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Potassium *N*-Nitramino-5*H*-Tetrazolates – Powerful Green Primary Explosives with High Initiation Capabilities

Norbert Szimhardt,[a] Maximilian H. H. Wurzenberger,[a] Philipp Spieß,[a] Thomas M. Klapötke,[a] and Jörg Stierstorfer*[a]

Abstract: Since the nowadays used lead-based primary explosives, lead azide, picrate and styphnate suffer from various environmental and toxic issues, there is a great need for new green materials. Therefore, two highly promising lead-free primary explosives potassium 1-(*N*-nitramino)-5*H*-tetrazolate (**1**, 1-KNAT) and potassium 2-(*N*-nitramino)-5*H*-tetrazolate (**2**, 2-KNAT) have been synthesized and characterized. Both isomers show superior energetic performance, initiation capability and were comprehensively analyzed by low-temperature X-ray diffraction, IR, multinuclear NMR spectroscopy, elemental analysis, and DTA. Sensitivity determinations toward impact, friction, and electrostatic discharge revealed its highly powerful, but also sensitive character. In addition, their potential as lead-free primaries were evaluated in initiation tests of PETN or RDX filled detonators confirming their great suitability as lead-free primary explosives.

Keywords: Lead-free Primary Explosives · Tetrazoles · Structure Elucidation · Nitramines · Potassium Salts

1 Introduction

In the field of high energy density materials (HEDM), the challenge has always been to find an ideal balance between high performance and molecular stability. By combining synthetic and theoretical studies, various strategies for the design of new energetic materials have become established [1–4]. However, driven by mounting demands for environmental sustainability and superior performance, considerable research is now focused on promoting the generation of eco-friendly and safe HEDM [2, 5, 6]. At least since the REACH (Registration, Evaluation, Authorization, and Restriction of Chemicals) [7] regulation in 2011, the restriction or even the prohibition of lead azide (LA) and lead styphnate (LS), which have been put on the candidate list, seems very likely in future. During the research for green primary explosives for both military and civilian purposes, metal-organic compounds have received considerable attention [8–10]. The formation of energetic salts seems to be extremely useful for triggering the individual behavior because of a crystal package and a pronounced cation-anion packing [11]. Among the alkali cations, potassium is considered the best as it combines environmental safety, good coordination, high availability, and low costs [12]. Up to now, several promising potassium-based primaries have been reported and investigated as potential substitutes for the commonly used lead-containing primary explosives (Chart 1) [13–17]. KDBNF is currently widely used in lead-free primer and igniter systems [17]. With KDNP in comparison, the temperature stability could be further improved, whereby also suitable properties for application as possible LS alternative could be shown [13]. In 2014, Fischer *et al.* reported K₂DNABT, a highly powerful green primary explosive, which combined good thermal stability and initiation capability, but shows increased sensitivity issues [14]. With the introduction of the nitramino group, the detonation properties and ease of salt formation could be significantly enhanced [18]. Nevertheless, a seven-step synthesis reduces the usability for industrial processes in order to replace the easily accessible lead compounds. From this point of view, a simpler and shorter synthesis would be very desirable.

Mentally separating the symmetrical K₂DNABT system into two molecules, leads to a mononitraminotetrazolate, which is noticeably easier to synthesize and shows comparable energetic parameters to the parent dinitraminotetrazolate compound. Almost two decades ago, first approaches to synthesize the silver and ammonium salts of 1-(*N*-nitramino)-5*H*-tetrazolate and 2-(*N*-nitramino)-5*H*-tetrazolate salts have been reported using alkyl nitrates as the nitrating reagent [19]. The salts were hardly characterized and suffer from an extreme lack of data (XRD, NMR spectroscopy, sensitivities, etc.). In order to close this gap and due to the expected enormous sensitivity of the silver salts and the probably undesirable good solubility of the ammonium salts, the previously unknown environmentally friendly po-

[a] *N. Szimhardt, M. H. H. Wurzenberger, P. Spieß, T. M. Klapötke, J. Stierstorfer*
Department of Chemistry, Energetic Materials Research
Ludwig Maximilian University
Butenandtstr. 5–13 (D), 81377 München (Germany)
**e-mail: jstch@cup.uni-muenchen.de*

N. Szimhardt, M. H. H. Wurzenberger, P. Spieß, T. M. Klapötke, J. Stierstorfer

tassium salts were selected as target molecules. Therefore, in our continuing efforts toward environmentally benign materials, we have now prepared and characterized the manageable potassium salts 1-KNAT (**1**) and the corresponding isomeric 2-KNAT (**2**) by an alternative synthetic route. Both compounds show promising energetic and physicochemical properties competitive with those of LA.
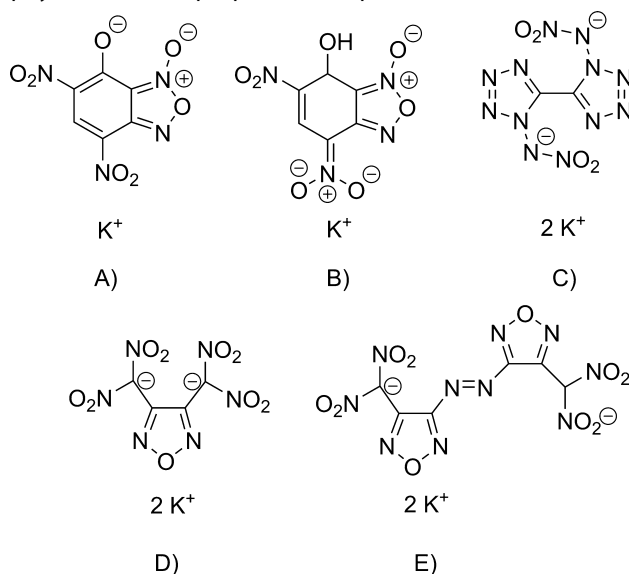
2 Experimental Section

More information on the general methods and synthesis of the starting compounds can be found in the Supporting Information.

Caution! All investigated compounds are highly powerful energetic materials, which show increased sensitivities toward various stimuli (e.g. elevated temperatures, impact, friction, or electrostatic discharge). Although no hazards occurred, proper security precautions (safety glasses, face shield, earthed equipment and shoes, leather jacket, Kevlar gloves, Kevlar sleeves, and ear plugs) have to be worn while synthesizing and handling the described compounds.

2.1 General Procedure for the Potassium N-Nitramino-5H-Tetrazolates 1 and 2

Under nitrogen atmosphere, the corresponding amino-5H-tetrazole was dissolved in dry acetonitrile and cooled to 0 °C. NO_2BF_4 was added portion wise, and after complete addition, the ice bath was removed. After stirring overnight, acetonitrile was removed under reduced pressure. The obtained residue was dissolved in a small amount of EtOH and one equivalent of KOEt dissolved in EtOH was added under ice cooling. Colorless precipitation was observed, filtered off, and a second equivalent of KOEt in EtOH was added to the filtrate under the same cooling conditions. After filtration,

the slightly yellow residue was washed with cold EtOH to obtain the corresponding potassium nitramino-5H-tetrazolate. The obtained solid material was further dried overnight at 110 °C.

### 2.2 Potassium 1-(N-Nitramino)-5H-Tetrazolate (1)

Following the general procedure 1-amino-5H-tetrazole (0.50 g, 5.80 mmol), dissolved in acetonitrile (20 mL), reacts with NO_2BF_4 (0.85 g, 7.00 mmol) to obtain **1** in form of a colorless solid (0.63 g, 3.80 mmol, 64 %). Single crystals suitable for X-ray diffraction were obtained by recrystallization from acetonitrile.

DTA (5 °C min⁻¹): onset: 180 °C (exothermic decomposition after melting); IR (ATR, cm⁻¹): $\tilde{v}$ = 3136 (m), 1676 (w), 1572 (w), 1500 (w), 1480 (vw), 1463 (m), 1410 (m), 1384 (s), 1306 (vs), 1276 (s), 1198 (m), 1176 (m), 1161 (s), 1105 (m), 1092 (s), 1007 (m), 957 (m), 925 (w), 891 (m), 867 (s), 820 (w), 775 (s), 725 (m), 725 (m), 717 (m), 687 (w), 654 (s), 535 (w), 472 (w), 453 (m); ¹H NMR (DMSO-d_6, 25 °C, ppm) δ: 9.18 (s, 1H, C—H); ¹³C NMR (DMSO-d_6, 25 °C, ppm) δ: 142.2 (s, 1C, CN_4); ¹⁴N NMR (DMSO-d_6, 25 °C, ppm): δ = 4.2 (N6); ¹⁵N NMR (DMSO-d_6, 25 °C, ppm): δ 2.8 (d, $^3J_{N-H}$ = 2.8 Hz, N3), −4.9 (s, N6), −14.3 (d, $^3J_{N-H}$ = 0.8 Hz, N2), −54.3 (d, $^2J_{N-H}$ = 12.2 Hz, N4), −116.1 (d, $^2J_{N-H}$ = 8.4 Hz, N1), −122.7 (s, N5); EA: ($CHKN_5O_2$, 167.98) calc.: C 7.14, H 0.60, N 49.98 %; found: C 7.40, H 0.89, N 47.02 %; ball drop impact tester: < 4 mJ; BAM drophammer: < 1 J; friction tester: < 0.1 N; ESD: 0.89 mJ (at grain size < 100 μm).

2.3 Potassium 2-(N-Nitramino)-5H-Tetrazolate (2)

Following the general procedure 2-amino-5H-tetrazole (0.82 g, 7.50 mmol) dissolved in 20 mL acetonitrile, reacts with NO_2BF_4 (1.40 g, 10.5 mmol) to obtain **2** as a yellowish solid (0.77 g, 4.60 mmol, 48 %). Single crystals suitable for X-ray diffraction were obtained by recrystallization from acetonitrile.

DTA (5 °C min⁻¹): 176 °C (exothermic decomposition after melting); IR (ATR, cm⁻¹): $\tilde{v}$ = 3136 (w), 1814 (vw), 1572 (vw), 1505 (vw), 1481 (w), 1423 (s), 1371 (w), 1334 (s), 1272 (vs), 1262 (vs), 1220 (s), 1166 (m), 1130 (s), 1030 (s), 1009 (m), 1006 (m), 1003 (m), 910 (m), 892 (s), 778 (m), 730 (w), 705 (m), 677 (m), 677 (m); ¹H NMR (DMSO-d_6, 25 °C, ppm) δ: 8.77 (s, 1H, −CH); ¹³C NMR (DMSO-d_6, 25 °C, ppm) δ: 151.3 (s, 1 C, $CN4$); ¹⁴N NMR (DMSO-d_6, 25 °C, ppm): δ = −3.1 (N6); ¹⁵N NMR (DMSO-d_6, 25 °C, ppm): δ: −4.00 (s, N6), −7.8 (d, $^3J_{N-H}$ = 1.5 Hz, N3), −54.4 (d, $^2J_{N-H}$ = 12.4 Hz, N4), −76.2 (d, $^3J_{N-H}$ = 7.1 Hz, N2), −76.8 (d, $^2J_{N-H}$ = 14.4 Hz, N1), −113.1 (s, N5); EA: ($CHKN_5O_2$, 167.98) calc.: C 7.14, H 0.60, N 49.98 %; found: C 7.65, H 0.78, N 45.29 %; ball drop impact tester: < 4 mJ; BAM drophammer: 5 J; friction tester: < 0.1 ; ESD: 8.2 mJ (at grain size < 100 μm).
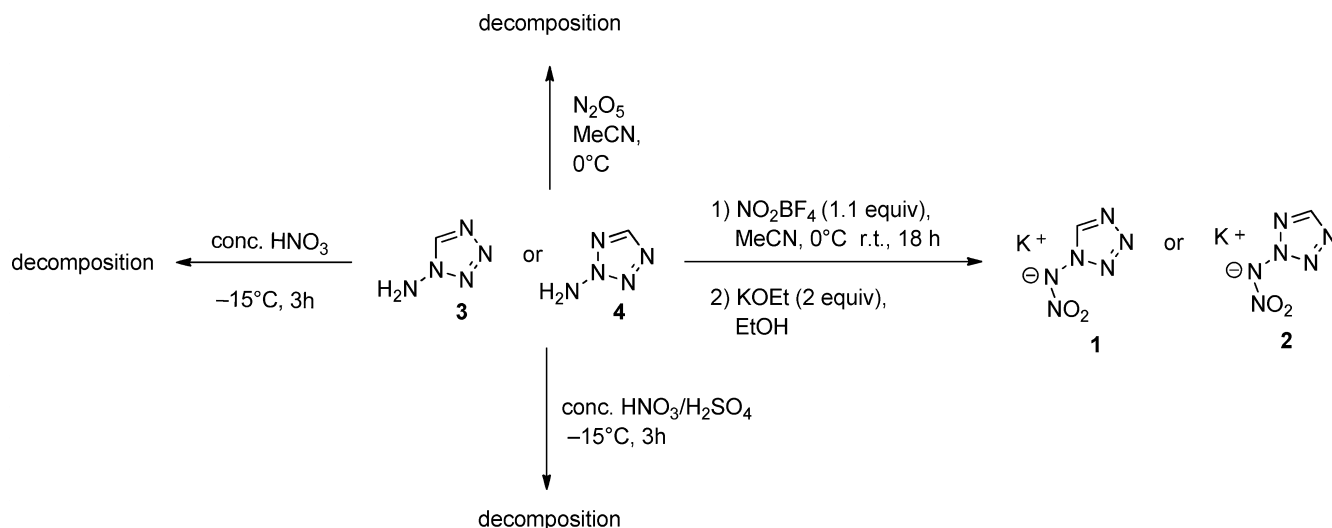
Scheme 1. Different reaction routes using various nitration reagents starting from 1-amino-5*H*-tetrazole and 2-amino-5*H*-tetrazole.

3 Results and Discussion

3.1 Synthesis

The starting materials 1-amino-5*H*-tetrazole and 2-amino-5*H*-tetrazole have been synthesized according to literature modified procedures (more details can be found in the SI). Several direct nitration procedures of 1-amino-5*H*-tetrazole and 2-amino-5*H*-tetrazole with N_2O_5, 100% nitric acid and mixed acids have been approached in order to synthesize **1** and **2** in a more convenient way but were unfortunately unsuccessful (Scheme 1). During the addition step or further by quenching the acid mixtures, gas evolution could be observed. The gas evolution is a reliable indicator for decomposition of the starting material, which can be attributed to the relatively labile N–N bonds of 1-amino-5*H*-tetrazole and 2-amino-5*H*-tetrazole, which break under these harsh reaction conditions, releasing nitrogen gas. This work, deals with the successful nitration with the mild nitration reagent NO_2BF_4, as an alternative method described in the literature [19]. The corresponding salts **1** and **2** were obtained by the stoichiometric addition of potassium ethanolate, after the previous precipitation of KBF_4. Unfortunately, NO_2BF_4 is a relatively expensive reagent and decomposes under hydrolysis fuming on air. This complicates the storage and practicability of NO_2BF_4. Hence, further research into other nitration methods using inexpensive reagents is highly desirable in order to compete with existing inexpensive lead compounds concerning the production for industrial purposes. By protecting the weak point, the amino group of the aminotetrazoles with a protecting group (e.g. carbamate functionality), harsh nitration conditions might be tolerated without observed decomposition. The addition of an excess of base might cleave the nitrated aminotetrazoles and could give access to the potassium salts. Further research

studies in this area should be carried out to make these compounds economically attractive. As the used starting material 1-amino-5*H*-tetrazole is accessible through a selective synthetic route from standard feedstock without distillation or column chromatography, compound **1** indicates a great potential to compete in industrial purposes with existing used primaries.

The structural and molecular composition of **1** and **2** were confirmed by elemental analysis, X-ray diffraction, IR, and multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{14}N, and ^{15}N). Both isomers can easily be differentiated by NMR and IR analysis (Figure S1). Six nitrogen resonances were observed in each proton coupled ^{15}N NMR spectrum of **1** and **2** (Figure 1).

3.2 Crystal Structures

Low-temperature X-ray diffraction was used to characterize **1** and **2**. The crystal structures were uploaded to the CSD database and can be obtained free of charge with the CCDC no. 1849956 (**1**) and 1849957 (**2**). Details to the measurement and refinement data are given in the SI. Compound **1** crystallizes in the form of colorless blocks in the monoclinic space group $P2_1/c$ with a density of 1.973 g cm^{-1} (143 K) and four molecules per unit cell. The molecular structure and coordination environment around the potassium cation of **1** are shown in Figures 2 and 3. The alkali metal is sevenfold coordinated by four different 1-nitraminotetrazolates, which bind with atoms N3, N4, O1, or O2.

Compound **2** is shown in Figure 4 and crystallizes in the form of colorless rods in the orthorhombic space group *Pbca* with eight formula units per unit cell and a calculated density of 1.983 g cm^{-1} (143 K). The densities of both iso-
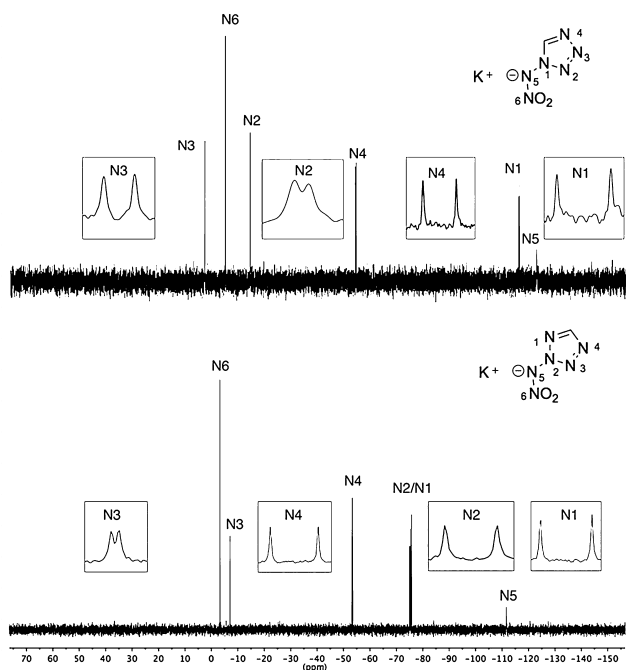
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Figure 1. Proton-coupled ^{15}N NMR spectra of compound **1** and **2**.
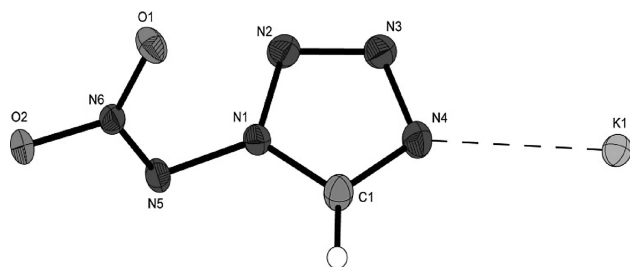

Figure 2. Molecular structure of **1**. Thermal ellipsoids of non-hydrogen atoms in all structures are set to the 50% probability level. Selected bond lengths (pm): C1–H1 92.8(16), N1–C1 133.0(2), N4–C1 131.5(2), N3–N4 136.65(18), N2–N3 129.8(2), N1–N2 134.70(17), 140.47(19), N5–N6 131.81(18), N1–N5 140.5(19), O1–N6 124.70(15), O2–N6 127.10(17).
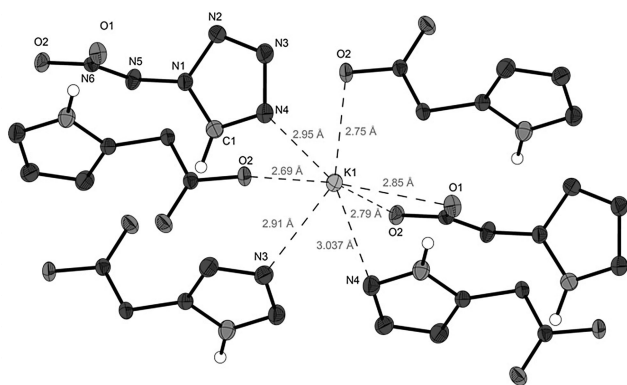

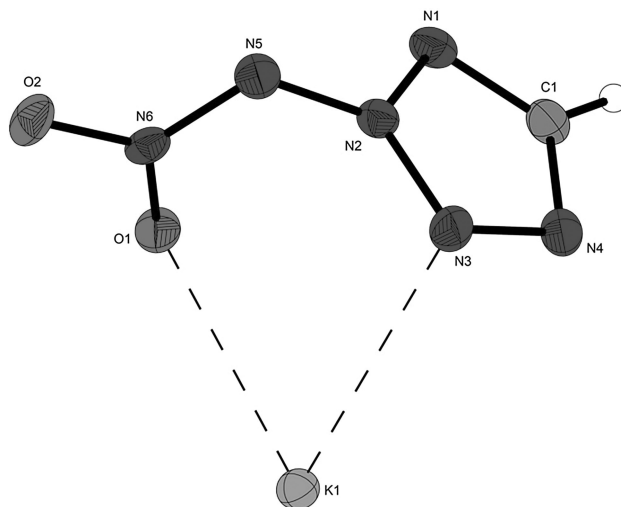**Figure 3.** Coordination environment of the potassium cation in **1**.

Figure 4. Molecular structure of **2**. Selected bond lengths (pm): C1–H1 94.7(17), N1–C1 132.1(2), N4–C1 134.11(19), N1–N2 132.50(17), N2–N3 131.75(17), N2–N5 139.37 (17), N3–N4 132.14(18), N5–N6 133.40(17), O1–N6 124.94(15), O2–N6 124.46(16).

mers are slightly lower in comparison to K$_2$DNABT (2.172 g cm^{-3} (100 K)) [14]. In both molecules, the nitro groups are twisted by 109.12° (**1**) and 108.06° (**2**) out of the ring plane, while N5 is almost planar to the tetrazole ring. A comparison of the bond lengths shows that the bond length in **1** between N5 and N6 is slightly shorter with 131.8 pm than in **2** (133.4 pm). These values lie between N–N single and double bonds [20], which reflects the electron-withdrawing effect of the nitro group on the amide moiety. The weakest bond in both molecules is between N1–N5 with 140.5 pm (**1**) and 139.4 pm (**2**). (Further details on the crystal structure can be found in the Supporting Information.)

3.3 Scanning Electron Microscopy (SEM) and Energy-Dispersive X-Ray Spectroscopy (EDX)

Scanning electron microscopy in combination with energy dispersive X-ray spectroscopy was used to determine the morphology, grain size and chemical composition, which can strongly influence the observed sensitivities performed.

Due to the simpler synthesis, the associated lower costs and the more promising characteristics of compound **1** compared to **2**, only this salt was measured by SEM and EDX. Compound **1** shows the consistency of small tubes with cavities (Figure 5). Aside from insignificant trace amounts of silicon, the EDX spectrum only shows elements which are actually present in the molecular structure. No contamination of fluorine or boron was detected.

3.4 Physicochemical Properties

Since all materials investigated are highly energetic compounds, their physicochemical properties were explored. The thermal behavior of compound **1** and **2** was investigated using DTA (Figure 6). Violent detonations could be observed for 1 ant 180 °C, and 176 °C for compund 2, after melting of both compounds. The decomposition peak of compound 2 is relatively broad due to the small amount of substance used for the measurement.
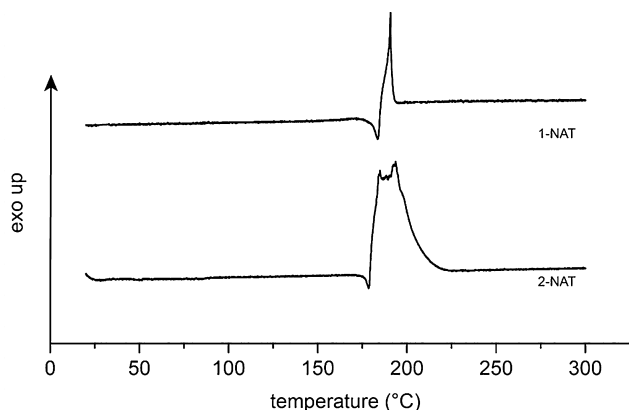
Figure 6. DTA plots of compound **1** and **2**.

To evaluate the potential of **1** and **2** as suitable green primary explosives, the sensitivities toward impact, friction, electrostatic discharge next to thermal stability and detonation performance were investigated (Table 1). The friction, impact, and electrostatic sensitivities of **1** and **2** are comparable to those of LA and K$_2$DNABT [14]. The measured friction and ball drop impact sensitivities correspond to the

Figure 5. SEM image (800 × magnitude (left) and 2500 × magnitude (right)) and EDX spectrum of compound **1**.

Table 1. Explosive and detonation parameters of **1** and **2** in comparison to K$_2$DNABT and LA.

Formula	**1** CHKN$_6$O$_2$	**2** CHKN$_6$O$_2$	K$_2$DNABT [14] C$_2$K$_2$N$_{12}$O$_4$	Pb(N$_3$)$_2$ [22] N$_6$Pb
IS[a] [J]	< 1	5	1	2.4–4
FS[b] [N]	< 0.1	< 0.1	< 0.1	0.1–1.0
ESD[c] [mJ]	0.9	8.2	< 0.1	< 5.0
BDIS	< 4[o]	< 4[o]	31.1[p]	53.3[q]
Ω_{CO2}[d] [%]	−6.2	−6.2	−4.8	−11.0
T_{dec}[e] [°C]	180	176	200	320–360
δ[f] [g cm^{-3}]	1.928	1.938	2.172	4.80[n]
$\Delta_f H°$[g] [kJ mol^{-1}]	93.4	77.9	326.4	450.1[n]
$\Delta_f U°$[h] [kJ kg^{-1}]	621.7	529.6	1035.6	1574.9[n]
EXPLO5 6.04 values:				
$-\Delta_{ex}H°$[i] [kJ kg^{-1}]	4616	4526	4959	1575
T_{det}[j] [K]	3259	3209	3417	3285
P_{CJ}[k] [GPa]	25.0	25.1	32.5	34.9
V_{det}[l] [ms^{-1}]	7858	7882	8691	6077
V_0[m] [dm^3 kg^{-1}]	410	409	485	252

[a] Impact sensitivity (BAM drop-hammer (1 of 6)). [b] Friction sensitivity (BAM friction tester (1 of 6)). [c] Electrostatic discharge device (OZM research). [d] Oxygen balance ($\Omega = (xO - 2yC - 1/2zH)$ M/1600). [e] Onset temperatures measured by DTA ($\beta = 5$ °C min^{-1}). [f] X-ray densities converted to RT. [g] Calculated enthalpy of formation. [h] Calculated energy of formation. [i] Heat of explosion. [j] Temperature of detonation. [k] Detonation pressure. [l] Detonation velocity. [m] Gas volume after detonation (assuming only gaseous products). [n] from EXPLO5 database. [o] ball drop impact sensitivity determined with the OZM ball drop tester applying the 1 of 6 method in accordance with the MIL-STD 1751A (method 1016). [p] E_{50} ball drop impact sensitivity determined with the OZM ball drop tester applying the Probit method with 10 trials at 6 different heights. [q] E_{50} ball drop impact sensitivity of dextrinated LA [22].

lowest possible determinable values for the equipment used, which underlines the highly sensitive nature of these synthesized compounds. Interestingly, and to our surprise, compound **2** was slightly less sensitive toward impact than **1**. The detonation parameters of **1** and **2** were calculated using the latest EXPLO5 6.04 computer code [21]. Both compounds have very high positive heats of formation, as shown in Table 1.

As expected, the enthalpy of formation and energy of formation values are lower than for the double potassium salt K$_2$DNABT [14]. The nitramino-5*H*-tetrazolate isomers outperform easily lead azide in performance parameters such as heat of explosion, detonation velocity and gas volume after detonation [22]. Nevertheless, the values are still below those of K$_2$DNABT, which can be attributed to the higher density and higher heat of formation. The value for the temperature of detonation is in the range of lead azide. From the point of view of detonation pressure, both isomers exhibit detonation pressures 10 GPa lower than for lead azide and 7,5 GPa lower than for K$_2$DNABT.

In order to determine the compounds' deflagration to detonation transition (DDT) capability, hot needle (HN) and hot plate (HP) tests were performed (Figure 7). The HN test
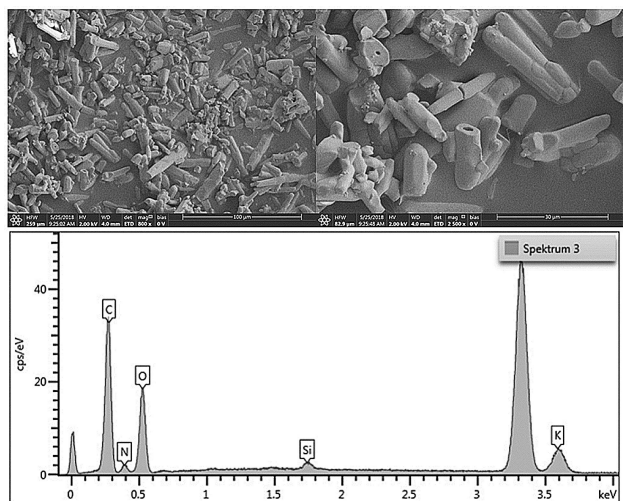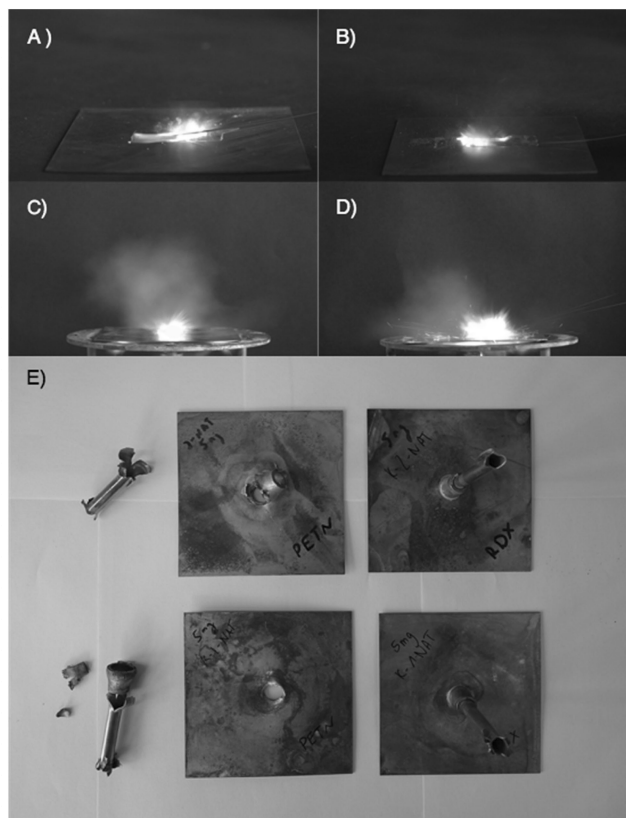
Figure 7. A) and B) HN test of **1** and **2**; C) and D) HP test of **1** and **2**; E) Positive PETN (left) and RDX (right) initiation tests with 5 mg of compound **1** (bottom) and **2** (top).

was performed by the fixation of each compound underneath adhesive tape. The following penetration of **1** and **2** with a red-heated needle resulted in a vast detonation, which indicates their great potential as valuable primary explosives. The safe and straightforward HP test shows the behavior of the unconfined samples toward fast heating. Both compounds detonated also violently during the hot plate test with a slight bending of the plates.

3.5 Toxicity

To estimate the potential environmental impact of compound **1** and **2**, toxicity measurements were carried out using the luminesce marine bacterium *Vibrio fischeri* [23]. Our studies show that, after a time period of 30 min 85 % of the bacteria were unaffected at a concentration of 1.60 g L^{-1} (**1**) and 1.61 g L^{-1} (**2**). Due to the extreme non-toxicity of the compounds, no reasonably EC_{50} value could be determined with the dilution series used. Nevertheless, with values clearly over 1.00 g L^{-1}, both compounds can be considered as non-toxic (toxicity level after 30 min incubation: very toxic < 0.10 g L^{-1}, toxic 0.10–1.00 g L^{-1}, non-toxic > 1.00 g L^{-1}) [24].

4 Conclusions

Potassium 1-(*N*-nitramino)-5*H*-tetrazolate (**1**, 1-KNAT) and its isomeric counterpart potassium 2-(*N*-nitramino)-5*H*-tetrazolate (**2**, 2-KNAT), two new promising primary explosives, could by synthesized through direct nitration of 1-amino-5*H*-tetrazole and 2-amino-5*H*-tetrazole and subsequent addition of potassium ethanolate in a one-step reaction. The potassium salts that could be prepared by an alternative route compared to the literature-known ammonium and silver salts represent a good compromise between solubility, sensitivity, performance, and environmental compatibility. Since the compounds known from literature have been very poorly analyzed, this work carries out an extensive analytical study of the two potassium salts in order to close this gap. Both compounds were characterized by low-temperature X-ray diffraction and showed, unfortunately, a slightly lower density compared to K_2DNABT. In addition, the compounds were analyzed by vibrational (IR) and multinuclear NMR spectroscopy, as well as by EA. To identify impurity residues and to investigate the morphology, grain size and crystal habit of **1**, the latter was measured with scanning electron microscopy and energy dispersive X-ray spectroscopy. Thermal stability measurements by DTA showed satisfying exothermic decomposition temperatures around 180 °C. The measured sensitivities toward friction and impact, underline the highly sensitive character of the two isomers while remaining safe to handle. The calculations of the energetic properties of 1-KNAT and 2-KNAT, show their excellent performance in comparison to lead azide, outperforming LA in several important parameters. Easy thermal initiation was proven by hot plate and hot needle tests and an excellent secondary explosive initiation capability was observed. Only 5 mg of the two compounds were sufficient to initiate PETN and RDX reliably. Toxicity measurements using *Vibrio fischeri* showed the non-toxic character of the environmentally benign potassium salts. 1-KNAT can be considered as a promising lead-free green primary explosive for potential future initiation systems due to its simpler synthesis (starting material is more easily accessible) and better sensitivity values compared to **2**.

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