

# A GENUINELY MULTIDISCIPLINARY JOURNAL

# CHEMPLUSCHEM

# CENTERING ON CHEMISTRY

# **Accepted Article**

**Title:** Isomers of Dinitropyrazoles: Synthesis, Comparison and Tuning of Their Physico-Chemical Properties

Authors: Joerg Stierstorfer, Thomas M. Klapötke, Marc F Bölter, and Alexander Harter

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemPlusChem 10.1002/cplu.201800318

Link to VoR: http://dx.doi.org/10.1002/cplu.201800318



# WILEY-VCH

www.chempluschem.org

# Isomers of Dinitropyrazoles: Synthesis, Comparison and Tuning of Their Physico-Chemical Properties

Marc F. Bölter,<sup>[a]</sup> Alexander Harter,<sup>[a]</sup> Thomas M. Klapötke,<sup>\*[a]</sup> and Jörg Stierstorfer<sup>[a]</sup>

**Abstract:** Three isomeric dinitropyrazoles (DNPs) were synthesized starting from easy available 1*H*-pyrazole by slightly improved methods than described in literature. 3,4-Dinitropyrazole (**3**), 1,3-dinitropyrazole (**4**), and 3,5-dinitropyrazole (**5**) were obtained and compared to each other with respect to thermal stability, crystallography, sensitivity and energetic performance. The two isomers (**3** and **4**) show high densities (1.79 and 1.76 g cm<sup>-3</sup>) and interesting thermal behavior as melt-castable materials (**3**: T<sub>melt.</sub> = 71 °C, T<sub>dec.</sub> = 285 °C; **5**: T<sub>melt.</sub> = 68 °C, T<sub>dec.</sub> = 171 °C). Further, eight salts (sodium, potassium, ammonium, hydrazinium, hydroxylammonium, guanidinium, aminoguanidinium and TATOT) of **3** and **5** were synthesized in order to tune performance and sensitivity values. The obtained compounds were characterized using

<sup>1</sup>H, <sup>13</sup>C, <sup>14</sup>N, <sup>15</sup>N NMR and IR spectroscopy as well as mass spectrometry, elemental analysis and thermal analysis (DSC). Crystal structures could be obtained of 14 compounds (**3-7**, **10-12** and **15-20**) by low temperature single crystal X-ray diffraction. Impact, friction and ESD values were also determined by standard methods. The sensitivity values range between 8.5 and 40 J for impact and 240 N and 360 N for friction and show mainly insensitive character. The energetic performances were calculated using recalculated X-ray densities, heats of formation and the EXPLO5 code and support the energetic character of the title compounds. The calculated energetic performances ( $V_{\rm D}$ : 6245–8610 m s<sup>-1</sup>;  $\rho_{\rm CJ}$ : 14.1–30.8 GPa) were compared to RDX.

# Accepted Manuscrip

### Introduction

Modern high energy density materials (HEDMs) have to fulfill different requirements depending on their application such as high energetic performance, high density, high heat of formation, low sensitivity toward external stimuli, thermal stability and environmental impact to replace the widely used RDX.<sup>[1]</sup> In contrast to the carcinogenic and hepatoxic RDX nitrogen-rich materials release mostly environmentally friendly dinitrogen after decomposition.<sup>[2]</sup> These goals could be achieved by azoles, such triazoles<sup>[4]</sup>, as tetrazoles<sup>[3]</sup>. imidazoles<sup>[5]</sup>, oxadiazoles<sup>[6]</sup>, furazanes<sup>[7]</sup> or pyrazoles<sup>[8]</sup>. In general the deprotonation of azoles by bases result in higher performances and thermal stabilities such as 5,5'-bistetrazole-1,1-dioxide dihydrate (V<sub>D</sub>: 8764 m s<sup>-1</sup>, T<sub>dec.</sub>: 214 °C) and its dihydroxylammonium salt (TKX-50, V<sub>D</sub>: 9698 m s<sup>-1</sup>, T<sub>dec.</sub>: 221 °C) or its potassium salt (T<sub>dec.</sub>: 335 °C).<sup>[3, 9]</sup> Nitrated pyrazoles arouse interest in the past due to their different

 [a] Prof. Dr. Thomas M. Klapötke, \* Marc F. Bölter, Alexander Harter, Dr. Jörg Stierstorfer
 Department of Chemistry
 University of Munich (LMU)
 Butenandtstr. 5–13 (D)
 81377 München (Germany)
 \* Fax: +49 89 2180 77492

E-Mail: tmk@cup.uni-muenchen.de

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. characteristics and achieve the requirements mentioned before (Figure 1).<sup>[10]</sup> The nitro groups decrease the electron density inside the pyrazole, whereas the acidity of the *N* bonded proton rises and the pKa value decreases (1*H*-pyrazole: 14.2; 3-nitropyrazole 9.81; 3,4-dinitropyrazole: 5.14, 3,5-dinitropyrazole: 3.14 and 3,4,5-trinitropyrazole: 2.35).<sup>[11]</sup> Hence, only the *C* nitrated dinitropyrazoles and trinitropyrazole (TNP) are acidic enough to get deprotonated by adding common bases (figure 1). Shreeve *et al.* reported a series of nitrogen-rich salts of TNP with rather high energetic properties, low sensitivities and high thermal stabilities.<sup>[8]</sup>



Figure 1. Overview of nitrated pyrazolates arranged according to their rising sensitivity and energetic performance.

Comparing the densities of di- and trinitrated pyrazoles the calculated density of TNP (1.867 g cm<sup>-3</sup>) is marginally higher than the ones of the two DNP isomers (1.76 and 1.79 g cm<sup>-3</sup>).<sup>[8]</sup> But the sensitivity values are with 17 J for impact and 92 N for friction higher than for TNP.<sup>[8]</sup> Nitrogen-rich salts of dinitrated pyrazoles (DNPs) have not been mentioned in the literature yet. In this work three different isomeric DNPs were synthesized by partly different

methods than literature and selected alkaline metal and nitrogenrich salts of 3,4-DNP and 3,5-DNP were prepared, intensively characterized and compared to each other.

### **Results and Discussion**

The synthesis of the three DNPs is described by. Janssen *et al.* starting from *N*-nitration of pyrazole, followed by thermal rearrangement in anisole (2) (Scheme 1).<sup>[12]</sup> A selective C4 nitration of compound 2 was carried out by using nitric acid and sulfuric acid yielding 3,4-DNP (3).<sup>[12a]</sup> Similar nitration conditions to the first step were used for the synthesis of 1,3-DNP (4).<sup>[12a]</sup> A further thermal rearrangement in benzonitrile and an easier work-up from literature gave **5** in good yields.<sup>[12a]</sup>

Starting from compounds **3** and **5** different ionic derivatives (**6**–**21**) were synthesized by deprotonation. The salts were prepared using sodium hydroxide, potassium hydroxide, ammonia, hydroxylamine, hydrazine, guanidine bicarbonate, aminoguanidine bicarbonate and TATOT (3,6,7-Triamino-[1,2,4]triazolo[4,3-b][1,2,4]triazole). Salts of compound **5** show a much better and faster crystallization behavior than the salts of compound **3**.



Scheme 1. Synthesis of 1,3-dinitropyrazole (4), 3,4-dinitropyrazole (3) and 3,5dinitropyrazole (5) as well as their ionic derivatives.

### **Crystal structures**

In this work the crystal structures of compounds **3–7**, **10–12** and **15–20** were obtained. Selected data and parameters from the low temperature X-ray data collection and refinements are given in the supporting information. Further information regarding the crystal-structure determinations have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. 1835056 (3), 1835054 (4), 1835062 (5), 1835053 (6), 1835066 (7), 1835061 (10), 1835065 (11), 1835063 (12), 1835060 (15), 1835055 (16), 1835057 (17), 1835059 (18), 1835058 (19) and 1835064 (20).

Dinitropyrazoles **3–5** crystallize in common space groups (**3**:  $P2_1/c$ ; **4**:  $P2_1/c$ ; **5**:  $Pca2_1$ ) with crystal densities between 1.796 g cm<sup>-3</sup> (**4**) and 1.827 g cm<sup>-3</sup> (**5**) at 173 K.



Figure 2. Molecular units of 3 (left) and 5 (right). Ellipsoids are drawn at the 50% probability level.

The molecular units of compounds 3-5 are shown in Figures 2 and 3.



Figure 3. Molecular unit of 4. Ellipsoids are drawn at the 50% probability level.

Compound **4** is disordered along the axis of rotation through atom N2. The bond lengths within the ring nitrogen atoms of the nitropyrazoles are between the values of a N–N single bond (1.47 Å) and a N=N double bond (1.25 Å). The nitro groups of **3** are most twisted toward the planar pyrazole ring due to their steric hindrance (**3**: –7.8(2)°, –78.83(18)°; **4**: –3.1(5)°, 17.1(8)°; **5**: – 1.7(4)°, –8.9(3)°). Further, 3,4-DNP (**3**) is stabilized due to hydrogen bonding resulting in a high decomposition temperature (T<sub>dec.</sub>: 285 °C). On the one hand classical hydrogen bonds are found involving N–H···N/O interactions and showing H···N/O distances between 2.9540(16) and 3.0572(16) Å.<sup>[13]</sup> Further, weak non-classical hydrogen bonds implicating C–H···O correlations are visible.

The molecular moieties of water free salts are depicted in Figures 4–7. The remaining crystal structures can be found in the supporting information. The potassium (**15**) and ammonium (**16**) salt of 3,5-DNP crystallize in the space group P–1. The crystal density of **15** shows the highest value of all compounds with 2.037 g cm<sup>-3</sup> whereas the density of **16** is 1.732 g cm<sup>-3</sup> at 173 K.



Figure 4. Molecular units of 15 (left) and 16 (right). Ellipsoids are drawn at the 50% probability level.

The bond lengths and angles of **15** and **16** are similar to the neutral compound **3**. Compound **16** is stabilized by various H-bonds between the ammonium cation and the anion e.g. N5-H5A...O3, N5-H5A...O1, N5-H5A...O4, N5-H5B...O2 N5-H5C...N1, N5-H5D...N2. The nitro groups of **16**  $(5.3^{\circ}; 5.1^{\circ})$  are more twisted toward the planar pyrazole ring system compared to the ammonium salt  $(2.8(2)^{\circ}; 1.3(2)^{\circ})$ .

The hydrazinium salts of both isomers (**10**, **18**) are crystallizing in the monoclinic space groups  $P2_1/c$  and  $P2_1/n$ , respectively. The nitro groups of hydrazinium salt **10** are further twisted toward the planar ring. The density of **10** (1.704 g cm<sup>-3</sup>) is higher than that of compound **18** (1.682 g cm<sup>-3</sup>). This relates to the slightly higher density of the neutral compounds **3** and **5**. The nitrogen bond

lengths of both hydrazines are very similar (**10**: N9–N10 1.444(4); **18**: N5–N6 1.446(2)) and are in the range of a typical N–N single bond.



Figure 5. Molecular units of **10** (left) and **18** (right). Ellipsoids are drawn at the 50% probability level.

Both hydrazinium cations show hydrogen bonding to the pyrazole ring nitrogen and to the oxygen of the nitro groups. The better hydrogen interaction of **18** leads to a higher decomposition temperature (figure 8).

Figures 6 and 7 depict the molecular units of the guanidinium derivatives (**11**, **12** and **20**). They all crystallize in the common space groups P-1 (**11**),  $P2_12_12_1$  (**12**) and C2/c (**20**) with densities of 1.657 g cm<sup>-3</sup> (**11**, 173 K), 1.647 g cm<sup>-3</sup> (**12**, 173 K) and 1.695 g cm<sup>-3</sup> (**20**, 100 K). The structure of **11** is dominated by strong hydrogen bonds involving all guanidinium protons and both nitro groups are twisted out of the pyrazole plane (O1–N3–C1–N1: 24.4(2)° and O4–N4–C2–C1: -168.89(16)°) due to their steric hindrance.



Figure 6. Molecular unit of 11. Ellipsoids are drawn at the 50% probability level.

Also the nitro groups of compound **12** are twisted toward the planar pyrazole ring with torsion angles of  $28.28(19)^{\circ}$  (O4–N4–C1–N1) and  $24.7(2)^{\circ}$  (O1–N3–C2–C3). Comparing the twist of the nitro groups of compound **12** and **20** they are only distorted slightly for the latter (-3.1(3)° and 4.3(2)°).





Figure 7. Molecular units of 12 (top) and 18 (bottom). Ellipsoids are drawn at the 50% probability level.

The N–N bond lengths of aminoguanidinium cations are close to a N–N single bond with distances between 1.4030(18) Å (**12**) and 1.410(2) Å (**20**). Both structures show hydrogen bonding involving all protons of the aminoguanidinium and the carbon bonded hydrogen.

### Spectroscopy

The three isomers **3–5** can easily be distinguished by <sup>1</sup>H, <sup>13</sup>C, <sup>14</sup>N and <sup>15</sup>N NMR spectroscopy as well as IR and Raman spectroscopy. Further a two dimensional <sup>1</sup>H/<sup>15</sup>N NMR HMBC spectrum was recorded for compound **4**.The NMR shifts of **3–5**, **8**, **11**, **16** and **19** are listed in table 1. In the <sup>1</sup>H NMR spectra, two hydrogen signals were observed for 1,3-DNP (9.09 and 7.44 ppm) and for 3,4-DNP (14.84 and 9.10 ppm) and one for 3,5-DNP (7.92 ppm). The reason for the missing N-H peak of 3,5-DNP might be the fact that the molecule is deprotonated in solution because of the high pK<sub>a</sub> = 3.14 value.<sup>[11a]</sup> In the <sup>13</sup>C NMR spectra, two signals were determined for 3,5-DNP (151.5 and 98.8 ppm) and three for 1,3-DNP (152.6, 130.0 and 104.7 ppm) and 3,4-DNP (148.2, 132.7 and 126.3 ppm).

### Table 1. NMR signals of compounds 3-5, 8, 11, 16 and 19.

compound	<sup>1</sup> H [ppm]	<sup>13</sup> C{ <sup>1</sup> H} [ppm]	<sup>15</sup> N [ppm]						
3	14.84, 9.10	148.2, 132.7,	-175.5, -85.0,						
		126.3	-26.1, -25.5						
4	9.09, 7.44	152.6, 130.0,	-113.5, -95.0,						
		104.7	-63.2, -25.1						
5	7.92	151.5, 98.9	-123.4, -26.4						
8	8.14, 7.12	163.5, 138.0,	-						
		125.8							
11	8.03, 6.94	157.9, 150.9,	-						
		138.1, 125.3							
16	7.30, 7.10	156.4, 98.3	-						
19	7.30, 6.93	157.9, 156.4,	-						
		98.4							

In the <sup>14</sup>N NMR spectra the resonances for the nitro groups of **3**–**15** are in the typical range between -10 and -40 ppm for carbon bonded and between -40 and -70 ppm for *N* nitrated species (**4**). The three isomers can further be distinguished by <sup>15</sup>N NMR spectroscopy (supporting information). The <sup>15</sup>N spectra of 3,5-DNP (**5**) shows two signals (-123.4 and -26.4 ppm) due to its symmetry and **3** (-175.5; -85.0, -26.1 and -25.5 ppm) and **4** (-113.5, -95.0, -63.2 and -25.1 ppm) show four, respectively. In the two dimensional HMBC NMR spectra the protons can be assigned to the carbon atoms (Figure 8). Due to the signal splitting into a doublet of doublet of the nitrogen atom at -113.5 ppm it can be assigned to the pyrazole nitrogen (N4). The larger coupling belongs to N–C–H (<sup>2</sup>J) and the smaller to the N–C–C–H (<sup>3</sup>J) coupling. The <sup>3</sup>J coupling of the proton at

9.09 ppm with the carbon bonded nitro group (N1) indicates the proton (a) to be bonded at C-4.



Figure 8. Two dimensional <sup>1</sup>H, <sup>15</sup>N HMBC spectrum of compound 3.

The characteristic absorption bands for nitro groups can be found at 1560/1329 cm<sup>-1</sup> for (3,5-DNP), 1518/1346 cm<sup>-1</sup> for (3,4-DNP) and 1351/1281 cm<sup>-1</sup> for 1,3-DNP. The bands at 1637 and 1548 cm<sup>-1</sup> were assigned to the *N*-nitro group of 1,3-DNP.

In the <sup>1</sup>H NMR spectra of 3,4-DNP salts **6–13** the hydrogen signal of DNP is observed between 8.03 and 8.30 ppm. For 3,5-DNP salts **14-21** the shift ranges from 7.28 to 7.30 ppm. In the <sup>13</sup>C NMR spectra, three resonances for the 3,4-DNP anion were observed and two for 3,5-DNP anion due to its symmetry. The signals range from 125.3–127.3 ppm (C-H), 136.9–139.1 ppm (C-NO<sub>2</sub>) and 150.3–163.5 ppm (C-NO<sub>2</sub>) for 3,4-DNP and from 98.3–98.4 ppm (C-H), 156.1–156.4 ppm (C-NO<sub>2</sub>) for 3,5-DNP.

IR spectra of compounds **6–21** were measured and the frequencies were assigned according to observed data reported in the literature.<sup>[14]</sup> The characteristic absorption bands for nitro groups of salts **6–21** were found in the region from 1527–1556 cm<sup>-1</sup> and 1335–1369 cm<sup>-1</sup>. Further the absorption bands of the primary amines were found for the nitrogen-rich cations (**8-13** and **16–21**) in the range of 3125 and 3580 cm<sup>-1</sup>. Triazole ring vibrations for **13** and **21** were found in the regions between 1583–1446 cm<sup>-1</sup>.<sup>[1h]</sup>

# Thermal Analysis, Sensitivities, Physicochemical and Energetic Properties

The different compounds were investigated in regard to their thermal behavior, sensitivities as well as their energetic properties. The decomposition temperatures were measured by differential scanning calorimetry (DSC) or differential thermal analysis (DTA) with a heating rate of 5 °C min<sup>-1</sup>. Heats of formation were calculated by the atomization method using electronic energies (CBS-4M method). The energetic parameters were calculated with EXPLO5 V6.03.<sup>[15]</sup>

The isomers **3–5** only differ in the position of the nitro groups. The melting and decomposition temperatures rise from the most instable 1,3-DNP (**4**) with 68 °C and 171 °C over compound (**3**) with 71 °C and 285 °C to compound (**5**) with 169 °C and decomposition temperature of 299 °C (Figure 9).



Figure 9. DSC plots of compounds 3–4 and DTA plot of 5 measured with a heating rate of 5  $^{\circ}$ C min<sup>-1</sup>. Critical temperatures are given as onset temperatures.

As expected all of the DNPs are not or less sensitive with IS values of 25 to 40 J, 360 N for friction sensitivity and ca. 1.5 J for electrostatic discharge sensitivity. 1,3-DNP (4) implies the lowest value of 25 J, which refers to the nitramino part, but is still higher than RDX (IS: 7.5 J). The densities of **3–5** are in between 1.76 and 1.79 g m<sup>-3</sup> at 298 K, which is nearby the density of RDX.<sup>[16]</sup> All three DNPs are isomers and therefore have the same nitrogen content and a negative oxygen balance. The compounds have positive heat of formations in the range of 73.2 kJ mol<sup>-1</sup> to 189.1 kJ mol<sup>-1</sup>. 3,5-DNP (**5**) represent the lowest value (73.2 kJ mol<sup>-1</sup>), followed by 3,4-DNP **3** (124.2 kJ mol<sup>-1</sup>) and **5** (189.1 kJ mol<sup>-1</sup>)

with the highest. The detonation pressures ( $p_{CJ}$ ) lie between 28.9 and 30.8 GPa increasing from compound (5) to compound (3). The detonation velocities ( $V_D$ ) show the same trend with values between 8279 m s<sup>-1</sup> and 8459 m s<sup>-1</sup>. Regarding the melting and decomposition behavior of the DNP salts they strongly vary with the corresponding cation (figure 10).





The sodium (6) and potassium (7) salts of 3,4-DNP compounds dehydrate at 80 °C or 88 °C followed by decomposition at 142 °C and 174 °C, respectively.

Beside compound **12**, which melts at 124 °C, all other decompose at temperatures between 101 °C and 180 °C with **13** as the highest. One reason could be the close position of the nitro groups destabilizing the molecule.

As shown in Table 2 all 3,4-DNP salts are insensitive toward impact, friction and electrostatic discharge. The two exceptions are the hydrazinium (IS: 10 J) and TATOT (IS: 30 J) salt, but nevertheless they are less sensitive than RDX (IS: 7.5 J) and are classified as less sensitive. All salts have friction sensitivity values of 360 N and the ESD value varies between 1.0 and 1.5 J, which also shows their insensitive behavior toward external stimuli. The heats of formation  $\Delta_{f} H^{\circ}$  lie in the range from negative values for the hydrates (6: -1071 kJ mol<sup>-1</sup>, 7: -675.4 kJ mol<sup>-1</sup>) to 221.2 kJ mol<sup>-1</sup> for **10**. The sodium (**6**), potassium (**7**) and guanidinium (11) salt have lower heat of formations compared to the neutral compound **3**. The densities lie between 1.61 and 1.74 g cm<sup>-3</sup> at 298 K with 6 as the highest. The calculated detonation pressures  $(p_{CJ})$  are in the range from 14.1 GPa (6) to 27.5 GPa (10). The highest p<sub>CJ</sub> value of 275 bar belongs to the hydrazinium salt (10) as well as the highest detonation velocity (V<sub>D</sub>) with a value of 8369 m s<sup>-1</sup>. Table 3 shows the properties of different 3,5-DNP salts compared to RDX. In contrast to the 3,4-DNP salts they have higher decomposition temperatures (Figure 10). Compound 15 and 16 show the best thermal stability with values of 307°C (15) and 300°C (16). One reason for the relatively high decomposition temperature is the hydrogen bonding of 16. The heats of formation lie between -298.7 kJ mol-1 (19) and 187.8 kJ mol<sup>-1</sup> (18). Therefore, the hydrazinium (18) and aminoguanidinium (19) salt have a higher heat of formation than the neutral compound 5 (Table 3).

Regarding sensitivity values most 3,5-DNP salts are not sensitive toward friction, impact and electrostatic discharge with exception of the water free potassium salt (IS: 8.5 J) and the hydrazinium (IS: 10 J) salt. The densities lie between 1.59 and 2.037 g cm<sup>-3</sup> at 298 K. The potassium salt of 3,5-DNP has the highest density, which is also higher than the neutral compound **5**. The calculated detonation pressures ( $p_{CJ}$ ) lie in the range from 19.1 GPa (**19**) to 29.6 GPa (**18**). The highest  $p_{CJ}$  value (29.6 GPa) and the highest detonation velocity ( $V_D$ : 8610 m s<sup>-1</sup>) were achieved for the hydrazinium salt (**18**).

Overall both hydrazinium salts (**10** and **18**) and the ammonium salt **16** perform nearly as well as RDX regarding its detonation properties ( $V_D$ = 8109–8610 m s<sup>-1</sup>) and are less sensitive. Further the ammonium salt is not sensitive toward impact, friction and electrostatic discharge and shows a high thermal stability of 300°C.

### **Toxicity Assessment**

To determine the toxicity to aquatic life of **5**, **7** and **15** using the luminescent marine bacterium *Vibrio fischeri* (see supporting information) was used.<sup>[17]</sup> The EC50 value (half-maximal effective concentration) of compound **5** and **7** are lower than that of RDX (see Tables 2 and 3), which implies that **5** and **7** is more toxic than RDX. Hence, the potassium salt **15** has a higher EC<sub>50</sub> value, which means that **15** is classified to be less toxic than RDX. Interestingly, the potassium salt of 3,5-DNP (**15**) is less toxic than the free acid (**5**).

### Conclusion

Nitropyrazoles are valuable energetic materials due to their large variety of substitution patterns. While mono-nitropyrazoles are

low energetic, trinitropyrazoles are characterized by an intensive synthetic protocol as well as higher sensitiveness which do not comply with new insensitive munitions regulations. Therefore in the present work, the three different dinitropyrazoles (3,4-DNP (3), 1,3-DNP (4) and 3,5-DNP (5) are synthesized, characterized and compared to each other. Their interesting thermal behavior, high detonation properties and rather low sensitivity was identified. In addition the potassium and sodium as well as six selected nitrogen-rich salts were synthesized of 3,4- (3) and 3,5-DNP (5). Densities vary between 1.59 and 1.99 g cm<sup>-3</sup>. Using EXPLO5, their detonation parameters were calculated. Their detonation velocity ranges from 6245 to 8610 m s<sup>-1</sup>. With exception of 9 (10 J), 15 (8.5 J) and 18 (10 J) their IS values are higher than 40 J. According to their rather high thermal stabilities, low sensitivity values and detonation performances they can be used as HEDM.

### **Experimental Section**

The complete experimental procedures for the synthesis of salts can be found in the supporting information.

**CAUTION!** All investigated compounds are potentially explosive energetic materials, although no hazards were observed during preparation and handling these compounds. Nevertheless, this necessitates additional meticulous safety precautions (earthed equipment, Kevlar<sup>®</sup> gloves, Kevlar<sup>®</sup> sleeves, face shield, leather coat, and ear plugs).

1-*N*-Nitropyrazole (1):<sup>[12b]</sup> 1*H*-Pyrazole (30.0 g, 495 mmol, 1.0 eq.) was dissolved in concentrated acetic acid (90 mL) and was cooled to 10 °C. Subsequently, fuming nitric acid (100 %, 21 mL, 504 mmol, 1.1 eq.) was added dropwise over 1 h, while keeping the temperature at 10 °C. The suspension was stirred for 30 min at 10 °C. Afterwards, the mixture was allowed to warm to room temperature and acetic anhydride (60 mL, 636 mmol, 1.4 eq.) was added slowly. The suspension was stirred for 1 h to receive a yellow solution, which was poured on ice afterwards. The resulting precipitate was filtered and dried on air to obtain 1 as a colorless solid (49.5 g, 438 mmol, 88 %).

<sup>1</sup>**H NMR** (400MHz, DMSO *d*<sub>6</sub>): δ (ppm) = 8.79 (dd, 1H, <sup>3</sup>J = 3.0 Hz, <sup>3</sup>J = 1.7 Hz, NO<sub>2</sub>-N-CH), 7.87 (s, 1H, N=CH), 6.70 (dd, 1H, <sup>3</sup>J = 3.0 Hz, <sup>3</sup>J = 1.7 Hz, CH); <sup>13</sup>**C NMR** (101 MHz, DMSO *d*<sub>6</sub>): δ (ppm) = 141.5 (NO<sub>2</sub>-N-CH), 126.8 (N=CH), 109.7 (C-H). **IR** (ATR, rel. int.):  $\tilde{v}$  (cm<sup>-1</sup>) = 3150 (w), 3121 (m), 1739 (w), 1608 (m), 1528 (w), 1477 (w), 1404 (w), 1371 (w), 1317 (m), 1283 (m), 1253 (m), 1228 (m), 1160 (m), 1062 (m), 1028 (m), 936 (m), 903 (m), 774 (s), 630 (s), 563 (m), 457 (m).

**5-Nitropyrazole (2):**<sup>[12a]</sup> Compound **1** (12.5 g, 111 mmol, 1.0 eq.) was suspended in anisole (250 mL) and heated for 16 h at 145 °C. Afterwards, the solution was cooled to 0 °C and the resulting precipitate was filtered, washed with cold anisole and dried on air. Compound **2** was obtained as a yellowish solid (9.91 g, 87.7 mmol, 79 %).

<sup>1</sup>**H NMR** (400 MHz, DMSO *d<sub>6</sub>*): δ (ppm) = 13.94 (s, 1H, NH), 8.02 (d, 1H,  ${}^{3}J = 2.5$  Hz, N=CH), 7.03 (d, 1H,  ${}^{3}J = 2.5$  Hz, CH);  ${}^{13}$ **C NMR** (101 MHz, DMSO *d<sub>6</sub>*): δ (ppm) = 156.3 (C-NO<sub>2</sub>), 132.3 (N=CH), 101.8 (CH); **IR** (ATR, rel. int.):  $\tilde{\nu}$  (cm<sup>-1</sup>) = 3141 (m), 3021 (w), 2974 (w), 2926 (m), 2882 (m), 1556 (s), 1510 (s), 1422 (m), 1379 (s), 1350 (s), 1249 (m), 1209 (m), 1144 (w), 1090 (m), 1048 (m), 990 (m), 928 (w), 903 (w), 821 (s), 783 (s), 752 (s), 613 (m), 537 (w).

**3,4-Dinitropyrazole (3):**<sup>[12a]</sup> Compound **2** (9.0 g, 79.6 mmol, 1.0 eq.) was dissolved in concentrated sulfuric acid (96 %, 15 mL) and the viscous solution was cooled to 0 °C. Subsequently, concentrated nitric acid (100 %, 10 mL) was added drop wise over 30 min, while keeping the temperature at 0 °C. Afterwards, further sulfuric acid (96 %, 30 mL) was added and the solution was allowed to warm to room temperature and heated at 80 °C for 3 h. The mixture was poured on ice and was extracted with diethyl ether (3x50 mL). The combined organic layers were dried over magnesium sulfate and the solvent was concentrated in vacuum. The residue was allowed to stand for crystallization. Compound (3) was obtained as yellowish crystals (8.56 g, 54.2 mmol, 68 %).

Table 2. Energetic Properties and detonation parameters of compounds 3-11 compared to RDX

	3	4	5	6·2H₂O	7·2H₂O	8	9	10	11	RDX
Formula	$C_3H_2N_4O_4$	$C_3H_2N_4O_4$	$C_3H_2N_4O_4$	C₃H₅N₄O <sub>6</sub> Na	C₃H₅N₄O <sub>6</sub> K	$C_3H_5N_5O_4$	$C_3H_5N_5O_5$	$C_3H_6N_6O_4$	C <sub>4</sub> H <sub>7</sub> N <sub>7</sub> O <sub>4</sub>	$C_3H_6N_6O_6$
FW [g mol <sup>-1</sup> ]	158.07	158.07	158.07	216.08	232.19	175.03	191.03	190.05	217.06	221.12
IS [J] <sup>a</sup>	40	25	25	40	40	40	10	40	40	7.5
<i>F</i> S [N] <sup>b</sup>	360	360	360	360	360	360	360	360	360	120
ESD [J] <sup>c</sup>	1.5	1.0	1.5	1.0	1.5	1.5	1.0	1.0	1.0	0.2
N [%] <sup>d</sup>	35.44	35.44	35.44	25.93	24.13	40.00	36.65	44.20	45.15	37.84
Ω [%] <sup>e</sup>	-30.36	-30.36	-30.36	-22.1	-20.7	-41.1	-29.3	-42.08	-55.26	-21.6
$T_{\text{dec.}} [^{\circ}C]^{f}$	71 (m.p.) 285 (dec.)	68 (m.p.) 171 (dec.)	169 (m.p.) 299 (dec.)	80 (H <sub>2</sub> O) 142 (dec.)	88 (H <sub>2</sub> O) 174 (dec.)	127	101	117	139 (m.p.) 156 (dec.)	205 <sup>[18]</sup>
ρ [g cm <sup>-3</sup> ] (298K) <sup>g</sup>	1.79	1.76	1.78	1.74	1.72	1.69°	1.72°	1.67	1.63	1.81 <sup>[16]</sup>
Δ <sub>f</sub> <i>H</i> ° [kJ mol⁻¹] <sup>h</sup>	124.2	189.1	73.2	-1071	-675.4	-	-	221.2	40.4	70.3
$\Delta_{\rm f} U^{\circ}  [\rm kJ \ kg^{-1}]^i$	864	1274	542	-4871	-2829	-	-	1268	288.7	417.0
EXPLO5 V6.03 \	/alues: <sup>g</sup>									
–Δ <sub>E</sub> U° [kJ kg <sup>−1</sup> ] <sup>j</sup>	5409	5752	5106	2070	3543	-	-	5402	3975	5845
<i>T</i> <sub>E</sub> [K] <sup><i>k</i></sup>	3956	4183	3786	1841	2665	-	-	3573	2866	3810
<i>р</i> <sub>СЈ</sub> [GPa] <sup>/</sup>	30.6	30.8	28.9	14.1	17.8	-	-	27.6	21.1	34.5
<i>D</i> [m s <sup>-1</sup> ] <sup>m</sup>	8426	8459	8279	6245	6800	-	-	8369	7585	8861
<i>V</i> <sub>0</sub> [L kg <sup>-1</sup> ] <sup>n</sup>	711	721	428	612	581	-	-	832	815	785
Toxicity:										
<i>EC</i> 50 (15 min) [a L <sup>-1</sup> ]	-	-	0.27	-	0.10	-	-	-	-	0.327
<i>EC<sub>50</sub></i> (30 min) [a L <sup>-1</sup> ]	-	-	0.19	-	0.08	-	-	-	-	0.239

<sup>a</sup> impact sensitivity (BAM drophammer, 1 of 6); <sup>b</sup> friction sensitivity (BAM friction tester, 1 of 6); <sup>c</sup> electrostatic discharge device (OZM); <sup>d</sup> nitrogen content; <sup>e</sup> oxygen balance; <sup>1</sup> decomposition temperature from DSC ( $\beta$  = 5°C); <sup>g</sup> recalculated from low temperature X-ray densities ( $\rho_{299K} = \rho_T / (1+\alpha_V(298-T_0); \alpha_V = 1.5 10^{-4} \text{ K}^{-1})$ ; <sup>h</sup> calculated (CBS-4M) heat of formation; <sup>i</sup> calculated energy of formation; <sup>j</sup> energy of explosion; <sup>k</sup> explosion temperature; <sup>l</sup> detonation pressure; <sup>m</sup> detonation velocity; " assuming only gaseous products; o measured pycnometrically at room temperature

Table 3.	Energetic	Properties	and	detonation	parameters	of (	compounds	12-21.
1 4 5 1 5 5 1	Energene	1 10001100	ana	aotoriation	puluinotoro	· · ·	oompoundo	

	12	13	14-2H₂O	15	16	17	18	19·H₂O	20	21
Formula	$C_4H_8N_8O_4$	$C_6H_8N_{12}O_4$	C₃H₅N₄O <sub>6</sub> Na	C₃HN₄O₄ K	$C_3H_5N_5O_4$	$C_3H_8N_6O_4$	$C_3H_6N_6O_4$	$C_4H_9N_7O_5$	$C_4H_8N_8O_4$	$C_6H_8N_{12}O_4$
FW [g mol <sup>-1</sup> ]	232.18	312.08	216.08	196.16	175.03	191.03	190.05	217.06	232.18	312.08
/S [J] <sup>a</sup>	40	30	40	8.5	40	40	10	40	40	40
<i>F</i> S [N] <sup>b</sup>	360	360	360	240	360	360	360	360	360	360
ESD [J] <sup>c</sup>	1.5	1.5	1.5	0.4	1.5	1.0	1.0	1.0	1.0	1.0
N [%] <sup>d</sup>	48.27	53.84	25.93	28.56	40.00	36.65	44.20	45.15	48.27	53.84
Ω [%] <sup>e</sup>	-55.2	-61.5	-22.1	-25.5	-41.1	-29.3	-42.1	-55.3	-55.2	-61.5
$T_{\text{dec.}} [^{\circ}C]^{f}$	124 (m.p.) 146 (dec.)	180	99 (H <sub>2</sub> O) 297	307	251 (m.p.) 300 (dec.)	141	200	236 (m.p.) 295 (dec.)	226 (m.p.) 232 (dec.)	225 (m.p.) 234 (dec.)
ρ [g cm <sup>-3</sup> ] (298K) <sup>g</sup>	1.61	1.71°	1.72°	1.99	1.70	1.72°	1.74	1.59	1.64	1.62°
∆ <sub>f</sub> <i>H</i> ° [kJ mol <sup>–1</sup> ] <sup>h</sup>	149.4	-	-	-194.8	34.0	-	187.8	-298.7	108.1	-
∆ <sub>f</sub> <i>U</i> ° [kJ kg <sup>−1</sup> ] <sup>i</sup>	750.3	-	-	-936.1	293.4	-	1091.8	-1159.4	572.4	-
EXPLO5 V6.03 v	alues: <sup>g</sup>									
–Δ <sub>E</sub> U° [kJ kg <sup>−1</sup> ] <sup>j</sup>	4273	-	-	4235	4764	-	5315	3295	4113	-
$T_{E}  [K]^k$	2982	-	-	3064	3298	-	3481	2486	2893	-
<i>р</i> сј [GPa] <sup>/</sup>	22.2	-	-	22.5	25.9	-	29.6	19.1	22.6	-
<i>D</i> [m s <sup>-1</sup> ] <sup><i>m</i></sup>	7788	-	-	7557	8109	-	8610	7319	7848	-
<i>V</i> <sub>0</sub> [L kg <sup>-1</sup> ] <sup>n</sup>	841	-	-	397	794	-	823	488	473	-
Toxicity:										
<i>EC<sub>50</sub></i> (15 min) [g L <sup>-1</sup> ]	-	-	-	1.21	-	-	-	-	-	-
EC <sub>50</sub> (30 min)	-	-	-	0.95	-	-	-	-	-	-

lg L' a

<sup>y -</sup> j <sup>7</sup> impact sensitivity (BAM drophammer, 1 of 6); <sup>b</sup> friction sensitivity (BAM friction tester, 1 of 6); <sup>c</sup> electrostatic discharge device (OZM); <sup>d</sup> nitrogen content; <sup>e</sup> xygen balance; <sup>f</sup> decomposition temperature from DSC (β = 5°C); <sup>g</sup> recalculated from low temperature X-ray densities (p<sub>298K</sub> = p<sub>T</sub> / (1+αν(298-T₀); αν = 1.5 sygen balance; <sup>*t*</sup> decomposition temperature from DSC ( $\beta = 5^{\circ}$ C); <sup>*g*</sup> recalculated from low temperature X-ray densities (p<sub>298K</sub> – p<sub>1</sub> / () () (100 (200 - 10), 0V - 1.0) 10<sup>-4</sup> K<sup>-1</sup>; <sup>*h*</sup> calculated (CBS-4M) heat of formation; <sup>*t*</sup> calculated energy of formation; <sup>*t*</sup> energy of explosion; <sup>*k*</sup> explosion temperature; <sup>*t*</sup> detonation pressure; <sup>*m*</sup> detonation velocity; " assuming only gaseous products; o measured pycnometrically at room temperature.

1,3-Dinitropyrazole (4):<sup>[12a]</sup> Compound 2 (5.0 g, 43 mmol 1.0 eq.) was suspended in acetic acid (100 %, 31 mL) and concentrated nitric acid (100 %, 4.14 mL) was added at r.t. to the suspension. The reaction was stirred for 30 min. at which the solution turned purple. Afterwards acetic anhydride (10 mL) was added and the solution was stirred for 24 h at room temperature. The mixture was poured on ice and extracted with ethyl acetate (3x50 mL). The combined organic layers were dried over magnesium sulfate and the solvent was concentrated in vacuum. The residue was stand for crystallization to give 4 as yellowish needles (5.77 g, 36.6 mmol, 85 %).

<sup>1</sup>H NMR (400 MHz, DMSO d<sub>6</sub>): δ (ppm) = 9.09 (s, 1H, CH), 7.44 (s, 1H, CH); <sup>13</sup>C NMR (101 MHz, DMSO *d*<sub>6</sub>): δ (ppm) = 152.55 (N=C-NO<sub>2</sub>), 129.97 (CH),

104.73 (CH); <sup>14</sup>N NMR (DMSO *d<sub>b</sub>*): δ (ppm) = -62.4 (*N*-NO<sub>2</sub>), -23.5 (*C*-NO<sub>2</sub>); <sup>15</sup>N NMR (DMSO *d<sub>b</sub>*): δ (ppm) = -113.5 (N), -95.0 (N-NO<sub>2</sub>), -63.2 (*N*-NO<sub>2</sub>), -25.1 (*C*-NO<sub>2</sub>); **IR** (ATR, rel. int.):  $\tilde{v}$  (cm<sup>-1</sup>) = 3170 (w), 3156 (w), 1740 (w), 1637 (m), 1548 (m), 1515 (w), 1471 (w), 1435 (w), 1398 (m), 1351 (m), 1323 (m), 1281 (s), 1237 (s), 1113 (s), 1039 (s), 983 (m), 961 (m), 899 (w), 810 (s), 781 (s), 753 (s), 616 (w), 567 (m), 523 (w), 485 (w); **Raman** (1064 nm, 200 mW, cm<sup>-1</sup>):  $\tilde{v} = 3173(17)$ , 3159(11), 2836(8), 2753(5), 1638(16), 1549(22), 1521(17), 1474(14), 1437(58), 1400(100), 1320(21), 1324(21), 1289(31), 1238(16), 1212(10), 1116(13), 1102(11), 1044(10), 986 (25), 964(37), 932(9), 986(9), 823(17), 788(9), 569(9); **Elemental analysis**: calcd. (%) for C<sub>3</sub>H<sub>2</sub>N<sub>4</sub>O<sub>4</sub> (M = 158.07 g mol<sup>-1</sup>): C 22.80, H 1.28, N 35.44; found: C 23.8, H 1.37, N 35.34;; **DSC** (5 °C min<sup>-1</sup>): Tmet. = 68 °C, Tdec. = 175 °C. **Sensitivities** (grain size: < 100 µm): **BAM impact**: 25 J, **BAM friction**: 360 N, **ESD**: 1.0 J.

**3,5-Dinitropyrazole (5):**<sup>[12a]</sup> Compound **4** (9.0 g, 56.6 mmol, 1.0 eq.) was suspended in benzonitrile (250 mL) and heated at 180 °C for 3 hours. After cooling down the solution aqueous sodium hydroxide (2 M, 200 mL) was added and the precipitate was collected by filtration. The precipitate was acidified with conc. HCI to pH=1 and extracted with diethyl ether (3x100 mL). The combined organic layers were dried over magnesium sulfate and the solvent removed to yield **5** (7.0 g, 44 mmol, 78 %).

**H** NMR (400 MHz, DMSO *d<sub>b</sub>*): δ (ppm) = 7.92 (s, 1H, CH) <sup>13</sup>C NMR (101 MHz, DMSO *d<sub>b</sub>*): δ (ppm) = 151.53 (N=C-NO<sub>2</sub>), 99.78 (CH); <sup>14</sup>N NMR (DMSO *d<sub>b</sub>*): δ (ppm) = -24.8 (NO<sub>2</sub>); <sup>15</sup>N NMR (DMSO *d<sub>b</sub>*): δ (ppm) = -123.4 (N), -26.4 (NO<sub>2</sub>); **IR** (ATR, rel. int.):  $\tilde{v}$  (cm<sup>-1</sup>) = 3156 (w), 1712 (w), 1640 (m), 1550 (m), 1510 (m), 1436 (w), 1398 (m), 1329 (m), 1282 (s), 1237 (s), 1174 (w), 1111 (s), 1039 (s), 983 (m), 809 (s), 779 (s), 751 (s), 618 (w); Raman (1064 nm, 200 mW, cm<sup>-1</sup>):  $\tilde{v}$  = 3151(4), 1600(2), 1576(4), 1571(4), 1552(9), 1541(8), 1504(2), 1486(3), 1447(15), 1442(14),1431(11), 1401(100), 1358(4), 1341(5), 1273(4), 1196(4), 1025(1), 1015(3), 1005(3), 985(4), 848(1), 833(1), 762(1), 350(4), 286(6), 96(25), 75(6); Elemental analysis: calcd. (%) for C<sub>3</sub>H<sub>2</sub>N<sub>4</sub>Q<sub>4</sub> (M = 158.07 g mol<sup>-1</sup>): C 22.80, H 1.28, N 35.44; found: C 23.04, H 1.28, N 35.76; **DTA** (5 °C min<sup>-1</sup>): T<sub>melt</sub>. = 171 °C, T<sub>dec</sub>. = 299 °C; **Sensitivities** (grain size: < 100 µm): **BAM impact**: 25 J, **BAM** friction: 360 N, **ESD**: 1.0 J.

### Acknowledgements

Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the Office of Naval Research (ONR) under grant no. ONR.N00014-16-1-2062 is gratefully acknowledged. The authors acknowledge collaborations with Dr. Mila Krupka (OZM Research, Czech Republic) in the development of new testing and evaluation methods for energetic materials and with Dr. Muhamed Suceska (Brodarski Institute, Croatia) in the development of new computational codes to predict the detonation and propulsion parameters of novel explosives. We are indebted to and thank Drs. Betsy M. Rice, Jesse Sabatini and Brad Forch (ARL, Aberdeen, Proving Ground, MD) for many inspired discussions. We thank Mr. Stefan Huber for help with the sensitivity testing and Mrs. Cornelia C. Unger for the toxicity measurements.

Parts of this work were presented on the NTREM conference 2017.  $^{\left[ 19\right] }$ 

**Keywords:** Energetic materials • Pyrazoles • Nitration• Structure Elucidation • Cations

a) P. Yin, L. A. Mitchell, D. A. Parrish, J. M. Shreeve, *Chem. Asian J.* 2017, *12*, 378–384; b) R. Haiges, K. O. Christe, *Inorg. Chem.* 2013, *52*, 7249–7260; c) G. A. Parker, G. Reddy, M. A. Major, *Int. J. Tox.* 2006, *25*, 373– 378; d) R. Meyer, J. Köhler, A. Homburg, *Explosives*, Wiley-VCH, Weinheim, 2016; e) M. Zhang, W. Fu, C. Li, H. Gao, L. Tang, Z. Zhou, *Eur. J. Inorg. Chem.* 2017, 2017, 2883–2891; f) V. Thottempudi, H. Gao, J. M. Shreeve, *J. Am. Chem. Soc.* 2011, *133*, 6464–6471; g) H. Xue, S. W. Arritt, B. Twamley, J. M. Shreeve, *Inorg. Chem.* 2004, *43*, 7972–7977; h) T. M. Klapötke, P. C. Schmid, S. Schnell, J. Stierstorfer, *Chem. Eur. J.* 2015, *21*, 9219–9228; i) T. M. Klapötke, *High Energy Density Materials*, Springer, Berlin, Heidelberg, 2007.

[1]

- a) L. M. Sweeney, C. P. Gut, M. L. Gargas, G. Reddy, L. R. Williams, M. S. Johnson, *Reg. Tox. Pharmacol.* 2012, 62, 107–114; b) J. Giles, *Nature* 2004, 427, 580–581; c) M. B. Talawar, R. Sivabalan, T. Mukundan, H. Muthurajan, A. K. Sikder, B. R. Gandhe, A. S. Rao, *J. Hazard. Mater.* 2009, 161, 589–607.
- [3] N. Fischer, D. Fischer, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, J. Mat. Chem. 2012, 22, 20418–20422.
- [4] T. M. Klapötke, P. C. Schmid, S. Schnell, J. Stierstorfer, J. Mat. Chem. A 2015, 3, 2658–2668.
- [5] T. M. Klapötke, A. Preimesser, J. Stierstorfer, Z. anorg. allg. Chem. 2012, 638, 1278–1286.
- [6] H. Wei, C. He, J. Zhang, J. M. Shreeve, Angew. Chem. Int. Ed. 2015, 54, 9367–9371.
- [7] Y. Liu, J. Zhang, K. Wang, J. Li, Q. Zhang, J. M. Shreeve, Angew. Chem. Int. Ed.2016, 55, 11548–11551.
- [8] Y. Zhang, Y. Guo, Y.-H. Joo, D. A. Parrish, J. M. Shreeve, *Chem. Eur. J.* **2010**, *16*, 10778–10784.
- a) T. M. Klapötke, M. Leroux, P. C. Schmid, J. Stierstorfer, *Chem. Asian J.* 2016, *11*, 844–851; b) N. Fischer, T. M. Klapötke, M. Reymann, J. Stierstorfer, *Eur. J. Inorg. Chem.* 2013, 2013, 2167–2180.
- [10] P. Yin, J. Zhang, D. A. Parrish, J. M. Shreeve, *Chem. Eur. J.* 2014, 20, 16529–16536.
- a) J. Catalan, J. Elguero, Adv. Heterocycl. Chem., 1987, Vol. 41, 187–274; b) G. Hervé, C. Roussel, H. Graindorge, Angew. Chem. Int. Ed. 2010, 49, 3177–3181.
- [12] a) J. W. A. M. Janssen, H. J. Koeners, C. G. Kruse, C. L.
  Habrakern, J. Org. Chem. 1973, 38, 1777–1782; b) R.
  Hüttel, F. Büchele, P. Jochum, Chem. Ber. 1955, 88, 1577–1585.
- [13] S. Thomas, Angew. Chem. Int. Ed. 2002, 41, 48–76.
- [14] M. Hesse, H. Meier, B. Zeeh, Spektroskopische Methoden in der Organischen Chemie, 7<sup>th</sup> edn., Thieme, Stuttgart, New York, **2005**.
- [15] T. Altenburger, T. M. Klapötke, A. Penger, J. Stierstorfer, Z. anorg. allg. Chem. 2010, 636, 463–471.
- [16] C. S. Choi, E. Prince, *Acta Cryst. B* **1972**, *28*, 2857–2862.
- [17] G. I. Sunahara, S. Dodard, M. Sarrazin, L. Paquet, G. Ampleman, S. Thiboutot, J. Hawari, A. Y. Renoux, *Ecotoxicol. Environ. Saf.* **1998**, *39*, 185–194.
- [18] H. Maruizumi, D. Fukuma, K. Shirota, N. Kubota, Propellants, Explos., Pyrotech. **1982**, 7, 40–45.
- [19] M. F. Bölter, T. M. Klapötke, J. Stierstorfer, Proceedings of the seminar on New Trends in Research of Energetic Materials, Czech Republic, 2017, 538–547.

Received: ((will be filled in by the editorial staff)) Revised: ((will be filled in by the editorial staff)) Published online: ((will be filled in by the editorial staff))

# **Table of Contents**

# **FULL PAPER**

Three different isomeric dinitropyrazoles are synthesized, characterized and compared to each other. They show good thermal and physical stability well as as appropriate energetic performances. Several ionic derivatives were additionally prepared to tune performance and sensitivity values.



### N-Heterocycles

Thomas M. Klapötke,<sup>\*</sup> Marc F. Bölter, Alexander Harter, Jörg Stierstorfer

Isomers of Dinitropyrazoles: Synthesis, Comparison and Tuning of Their Physico-Chemical Properties