 (s), 416 (m) cm⁻¹. ⁶Li{H} NMR (DMSO-*d*₆, 25 °C): δ = -1.0 (s, Li) ppm. ¹⁴N{H} NMR (DMSO-*d*₆, 25 °C): δ = -16.4 (br s, NO₂), -19.2 (br s, NO₂)

ppm. $^{13}\text{C}\{\text{H}\}$ NMR (DMSO- d_6 , 25 °C): $\delta = 150.6$ (s, C-NO₂), 137.3 (s, CH), 125.4 (s, C-NO₂) ppm. $^1\text{H}\{\text{H}\}$ NMR (DMSO- d_6 , 25 °C): $\delta = 8.19$ (s, 1H, CH), 4.11 (br s, 2H, H₂O) ppm. EA (LiC₃H₃N₄O₅, 182.02): calcd. N 30.78, C 19.80, H 1.66%; found N 29.38, C 19.81, H 1.96%. DTA (5 °C min⁻¹): 141 (endothermic, followed by exothermic signal) °C. FS (> 1000 μm): 288 N. IS (> 1000 μm): 15 J. ESD (> 1000 μm): 0.2 J.

Lithium 3,5-dinitropyrazolate (12)·2.5 H₂O: The target salt was accessed by stirring a suspension of 3,5-dinitro-1H-pyrazole (0.50 g, 3 mmol, 1 eq.) and lithium hydroxide (77 mg, 3 mmol, 1 eq.) in water (5 mL) at room temperature for one hour. Afterwards, the reaction mixture was filtered and the solvent was removed from the filtrate on a rotary evaporator. Recrystallization of the resulting solid from ethyl acetate (27 mL) afforded colorless crystals (0.49 g, 2 mmol, 74%).

IR (ATR): $\tilde{\nu} = 3599$ (m), 3537 (m), 3211 (m), 3158 (m), 2808 (w), 2610 (w), 1640 (m), 1570 (m), 1531 (s), 1513 (s), 1473 (s), 1444 (s), 1351 (vs), 1318 (vs), 1274 (s), 1205 (m), 1172 (m), 1075 (w), 1016 (s), 998 (m), 834 (s), 822 (s), 749 (s), 667 (vw), 590 (m), 557 (m), 512 (w) cm⁻¹. $^7\text{Li}\{\text{H}\}$ NMR (DMSO- d_6 , 25 °C): $\delta = 1.7$ (s, Li) ppm. $^{14}\text{N}\{\text{H}\}$ NMR (DMSO- d_6 , 25 °C): $\delta = -11.8$ (br s, NO₂) ppm. $^{13}\text{C}\{\text{H}\}$ NMR (DMSO- d_6 , 25 °C): $\delta = 155.8$ (s, C-NO₂), 98.6 (s, CH) ppm. $^1\text{H}\{\text{H}\}$ NMR (DMSO- d_6 , 25 °C): $\delta = 7.37$ (s, 1H, CH), 3.64 (br s, 5H, H₂O) ppm. EA (LiC₃H₆N₄O_{6.5}, 209.04): calcd. N 26.80, C 17.24, H 2.89%; found N 26.07, C 17.02, H 2.90%. DTA (5 °C min⁻¹): 61 (endothermic), 321 (exothermic) °C. FS (< 100 μm): > 360 N. IS (< 100 μm): 35 J. ESD (100–500 μm): 0.2 J.

Lithium 4-amino-3,5-dinitropyrazolate·1.5 H₂O (13): After a reaction mixture consisting of 4-amino-3,5-dinitro-1H-pyrazole (0.50 g, 3 mmol, 1 eq.) and lithium hydroxide (68 mg, 3 mmol, 1 eq.) in water (5 mL) had been stirred at room temperature for one hour, it was filtered and the solvent was evaporated from the filtrate in vacuo. By recrystallization of the residue from ethanol (5 mL), orange crystals were obtained (0.31 g, 2 mmol, 53%).

IR (ATR): $\tilde{\nu} = 3517$ (w), 3436 (m), 3324 (s), 3182 (m), 1639 (s), 1578 (w), 1509 (w), 1466 (s), 1427 (s), 1303 (vs), 1287 (vs), 1257 (s), 1233 (s), 1208 (s), 1146 (m), 928 (m), 842 (m), 829 (s), 758 (m), 724 (w), 674 (w), 648 (w), 551 (w), 528 (m), 498 (m), 434 (m), 427 (m), 414 (m) cm⁻¹. $^7\text{Li}\{\text{H}\}$ NMR (DMSO- d_6 , 25 °C): $\delta = -1.0$ (s, Li) ppm. $^{14}\text{N}\{\text{H}\}$ NMR (DMSO- d_6 , 25 °C): $\delta = -20.4$ (br s, NO₂) ppm. $^{13}\text{C}\{\text{H}\}$ NMR (DMSO- d_6 , 25 °C): $\delta = 142.8$ (s, C-NO₂), 131.5 (s, C-NH₂) ppm. $^1\text{H}\{\text{H}\}$ NMR (DMSO- d_6 , 25 °C): $\delta = 6.68$ (br s, 2H, NH₂), 3.64 (br s, 3H, H₂O) ppm. EA (LiC₃H₅N₅O_{5.5}, 206.04): calcd. N 33.99, C 17.49, H 2.45%; found N 34.27, C 17.79, H 2.31%. DTA (5 °C min⁻¹): 93 (endothermic), 132 (endothermic), 168 (exothermic) °C. FS (100–500 μm): 360 N. IS (100–500 μm): > 40 J. ESD (100–500 μm): 1.5 J.

Lithium 3,4,5-trinitropyrazolate·H₂O (14): 3,4,5-Trinitro-1H-pyrazole (0.25 g, 1 mmol, 2 eq.) was reacted with lithium carbonate (46 mg, 1 mmol, 1 eq.) in ethanol (10 mL) at room temperature overnight before the solvent was removed on a rotary evaporator. A yellow-brown solid was gained, which was recrystallized from ethanol (10 mL).

Lithium 4-oxo-3,5-dinitropyrazolate·2 H₂O (15): 4-Hydroxy-3,5-dinitro-1H-pyrazole (0.60 g, 3 mmol, 1 eq.) and lithium hydroxide (83 mg, 3 mmol, 1 eq.) were dissolved in water/methanol (1:1, 10 mL) and the solution heated at 80 °C for 15 minutes. The mother liquor was reduced in vacuo until yellow-orange crystals (0.64 g, 3 mmol, 86%) precipitated from solution.

IR (ATR): $\tilde{\nu} = 3500$ (w), 3400 (w), 3109 (m), 1680 (vw), 1617 (s), 1447 (m), 1389 (s), 1298 (vs), 1250 (s), 1207 (s), 982 (s), 855 (m), 835 (m), 799 (m), 761 (s), 738 (m), 603 (s), 546 (s), 531 (s), 519 (s), 467 (s) cm⁻¹. $^7\text{Li}\{\text{H}\}$ NMR (DMSO- d_6 , 25 °C): $\delta = 1.8$ (s, Li) ppm. $^{14}\text{N}\{\text{H}\}$ NMR (DMSO- d_6 , 25 °C): $\delta = -23.2$ (br s, NO₂) ppm. $^{13}\text{C}\{\text{H}\}$ NMR (DMSO- d_6 , 25 °C): $\delta = 142.1$ (s, C-O), 140.7 (s, C-NO₂) ppm. $^1\text{H}\{\text{H}\}$ NMR (DMSO-

d_6 , 25 °C): $\delta = 5.06$ (br s, 4H, H₂O) ppm. EA (LiC₃H₃N₄O₇, 216.03): calcd. N 25.94, C 16.68, H 2.33%; found N 25.86, C 16.76, H 2.39%. DTA (5 °C min⁻¹): 109 (endothermic), 189 (exothermic), 269 (exothermic) °C. FS (< 100 μm): > 360 N. IS (< 100 μm): > 40 J. ESD (< 100 μm): 0.2 J.

Deposition Numbers 2021636 (for 11), 2021637 (for 12·3 H₂O), 1998248 (for 13), 2021635 (for 14), and 2021634 (for 15) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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