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Energetic derivatives of 3,3′,5,5′-tetranitro-4,4′-bipyrazole (TNBPz): Synthesis, characterization and properties

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ABSTRACT

3,3‘,5,5‘-Tetranitro-4,4‘-bipyrazole monohydrate (TNBPz, **1**·H_2O) is an excellent precursor for the synthesis of new energetic materials (**2–12**). Several nitrogen-rich salts (e.g. guanidinium, aminoguanidinium, hydrazinium, ammonium and hydroxylammonium) were prepared from **1**·H_2O by neutralization reactions. In addition, the *N*-methylation and *N*-amination of compound TNBPz was investigated and is reported. All new synthesized energetic materials were fully characterized by NMR (^1H, ^{13}C, ^{14}N, and ^{15}N) spectroscopy, infrared spectroscopy, differential thermal analysis (DTA) and elemental analysis. Compounds **2**, **4–8** and **10** were characterized with single crystal X-ray diffraction. The heats of formation for compounds **2**, **4–6**, **8**, **11** and **12** were calculated using the atomization method based on CBS-4 M enthalpies. Several detonation parameters, such as detonation pressure, velocity and energy, were calculated by using the X-ray densities and the calculated standard molar enthalpies of formation. The sensitivities of all energetic materials toward external stimuli were tested according to the BAM standards. In addition, the toxicity toward vibrio fischeri bacteria of few energetic salts (**3** and **4**) is reported.

1. Introduction

The research on new energetic materials has increased in the last decades due to arising safety regulations [1]. The key to the development of new energetic materials is to design high-energy density materials with good detonation parameters and low sensitivity [2]. Currently used high explosives (e.g. TNT and RDX) show high toxicity which makes the research on new energetic materials based on nitrogen-rich heterocycles very attractive. The functionalization of azoles with different explosphore groups (e.g. $-NO_2$, $-ONO_2$, $-NHNO_2$, $-C(NO_2)_3$) is a good approach for the synthesis of new high-energy dense materials [3]. There are a few strategies that can be used by the design of new energetic materials in order to combine performance with sensitivity; formation of nitrogen-rich the salts, introduction of alternating NO_2/NH_2 groups in the molecule and the introduction of a conjugation [4,5].

The chemistry of C-nitrated nitrogen-rich heterocyclic rings has been extensively investigated in the last decade [6]. Fig. 1 shows a few examples of polynitrated nitrogen-rich heterocycles which exhibit very interesting properties, such as high detonation velocities and pressure, but show also good stability toward external stimuli. The formation of nitrogen-rich salts with polynitrated pyrazole derivatives leads mostly to the formation of energetic materials with high densities and good thermal stability as a result of their electrostatic lattice energy [7,8]. Using nitrogen-rich cations for the formation of energetic salts involving nitrated azoles leads to a stabilization of the structure, due to the high positive heat of formation of the cation and the potential intra- and intermolecular hydrogen bond formation [9–12].

However, the functionalization of 3,3′,5,5′-tetranitro-4,4‘-bipyrazole monohydrate (TNBPz, **1**·H_2O) has not been reported and their energetic derivatives are not known. The extensive synthesis of compound **1**·H_2O was recently reported and it exhibits excellent properties to be a starting material for new energetic materials [13]. In our study the formation of energetic salts with **1**·H_2O and the *N*-methylation and *N*-amination of **1**·H_2O was investigated. Many energetic materials were reported (**2–12**) and fully characterized. All new synthesized energetic materials were experimentally and theoretically investigated.

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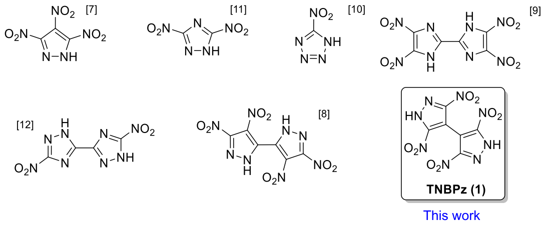


Fig. 1. Literature known fully C-nitrated heterocyclic compounds and the investigated nitro pyrazole $1{\cdot}H_2O$ during this work.

2. Results and discussion

2.1. Synthesis

The starting material 3,3′,5,5′-tetranitro-4,4′-bipyrazole monohydrate (TNBPz, $\mathbf{1}{\cdot}H_2O$) was obtained by nitration of the 4,4′-bipyrazole scaffold. The synthesis of $\mathbf{1}{\cdot}H_2O$ has been reported previously in the literature [13]. Numerous new energetic compounds (**2–12**) were obtained by reacting TNBPz ($\mathbf{1}{\cdot}H_2O$) with several nitrogen-rich bases or further N-functionalizing TNBPz (Scheme 1). The resulting salts were isolated in good yields and are stable at room temperature.

The N-functionalization of TNBPz ($\mathbf{1}{\cdot}H_2O$) e.g. N-methylation and N-amination was extensively investigated. The synthesis of 1,1′-dimethyl-3,3′,5,5′-tetranitro-4,4′-bipyrazole ((Me)$_2$TNBPz, 2) has been previously reported in the literature, however, we present a new and simpler procedure [14]. Hence, compound **2** was obtained by simple N-methylation of $\mathbf{1}{\cdot}H_2O$ with an excess of dimethyl sulfate in the presence of a weak base. In addition, the N-amination of compound $\mathbf{11}{\cdot}H_2O$ was investigated and the effect of the amination reagent was extensively investigated. For this type of reactions, the well-known amination reagents hydroxylamine-O-sulfonic acid (HOSA) and O-p-toluene sulfonylhydroxylamine (TOSA) were selected. The reaction of compound $\mathbf{1}{\cdot}H_2O$ with HOSA in the presence of a buffer solution ($NaOH/KH_2PO_4$) did not yield the expected 1,1′-diamino-3,3′,5,5′-tetranitro-4,4′-bipyrazole ((NH_2)$_2$TNBPz, 12) but resulted in the formation of the potassium salt of 4-(1-amino-3,5-dinitropyrazolyl)–3′,5′-dinitropyra-zolate (11). Further study of this reaction did not provide the desired compound **12**. Hence, TNBPz was reacted furtherly with TOSA in an CH_3CN/DCM solution with the presence of 1,8-diazabicyclo[5.4.0]undec-7-en (DBU). This resulted in 1,1′-diamino-3,3′,5,5′-tetranitro-4,4′-bipyrazole ((NH_2)$_2$TNBPz, 12). All reactions are shown in Scheme 1.

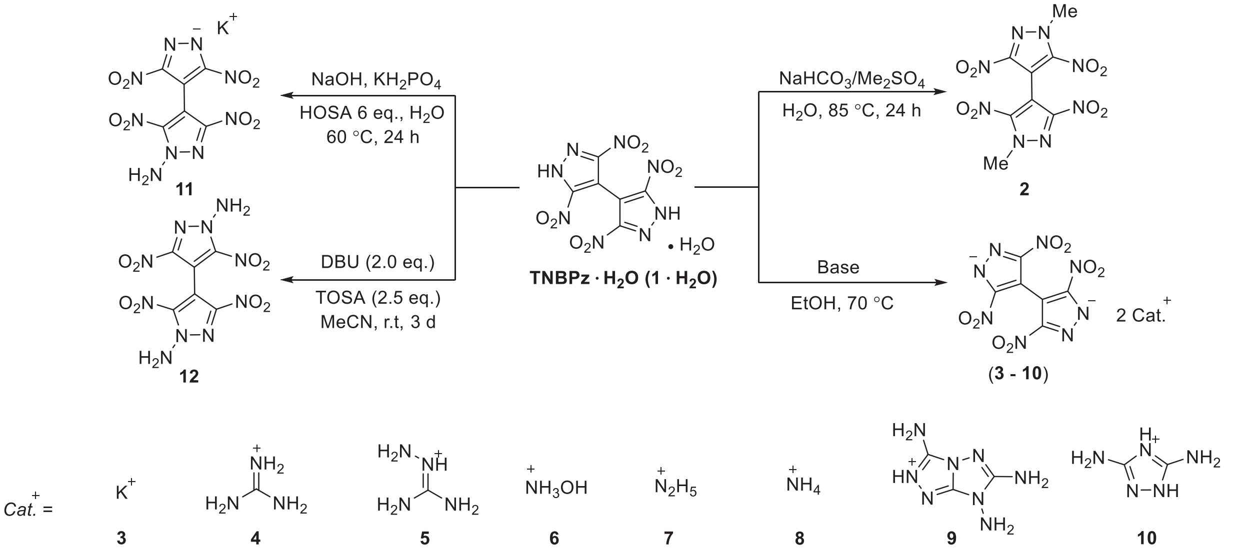
2.2. Crystal structures

During this work the crystal structures of 2, 4–7 and 10 were determined by low-temperature X-ray diffraction. Selected data and parameters from the low-temperature X-ray data collection, refinements and CCDC numbers are given in the Supporting Information (Tables S1 and S2). Compounds **2**, **4–6**, and 10 (Fig. S2) crystallize anhydrously whereas compound **7** (Fig. S1) crystallizes as a hemihydrate. Of course, it was tried to grow single crystals of the aminated products 11 and 12. While we were able to measure low quality crystals of 11 (a depiction of the molecular unit is shown in Fig. S3) all attempts failed for 12. The structure of 11 is similar to those of the mono-rubidium and cesium salt of the tetranitro-bipyrazole, which were published recently [15].

Compound **2** crystallizes in the monoclinic space group *Cc* with four formulas per unit cell. The lattice parameters are a=8.9141(5) Å, b=22.3417(15) Å, c=7.8114(4) Å and β = 124.432(2)°, giving a cell volume of 1283.13(13) Å^3 with calculated density of 1.771 g/cm^3. The asymmetric unit includes one unit of 2. It itself consists out of two planar pyrazole-rings ($|\Theta_{\text{out of plane}}| \leq 1.1°$) with averaged dihedral angle of 73.2° between both. This twist is higher compared to that found in solvent free TNBPz (71.44(5)°), but lower in comparison to TNBPz·H_2O ($1{\cdot}H_2O$) (78.99(6)°) [11]. The bond lengths and angles found in the pyrazole-rings are similar to those of the ionic derivatives of the TNBPz monoanion (e.g. compound **6**), but are generally more distinct in each ring due to the abolished indistinguishability of the nitrogen through the methyl-groups. The lengths of the nitrogen-nitrogen bonds are 1.330 Å and 1.340 Å. In comparison the carbon-nitrogen bonds closer to the methyl-group are longer with each having a length of 1.355 Å, while the other carbon-nitrogen bonds are shorter (1.325 Å, 1.329 Å). In return the carbon-carbon bonds closer to the methyl-group with lengths of 1.382 Å and 1.384 Å are shorter compared to the other carbon-carbon bonds with lengths of 1.399 Å and 1.403 Å. The angles at the ring-nitrogen are not similar anymore, with methylated nitrogen are widened (110.58°,111.72°) and the angles at the other nitrogen are compressed (104.56°, 104.91°) compared to those found in 6. The bond angles at the nitro-carbon more distant to the methyl-group are very similar to those of compound **6** (113.9°, 114.1°), while the nitro-carbon closer to the methyl-group are slightly compressed (109.4°, 109,6°). The carbon-carbon bond between the rings and the carbon-nitrogen bonds of the nitro-groups have aromatic character with a length of 1.465 Å and 1.438–1.447 Å, respectively. Compared to the nitro-groups the carbon-nitrogen bonds of the methyl-groups possess higher length of 1.469 Å and 1.472 Å, showing that they are in contrast not a part of the aromatic system (Fig. 2). The nitrogen of the nitro-groups and carbon of the methyl-groups lie in the plane of its pyrazol ring ($|\Theta_{\text{out of plane}}| \leq$ 3.8°).

The crystal structure of bis(guanidinium) 3,3′,5,5′-tetranitro-4,4′-bipyrazolate (**4**) is shown in Fig. 3 with bond lengths and angles. Compound **3** crystalizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The volume of the unit cell is 1721.9(4) Å^3 with lattice constants a=10.7792(15), b=17.441(12), c=9.6177(15) Å and β=107.766(15)°. The calculated density at 298 K is 1.63 g/cm^3. The molecule of 4 can be divided in two components: the biyprazolate anion and the guanidinium cations. The bond lengths between the carbon and the nitrogen atoms in the guanidinium cation exhibit similar values of 1.32 Å and 1.34 Å. The average bond angle between the carbon atom and the nitrogen atoms in the cation is around 120°. Both pyrazole rings and their nitro groups have a similar arrangement. The planes which are defined through each ring are twisted by 63.4(3)° (C3–C2–C5–C6) to each other. The N–O bonds of the nitro groups show the standard length for nitro groups of 1.24 Å [15]. The bond lengths between N3–C1 of 1.433(3) Å, N4–C3 of 1.431(3) Å, N7–C4 of 1.432(3) Å and N8–C6 of 1.434(3) Å are close to the standard value for C–N single bonds of 1.47 Å [16]. The bonds between N1–N2 (1.346(3) Å), N1–C1 (1.347(3) Å) and N2–C3 (1.349(3) Å) all have similar lengths. The bonds between C1–C2 and C2–C3 have lengths of 1.393(3) Å and 1.391(3) Å. So, they all have the standard length for aromatic systems of these elements. The bond lengths and angles differ slightly from the ones of the anhydrous pyrazole [17]. The distance between C2 and C5, the atoms which connect both rings, is with 1.467(3) Å between the standard length for C=C double bonds and C–C single bonds. A comparable C–C bond length between two nitrogen-rich aromatic rings can be observed in TKX-50 with 1.444(3) Å [18]. The angles in the ring (106.96(18)° (N2–N1–C1), 113.36(19)° (N1–C1–C2)) coincide with the different bond lengths (1.346(3) Å (N1–N2), 1.391(3) Å (C2–C3)). This means the rings are slightly deformed. The angles in the nitro groups and between the nitro groups and the ring differ just very slightly among the four nitro groups (O3–N4–O4 123.0(2)°, O3–N4–C3 119.70(19)°, O5–N7–O6 122.82(19)°, O5–N7–C4 118.86(18)°, O1–N3–O2 123.1(2)°, O1–N3–C1 118.59(19)°, O7–N8–O8 123.03(19)°, O7–N8–C6 118.58(18)°. The torsion angles show that both pyrazole rings are twisted to each other.

Compound **5** (Fig. 4) crystallizes in the orthorhombic space group *Pccn* with a cell volume of 1802.61(6) Å^3 and four formula units per cell. The cell constants are a=10.2845(2) Å, b=18.8916(4) Å and c=9.2779(2) Å. The calculated density at 298 K is 1.66 g/cm^3. The different cation has no influence on the structure of the bipyrazolate, compared to compound **4**. The rings are twisted by 56.04° (C1–C2–C2′–C3′)



Scheme 1. Synthesis of the energetic compounds **2–12** based on 3,3′,5,5′-tetranitro-4,4′-bipyrazole monohydrate ($\mathbf{1}\cdot H_2O$).

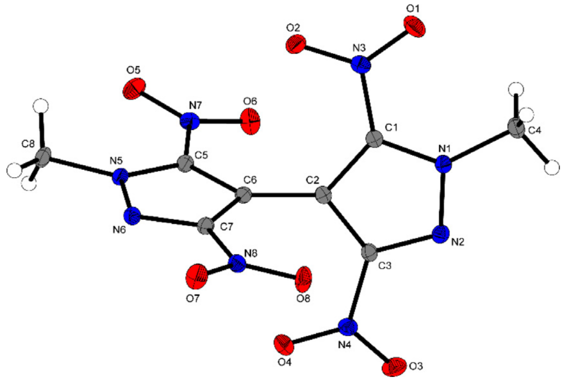


Fig. 2. Molecular unit of 1,1′-dimethyl-3,3′,5,5′-tetranitro-4,4′-bipyrazole (2) in the crystalline state. Ellipsoids correspond to 50% probability levels. Hydrogen radii are arbitrary. Selected bond lengths (Å) and angles (deg): N1–N2 1.329(3), N1–C1 1.356(4), N1–C4 1.466(4), C1–C2 1.382(3), C2–C6 1.465(4), C6–C7 1.399(3), O1–N3 1.231(3), N3–C1 1.438(3), N2–N1–C1 110.7(2), N2–N1–C4 118.1(2), C1–N1–C4 131.2(2), N2–C3–N4 118.6(2), O1–N3–C1 118.2(3), C1–C2–C6 129.2(2), C2–C6–C7 129.2(3), C1–N1–N2–C3 –0.8(3), C4–N1–N2–C3 178.2(2), C4–N1–C1–N3 1.6(4), N2–N1–C1–C2 1.1(3), C1–C2–C6–C7 –104.2(3), C1–C2–C6–C5 74.4(4), O1–N3–C1–N1 –13.7(4).

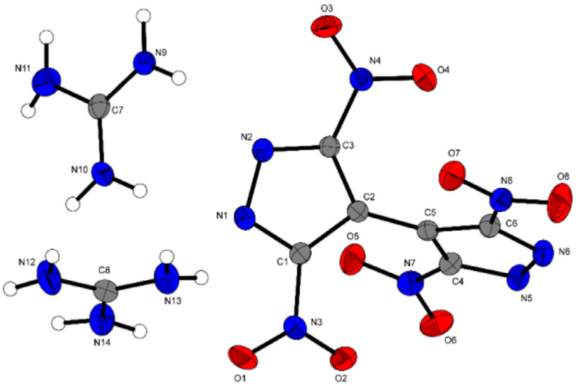


Fig. 3. Molecular unit of bis(guanidinium) 3,3′,5,5′-tetranitro-4,4′-bipyrazolate (4) in the crystalline state. Ellipsoids correspond to 50% probability levels. Hydrogen radii are arbitrary. Selected bond lengths (Å) and angles (deg): O1–N3 1.229(3), N1–N2 1.346(3), N1–C1 1.347(3), C1–C2 1.393(3), C2–C5 1.467(3), N2–C3 1.349(3), N3–C1 1.433(3), N9–C7 1.320(3), N10–C7 1.316(4), N2–N1–C1 106.96(18), N1–C1–N3 118.7(2), O1–N3–C1 118.3(2), C1–C2–C5 129.60(19), N10–C7–N11 119.6(2), C1–N1–N2–C3 –0.8(2), N2–N1–C1–N3 –179.87(17), N2–N1–C1–C2 1.4(2), O1–N3–C1–C2 170.0(2), C1–C2–C5–C6 –115.4(3), C3–C2–C5–C4 –122.1(3), C3–C2–C5–C6 63.4(3).

against each other. The bonds between N1−N2 (1.3398(13) Å), N1−C1 (1.3475(13) Å), N2−C3 (1.3441(14) Å), C1−C2 (1.3934(15) Å) and C2−C3 (1.3964(14) Å) have aromatic character [16]. The bonds between N1′−N2′, N1′−C1′, N2′−C3′, C1′−C2′ and C2′−C3′ have the same length. The bond between C2 and C2′ is with 1.4623(14) Å between the standard length for C–C double bonds and C–C single bonds [16]. The rings are slightly deformed and the oxygens are slightly displaced out of the plane. The bonds between C4 and the surrounding nitrogen atoms N5, N7 and N8 have the typical length for aromatic bonds. The N5−N6 bond is with a length of 1.4062(16) Å between a single and an aromatic bond [16]. The bond angles between N5−C4−N8, N7−C4−N8, N5−C4−N7 and N6−N5−C4 defer slightly from 120°.

Compound **6** crystallizes orthorhombic space group $Pca2_1$ with 16 formulas per unit cell. The lattice parameters are a=17.1257(5) Å, b=9.8507(3) Å and c=33.8680(11) Å, giving a cell volume of 5713.5(3) Å^3. The calculated density is 1.768 g/cm^3, which is slightly lower than the density of anhydrous TNBPy (1.820 g/cm^3) and TNBPy·H$_2$O ($\mathbf{1}\cdot H_2O$) (1.830 g/cm^3) [13].

The asymmetric unit includes four units of **6**. The anions consist each out of two planar pyrazole-rings ($|\Theta_{\text{out of plane}}| \le 2.2°$) with averaged dihedral angle of 70.8° between both. This twist is lower compared to that found in anhydrous TNBPy (71.44(5)°) and TNBPy·H$_2$O ($\mathbf{1}\cdot H_2O$) (78.99(6)°) [13]. The carbon-carbon bond in the pyrazole-rings have an medium length of 1.388 Å. The carbon-nitrogen and nitrogen-nitrogen bond lengths are very similar with 1.342 Å and 1.345 Å on average, respectively. The medium bond length between the ring-connecting carbon is 1.465 Å, which sustainably smaller than a typical carbon-carbon single bond, displaying its aromatic character. Similarly, the carbon-nitrogen bond to the nitro-groups have a reduced length of 1.430 Å on average, also showing their affiliation to the aromatic system. The medium bond angle located at one nitrogen of the pyrazole-rings is 106.9°, nearly matching the angle of an equilateral pentagon (108°). In comparison the bond angles at the nitro-carbons are widened (averaged 113.3°), while bond angles located at the ring-connecting carbon are compressed (averaged. 99.8°). All nitrogen of the nitro-groups

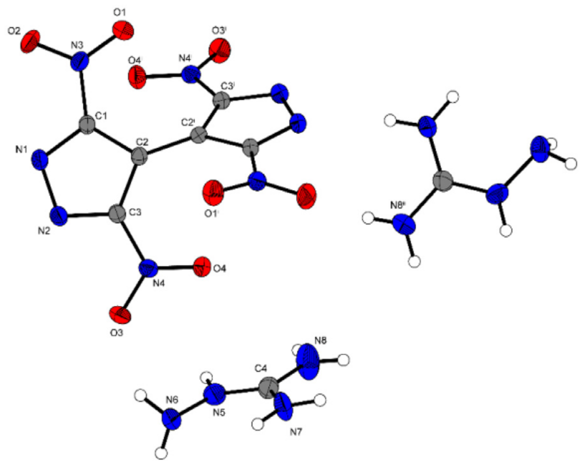


Fig. 4. Molecular unit of bis(aminoguanidinium) 3,3′,5,5′-tetranitro-4,4′-bipyrazolate (5) in the crystalline state. Ellipsoids correspond to 50% probability levels. Hydrogen radii are arbitrary. Selected bond lengths (Å) and angles (deg): N1–N2 1.3398(13), N1–C1 1.3475(13), C1–C2 1.3934(15), C2–C2′ 1.4623(14), N8–C4 1.3280(18), N2–N1–C1 106.98(9), N1–N2–C3 106.87(9), C1–C2–C3 99.11(8), C1–C2–C2′ 130.42(9), N7–C4–N8 119.66(13), C1–N1–N2–C3 0.34(11), C1–C2–C2′–C1′ 130.13(13), C61–N5–C4–N8 –176.91(13).

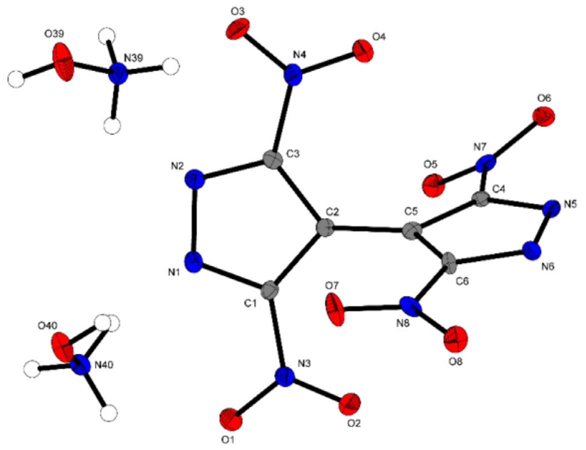


Fig. 5. Molecular unit of bis(hydroxylammonium) 3,3′,5,5′-tetranitro-4,4′-bipyrazolate (6) in the crystalline state. Ellipsoids correspond to 50% probability levels. Hydrogen radii are arbitrary. Selected bond lengths (Å) and angles [deg.]: N1–N2 1.348(7), N1–C1 1.341(7), C1–C2 1.395(7), C2–C5 1.461(7), N3–C1 1.424(7), N4–C3 1.430(7), O39–N39 1.408(7), O3–N4 1.243(6), N2–N1–C1 107.4(5), N3–C1–C2 128.2(5), C1–C2–C5 131.2(5), C3–C2–C5 129.2(5), C3–C2–C5 129.2(5), C1–N1–N2–C3 1.2(6), N2–N1–C1–N3 179.9(5), N2–N1–C1–N3 179.9(5), N1–N2–C3–N4 178.8(4), C1–C2–C5–C4 117.6(8), C1–C2–C5–C6 –66.3(9).

nearly lies in the plane of its pyrazole-ring ($|\Theta_{\text{out of plane}}| \leq 6.9°$), while the oxygen shows different amount of rotation against this plane ($0.2° \leq |\Theta_{\text{out of plane}}| \leq 30.7°$) (Fig. 5).

2.3. ^{15}N nmr spectroscopy

All synthesized compounds were characterized via multinuclear ^{1}H, ^{13}C and ^{14}N NMR spectroscopy, elemental analysis, vibrational spectroscopy (IR), and mass spectrometry. In addition, the ^{15}N NMR spectra of potassium 4-(1-amino-3,5-dinitropyrazolyl)–3′,5′-dinitro-pyrazolate (11) and 1,1′-diamino-3,3′,5,5′-tetranitro-4,4‘-bipyrazole (12) were recorded and the spectrum is shown in Fig. 6. Compound **11** exhibits nine resonances in the ^{15}N NMR spectrum. All eight resonances for the nitro groups and the pyrazole nitrogen atoms are observed in the range between −16.1 ppm and 165.2 ppm. The amino group is observed at −284.4 ppm as a triplet with a coupling constant of $^{1}J_{NH}$=73.6 Hz. ^{15}N NMR spectrum of 12 exhibits five resonances; both nitro groups show resonances at −26.1 (N1) and −32.4 (N2) ppm, both N atoms of the pyrazole ring-system are observed at −81.4 (N3) ppm and −163.0 (N4) ppm, whereas the amino groups are visible at −283.3 (N5) ppm. The NH_2 groups are observed as a singlet resonance in the ^{1}H coupled ^{15}N spectrum and not as the expected triplet resonance. Possible reason for this result is the potential ^{1}H/^{2}D exchange of $(NH_2)_2$TNBPz (12) with the d_6-DMSO solvent, in which the sample was measured Table 1.

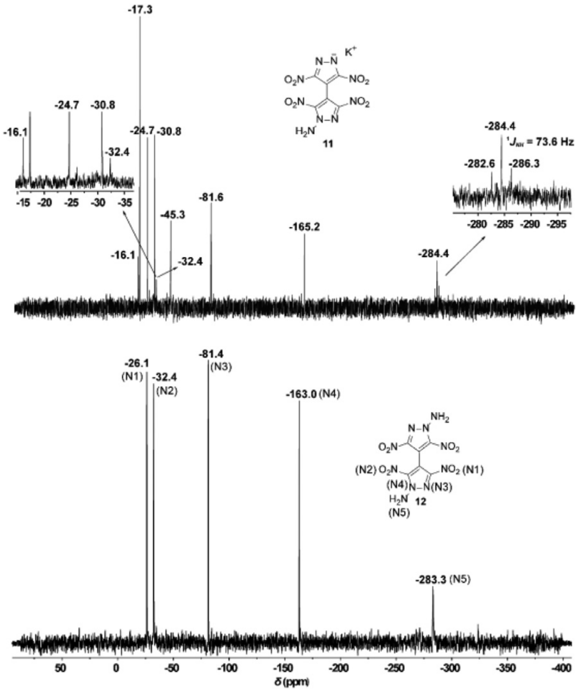


Fig. 6. ^{15}N NMR spectra of potassium 4-(1-amino-3,5-dinitropyrazolyl)–3′,5′-dinitropyrazolate (11) and 1,1′-diamino-3,3′,5,5′-tetranitro-4,4′-bipyrazole (12) in d_6-DMSO.

Table 1
Toxicity assessment results for compounds **3** and **4**.

	EC_{50} (g/L) (15 min)	EC_{50} (g/L) (30 min)	Toxicity level[a]
3	>>1.64	>>1.64	+
4	2.06	1.49	+

[a] Toxicity level (incubation 30 min): Very toxic (–) < 0.10 g/L; Toxic (o) 0.10–1.00 g/L; Less toxic (+) > 1.00 g/L.

2.4. Toxicity assessments

To get a first impression how toxic the nitrated bipyrazole salts **11** and **12** act towards the aquatic environment, they were exposed to *Vibrio fischeri* bacteria strains. These bioluminescent bacteria strains are naturally found in the seas, therefore the measurements with different concentrations of the desired compounds are carried out in a stock solution of 2% NaCl at 15 °C ± 0.3 °C [19]. The bioluminescence of the bacteria was measured after 15 min and 30 min exposure time with the compounds again and leads to the EC_{50} (effective concentration, were the bioluminescence is decreased to 50%). At first, they were classified as nontoxic (> 1.00 g/L); toxic (0.10–1.00 g/L) and very toxic (< 0.10 g/L) [20]. For the guanidinium salt **4**, EC_{50} values of 2.09 g/L (15 min) and 1.49 g/L (30 min) were measured, the potassium salt **3** of the same TNBPz anion led to values of 1.66 g/L and 1.27 g/L. Therefore, this

Table 2
Physico-chemical properties of **2, 4–6, 8, 11,** and **12**.

Compound	**2**	**4**	**5**	**6**	**8**	**11**	**12**
IS[a] (J)	10	40	10	5	10	10	15
FS[b] (N)	350	> 360	> 360	324	360	48	324
ESD[c] (J)	0.041	1.50	1.25	0.20	0.50	0.025	0.013
Ω[d] (%)	−51.4	−51.8	−51.9	−25.3	−36.8	−23.9	−27.9
T_m[e] (C)	186	251	179	–	–	–	234
T_{dec}[f] (C)	270	300	210	194	276	280	244
ρ[g] (g/cm^3)	1.72	1.63	1.66	1.72	1.69	2.00	1.75[*]
ΔH_f°[h] (kJ/mol)	200.9	88.8	308.5	236.7	108.7	139.3	464.5
EXPLO5 6.03							
$-\Delta_E U^{\circ}$[i] (kJ/kg)	4795	3903	4224	5657	4759	5172	5540
$T_{\text{C-J}}$[j] (K)	4041	2909	3009	3934	3421	3633	4114
$p_{\text{C-J}}$[k] (kbar)	242	208	231	302	258	318	305
$D_{\text{C-J}}$[l] (m/s)	7711	7484	7866	8456	8003	8517	8469
V[m] (dm^3/kg)	693	474	467	770	452	560	738

[a] Impact sensitivity (BAM drophammer, method 1 of 6);
[b] Friction sensitivity (BAM drophammer, method 1 of 6);
[c] Electrostatic discharge device (OZM research);
[d] Oxygen balance;
[e] Melting point (DTA, $\beta = 5$ °C/min);
[f] Temperature of decomposition (DTA, $\beta = 5$ °C/min);
[g] Density at 298 K;
[h] Standard molar enthalpy of formation;
[i] Detonation energy;
[j] Detonation temperature;
[k] Detonation pressure;
[l] Detonation velocity;
[m] Volume of detonation gasses at standard temperature and pressure conditions;
[*] Pycnometric density measurement.

anion is considered as not-toxic. This is in quite good agreement with the potassium salt of the TriNBPz anion (EC$_{50}$ (15 min)=2.86 g/L; EC$_{50}$ (30 min)=1.42 g/L) [21]. Eventually, compared to the corresponding monomer, the potassium salt of the 3,4-dinitropyrazole, this is an interesting finding, because it has an EC$_{50}$ value of 1.21 g/L and 0.95 g/L, respectively and is considered as toxic [22]. The values for the potassium salts of the corresponding N-oxides are suggesting that they are even more toxic [23]. The common used secondary explosive RDX is more toxic towards the bacteria strain compared to the herein presented compounds (EC$_{50}$ (15 min)=0.33 g/L; EC$_{50}$ (30 min)=0.24g/L) [20,24].

2.5. Physical and detonation properties

Since all synthesized compounds (**2**–**12**) in this work are energetic materials their properties were investigated. In addition, all theoretically and experimentally determined detonation properties for compounds **2, 4**–**6**, **8**, **11**, and **12** are reported in Table 2. The thermal behavior of all compounds was determined with OZM Research DTA 552-Ex instrument at a heating rate of 5 °C/min. In the case of all TNBPz based energetic materials compounds **2** (T_{dec}=270 °C), 4 (T_{dec}=300 °C), 8 (T_{dec}=276 °C) and 11 (T_{dec}=280 °C) show the highest thermal stability, whereas 2 and 4 decompose prior melting at 186 °C and 251 °C, respectively. Comparison of the hydroxylammonium salts ((NH_3OH)HTriNBPz (6 T_{dec}=230 °C), (NH_3OH)HTNBPz (15 T_{dec}=201 °C) and $(NH_3OH)_2$TNBPz (16 T_{dec}=194 °C) to each other shows that the TNBPz monoanion based salt exhibits better thermal stability than the related hydroxylammonium salts [21].

The plotted DTAs of compounds **7–9**, **11** and **12** are presented in Fig. 7. The ionic compounds **7** (215 °C), **8** (276 °C), **9** (250 °C) and **11** (280 °C) show sharp decomposition signals in the DTA plots, whereas the organic compound $(NH_2)_2$TNBPz (**12**) decomposes at 244 °C prior melting (234 °C).

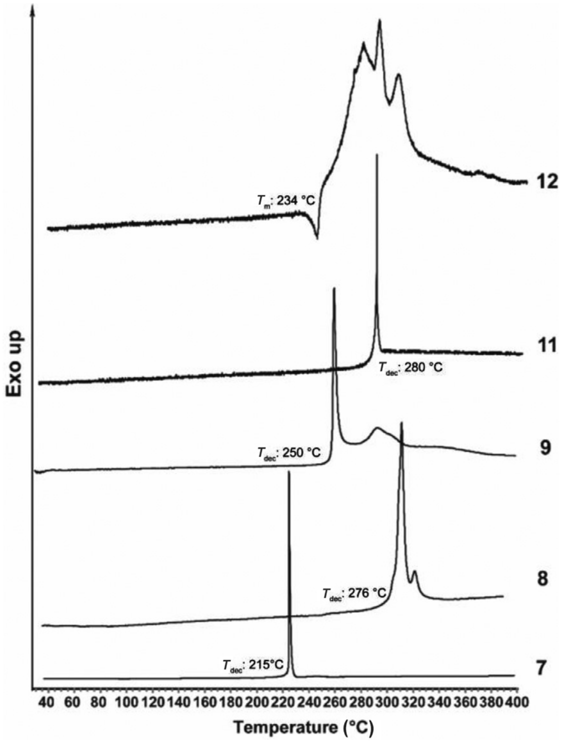
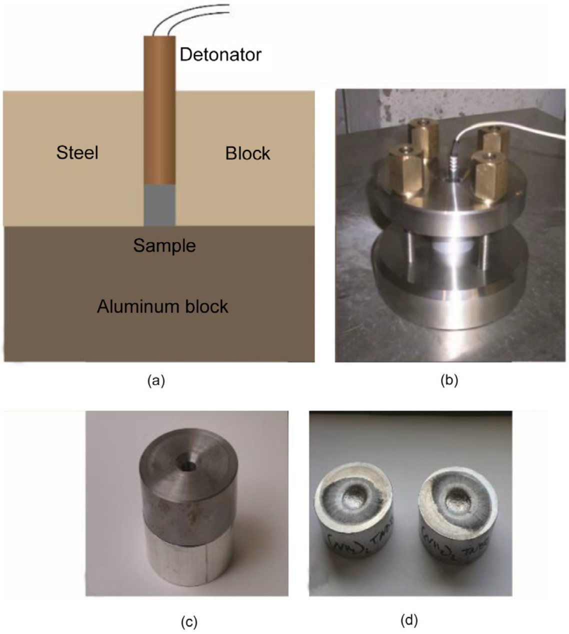


Fig. 7. DTA plots for selected compounds (Heating rate: 5 °C/min, critical temperatures are given as onset temperatures).

The lowest room temperature densities for the TNBPz based ionic derivatives are 1.66 g/cm^3 for compound **5** and 1.63 g/cm^3 for compound **4**. The highest reported density for the TNBPz based energetic derivatives is of the potassium salt **11** with 2.00 g/cm^3, followed by 1.75 g/cm^3 for compound **12**.

Experimentally determined sensitivities toward impact, friction and electrostatic discharge are also reported in Table 2. The determined sensitivities vary for impact from 5 J to 40 J, for friction from 48 N to >



(a) (b)

(c) (d)

Fig. 8. SSRT results. (a) Schematical illustration. (b) Photograph of the setup. (c) Aluminum block and steel block filled with compound **12**. (d) Dented aluminum block after initiation of the explosive with a commercial detonator.

360 N and for electrostatic discharge from 0.013 J up to 1.50 J. The most impact sensitive material is the hydroxylammonium salt **6** with 5 J. The most impact insensitive compound with 40 J is the guanidinium salt **4**. The energetic materials 2 (10 J), 5 (10 J), 8 (10 J), 11 (10 J) and 12 (15 J) exhibit moderate impact sensitivity values. In addition, the most synthesized ionic and neutral polynitrated bipyrazole derivatives exhibit low sensitivity toward friction. Only compound **12** shows high friction sensitivity with value of 48 N. In contrast to these results, the most sensitive compound to ESD is **12** with 0.013 J, followed by the potassium salt **11** with 0.025 J.

For the most synthesized energetic materials positive standard molar enthalpies of formation were calculated. The highest calculated enthalpy of formation for a TNBPz based derivative is 464.5 kJ/mol (12). The lowest positive enthalpy of formation was observed for the guanidinium salt **4** (88.8 kJ/mol). Using the room temperature densities [25] and the determined enthalpies of formation, several detonation properties were calculated for compounds **2**, **4–6**, **8**, **11**, and **12** by using the EXPLO5 code (6.03 Version) [26]. The calculated values for the detonation energy $(-_{\Delta E}U^{\circ})$ range from 3900 kJ/kg to 5700 kJ/kg. The highest values were calculated for compounds **5** (5657 kJ/kg), **11** (5172 kJ/kg) and **12** (5540 kJ/kg), whereas the lowest were determined for the guanidinium salt **4** with 3903 kJ/kg. In addition, the best performing compounds regarding calculated detonation pressure ($p_{\text{C-J}}$) and detonation velocity ($D_{\text{C-J}}$) are the ionic compounds **6** ($p_{\text{C-J}}$=328 kbar, $D_{\text{C-J}}$=8673 m/s $^{-}$), 11 ($p_{\text{C-J}}$=318 kbar, $D_{\text{C-J}}$=8517 m/s) and the N-aminated compound **12** ($p_{\text{C-J}}$=305 kbar, $D_{\text{C-J}}$=8469 m/s).

Additionally, the explosive performance (explosiveness) of 1,1′-diamino-3,3′,5,5′-tetranitro-4,4′-bipyrazole ($(NH_2)_2$TNBPz, **12**) was investigated in the small scale by the small-scale shock reactivity test (SSRT). For this purpose, a specific amount of the sample was put in a calendric whole in a steel block on the top of an aluminum block. Compound **12** was pressed at a consolidation dead load of 3 t with a dwell time of 5 s into a perforated steel block. The sample was initiated by a commercially available detonator (Orica-DYNADET C2–0 ms). The set-up for this test is shown in Fig. 8 and has been previously reported in the literature [25].

Table 3
The SSRT for 12 compared to HNS, PYX and TKX-55 [27].

	HNS	PYX	TKX-55	12
m_E (mg)[a]	469	474	496	472
m (mg)[b]	672	637	641	786

[a] Mass of the explosive: $m_E = V_s\ \rho\ 0.95$;
[b] Mass of SiO_2.

The obtained results after the initiation of compound **12** are shown in Fig. 8(d). The dent size was filled with a fine powdered SiO_2 sand and the resulting weight of SiO_2 was reported. The results for **12** are shown together with the corresponding value for HNS, PYX and TKX-55 in Table 3. The obtained value for $(NH_2)_2$TNBPz (**12**, 786 mg) compared to HNS (672 mg), PYX (637 mg) and TKX-55 (641 mg) shows that the explosive performance of double aminated 12 higher is than the heat resisting explosives HNS, PYX and TKX-55.

3. Experimental part

3.1. General information

^{1}H, ^{13}C, ^{14}N and ^{15}N NMR spectra were recorded on JEOL 270 and BRUKER AMX 400 instruments. The samples were measured at room temperature in standard NMR tubes (Φ 5 mm). Chemical shifts are reported as δ values in ppm relative to the residual solvent peaks of d_6-DMSO (δ H: 2.50, δ C: 39.5). Solvent residual signals and chemical shifts for NMR solvents were referenced against tetramethylsilane (TMS, δ=0 ppm) and nitromethane. Unless stated otherwise, coupling constants were reported in hertz (Hz) and for the characterization of the observed signal multiplicities the following abbreviations were used: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sept (septet), m (multiplet) and br (broad). Low resolution mass spectra were recorded on a JEOL JMS-700 MStation mass spectrometer (EI+/DEI+). Infrared spectra (IR) were recorded from 4500 cm^{-1} to 650 cm^{-1} on a PERKIN ELMER Spectrum BX-59, 343 instrument with SMITHS DETECTION DuraSamplIR II Diamond ATR sensor. The absorption bands are reported in wavenumbers (cm^{-1}). Elemental analysis was carried out by the department's internal micro analytical laboratory on an Elementar Vario el by pyrolysis of the sample and subsequent analysis of the formed gasses. Decomposition temperatures were measured via differential thermal analysis (DTA) with an OZM Research DTA 552-Ex instrument at a heating rate of 5 °C/min and in a range of room temperature to 400 °C. All sensitivities toward impact (IS) and friction (FS) were determined according to BAM (German: Bundesanstalt für Materialforschung und -prüfung) standards using a BAM drop hammer and a BAM friction apparatus [28]. All energetic compounds were tested for sensitivity towards electrical discharge using an Electric Spark Tester ESD 2010 EN.

3.2. Synthesis

3.2.1. 1,1′-Dimethyl-3,3′,5,5′-tetranitro-4,4′-bipyrazole (2)

3,3′,5,5′-Tetranitro-4,4′-bipyrazole monohydrate (500 mg, 1.51 mmol) was dissolved in water (10 mL) and $NaHCO_3$ (260 mg, 3.1 mmol) was added. The yellow solution was then heated to 65 °C and dimethyl sulfate (0.60 mL, 6.0 mmol) was added dropwise. The reaction mixture was stirred for 12 h at 85 °C. The white precipitate was filtered, washed with small amount of ice-water and tried on air to yield **2** (450 mg, 1.32 mmol, 88%) as a white solid.

DTA (5 °C/min): 186 (melt), 270 °C (exo); DTA (5 °C/min): 186 °C (melt), 270 °C (exo); BAM: drop hammer: 10 J (100–500 μm); friction tester: 360 N (100–500 μm); ESD: 41 μJ (100–500 μm). IR (ATR), $\tilde{\nu}$ (cm^{-1})=1566 (s), 1553 (w), 1504 (vs), 1428 (s), 1328 (vs), 1292 (s), 1011 (m), 890 (m), 876 (m), 767 (m), 767 (m), 694 (m). ^{1}H

NMR (d_6-DMSO, 400 MHz, ppm) δ=4.40 (s, 6H). ^{13}C NMR (d_6-DMSO, 101 MHz, ppm) δ=149.4, 144.0, 101.8. ^{14}N NMR (d_6-DMSO, 29 MHz, ppm) δ=−32. Elem. Anal. ($C_6H_6N_8O_8$, 342.18 g/mol) calcd: C 28.08%, H 1.77%, N 32.75%. Found: C 27.97%, H 1.61%, N 32.52%.

3.2.2. Dipotassium 3,3′,5,5′-tetranitro-4,4′-bipyrazolate monohydrated (3·H_2O)

3,3′,5,5′-Tetranitro-4,4′-bipyrazole monohydrate (665 mg, 2.0 mmol, 2.0 eq) was dissolved in a mixture of EtOH (10 mL) and water (5 mL) and to the solution was added potassium carbonate (277 mg, 2.00 mmol, 2.0 eq). The mixture was heated to reflux for 30 mins and after cooling down to room temperature the solvent was removed in vacuo to yield compound **3**·H_2O as yellow solid (716 mg, 1.75 mmol, 97%).

BAM: drop hammer: 1.5 J (100–500 µm); friction tester: 120 N (100–500 µm); ESD: 0.16 J (100–500 µm). IR (ATR), $\tilde{\nu}$ (cm^{-1})=3454 (m), 3425 (m), 3359 (m), 3195 (br), 1678 (m), 1654 (s), 1546 (s), 1494 (m), 1477 (m), 1378 (vs), 1325 (vs), 1298 (s), 1179 (m), 1021 (m), 993 (s), 855 (s), 835 (s); ^{1}H NMR (d_6-DMSO, 400 MHz, ppm) δ=3.33 (s, H_2O). ^{13}C NMR (d_6-DMSO, 101 MHz, ppm) δ=153.9, 104.4. ^{14}N NMR (d_6-DMSO, 29 MHz, ppm) δ=−14.

Compound **3**·H_2O was dried in vacuo for 6 h to yield the anhydrous dipotassium 3,3′,5,5′-tetranitro-4,4′-bipyrazolate (3).

Elem. Anal. ($C_6K_2N_8O_8$, 390.31 g/mol) calcd.: C 18.46%, H 0.00%, N 28.71%. Found: C 18.15%, H 0.00%, N 27.82%.

*3.2.3. Bis(guanidinium) 3,3′,5,5′-tetranitro-4,4′-bipyrazolate **(4)***

3,3′,5,5′-Tetranitro-4,4′-bipyrazole monohydrate (166 mg, 0.5 mmol, 1.0 eq) was solved in ethanol (10 mL) and the solution was heated to 75 °C. Guanidine carbonate (91 mg, 0.5 mmol, 1.0 eq) was added. Filtration and removing the solvent at room temperature yielded the product as yellow crystals (23, 216 mg, 0.50 mmol, 100%).

DTA (5 °C/min): 251 (melt), 300 °C (exo); BAM: drop hammer: 40 J (100–500 µm); friction tester: >360 N (100–500 µm); ESD: 1.50 J (100–500 µm). IR (ATR), $\tilde{\nu}$ (cm^{-1})=3430 (s), 3375 (m), 3154 (m), 2797 (w), 1634 (s), 1574 (w), 1528 (m), 1474 (s), 1402 (m), 1377 (m), 1336 (vs), 1310 (s), 1300 (vs), 1166 (w), 1001 (m), 846 (s), 772 (vw), 713 (w), 692 (w), 614 (vw), 549 (vw), 524 (vw). Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu}$ (cm^{-1})=1631 (13), 1505 (11), 1478 (5), 1385 (72), 1360 (45), 1321 (26), 1282 (13), 1216 (7), 1169 (100), 1009 (17), 830 (35), 816 (3),776 (2), 761 (5), 671 (4), 526 (6), 381 (3), 307 (5), 277 (9), 121 (35). ^{1}H NMR (d_6-DMSO, 400 MHz, ppm) δ=6.93 (s, 12H). ^{13}C NMR (d_6-DMSO, 101 MHz, ppm) δ=157.9, 153.8, 104.3. ^{14}N NMR (d_6-DMSO, 29 MHz, ppm) δ=−17. Elem. Anal. ($C_8H_{12}N_{14}O_8$, 432.27 g/mol) calcd: C 22.23%, H 2.80%, N 45.36%. Found: C 22.51%, H 2.84%, N 45.31%.

*3.2.4. Bis(aminoguanidinium) 3,3′,5,5′-tetranitro-4,4′-bipyrazolate **(5)***

3,3′,5,5′-Tetranitro-4,4′-bipyrazole monohydrate (332 mg, 1.00 mmol, 1.0 eq) was solved in ethanol (20 mL) and water (10 mL). The solution was heated to 75 °C. Aminoguanidine bicarbonate (273 mg, 2.0 mmol, 2.0 eq.) was added. Filtration and removing the solvent at room temperature results the product as yellow crystals (**5**, 463 mg, 1.00 mmol, 100%).

DTA (5 °C/min): 179 (melt), 210 °C (exo); BAM: drop hammer: 10 J (100–500 µm); friction tester: >360 N (100–500 µm); ESD: 1.25 J (100–500 µm). IR (ATR), $\tilde{\nu}$ (cm^{-1})=3476 (w), 3430 (m), 3354 (m), 3319 (m), 3167 (w), 2827 (w), 1670 (s), 1532 (m), 1478 (s), 1405 (w), 1379 (m), 1338 (vs), 1309 (s), 1217 (w), 1160 (w), 1078 (vw), 998 (m), 844 (s), 759 (vw), 708 (w), 633 (w), 517 (vw). Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu}$ (cm^{-1})=1627 (17), 1506 (11), 1481 (8), 1407 (29), 1388 (100), 1362 (49), 1318 (26), 1312 (23), 1280 (15), 1215 (11), 1178 (80), 1162 (60), 1023 (5), 1000 (6), 971 (7), 832 (48), 814 (4), 761 (7), 667 (4), 633 (3), 501 (5), 307 (4), 293 (6), 279 (9), 194 (8), 155 (13). ^{1}H NMR (d_6-DMSO, 400 MHz, ppm) δ=8.58 (s, 2H), 7.27 (s, 4H), 6.76 (s, 4H), 4.69 (s, 4H). ^{13}C NMR (d_6-DMSO, 101 MHz, ppm) δ=159.2, 154.3, 104.7. ^{14}N NMR (d_6-DMSO, 29 MHz, ppm) δ=−19. Elem. Anal. ($C_8H_{14}N_{16}O_8$, 462.30 g/mol) calcd: C 20.78%, H 3.05%, N 48.48%. Found: C 21.04%, H 3.07%, N 48.25%.

*3.2.5. Bis(hydroxylammonium) 3,3′,5,5′-tetranitro-4,4′-bipyrazolate **(6)***

3,3′,5,5′-Tetranitro-4,4′-bipyrazole monohydrate (500 mg, 1.50 mmol, 1.00 eq) was dissolved in Et_2O (20 mL) and EtOH (5 mL). Aqueous NH_2OH (241 mg, 50-wt%, 6.00 mmol, 4.00 eq) was added dropwise and the resulting reaction mixture was stirred for 1 h at room temperature. Removal of the solvents in vacuo afforded compound **6** as a yellow solid (570 mg, 1.50 mmol, 100%).

DTA (5 °C/min): 194 °C (exo); BAM: drop hammer: 5 J (100–500 µm); friction tester: 324 N (100–500 µm); ESD: 200 mJ (100–500 µm). IR (ATR), $\tilde{\nu}$ (cm^{-1})=3138 (br), 2605 (br), 1538 (m), 1481 (s), 1393 (s), 1341 (vs), 1311 (vs), 1191 (m), 1028 (m), 1004 (s), 850 (vs), 769 (w), 692 (w). ^{1}H NMR (d_6-DMSO, 400 MHz, ppm) δ=10.13 (s, 6H), 9.96 (s, 2H). ^{13}C NMR (d_6-DMSO, 101 MHz, ppm) δ=153.6, 104.1. ^{14}N NMR (d_6-DMSO, 29 MHz, ppm) δ=−14. Elem. Anal. ($C_6H_8N_{10}O_{10}$, 380.19 g/mol) calcd: C 18.95%, H 2.12%, N 36.84%. Found: C 19.40%, H 2.00%, N 36.34%.

*3.2.6. Bis(hydrazinium) 3,3′,5,5′-tetranitro-4,4′-bipyrazolate **(7)***

3,3′,5,5′-Tetranitro-4,4′-bipyrazole monohydrate (499 mg, 1.5 mmol, 1.0 eq) was solved in ethanol (12 mL). The solution was heated to 75 °C. Hydrazine hydrate (150 mg, 3.0 mmol, 2.0 eq) was added. Filtration and removing the solvent at room temperature results the product as yellow crystals (**7**, 567 mg, 1.50 mmol, 100%).

BAM: drop hammer: 4 J (100–500 µm); friction tester: 216 N (100–500 µm); ESD: 0.25 J (100–500 µm). IR (ATR), $\tilde{\nu}$ (cm^{-1})=3339 (vw), 3205 (w), 2592 (m), 1610 (w), 1530 (m), 1474 (s), 1374 (m), 1340 (vs), 1315 (vs), 1303 (s), 1284 (s), 1180 (m), 1089 (m), 1002 (m), 947 (m), 845 (vs), 772 (w), 760 (w), 713 (w), 689 (w), 630 (w), 591 (w), 521 (w). Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu}$ (cm^{-1})=1625 (32), 1514 (7), 1478 (5), 1395 (100), 1364 (68), 1327 (28), 1320 (27), 1286 (17), 1217 (10), 1192 (94), 1182 (90), 1025 (6), 1003 (5), 951 (3), 833 (57), 814 (2), 775 (3), 761 (12), 668 (5), 596 (2), 526 (2), 375 (4), 309 (8), 282 (9), 175 (9), 113 (4). ^{1}H NMR (d_6-DMSO, 400 MHz, ppm) δ=6.33 (s, 10H). ^{13}C NMR (d_6-DMSO, 101 MHz, ppm) δ=153.0, 103.6. ^{14}N NMR (d_6-DMSO, 29 MHz, ppm) δ=−17. Elem. Anal. ($C_6H_{10}N_{12}O_8$, 378.22 g/mol) calcd: C 19.05%, H 2.67%, N 44.44%. Found: C 19.31%, H 2.98%, N 42.06%.

*3.2.7. Bis(ammonium) 3,3′,5,5′-tetranitro-4,4′-bipyrazolate **(8)***

3,3′,5,5′-Tetranitro-4,4′-bipyrazole monohydrate (332 mg, 1.00 mmol, 1.0 eq) was solved in ethanol (10 mL). The solution was heated to 75 °C. Ammonium carbonate (96 mg, 1.0 mmol, 2.0 eq) was added. Filtration and removing the solvent at room temperature gave the product as yellow crystals (368 mg, 1.00 mmol, 100%).

DTA (5 °C/min): 276 °C (exo); BAM: drop hammer: 10 J (100–500 µm); friction tester: >360 N (100–500 µm); ESD: 0.50 J (100–500 µm). IR (ATR), $\tilde{\nu}$ (cm^{-1})=3635 (vw), 3482 (vw), 3246 (w), 2897 (w), 2775 (w), 1824 (vw), 1645 (vw), 1540 (m), 1483 (s), 1422 (s), 1401 (s), 1341 (vs), 1310 (s), 1182 (m), 1080 (vw), 1046 (vw), 1026 (w), 1003 (s), 841 (s), 772 (w), 758 (w), 696 (m), 591 (m), 513 (w). Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu}$ (cm^{-1})=1644 (12), 1526 (10), 1397 (100), 1318 (20), 1288 (8), 1216 (9), 1186 (75), 1025 (4), 1003 (5), 829 (38), 760 (7), 669 (3), 592 (4), 527 (4), 374 (4), 278 (12). ^{1}H NMR (d_6-DMSO, 400 MHz, ppm) δ=5.65 (s, 8H). ^{13}C NMR (d_6-DMSO, 101 MHz, ppm) δ=151.7, 102.4. ^{14}N NMR (d_6-DMSO, 29 MHz, ppm) δ=−17, −357. Elem. Anal. ($C_6H_8N_{10}O_8$, 348.19 g/mol) calcd: C 20.70%, H 2.32%, N 40.23%. Found: C 20.59%, H 2.46%, N 39.33%.

*3.2.8. Bis(3,6,7-triamino-[1,2,4]triazolo[4,3-*b*][1,2,4]triazolium) 3,3′,5,5′-tetranitro-4,4′-bipyrazolate **(9)***

3,3′,5,5′-Tetranitro-4,4′-bipyrazole monohydrate (450 mg, 1.36 mmol, 1.0 eq) was dissolved in EtOH (20 mL) and water (10 mL). The solution was heated to 80 °C and 3,6,7-triamino-[1,2,4]triazolo[4,3-*b*][1,2,4]triazole (TATOT, 419 mg, 2.72 mmol, 2.0 eq) was added. The reaction mixture was stirred at the same temperature for 30 min and then cooled to room temperature. The solvent was removed in vacuo to yield compound **9** as a yellow powder (812 mg, 1.31 mmol, 96%).

BAM: drop hammer: > 40 J (100–500 µm); friction tester: 360 N (100–500 µm); ESD: 63 mJ (100–500 µm). *IR* (ATR), $\tilde{\nu}$ (cm^{-1})=3462 (m), 3349 (m), 3228 (vw), 3117 (w), 1673 (s), 1642 (s), 1594 (vw), 1571 (vw), 1547 (m), 1496 (m) 1418 (vw), 1387 (m), 1328 (vs), 1303 (vs), 1178 (m), 1120 (vw), 1080 (vw), 1026 (s), 1002 (m), 921 (m), 839 (vs), 770 (vw), 707 (m), 593 (m). ^{1}H NMR (d_6-DMSO, 400 MHz, ppm) δ =13.36 (s, 2H), 8.18 (s, 4H), 7.23 (s, 4H), 5.77 (s, 4H). ^{13}C NMR (d_6-DMSO, 101 MHz, ppm) δ=160.2, 153.8, 147.4, 141.2, 104.3. ^{14}N NMR (d_6-DMSO, 29 MHz, ppm) δ=−17. Elem. Anal. ($C_{12}H_{14}N_{24}O_8$, 622.40 g/mol) calcd: C 23.16%, H 2.27%, N 54.01%. Found: C 23.43%, H 2.08%, N 53.78%.

3.2.9. *Bis(3,5-diamino-1,2,4-triazolium) 3,3′,5,5′-tetranitro-4,4′-bipyrazolate* ***(10)***

3,3′,5,5′-Tetranitro-4,4′-bipyrazole monohydrate (416 mg, 1.25 mmol, 1.0 eq) was dissolved in a mixture of EtOH (10 mL) and water (5 mL) and the solution was heated to 80 °C. 3,5-Diamino-1,2,4-triazole (248 mg, 2.50 mmol, 2.0 eq) was added and the reaction mixture was stirred for 30 mins. After cooling the solvent was removed in vacuo and compound **10** was obtained as yellow solid (631 mg, 1.23 mmol, 99%).

DTA (5 °C/min): 252 °C (melt), 289 °C (exo); BAM: drop hammer: > 40 J (100–500 µm); friction tester: > 360 N (100–500 µm); ESD: 0.61 (100–500 µm). IR (ATR), $\tilde{\nu}$ (cm^{-1})=3456 (m), 3359 (m), 1682 (w), 1659 (s), 1610 (vw), 1596 (vw), 1538 (m), 1489 (m), 1412 (w), 1390 (m), 1338 (vs), 1300 (s), 1180 (w), 1019 (m), 1002 (m), 845 (s); ^{1}H NMR (d_6-DMSO, 400 MHz, ppm) δ=7.37 (br, 4H). ^{13}C NMR (d_6-DMSO, 101 MHz, ppm) δ=153.7, 151.7, 104.2. ^{14}N NMR (d_6-DMSO, 29 MHz, ppm) δ=−17. Elem. Anal. ($C_{10}H_{12}N_{18}O_8$, 512.32 g/mol) calcd: C 23.44%, H 2.36%, N 49.21%. Found: C 23.29%, H 2.25%, N 48.20%.

3.2.10. *Potassium 4-(1-amino-3,5-dinitropyrazolyl)−3′,5′-dinitropyrazolate* ***(11)***

Sodium hydroxide (1.02 g, 25.0 mmol) and potassium dihydrogen phosphate (3.77 g, 28.0 mmol) were dissolved in water (15 mL) and TNBPz • H_2O (500 mg, 1.50 mmol) was added. The reaction mixture was heated to 60 °C and hydroxylamine-*O*-sulfonic acid (1.70 g, 15.0 mmol, 10.0 eq.) was added slowly. The suspension was stirred overnight at 60 °C. The formed precipitate was filtered, washed with small amount of water and dried on air to yield compound **11** (377 mg, 69%) as a yellow powder.

DTA (5 °C/min): 280 °C (exo); BAM: drop hammer: 10 J (100–500 µm); friction tester: 48 N (100–500 µm); ESD: 25 µJ (100–500 µm). IR (ATR), $\tilde{\nu}$ (cm^{-1})=3347 (w), 3043 (br), 1534 (s), 1481 (s), 1399 (s), 1368 (s), 1325 (vs), 1310 (vs), 1007 (m), 847 (vs), 756 (m), 741 (m). ^{1}H NMR (d_6-DMSO, 400 MHz, ppm) δ =7.86 (s, 2H). ^{13}C NMR (d_6-DMSO, 101 MHz, ppm) δ =153.9, 153.7, 145.3, 139.7, 106.1, 97.9. ^{14}N NMR (d_6-DMSO, 29 MHz, ppm) δ=−33. Elem. Anal. ($C_6H_2KN_9O_8$, 367.24 g/mol) calcd: C 19.62%, H 0.55%, N 34.33%. Found: C 19.72%, H 0.74%, N 33.95%.

3.2.11. *1,1′-Diamino-3,3′,5,5′-tetranitro-4,4′-bipyrazole* ***(12)***

3,3′,5,5′-Tetranitro-4,4′-bipyrazole monohydrate (2.00 g, 6.00 mmol, 1.0 eq) was dissolved in acetonitrile (100 mL) and 1,8-diazabicyclo[5.4.0]undec-7-en (DBU, 1.85 mL, 12.3 mmol, 2.05 eq) was added. The resulting solution was stirred for 1 h at room temperature and a freshly prepared solution of *O*-*p*-toluene sulfonylhydrohylamine (TOSA, 2.8 eq) in DCM was added in one portion. The resulting reaction mixture was stirred for 2 d at room temperature and the solvent was removed in vacuo. The resulting crude product was recrystallized from EtOH/H_2O to result in compound **12** (1.80 g, 87%) as a pale yellow solid.

DTA (5 °C/min): 234 °C (melt), 244 °C (exo); BAM: drop hammer: 15 J (100–500 µm); friction tester: 324 N (100–500 µm); ESD: 13 µJ (100–500 µm). IR (ATR), $\tilde{\nu}$ (cm^{-1})=3338 (m). 3273 (m), 1551 (s), 1490 (s), 1430 (m), 1380 (m), 1324 (vs), 1132 (m), 1104 (w), 1012 (m), 932 (w), 869 (s), 731 (m). ^{1}H NMR (d_6-DMSO, 400 MHz, ppm) δ=8.03 (s, 4H). ^{13}C NMR (d_6-DMSO, 101 MHz, ppm) δ=145.5, 140.1, 100.5. ^{14}N NMR (d_6-DMSO, 29 MHz, ppm) δ=−32. ^{15}N NMR (d_6-DMSO, 41 MHz, ppm) δ=−26.1 (N1), −32.4 (N2), −81.4 (N3), −163.0 (N4), −283.3 (N5). Elem. Anal. ($C_8H_4N_{10}O_8$, 344.16 g/mol) calcd: C 20.94%, H 1.17%, N 40.70%. Found: C 21.21%, H 1.25%, N 40.50%. *m/z* (DEI$^+$): 344.03 [M]$^+$, 210.02, 103.00, 77.00.

4. Conclusions

During this work the energetic functionalization of TNBPz ($\mathbf{1}\cdot H_2O$) was achieved. We report the neutralization reactions of TNBPz with different nitrogen-rich bases, which yielded many different ionic based energetic materials. In addition, the N-methylation and N-amination of $\mathbf{1}\cdot H_2O$ is reported. All new synthesized compounds were obtained from good to excellent yields. The N-methylation of TNBPz ($\mathbf{1}\cdot H_2O$) was achieved with dimethyl sulfate at elevated temperatures. The mono N-amination of TNBPz ($\mathbf{1}\cdot H_2O$) was obtained by reacting $\mathbf{1}\cdot H_2O$ with hydroxylamine-*O*-sulfonic acid (HOSA) in a NaOH/KH_2PO_4 buffer solution at 60 °C. Whereas, the double N-amination of TNBPz was obtained by reacting $\mathbf{1}\cdot H_2O$ with O-p-toluenesulfonylhydroxylamine (TOSA). All synthesized compounds were extensively investigated and the physico-chemical properties of the following compounds **2**, **4–6**, **8**, **11** and 12 are reported. From all synthesized energetic compounds, the ionic derivatives **6** ($p_{\text{C-J}}$=302 kbar, $D_{\text{C-J}}$=8456 m/s), **11** ($p_{\text{C-J}}$=318 kbar, $D_{\text{C-J}}$=8517 m/s) and the N-aminated **12** ($p_{\text{C-J}}$=305 kbar, $D_{\text{C-J}}$=8469 m/s) show the best performance. The hydroxylammonium salt **6** (*IS*=5 J) exhibits the highest impact sensitivity, whereas the potassium salt **11** (*FS*=48 N) is the compound with the highest friction sensitivity. Finally, the toxicity of compounds **3** and **4** toward aquatic bacteria (Vibrio fisheri) was investigated and the obtained results show that the ionic derivatives based on TNBPz are not toxic.

Declaration of Competing Interest

Jörg Stierstorfer and Thomas M. Klapötke are editorial board members for FirePhysChem and were not involved in the editorial review or the decision to publish this article. All authors declare that there are no competing interests.

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Supplementary materials

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