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Alkyl-Bridged Nitropyrazoles – Adjustment of Performance and Sensitivity Parameters

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Starting from 3,5-dinitro-4-methylaminopyrazole (**2**), six different energetic salts and three new derivatives of methylene bridged nitropyrazoles were synthesized. The derivatives bear a methylamino (**4**), methylnitramino (**5**), and azido group (**7**). All compounds were intensively characterized using single crystal X-ray diffraction, multinuclear NMR spectroscopy, IR spectroscopy, mass spectrometry, elemental analysis and DTA/TGA measurements. The sensitivities were determined according to BAM standard methods and the energetic properties calculated using the EXPLO5 code. The energetic salts were compared with each other and with **ANTA** in terms of their energetic properties. On the basis of the methyl- and ethyl bridged derivatives, it was shown how the introduction of methylamino (**4**) and methylnitramino (**5**) groups in an alkyl-bridged nitropyrazole system modify its properties (performance & sensitivities). In addition, azido compound **7** was contrasted with its literature-known constitutional isomer and investigated for its suitability as a potential metal-free primary explosive.

Introduction

The research and development of energetic materials looks back on a long history of innovation. More recently, the aspect of toxicity and environmental compatibility has moved into focus.[1] Nevertheless, striving for better-performing compounds is still a major priority. One of the most common strategies is the use of poly-nitro compounds such as nitropyrazoles, which are reported to be powerful energetic materials.[2] These compounds find use in all areas of energetic materials.[3,4] In addition to the beneficial properties that a nitro group implies, such as positive oxygen balance and increase in density, the reduced stability and enthalpy of formation,[5] as well as the increasing acidity[6] of the compounds are common disadvantages. High acidity often causes compatibility problems with other substances or in formulations, which can be overcome, for example, by *N*-alkylation of the acidic NH position as in 1-methyl-2,4,5-trinitroimidazole[7] or 1-methyl-3,4,5-trinitropyrazole.[8] In the same way, the insertion of an alkyl bridge is also possible. Ethyl- and methyl-bridged aminodinitro- or trinitropyrazoles can be found as examples in the literature.[5,9,10] These compounds are characterized not only by high thermal stability (e.g. bis(4-amino-3,5-dinitropyrazolyl)ethane T_{dec} = 311 °C), but in the case of bis(3,4,5-trinitropyrazolyl)methane **BTNPM** also by a particularly high performance (V_{det} = 9292 m s^{-1}), which is in the range of the famous explosive CL-20. However, the impact sensitivity of **BTNPM** is critical. With a value of 4 J, it is at the lower accepted limit for secondary explosives,[11] making safe industrial handling difficult. Comparing the compound to its ethyl-bridged analog (bis(3,4,5-trinitropyrazolyl)ethane) **BTNPE** (Figure 1), the effect of the alkyl chain elongation is not only an improvement in sensitivity (**BTNPM** IS: 4 J, FS: 144 N; **BTNPE** IS: 25 J, FS: 160 N), but also in thermal stability (**BTNPM** T_d = 205 °C; **BTNPE** T_d = 250 °C). In this work, we investigated how the introduction of methylamino and methylnitramino groups into alkyl-bridged nitropyrazoles affects the energetic properties. The introduction of methyl groups or alkyl chains, which increase the molecular degrees of freedom, can partially influence the melting point of a compound.[2,12,13] Therefore, we were also interested if this concept would turn our compounds into potential melt cast explosives.

Di- and trinitropyrazoles are not stable towards nucleophiles, as they undergo a nucleophilic nitro group replacement. The substituent in the N1 position determines which nitro group is replaced. In the case of *N*-unsubstituted 3,4,5-trinitropyrazole **TNP** the nitro group at the C4 position is functionalized, while the *N*-substituted **TNP** provides access to C5 functionalization (Figure 2A).[14,15] These rules also affect bridged **TNP**, causing for example **BTNPM** to be unstable towards bases such as NaOH or KOH due to nucleophilic attack of a hydroxide anion (Figure 2B).

On the other hand, this property can be utilized to establish new compounds. This work involves the reaction of **BTNPM** with an azide anion as a nucleophile and the characterization of the obtained product as a potential primary explosive.

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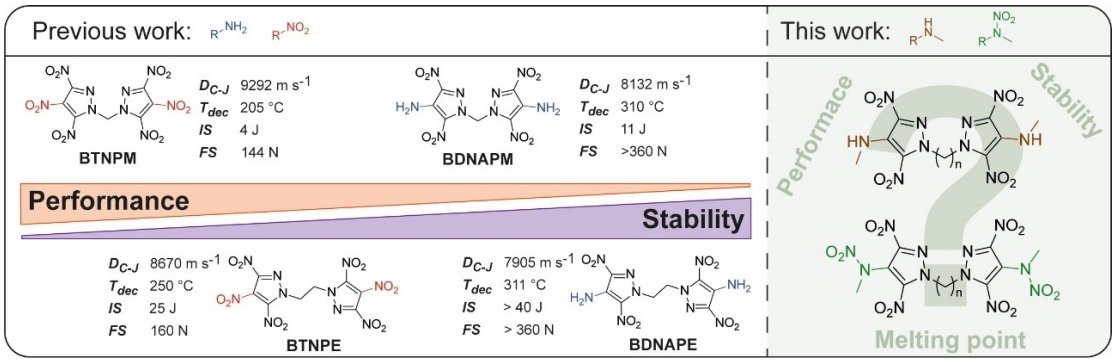


Figure 1. Different alkyl bridged nitropyrazoles with trends in terms of their performance and stability.

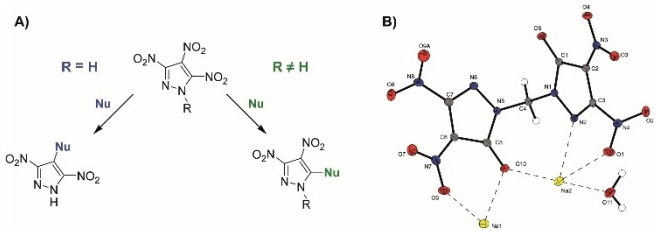


Figure 2. A) Reaction of 3,4,5-trinitropyrazole with nucleophiles; **B)** Molecular unit cell of disodium bis(3,4-dinitro-5-oxypyrazolyl)methane semihydrate **Na_2BDNOPM**. Reaction conditions: **BTNPM** 1 eq., NaOH 4 equiv. in boiling water (10 min).

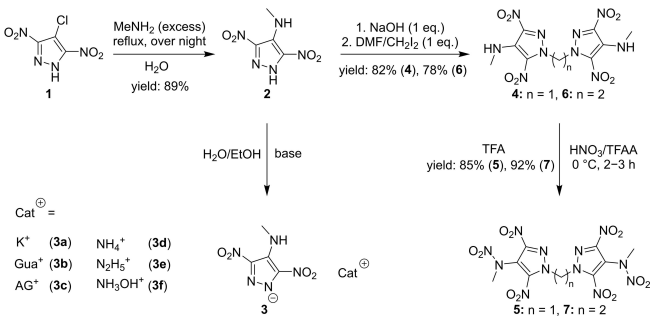
Results and Discussion

Synthesis

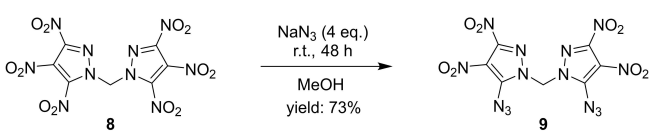
The synthesis starts with literature known 4-chloro-3,5-dinitropyrazole (**1**) prepared by chlorination of pyrazole[16,17] followed by a nitration at 100 °C using mixed acid.[14,18] The synthesis of 3,5-dinitro-4-methylaminopyrazole (**2**) was described by Dalinger et al.[14] For the substitution reaction, commercially available 40% aqueous solution of methylamine was used as *N*-nucleophile. The reaction was performed in a stainless steel autoclave yielding 65% of the desired product. In the course of this work, it was found, that longer reaction times (16 h, overnight) could avoid the use of a steel bomb. At the same time, methylamine equivalents could be reduced by half (from 20 equiv. to 10 equiv.) and the yield increased to 89%. Depending on the method of drying at the end of work-up, **2** can be obtained as a hydrate in form of a yellow powder (air-dried) or as an anhydrous, orange powder (dried at 50 °C, over night).

Starting from the anhydrous compound, six different ionic derivatives (**3a**–**3f**) were synthesized by simple acid-base chemistry. The salts were prepared in a water/ethanol mixture using a stoichiometric amount of the corresponding base while heating at 80 °C for 10 min. Sodium salt of **2** was further treated with diiodomethane or dibromoethane in DMF to give bis(3,5-dinitro-4-methylaminopyrazol-1-yl)methane (**4**) or -ethane (**6**) in an impressive yield of 82% and 78% respectively, over two steps. During work-up, it is important to quench slowly onto water under vigorous stirring to avoid the formation of sticky agglutinations. Many attempts have been made to nitrate **4**. Nitration with fuming nitric acid, mixed acid and acetyl nitrate under various conditions including reaction time and temperature failed. Bis(3,5-dinitro-4-methylnitraminopyrazol-1-yl)methane (**5**) and -ethane (**7**) were obtained through application of trifluoroacetyl nitrate as nitrating agent. For the high yield (85% and 92%) and purity, the use of trifluoroacetic acid as a solvent was necessary (Scheme 1).

For the synthesis of bis(5-azido-3,4-dinitropyrazol-1-yl)methane (**9**), bis(3,4,5-trinitropyrazol-1-ly)methane (**8**), prepared according to Fischer et al.,[9] was reacted with an excess of sodium azide at room temperature. In this process, the nitro group at the C5-position is substituted by an azido group in a nucleophilic substitution reaction (Scheme 2). After about 20 min, the suspension turns into a dark brown color. The complete reaction is achieved, when the color changes to yellowish-beige (approx. 48 h). By recrystallization from hot



Scheme 1. Synthesis of bis(3,5-dinitro-4-methylaminopyrazolyl)methane (**4**) and –ethane (**6**), bis(3,5-dinitro-4-methylnitraminopyrazolyl)methane (**5**) and –ethane (**7**) and energetic salts (**3a**-**3f**).



Scheme 2. Synthesis of bis(5-azido-3,4-dinitropyrazolyl)methane (**9**).

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ethanol and the required amount of acetonitrile until complete dissolution, the former powdery product can be transformed into a fine microcrystalline form.

Crystal structures

Suitable crystals could be obtained for compounds **2**, **3a**–**3f**, **4**–**7**, and **9** by recrystallization (**2**, **3b**, **3c**, **3e**: ethanol/water; **4**: acetone; **5**: ethanol; **7**: acetonitrile; **9**: ethanol/acetonitrile) or directly (**3a**, **3d**, **3f**, **6**) from the reaction mixture. Information on the X-ray measurements and refinements are given in the Supporting Information. Further information regarding the X-ray structure determinations were deposited in the CCDC database with the numbers: **Na_2BDNOPM**: 2076051, **2**: 2176049, **2Na**: 2176043, **3a**: 2176052, **3b**: 2176050, **3c**: 2176045, **3d**: 2176044, **3e**: 2176048, **3f**: 2176047, **4**: 2176046, **5**: 2176054, **6**: 2226156, **7**: 2226155, **9**: 2176053.

Ellipsoids of non-hydrogen atoms in all structures are drawn at the 50% probability level.

The crystal structures of the obtained six salts of 3,5-dinitro-4-methylaminopyrazole (**3**) are shown in Figure 3. None of the compounds does involve water molecules in the structures.

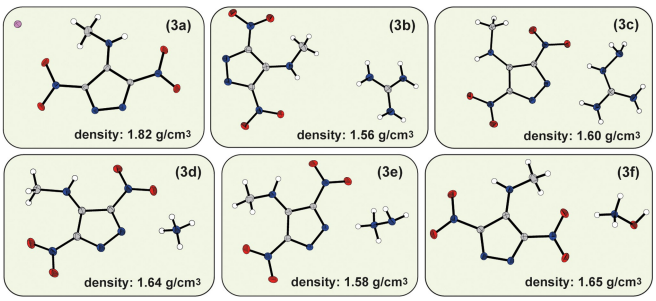

Figure 3. Molecular units of energetic salts **3a**–**3f**.

Deprotonation during salts formation occurs at the pyrazole ring, since the ring carries the most acidic proton.

Compound **4** and **6** crystallize from acetone or ethanol in form of yellow platelets or blocks in common space groups (**4**: *P*-1; **6**: *P*bca) with two and four molecules per unit cell, a cell volume of 715.73(4) Å^3 and 1535.77(19) Å^3 and a calculated density of 1.792 g cm^{-3} at 107 K and 1.731 g cm^{-3} at 173 K, respectively. Molecular units and extended structures are illustrated in Figure 4.

In both structures all pyrazole ring bonds lengths (e.g. **4**: N1–C1 1.386(3) Å, C1–C2 1.401(3) Å, N7–N6 1.318(2) Å; 6: C1–N2 1.332(2), C2–C3 1.413(3), N1–N2 1.317(2)) are in the typical range for substituted pyrazoles.[19] Bond lengths for the methylene bridge are found to be 1.443(3) Å for C5–N1 and 1.497(2) Å for C5–N6 and for the ethylene bridge 1.465(2) Å. The rings in structure **4** are twisted approximately orthogonally (N2–N1–C5–N6 98.82(19)° and N7–N6–C5–N1 5.5(3)°) to each other. The hydrogens of the methylamino groups (**4**: N4H, N9H; **6**: N5H) form a hydrogen bond to the oxygen atoms O4 and O8 (**4**) or O3 (**6**) from the respective nitro groups. Only one of the methyl group hydrogens in structure **4** forms non-classical hydrogen bonds to the nitro group oxygen atom O6 (H9 C–O6 2.269 Å).

Compound **5** and **7** crystallize from hot ethanol or acetonitrile in form of colorless platelets in the common space group *P*-1 with eight and one molecules per unit cell, a cell volume of 3609.2(3) Å^3 and 463.97(6) Å^3 and a calculated density of 1.753 g cm^{-3} and 1.755 g cm^{-3} at 173 K, respectively. Molecular units and extended structures are illustrated in Figure 5.

The values for the bond lengths of the pyrazole rings and the bridge are comparable to those of **4** and **6**. The position of the two pyrazole rings relative to each other changes from

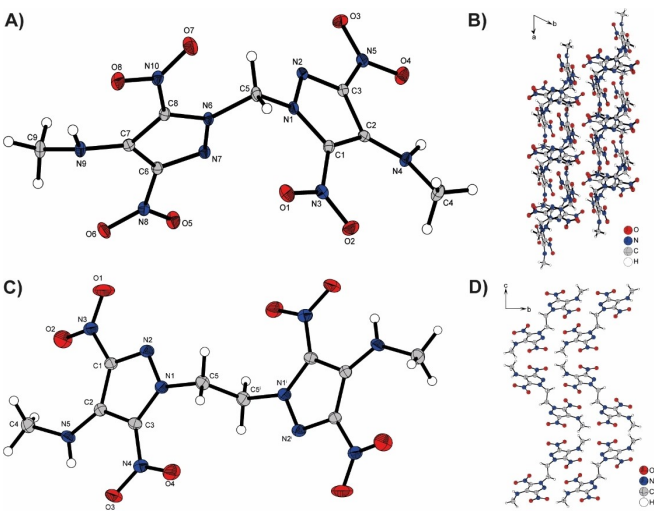

Figure 4. Molecular unit of compound **4** (A) and **6** (C) and extended structures (**4**: B; **6**: D) in the crystalline state. Symmetry code for C: 1-x, 1-y, 1-z.

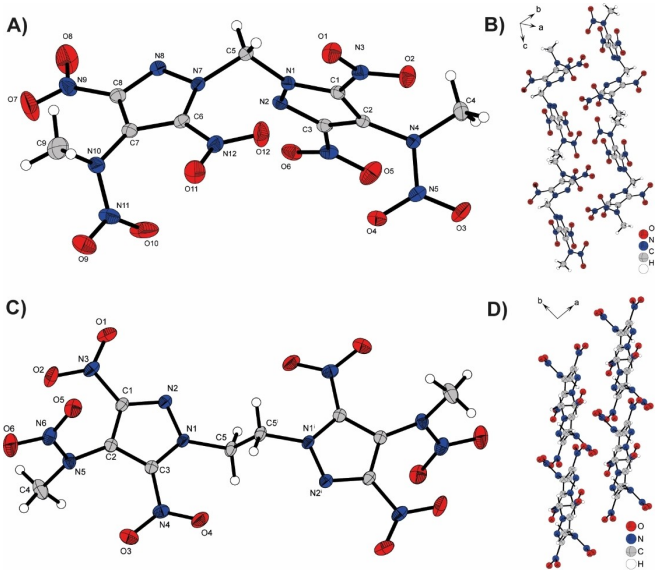

Figure 5. Molecular unit of compound **5** (A) and **7** (C) and extended structures (**5**: B; **7**: D) in the crystalline state. Symmetry code for C: 1-x, -y, 1-z.

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nearly orthogonal in **4** to 57.2(2) Å (N2–N1–C5–N7) and −113.33(18) (N8–N7–C5–N1). The addition of an electron-withdrawing nitro group on the methylamine distinctly lengthened the bond to the pyrazole ring from 1.362(3) Å (N9–C7, **4**) to 1.402(3) Å (N10–C7, **5**) or 1.338(2) Å (N5–C2, **6**) to 1.404(3) Å (N5–C2, **7**). The extended structure of **5** shows a zig-zag arrangement in the crystal. The layers are ordered according to an A-B-A layer principle, where B is rotated 180° with respect to A (Figure 5B). In contrast, **7** results in a layered structure with only one orientation of the molecules (Figure 5D).

Compound **9** crystallizes from hot ethanol/acetonitrile in form of colorless blocks in the monoclinic space group $P2_1/c$ with eight molecules per unit cell, a cell volume of 2984.87(19) $Å^3$ and a calculated density of 1.826 g cm^{-3} at 173 K. The molecular unit is illustrated in Figure 6.

In the asymmetric unit, compound **9** exhibits two different rotational isomers regarding the positioning of the pyrazole rings in respect to each other, which are to be represented in the crystal lattice equally. In the right structure (B) the azides are arranged in the same direction, whereas in the left structure (A) both azides point in different directions. Thereby structure A shows nearly an inversion symmetry at the C4 atom. Structure B demonstrates an approximate mirror plane along the C11 atom, with one pyrazole tilted more than the other. Three of the four azido groups are about in plane to the pyrazole ring (N6–N5–C3–C2 0.7(5)°, N20–N19–C10–C9 5.0(6)°, N27–N26–C14–C13 −7.6(6)°), while one azido group in structure (A) is rotated out of the plane (N13–N12–C7–C6 −26.9(5)°). The same applies to the nitro groups at the 4-position. The torsion angles of the nitro groups at C atoms C2, C6 and C9 are between 2 and 9 degrees (O3–N4–C2–C1 −8.4(4)°, O7–N11–C6–C5 −8.2(5)°, O15–N18–C9–C8 2.7(5)°). The nitro group at C13 (structure B) is twisted by 28° (O11–N25–C13–C12 −27.5(5)°).

Numerous attempts were undertaken to obtain individual isomers by recrystallization using a variety of solvents, including ethanol, methanol, acetonitrile, acetone, ethyl acetate, ether, and different solvent mixtures. However, the results were invariably the same. Rotamers are only observable in the solid phase, whereas in a solution, only a single set of signals is detectable in NMR spectra (Figure 7) owing to the unrestricted rotation of the CH_2 group.

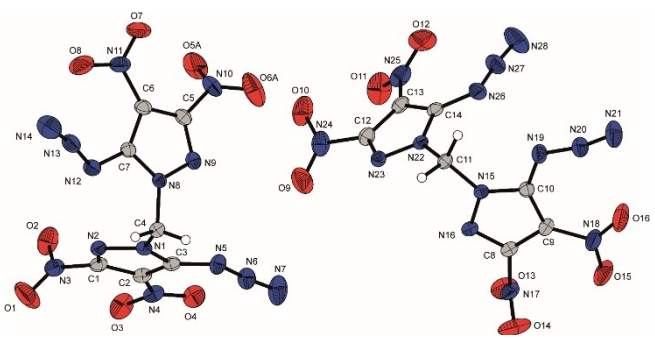

Figure 6. Asymmetric unit of compound **9** in the crystalline state.

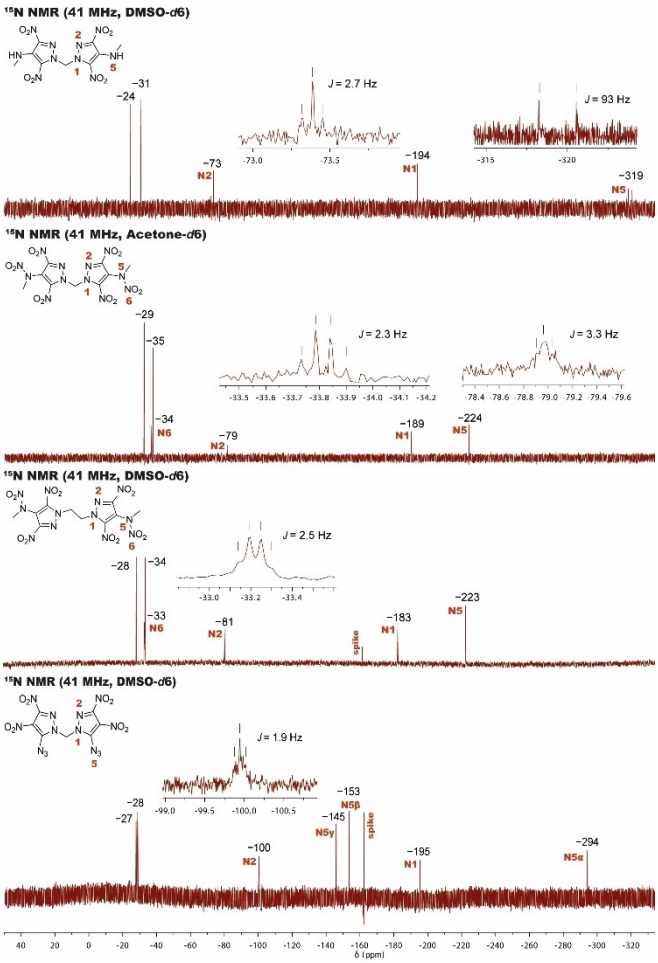

Figure 7. Proton coupled ^{15}N NMR spectra of compounds **4**, **5**, **7** and **9**.

Spectroscopy

All synthetized compounds (**2**–**7, 9**) were characterized by ^{1}H, ^{13}C, ^{14}N NMR spectroscopy, elemental analysis, mass spectrometry and IR spectroscopy. The methylene bridged compounds **4**, **5**, **7** and **9** were further characterized via ^{15}N NMR (Figure 7) and 2D $^{1}H/^{15}N$ NMR HMBC spectroscopy (more details on ^{1}H, ^{13}C and ^{15}N NMR can be found in the Supporting Information).

The measured ^{15}N NMRs are exemplary presented in Figure 7. The nitro group resonances found for compounds **4**, **5**, **7** and **9** are in the typical range between −10 and −50 ppm for carbon bonded species. The two pyrazole signals are found in the range of −73 to −100 and −189 to −195 ppm. The first signal splits a triplet due to the ^{3}J-coupling with the two protons of the methylene or ethylene bridge and thus can be assigned to N2. The methylamino signal in **5** at 319 ppm splits to a doublet. Nitration of the methylamino group (additional nitro group signal at −33.8 ppm for **5** or −33.2 ppm for **7** with quartet splitting) shifts this signal to the lower field (**5**: −223.5 ppm, **7**: −222.7 ppm). This and the absence of a doublet splitting indicates successful nitration. Compound **5** had to be measured in acetone-d_6 due to slow decomposition in DMSO-

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Table 1. Physicochemical properties and detonation parameters of **3a**–**3f** compared to **ANTA**.

	3a (K^+)	**3b** (G^+)	**3c** (AG^+)	**3d** (NH_4^+)	**3e** ($N_2H_5^+$)	**3f** (NH_3OH^+)	**ANTA**[22]
Formula	$C_4H_4KN_5O_4$	$C_5H_{10}N_8O_4$	$C_5H_{11}N_9O_4$	$C_4H_8N_6O_4$	$C_4H_9N_7O_4$	$C_4H_8N_6O_5$	$C_2H_3N_5O_2$
FW [g mol^{-1}]	225.21	246.19	261.20	204.15	219.16	220.15	129.08
IS[a] [J]	10	20	>40	15	15	10	>40[n]
FS[b] [N]	>360	>360	>360	>360	>360	>360	>360[n]
ESD[c] [J]	1.5	1	1	0.75	0.42	0.61	0.96
Ω_{CO2}[d] [%]	−46	−71	−70	−63	−62	−51	−43
T_{endo}[e] [°C]	/	/	157	/	/	/	/
T_{exo}[f] [°C]	280	245	188	240	203	188	220[n]
ρ[g] [g cm^{-3}]	1.824	1.558	1.600	1.638	1.582	1.651	1.820
$\Delta_f H°$[h] [kJ mol^{-1}]	−449.9	61.5	164.1	94.3	247.2	154.4	103.1
EXPLO5 V6.05 values							
$-\Delta_E U°$[i] [kJ kg^{-1}]	2733	3776	4037	4609	5060	5373	3952
$T_{C\text{-}J}$[j] [K]	2208	2622	2702	3029	3231	3458	2883
$p_{C\text{-}J}$[k] [GPa]	15.0	18.6	21.1	22.9	23.2	25.7	27.2
$D_{C\text{-}J}$[l] [m·s^{-1}]	6373	7307	7746	7836	7923	8089	8387
V^0[m] [dm^3·kg^{-1}]	514	838	854	832	861	824	790

[a] Impact sensitivity (BAM drophammer, method 1 of 6); [b] friction sensitivity (BAM friction tester, method 1 of 6); [c] electrostatic discharge sensitivity (OZM XSpark10); [d] oxygen balance toward carbon dioxide ($\Omega_{CO2} = (nO - 2xC - yH/2)(1600/FW)$); [e] endothermic event (DTA, $\beta = 5\,°C \cdot min^{-1}$); [f] temperature of decomposition (DTA, $\beta = 5\,°C \cdot min^{-1}$); [g] density at 298 K recalculated from X-ray data; [h] heat of formation (calculated using the atomization method and CBS-4 M enthalpies; [i] detonation energy; [j] detonation temperature; [k] detonation pressure; [l] detonation velocity; [m] volume of detonation gases at standard temperature and pressure conditions; [n] determined at LMU.

d_6. For compound **9**, three additional signals (−145.4, −153.0 and −293.7 ppm) for the azido groups are found in the ^{15}N spectrum in addition to the two pyrazole and two nitro group signals. The signal at −293.7 ppm can be clearly assigned to alpha nitrogen atom of the azide. In contrast to the usual covalently bonded azides, here, the beta and gamma nitrogen are assigned in reverse. The strong electronegativity of the nitro groups and the resulting electron withdrawing effects lead to electron-poor pyrazole moieties. This situation affects the terminal gamma nitrogen atom of the azide, therefore appearing to be slightly shifted to lower fields.[20,21] Evidence for the assignment of the beta nitrogen can be given by ^{14}N NMR. Due to symmetric surrounding, the beta nitrogen is the most easily observable of an azide in ^{14}N spectra. The assignment of the nitrogen signals was also confirmed by means of theoretical calculations (more details can be found in the Supporting Information).

Physicochemical properties

Compounds **3a**–**f**, **4**–**7** and **9** were investigated towards their physiochemical properties: thermal behavior, sensitivities towards impact, friction, electrostatic discharge and their detonation parameters. The thermal stabilities of all compounds were measured by differential thermal analysis (DTA) with a heating rate of 5 °C min^{-1}. The energetic salts **3a**, **b**, **d**, **e** show thermal stabilities above 200 °C, with the potassium salt being the most stable (280 °C). The salts **3c** and **f** decomposed already at 188 °C. Aminoguanidinium compound (**3c**) was found to be the only salt with a melting point (157 °C) (Table 1). By introducing a methylene or ethylene bridge between the pyrazole rings, the melting points right before decomposition could be achived. The comparison of the alkyl bridged compounds **4**–**7** with compound **9**, **BDNAPM** or **BTNPM** indicates, that not only the alkyl bridge is responsible for the melting point. The combination of the bridge and the methylation of amines is essential here. The melting points of compounds **4** and **5** are in a similar range (**4**: 173 °C; **5**: 166 °C). For ethyl bridged compounds **6** and **7** melting points can be found at 256 °C and 193 °C. However, in terms of thermal stability, these compounds perform worse than **BDNAPM** (310 °C) and **BTNPM** (205 °C) (**4**: 222 °C; **5**: 188 °C; **6**: 260 °C; **7**: 196 °C) (Figure 8). In the case of compounds **4** and **6**, the absence of interaction of the alternating nitro and amino groups, stabilizing **BDNAPM**, is responsible for the reduced thermostability. Compounds **5** and **7** are destabilized by the nitramine. The two azides in compound **9** drop the thermal stability to 149 °C (Figure 8).

All energetic salts **3a**–**f** were found to be insensitive towards friction. The impact sensitivity is within the acceptable range.

Also the bridged compounds **4** and **6** behave insensitive towards external stimuli (Table 2). The additional nitro group in compounds **5** and **7** increases the impact sensitivity to 4 J or 7.5 J, which corresponds to the impact sensitivity of **BTNPM**. The sensitivities for friction (240 N or 360 N) and ESD (0.61 J or 0.68 J) are decreased compared to **BTNPM**.

The densities of the salts range between 1.558 g cm^{-3} and 1.824 g cm^{-3}, with the potassium salt having the highest density, as expected. The densities for the neutral bridged compounds are in close range (**4**: 1.74 g cm^{-3}; **5**: 1.72 g cm^{-3}; **6**: 1.70 g cm^{-3}, **7**: 1.72 g cm^{-3}). The detonation velocity of the prepared compounds (**3**–**7**) does not exceed that of the compounds compared here (**ANTA**, **BDNAPM**, **BTNPM**), but it is within the acceptable level for secondary explosives. They range from 6373 m s^{-1} for **3a** to 8140 m s^{-1} for **5**. The same tendency is observed for the detonation pressures. Potassium salt (**3a**) shows the lowest value with 15 GPa and methylene bridged methylnitramine (**5**) the highest (28 GPa).

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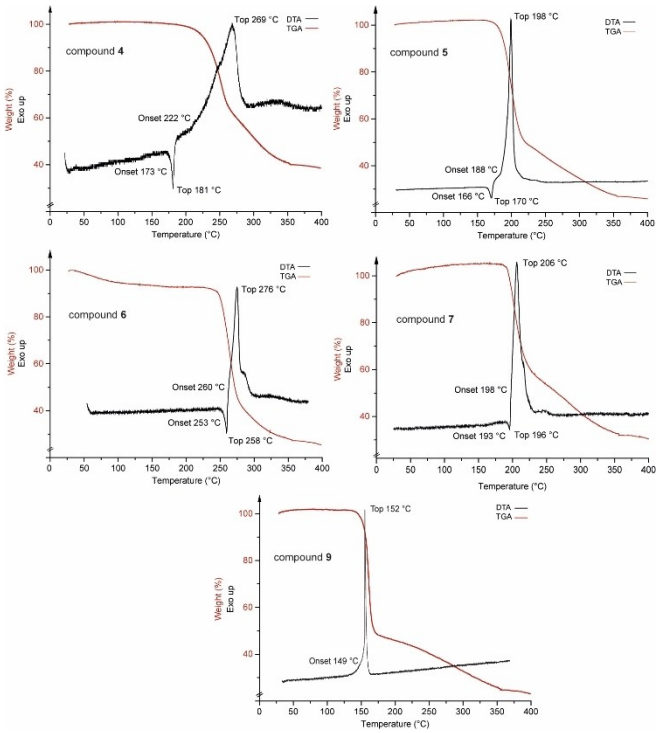

Figure 8. Combined DTA-TGA spectra of compounds **4**–**7** and **9**.

The comparison of compound **9** with its constitutional isomer **B4AzDNPM**, prepared by Korean group in year 2020,[23] provides significant differences (Figure 9). The terminal position of the azido group results in a slightly higher impact and friction resistance (**9**: IS: ≤ 1 J, FS: 20 N; **B4AzDNPM**: IS: 2 J, FS: 33 N). The thermal stability is formally decreased by 10 °C, but **B4AzDNPM** shows an endothermic peak directly before the decomposition point, which could hide the onset of decomposition, making the thermal stability comparable. Compound **9**, however, exceeds in terms of the detonation parameters. The slightly higher density (**9**: 1.79 g cm^{-3}, **B4AzDNPM**: 1.76 g cm^{-3}) and the heat of formation (**9**: 1042 kJ mol^{-1}, **B4AzDNPM**: 801 kJ mol^{-1}) of **9** increase the detonation velocity by approx. 300 m s^{-1} and the detonation pressure by approx. 3 GPa.

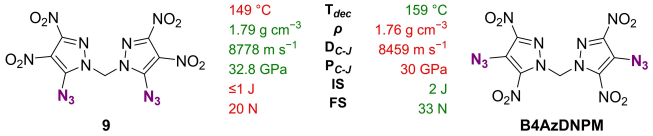

Figure 9. Comparison of energetic parameters of compound **9** and its constitutional isomer **B4AzDNPM**.

Hirshfeld analysis

By comparing the sensitivities of compounds **4** and **5**, it can be seen that the additional nitro group in compound **5** dramatically increases sensitivity towards impact and friction. Since the sensitivity of a compound depends partially on the intermolecular interactions, a Hirshfeld analysis was carried out for these compounds (Figure 10).

The stabilizing O···H interactions are present in both compounds in somewhat equal proportions (**4**: 37.7%, **5**: 38.4%). For the N···H interactions, which also contribute to the stabilization, the majority is present in compound **4** (**4**: 10.5%, **5**: 1.9%). Considering the O···N contacts and the repulsive O···O interactions, both of which have a destabilizing effect on the compounds, the amount for the methylnitramine **5** predominates (**4**: O···N 10.8%, O···O 11.9%; **5**: O···N 16.0%, O···O 21.6%), the number of repulsive interactions in compound **5** is much higher than in compound **4** and thus less balanced against the stabilizing effects, resulting in a high sensitivity towards mechanical stimuli.[24–26]

Initiation capability test

During the determinations of the thermal stability of compound **9** by DTA measurements, the test tube was completely

Table 2. Physicochemical properties and detonation parameters of **4**, **5**, **6**, **7** and **9** compared to **BDNAPM**, **BTNPM** and **B4AzDNPM**.

	4	**6**	**BDNAPM**[9]	**5**	**7**	**BTNPM**[9]	**9**	**B4AzDNPM**[23]
Formula	$C_9H_{10}N_{10}O_8$	$C_{10}H_{12}N_{10}O_8$	**$C_7H_6N_{10}O_8$**	$C_9H_8N_{12}O_{12}$	$C_{10}H_{10}N_{12}O_{12}$	**$C_7H_2N_{10}O_{12}$**	$C_7H_2N_{14}O_8$	**$C_7H_2N_{14}O_8$**
FW [g mol^{-1}]	386.24	400.27	**358.19**	476.24	490.26	**418.15**	410.18	**410.18**
IS[a] [J]	> 40	> 40	**11**	4	7.5	**4**	≤ 1	**2**
FS[b] [N]	> 360	> 360	**> 360**	240	360	**144**	20	**33**
ESD[c] [J]	> 1.5	> 1.5	**> 1.5**	0.61	0.68	**0.10**	0.42	/
Ω_{CO2}[d] [%]	−62	−72	**−40**	−34	−42	**−11**	−27	**−27**
T_{endo}[e] [°C]	173	253	/	166	193	/	/	**135**
T_{exo}[f] [°C]	222	260	**310**	188	196	**205**	149	**159**
ρ[g] [g cm^{-3}]	1.742	1.699	**1.802**	1.721	1.723	**1.934**	1.792	**1.76**
$\Delta_f H°$[h] [kJ mol^{-1}]	295.0	246.3	**205**	410.7	351.5	**379**	1042.5	**801**
EXPLO5 V6.05 values								
$-\Delta_E U°$[i] [kJ kg^{-1}]	4690	4459	**4742**	5492	5269	**6207**	5860[n]	/
T_{C-J}[j] [K]	3237	3058	**3443**	3941	3701	**4558**	4488[n]	/
p_{C-J}[k] [GPa]	24.1	21.7	**27.6**	28.0	26.5	**39.7**	32.8[n]	**30**
D_{C-J}[l] [m s^{-1}]	7776	7500	**8132**	8140	7984	**9292**	8778[n]	**8459**
V^0[m] [dm^3 kg^{-1}]	720	729	**708**	731	724	**709**	738[n]	/

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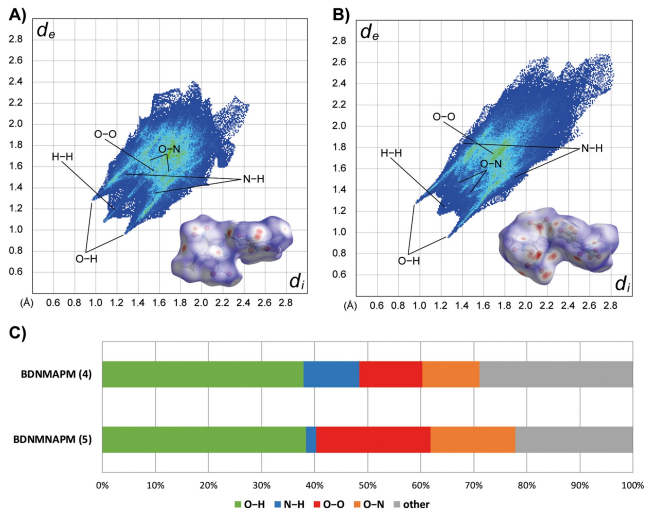

Figure 10. A) Two-dimensional Hirshfeld fingerprint plot and surface of compound **4**; **B)** Two-dimensional Hirshfeld fingerprint plot and surface of compound **5**; **C)** Population of close contacts of **4** and **5**.

Figure 11. A) Deflagration of **9** during hot plate test; **B)** Deflagration of **9** during hot needle test; **C)** Positive PETN initiation test with 50 mg of **9**.

fragmented by its detonative behavior during each measurement performed. Therefore, we decided to do hot plate and hot needle tests (Figure 11A, B), to get a first indication of its suitability as potential metal-free primary explosive. Due to the promising results, initiation capabilities were further evaluated in our classical setup (more information about the set up can be found in the Supporting Information). Pressed PETN was successfully initiated by 50 mg of compound **9**, loosely filled on top and fired with an electrical ignitor. The hole in the witness plate (Figure 11C) proved that compound **9** undergoes deflagration to detonation transition (DDT) under these conditions and possesses promising initiating capabilities that should be further evaluated.

Conclusions

The concept of methylene-bridged substituted pyrazoles to generate highly dense, non-acidic energetic materials was revisited in this work. 3,5-Dinitro-4-methylaminopyrazole was chosen as the starting compound, which was linked with diiodomethane or 1,2-dibromoethane and further nitrated. The obtained compounds **4**–**7** were intensively characterized. It was also possible to optimize the synthesis for the starting compound **2** (yield 89%, avoidance of autoclave conditions). In addition, the potassium salt and five selected nitrogen-rich salts were synthesized using **2** as starting material. In comparison, hydroxylammonium salt (**3f**) performs best with a calculated detonation velocity of 8089 m s^{-1} and pressure of 25.7 GPa. The potassium salt, in contrast, shows better thermal behavior (280 °C) and density (1.824 g cm^{-3}). Although melting points for **4**–**7** could be determined each (**4**: 173 °C; **5**: 166 °C; **6**: 253 °C; **7**: 193 °C) they are too high to be used as reasonable melt castable explosives. Also the decomposition temperatures are close (**4**: 222 °C; **5**: 188 °C; **6**: 260 °C; **7**: 196 °C). The introduction of methylamino and methylnitramino groups has been shown to have a thermally destabilizing effect on the present system. For example, the methylation of the amino group diminishes the decomposition temperature from 310 °C (**BDNAPM**) to 222 °C (**4**). However, the sensitivities were positively influenced. Compounds **4** and **6** appeared to be completely insensitive to impact and friction and compounds **5** and **7** indicated a lower friction sensitivity of 240 N or 360 N compared to **BTNPM** (FS: 144 N). Nitration of the methylamino group increased the detonation velocity (**4**: 7776 m s^{-1}, **5**: 8140 m s^{-1}, **6**: 7500 m s^{-1}, **7**: 7984 m s^{-1}) and pressure (**4**: 24.1 GPa, **5**: 28.0 GPa, **6**: 21.7 GPa, **7**: 26.5 GPa). The elongation by one carbon of the methylene bridge has a slightly negative effect on the detonation parameters (e.g. **5**: 8140 m s^{-1}**7**: 7984 m s^{-1}), but increases the thermal stability (e.g. **4**: 222 °C, **6**: 260 °C). A tad but positive effect on the sensitivities of compound **7** could also be reached (e.g. **IS**: **5**: 4 J, **7**: 7.5 J). The bridged azido compound **9** presented a relatively high detonation velocity of 8778 m s^{-1} and a sharp deflagration in the hot needle and hot plate tests. In addition, PETN could be successfully initiated with bis(5-azido-3,4-dinitropyrazol-1-yl)methane (**9**), which indicated its suitability as a potential metal-free primary explosive.

Deposition Numbers 2076051 (for Na2BDNOPM),2176049 (for DNMAP (2)), and 2176043 (for Na DNMAP (2Na)) 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.

Experimental Section

All chemical reagents and solvents were employed as received from Sigma-Aldrich, Acros Organics, ABCR and TCI. All information and details on analytical devices such as NMR, MS, EA, IR, DTA and calculation of the energetic properties as well as the synthesis of compound **2** and its salts are given in the Supporting Information.

Caution! Nitropyrazoles are potential energetic materials with sensitivities towards various stimuli. Therefore, meticulous security precautions (safety glasses, face shield, earthed equipment and shoes, Kevlar gloves and ear plugs) have to be applied while synthesizing and handling the described compounds.

Bis(3,5-dinitro-4-methylaminopyrazol-1-yl)methane (4)

To a solution of sodium 3,5-dinitro-4-methylaminopyrazolate monohydrate **(2Na)** (1.00 g, 4.40 mmol, 2 equiv.) in DMF (10 mL), diiodomethane (0.18 mL, 0.59 g, 2.20 mmol, 1 equiv.) was added and the reaction mixture was heated at 100 °C over night. The mixture was cooled down to ambient temperature, poured onto

water under stirring and iodine was removed with an excess amount of aqueous disodium thiosulfate solution. The suspension was filtered, washed with aqueous disodium thiosulfate solution and water to give bis-(3,5-dinitro-4-methylaminopyrazol-1-yl)methane **(4)** (0.788 g, 2.04 mmol, 93 %) after air-drying as a yellow powder.

DTA (5 °C min^{-1}) T_{melt} = 173 °C, T_{dec} = 220 °C; **^{1}H NMR** (400 MHz, DMSO-*d*6, 25 °C): δ (ppm) = 7.48 (q, ^{3}J = 5.3 Hz, 2H), 7.20 (s, 2H), 2.95 (d, ^{3}J = 5.4 Hz 6H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-*d*6, 25 °C): δ (ppm) = 143.1, 132.3, 130.9, 66.9, 33.0; **^{14}N{^{1}H} NMR** (29 MHz, DMSO-*d*6, 25 °C): δ (ppm) = −21, −31; **^{15}N NMR** (41 MHz, DMSO-*d*6, 25 °C): δ (ppm) = −24.4, −30.7, −73.4 (t, $^{2}J_{N,H}$ = 2.7 Hz), −193.8, −319.4 (d, $^{1}J_{N,H}$ = 93 Hz); **EA** ($C_9H_{10}N_{10}O_8$, 386.24 g/mol) calc. (found): C 27.99 (27.79), H 2.61 (2.62), N 36.26 (36.02) %; **HRMS** (EI+): *m/z* calculated for $C_9H_{10}N_{10}O_8$ [M]: 386.0683, found: 386.0675; **IR** (ATR, rel. int.): $\tilde{\nu}$ (cm^{-1}) = 3349 (m), 1619 (s), 1602 (s), 1532 (m), 1491 (s), 1442 (m), 1403 (m), 1389 (m), 1353 (s), 1301 (vs), 1279 (vs), 1213 (w), 1160 (w), 1114 (w), 1092 (w), 1026 (w), 1007 (w), 937 (w), 895 (s), 828 (m), 819 (m), 788 (w), 757 (m), 740 (m), 698 (w), 675 (w), 658 (m), 644 (m), 617 (m), 602 (m), 538 (w), 501 (w), 417 (vw), 405 (vw).

Bis(3,5-dinitro-4-methylnitraminopyrazol-1-yl)methane (5)

Bis-(3,5-dinitro-4-methylaminopyrazol-1-yl)methane **(4)** (1.00 g, 2.59 mmol, 1 equiv.) was dissolved in trifluoroacetic acid (10 mL) and cooled to 0 °C. Fuming nitric acid (3.8 mL, 91.1 mmol, 35 equiv.) and afterwards trifluoroacetic anhydride (1.3 mL, 9.34 mmol, 3.6 equiv.) were added dropwise and the reaction mixture was stirred on an ice-bath until everything was dissolved (approx. 2–3 h). The solution was poured onto ice-water (~30 mL), the precipitate was filtered off, washed with water and dried at 50 °C to give bis(3,5-dinitro-4-methylnitraminopyrazol-1-yl)methane **(5)** (1.05 g, 2.21 mmol, 85 %) as an off-white powder.

DTA (5 °C min^{-1}) T_{melt} = 166 °C, T_{dec} = 184 °C; **^{1}H NMR** (400 MHz, Aceton-*d*6, 25 °C): δ (ppm) = 7.76 (s, 2H), 3.76 (s, 6H); **^{13}C{^{1}H} NMR** (101 MHz, Aceton-*d*6, 25 °C): δ (ppm) = 148.7, 141.9, 115.8, 68.5, 40.9; **^{14}N{^{1}H} NMR** (29 MHz, Aceton-*d*6, 25 °C): δ (ppm) = −29, −33; **^{15}N NMR** (41 MHz, Aceton-*d*6, 25 °C): δ (ppm) = −29.4, −33.8 (q, $^{3}J_{N,H}$ = 2.3 Hz), −34.7, −79.0 (t, $^{2}J_{N,H}$ = 3.3 Hz), −189.0, −223.5; **EA** ($C_9H_8N_{12}O_{12}$, 476.24 g/mol) calc. (found): C 22.70 (22.60), H 1.69 (1.78), N 35.29 (35.03) %; **HRMS** (ESI−): *m/z* calculated for $C_9H_7N_{12}O_{12}$ [M–H]$^{-}$: 475.0312, found: 475.03118; **IR** (ATR, rel. int.): $\tilde{\nu}$ (cm^{-1}) = 1606 (m), 1571 (m), 1535 (s), 1458 (m), 1446 (m), 1428 (s), 1333 (s), 1321 (s), 1299 (s), 1276 (vs), 1206 (m), 1168 (w), 1135 (m), 1119 (m), 1081 (m), 994 (w), 958 (w), 900 (m), 887 (s), 832 (w), 827 (m), 802 (s), 794 (s), 772 (m), 752 (m), 711 (m), 694 (w), 662 (s), 634 (w), 618 (w), 602 (w), 533 (vw), 511 (w), 497 (m), 432 (w).

Bis(3,5-dinitro-4-methylaminopyrazol-1-yl)ethane (6)

To a solution of sodium 3,5-dinitro-4-methylaminopyrazolate monohydrate **(2Na)** (2.00 g, 8.81 mmol, 2 equiv.) in DMF (15 mL), 1,2-dibromoethane (0.42 mL, 0.91 g, 4.84 mmol, 1.1 equiv.) was added and the reaction mixture was heated at 90 °C over night. The mixture was cooled down to ambient temperature, poured onto water under stirring. The suspension was filtered, washed with water and a little amount of cold ethanol to remove the excess of 1,2-dibromoethane to give bis-(3,5-dinitro-4-methylaminopyrazol-1-yl)ethane **(6)** (1.37 g, 3.42 mmol, 78 %) after air-drying as a yellow powder.

DTA (5 °C min^{-1}) T_{melt} = 253 °C, T_{dec} = 260 °C;**^{1}H NMR** (400 MHz, DMSO-*d*6, 25 °C): δ (ppm) = 7.40 (q, ^{3}J = 5.3 Hz, 2H), 5.04 (s, 4H), 2.92 (d, ^{3}J = 5.4 Hz, 6H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-*d*6, 25 °C): δ (ppm) = 141.8, 132.9, 131.0, 53.4, 33.1; **EA** ($C_{10}H_{12}N_{10}O_8$, 400.27 g/mol) calc. (found): C 30.01 (29.96), H 3.02 (3.04), N 34.99 (34.76) %; **HRMS** (EI+): m/z calculated for $C_{10}H_{12}N_{10}O_8$ [M]: 400.0840, found: 400.0827; **IR** (ATR, rel. int.): $\tilde{\nu}$ (cm^{-1}) = 3326 (m), 1725 (vw), 1614 (s), 1533 (m), 1521 (m), 1472 (s), 1460 (s), 1435 (s), 1408 (s), 1386 (m), 1333 (s), 1313 (s), 1278 (vs), 1219 (s), 1194 (s), 1108 (s), 1030 (s), 889 (s), 828 (m), 769 (s), 751 (m), 743 (s), 620 (s), 602 (s), 509 (w), 486 (m), 456 (w), 407 (w).

Bis(3,5-dinitro-4-methylnitraminopyrazol-1-yl)ethane (7)

Bis-(3,5-dinitro-4-methylaminopyrazol-1-yl)methane **(6)** (1.00 g, 2.50 mmol, 1 equiv.) was dissolved in trifluoroacetic acid (10 mL) and cooled to 0 °C. Fuming nitric acid (4.0 mL, 95.9 mmol, 38 equiv.) and afterwards trifluoroacetic anhydride (1.5 mL, 10.8 mmol, 4.3 equiv.) were added dropwise and the reaction mixture was stirred on an ice-bath until everything was dissolved (approx. 2−3 h). The solution was poured onto ice-water (~30 mL), the precipitate was filtered off, washed with water and dried at 50 °C to give bis(3,5-dinitro-4-methylnitraminopyrazol-1-yl)ethane **(7)** (1.13 g, 2.31 mmol, 92 %) as an off-white powder.

DTA (5 °C min^{-1}) T_{melt} = 193 °C, T_{dec} = 196 °C; **^{1}H NMR** (400 MHz, Aceton-*d*6, 25 °C): δ (ppm) = 5.59 (s, 4H), 3.73 (s, 6H); **^{13}C{^{1}H} NMR** (101 MHz, Aceton-*d*6, 25 °C): δ (ppm) = 147.6, 141.9, 115.1, 53.9, 40.8; **^{14}N{^{1}H} NMR** (29 MHz, Aceton-*d*6, 25 °C): δ (ppm) = −29,−34; **^{15}N NMR** (41 MHz, DMSO-*d*6, 25 °C): δ (ppm) = −28.4, −33.2 (q, $^{3}J_{N,H}$ = 2.5 Hz), −33.8, −80.05, −182.6, −222.7; **EA** ($C_{10}H_{10}N_{12}O_{12}$, 490.26 g/mol) calc. (found): C 24.50 (24.47), H 2.06 (2.24), N 34.28 (34.01) %; **HRMS** (ESI+): m/z calculated for $C_{10}H_{10}N_{12}O_{12}$ [M]: 490.0541, found: 490.36152; **IR** (ATR, rel. int.): $\tilde{\nu}$ (cm^{-1}) = 1739 (w), 1603 (m), 1562 (m), 1527 (s), 1459 (s), 1449 (s), 1438 (s), 1423 (s), 1403 (w), 1377 (m), 1366 (m), 1352 (m), 1329 (vs), 1286 (vs), 1262 (s), 1218 (m), 1195 (m), 1160 (w), 1117 (m), 1065 (m), 950 (w), 892 (s), 826 (m), 792 (m), 785 (m), 771 (m), 754 (m), 730 (w), 691 (m), 667 (s), 641 (w), 599 (w), 537 (vw), 488 (m), 431 (m).

Bis(5-azido-3,4-dinitropyrazol-1-yl)methane (9)

Bis(3,4,5-trinitropyrazol-1-ly)methane **(8)** (2.50 g, 5.98 mmol, 1 equiv.) was suspended in methanol (25 mL) and sodium azide (1.56 g, 24.0 mmol, 4 equiv.) was added. The mixture was stirred at room temperature for 48 h. The solid residue was filtered off, washed with water and methanol and air-dried to give bis(5-azido-3,4-dinitropyrazol-1-yl)methane **(9)** (1.80 g, 4.39 mmol, 73 %) as a beige powder.

DTA (5 °C min^{-1}) T_{dec} = 149 °C; **^{1}H NMR** (400 MHz, DMSO-*d*6, 25 °C): δ (ppm) = 6.49 (s, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-*d*6, 25 °C): δ (ppm) = 147.9, 140.0, 118.2, 59.1; **^{14}N{^{1}H} NMR** (29 MHz, DMSO-*d*6, 25 °C): δ (ppm) = −27, −152, −154; **^{15}N NMR** (41 MHz, DMSO-*d*6, 25 °C): δ (ppm) = −27.3, −28.3, −99.9 (t, $^{2}J_{N,H}$ = 1.9 Hz), −145.4, −153.0, −194.9, −293.7; **EA** ($C_7H_2N_{14}O_8$, 410.18 g/mol) calc. (found): C 20.50 (20.67), H 0.49 (0.65), N 47.81 (47.97) %; **HRMS** (EI+): *m/z* calculated for $C_7H_2N_{14}O_8$ [M]: 410.0180, found: 410.0168; **IR** (ATR, rel. int.): $\tilde{\nu}$ (cm^{-1}) = 3031 (w), 2985 (w), 2156 (s), 1543 (vs), 1495 (vs), 1465 (s), 1454 (s), 1431 (s), 1415 (m), 1371 (s), 1335 (s), 1312 (s), 1275 (s), 1262 (s), 1200 (m), 1138 (s), 1078 (m), 1057 (m), 993 (m), 931 (m), 922 (m), 832 (s), 801 (s), 775 (m), 760 (s), 750 (s), 724 (m), 710 (m), 645 (m), 600 (m), 578 (m), 514 (m), 490 (m), 433 (m), 408 (m).

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: alkyl bridged pyrazoles · metal free primary explosives · nitropyrazoles · salt formation · secondary explosives

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