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1-Nitrimino-5-azidotetrazole: Extending Energetic Tetrazole Chemistry

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Azide and nitrimino functions are among the most energetic substituents that can be introduced to the skeleton to enhance the energetic properties of a compound. In this study, we report the successful synthesis of a compound that combines both, azide and nitrimino substituents directly attached to one tetrazole scaffold. 1-Nitrimino-5-azidotetrazole is prepared by nitration of 1-amino-5-azidotetrazole. Subsequent salination with ammonia and guanidinium carbonate yields two highly energetic derivatives. All energetic compounds, as well as the intermediate steps of an alternatively developed synthesis strategy, were analysed and characterized in detail. In addition to multinuclear NMR and IR spectroscopy, crystal structures of all key compounds were measured. The sensitivities (friction, impact, electrostatic discharge and thermal) were determined accordingly. In addition, the detonation parameters of all energetic substances were calculated with the EXPLO5 code, which was fed with the enthalpy of formation (atomization method based on CBS-4M) and the crystallographic densities.

Introduction

Alongside ever greater efforts to develop more powerful explosives, the environmental aspect in particular is a central factor for the development of new energetic materials.[1–3] For this, some basic properties should be fulfilled, whereby newly developed substances should be free of heavy metals and perchlorates. Compounds containing these components are demonstrably harmful to the environment and hazardous to humans' health.[4–5] Similarly, nitroaromatics, which despite being discovered and researched 150 years ago, still have an enormously wide range of applications.[6–7] In order to find possible substitutes, research has been conducted on nitrogen-rich heterocycles as basic building blocks the past years.[1,8] These have several advantages over other structural units. Firstly, the high nitrogen content of the compounds, which leads to the fact that after decomposition, most of the nitrogen is converted into elemental dinitrogen. In addition, unlike benzene, which serves as the basic building block for TNT, these heterocycles already have a considerable enthalpy of formation, which leads to improved explosion properties. In addition, many heterocycles are easily synthetically accessible.[9–11]

In principle, it should be noted that a clever increase of the nitrogen and oxygen content of explosives, often results in higher density but also higher amount of gaseous and mainly non-hazardous decomposition products (N_2, CO, CO_2). Not only therefore, from an environmental point of view, an all nitrogen compounds such as pentazole or its N-oxides would be the best possible energetic compound.[12–15] Research has focused for many years on the development of new tetrazole derivatives. Even unsubstituted 1H-tetrazole has a nitrogen content of almost 80% and an enthalpy of formation of 4732 kJ kg^{-1}.[16–17] By introducing suitable substituents to the tetrazole base, not only the nitrogen content but also the enthalpy of formation can be further tuned. However, the same applies for the substituents: the more nitrogen and oxygen, the better the impact on the environment and the resulting explosion parameters.[18]

Using this tactic: Combining tetrazole-based explosives with suitable (high N and O content), energy contributing substituents, major research successes have already been achieved (Figure 1).[19–21] Groups composed exclusively of nitrogen and oxygen have proved to be particularly attractive for use as substituents. Particularly suitable in this context are covalently bonded azides (only possible as C-substituents at tetrazoles), which, in addition to an energy contribution of 256 kJ mol^{-1}, also increase explosion properties and normally adjust sensitivities. In addition, azides are easy to install and their composition

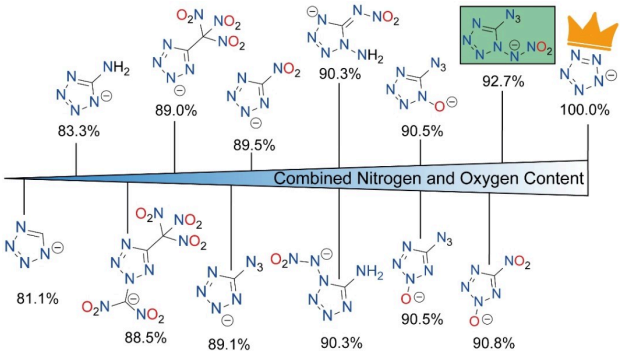

Figure 1. Single deprotonated monotetrazolates sorted by increasing combined nitrogen and oxygen content.

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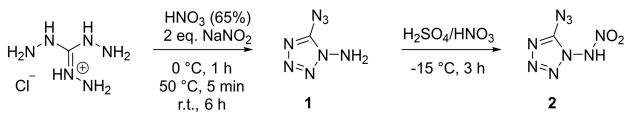
makes them particularly environmentally compatible, since they formally consist only of nitrogen.

In addition to azides, nitramines (or nitrimines) possess a favorable functionality, which in most cases can be introduced simply by nitration of amines.[22–23] The two oxygens contained in the nitramino not only increase the oxygen balance of the compound but also the density, since oxygen is heavier than the other components (mostly hydrogen, carbon and nitrogen). In addition, primary nitramines have another advantage. Although free nitramines (–N(*H*)NO_2) are often only stable to a limited extent, they can be functionalized by the formation of salts. The acidity of the proton is usually sufficient to deprotonate nitramines even with mild bases. The properties of the resulting compound can be further adjusted and adapted by the appropriate choice of cation.

In accordance with the modular principle, a various number of target compounds have already been successfully synthesized and investigated. In this study, we were focusing on the synthesis and characterization of 1-nitrimino-5-azidotetrazole (CHN_9O_2) and several ionic derivatives thereof. The parent compound (HNAAT, **2**) and the derivatives are high-energy explosives with a combined nitrogen and oxygen content of up to 91.5% and outstanding energetic parameters.

Results and Discussion

In general, tetrazoles with substitution at N1 are difficult to synthesize as soon as an electron-withdrawing group is located at position C1. Direct reactions of C-electron-withdrawing tetrazolates (e.g. 5-azidotetrazolate, 5-nitrotetrazolate or 5-cyanotetrazolate) with electrophiles always give the derivatives substituted at N2, as has been shown, for amination,[24–25] N-oxidation[21,26–27] or methylation[28–29] reactions. Consequently, two possible synthesis strategies arise for substitutions for particular tetrazolates at position N1. On the one hand, the functionality at position N1 can be introduced first, followed by the electron-withdrawing carbon function, or by reaction pathways that proceed via a selective mechanism, in which case rearrangement or selected ring closures automatically result in a substitution at position N1.[30] In the literature, the synthesis of 1-amino-5-azidotetrazole (**1**) is performed through double diazotization of triaminoguanidinium chloride (Scheme 1) with two equivalents of HNO_2.[31] By rapid quench with a base (Na_2CO_3), 1-amino-5-azidotetrazole (**1**) is obtained as the main product. We modified the published procedure and were able to push the yield to 26%. Despite the poor yield, only small quantities of starting materials (4 mmol) were reacted in one batch because of the formation of extremely sensitive byproducts (C_2N_{14} and 1-(aminoazidocarbamoyl)-5-azidotetrazole). The side species were removed using column chromatography.

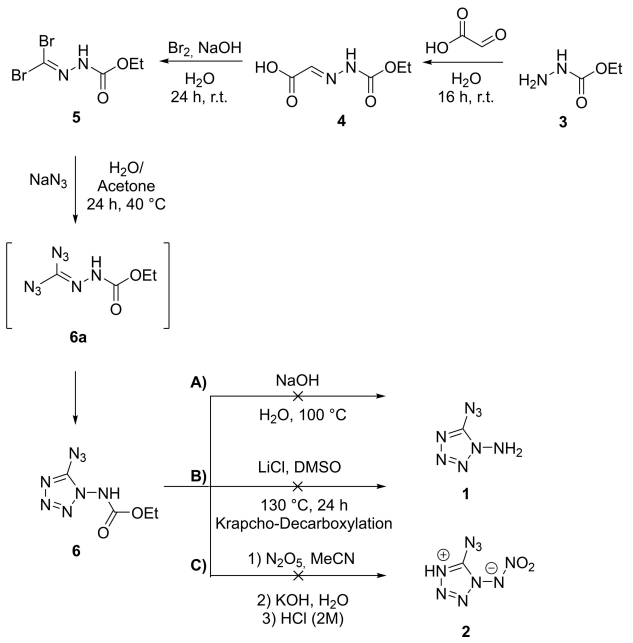


Scheme 1. Synthesis of 1-amino-5-azidotetrazole (**1**) through diazotization of triaminoguanidinium chloride and nitration using mixed acid to 1-nitrimino-5-azidotetrazole (**2**).

We had to do try several different nitration methods to obtain the desired 1-nitrimino-5-azidotetrazole (**2**). We did not obtain any reaction with nitric acid at different temperatures (−30–60 °C). Even aprotic nitration using NO_2BF_4 or N_2O_5 as nitrating agent in acetonitrile only yielded starting material. Finally, we applied a method that runs successfully for the N-nitration of 1,5-diaminotetrazole. In this process, nitration is performed with a sulfuric acid/nitric acid (1:1) mixture at −15 °C.[32] In our case, 1-amino-5-azidotetrazole (**1**) was added to the nitration mixture pre-dissolved in a small amount of concentrated sulfuric acid (Scheme 1). This method provided 1-nitrimino-5-azidotetrazole (**2**) in 54% yield in the form of a viscous oil. The nitration of the recently published isomeric 2-amino-5-azidotetrazole[24] through various methods (N_2O_5, NO_2BF_4 or mixed acid as for **1**) was not successful since only decomposition products were obtained.

Since the literature known synthesis of **1** includes, as above mentioned, the formation of several extremely sensitive 5-azidotetrazole derivatives and therefore has to be worked up through column chromatography, we tried to find another synthetic pathway toward **1**. The procedure should start from simple starting materials, involve as few synthesis steps as possible, deliver good yields, as well as not contain any extremely energetic or unstable intermediates. In addition, easy scalability should be achieved in order to be able to produce larger quantities of the compound. The sequence starts with ethyl carbazate (**3**), which can be easily synthesized by equimolar reaction of hydrazine hydrate with diethyl carbonate. Carbazate **3** undergoes condensation reaction with glyoxalic acid to precipitate hydrazone **4**. This reaction step was performed in a scale of up to 80 g. Bromine indicated decarboxylation of **4** under basic conditions results in the dibromo hydrazone **5**. We were also able to perform this step by replacing Br_2 by NBS, however, the yield is declining as a result. The subsequent bromo-azide exchange was carried out in a mixture of water and acetone and required a slight heating of the reaction solution to 40 °C (Scheme 2). The cyclization of the diazido hydrazone (**6a**) to the 5-azidotetrazole derivative **6** proceeded directly in solution. As the bromo-azide exchange was carried out at room temperature, only one bromine was substituted and after the in situ cyclization, the 5-bromotetrazole derivative was obtained, which was not studied in more detail. Similar observations were made recently for the reaction of dibromoformaldoxime with sodium azide.[20]

The main goal in the synthesis of 1-ethoxycarbamate-5-azidotetrazole was the better and easier accessibility of **1** and **2**, respectively. However, we were not successful with the deprotection of **6**. Our main synthetic approaches are shown in Scheme 2. Normally, ethyl carbamates can be cleaved in water under the exposure of a base at elevated temperature or of a strong acid.[33–34] However, our system was only deprotonated under basic conditions and the carbamate protecting group could not be removed. Acidic cleavage using TFA did yield starting material. Likewise, it could not be eliminated by Krapcho reaction, as was the case with recently published 1,1′-(diethoxycarbonyl)-diaminotetrazole.[35] Nor could the protect-



Scheme 2. Failed reaction attempts with 5-azidotetrazole carbamate **6**.

ing group be removed by previous nitration and basic work-up, as is successfully performed for K_2DNABT.[36]

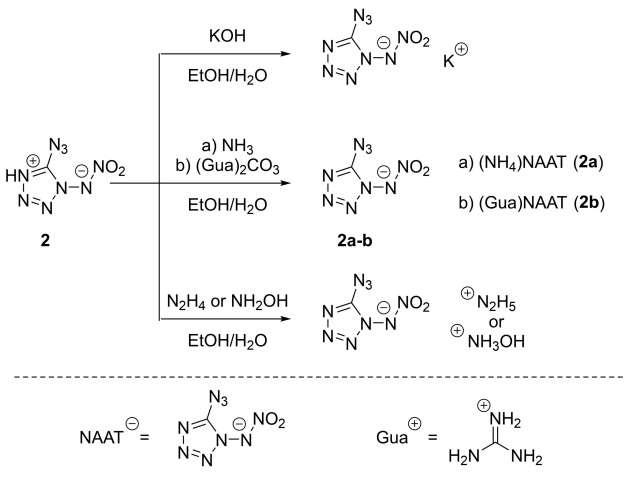
Despite the small amounts of 1-nitrimino-5-azidotetrazole (**2**), we were able to synthesize some new ionic nitrogen-rich derivatives. Sadly, we were only able to characterize the ammonium (**2a**) and the guanidinium (**2b**) derivative in more detail. Therefore, the oily free acid **2** was dissolved in ethanol and the respective bases were added. For the ammonium derivative **2a**, gaseous ammonia was bubbled through the solution, for the guanidinium derivative, $(Gua)_2CO_3$ dissolved in water was added equimolar (Scheme 3).

For the hydroxylammonium and hydrazinium derivatives, which are considered to exhibit the highest calculated detonation performance, it was only possible to isolate extremely hygroscopic salts, which could not be further characterized. In addition, we made some attempts to isolate the potassium derivative. However, after complete evaporation of the reaction solution, spontaneous detonation of the solidified potassium 1-nitrimino-5-azidotetrazolate occurred. Therefore, no more detailed analytical data on the potassium derivative are given in this paper. We also strongly recommend not to synthesize this compound, since detonative decomposition occurs even at the weakest external influences. The ionic derivatives **2a** and **2b** were obtained elemental analysis pure from the reduced reaction solution (**2a**) or after recrystallization from hot methanol (**2b**) in good to excellent yields.

Crystallographic investigations could be performed for all energetic solid derivatives (**2**, **2a**, **2b** and **6**). The crystal structures of **3** and **5** can be found in the Supporting Information. Deposition Numbers 2170430 (for **1**), 2170433 (for **2a**), 2170432 (for **2b**) and 2170434 (for **6**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre.

1-Amino-5-azidotetrazole (**1**) crystallizes in the orthorhombic space group $Pna2_1$ in the form of colorless plates. It shows a room temperature density of 1.636 g cm^{-3}. Therefore, it is 0.1 g cm^{-3} lower than for its isomer 2-amino-5-azidotetrazole ($\rho = 1.736$ g cm^{-3} @298 K)[24] and is also below the estimated value.[31] The molecule itself is planar. As expected for covalent azides, the N_3 is slightly bent by N6–N7–N8 = 172.1(5) ° The bond length of the amine bound to N1 (N1–N5 1.394(5) Å) is in between the bond length of a N–N single and double bond, suggesting an electron-donating effect of the N-amine. Due to the resulting three-dimensional structure, hydrogen bonds are formed with the two most electron-rich nitrogen atoms of the respective neighboring molecules (Figure 2). These are medium strength interactions in the range of d(H···A) = 2.27–2.37 Å, which are formed by both protons of the amino groups to N4 of the tetrazole ring and N_α of the azide function.

Ammonium 1-nitrimino-5-azidotetrazolate (**2a**) crystallizes in the monoclinic space group $P2_1/n$ with four molecular units per cell. The density is calculated to be 1.727 g cm^{-3} at 298 K



Scheme 3. Synthetic pathway toward the formation of ionic derivatives **2a** and **2b**.

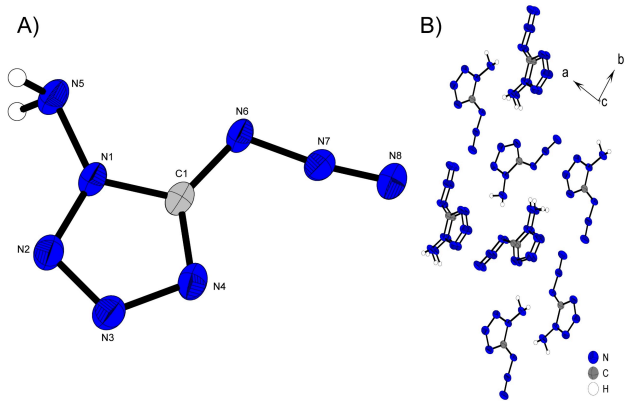


Figure 2. A) Molecular unit of **1** with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles [°]: N1–N5 1.394(5), C1–N6 1.379(6), N6–N7 1.271(5), N7–N8 1.109(5), N2–N1–N5 125.4(3), C1–N1–N5 1.121(8), N6–N7–N8 172.1(5), N4–C1–N6–N7 0.6(7); B) layer structure of **1** with view along the *c* axis.

(Figure 3). Through the introduction of the nitrimino function, the density could be raised about 0.14 g cm^{-3} compared with the density of ammonium 5-azidotetrazolate ($\rho = 1.585$ g cm^{-3} @298 K).[16] Despite nitration, the bond length N1-N5 is unchanged compared to **1** and, in addition, the nitro group of the nitrimine is orthogonal to the tetrazole ring (N6–N5–N1–N2 93.3(2) °), which indicates a still strong electron-donating effect of N5 toward the tetrazole. Each ammonium cation is coordinated by four anionic sites. Strong interactions are formed between the protons of NH_4^+ and N4, O1 and O2 of the anion with lengths d(H···A) of about 2.0 Å and somewhat weaker ones originating from N5 (N5···H10D–N10). Due to the introduction of the nitrimino group, the azide function no longer participates in intermolecular interactions and is rotated off the ammonium units in the crystal lattice.

The guanidinium derivative of 1-nitrimino-5-azidotetrazole crystallizes in the triclinic space group $P-1$ in the form of colorless needles. The density at room temperature is 1.656 g cm^{-3}. Therefore, its density is about 0.05 g cm^{-3} higher than for guanidinium 5-azidotetrazolate ($\rho = 1.610$ g cm^{-3} @298 K).[20] The nitro units of the nitramine groups are offset parallel to the planar guanidinium cations. Each guanidinium cation is saturated by four NAAT$^-$ anions, which follows a clear pattern. O1 and O2 or O2 and N5 of an anion unit coordinate in a pincer-like manner to one hydrogen atom each of two different amines of the same guanidinium cation. Thus, four hydrogens are already coated, which are found with distances of d(H···A) = 2.10–2.22 Å (Figure 4). The remaining two hydrogens of the guanidinium form moderate hydrogen bonds to N4 and N_α of the third and fourth coordinating anion units.

Compound **6** crystallizes in the monoclinic space group $P2_1/c$ in the form of colorless blocks. The density is 1.441 g cm^{-3} at 298 K, which is the lowest one included in this study. The structure is mainly characterized by one strong hydrogen bridge O1^i···H5–N5 (1.98 Å) (Figure 5). This results in the formation of chain-like molecular arrangements, which are arranged around this characteristic interaction. The respective neighboring molecules are twisted against each other, but form both regions where the azidotetrazole units overlap and the ester residues intersect.

We measured the sensitivities of all 5-azidotetrazole derivatives and calculated the performance parameters based on the crystallographic density and the CBS-4M heat of formation for **1**, **2**, **2a** and **2b** using the EXPLO5 code. Since **2** is a liquid, the density was measured using a gas pycnometer. For **6**, the calculations were omitted, since the compound is a precursor to the essential compounds of this study. Nevertheless, **6** is a high energetic material, which has been confirmed by the measurement of its sensitivities toward friction and impact (FS = 1.5 N, IS < 1 J). Further information about the thermal and mechanical sensitivity for **6** can be found in the Supporting Information and are not further discussed in here.

The combined nitrogen and oxygen content feature an impressive value for all investigated compounds, with the ammonium **2a** derivative even clearly exceeding 90% (91.5% for **2a**). Similarly, the N + O content of the guanidinium NAAT with 83.9% is one of the highest values for a mono-guanidinium derivative. The impact sensitivities for all compounds are clearly in the range of primary explosives (1–2 J). Due to its liquid nature, **2** has an impact sensitivity of < 1 J, but a friction sensitivity of > 360 N, similar to nitroglycerin. **1** and **2a** show equally extremely

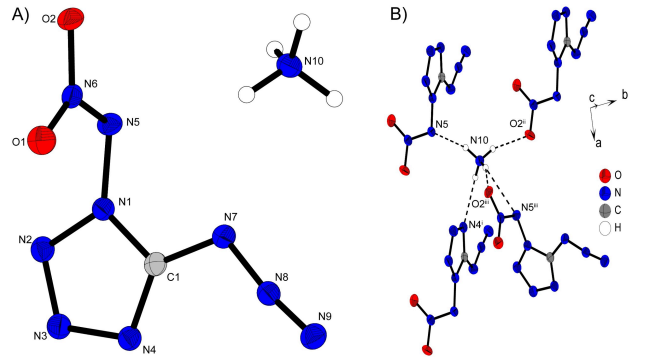


Figure 3. A) Molecular unit of **2a** with thermal ellipsoids drawn at the 50% probability level. Selected bond and intermolecular bond distances (Å) and angles [°]: N1–N5 1.394(2), N5–N6 1.345(2), C1–N7 1.383(2), N5···H10D–N10 2.30(2), N4^i···H10C–N10 2.16(2), O2^{ii}···H10B–N10 2.05(2), O2^{iii}···H10A–N10 2.03(2), N5–H10D–N10 148.9(2), N4^i–H10C–N10 148.5(2), O2^{ii}–H10B–N10 157.7(2), O2^{iii}–H10A–N10 163.0(2), N6–N5–N1–N2 93.3(2); B) Representation of the surrounding of a ammonium moiety within the crystal packing; Symmetry codes: (i) 1 + x, + y, + z, (ii) + x, 1 + y, + z, (iii) 1.5 – x, 0.5 + y, 1.5 – z.

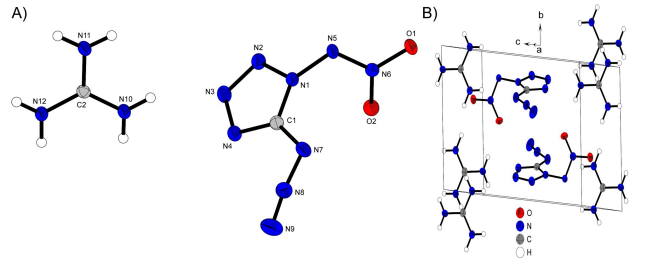


Figure 4. A) Molecular unit of **2b** with thermal ellipsoids drawn at the 50% probability level. Selected bond and intermolecular bond distances (Å) and angles [°]: N1–N5 1.398(2), N5–N6 1.332(2), C1–N7 1.390(2), N5···H12B–N12 2.20(3), O1···H11A–N11 2.10(3), N6–N7–N8 171.2(3), N5–H12B–N12 174.0(2), O1–H11A–N11 177.0(3), N10–C2–N12 120.2(2), N6–N5–N1–N2 107.7(2); B) layer structure of **2b** with view along the stated direction.

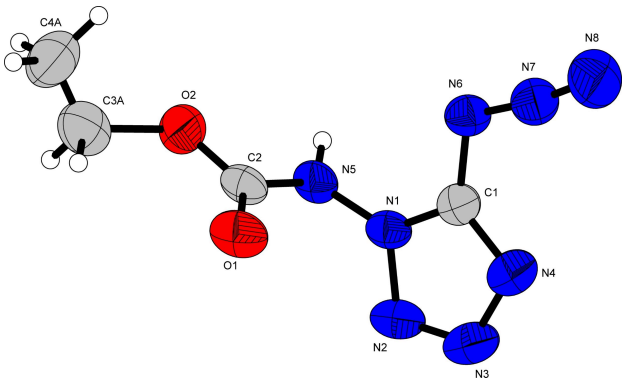


Figure 5. A) Molecular unit of **6** with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles [°]: N1–N5 1.356(3), N5–C2 1.359(3), C1–N6 1.387(4), N6–N7–N8 172.4(4), C2–N5–N1 117.3(2), N2–N1–N5–C2 85.8(3), N7–N6–C1–N4 2.1(5).

high friction sensitivities (4 N for **1** and 1 N for **2a**). All compounds are therefore more sensitive toward impact but less sensitive toward friction compared to lead azide (Table 1). In the case of guanidinium derivative **2b**, it could be increased to 30 N. **1** decomposes sharply at 165 °C. Due to the nitration and the salination with the selected cations, which are known from empirical experience to increase the decomposition temperature, we expected a similar if not even higher decomposition points then for **1**. Unfortunately, both ionic derivatives decompose shortly before 150 °C, whereby **2a** even decomposes denotatively.

Table 1. Physico-chemical properties of compounds **1**, **2**, **2a** and **2b** as well as lead azide.

	1	**2**	**2a**	**2b**	LA
IS [J][a]	1	<1	1	2	4
FS [N][b]	4	>360	1	30	<0.1
ESD [mJ][c]	75	–	20	125	<5
ρ [g cm^{-3}][d]	1.636	1.78*	1.727	1.656	4.8
N+O [%][e]	88.9	92.4	91.5	83.9	28.9
Ω [%][f]	−25.4	4.7	−8.5	−20.9	−11.0
T_{dec} [°C][g]	165	85	145	149	315
$\Delta_f H°$ [kJ mol^{-1}][h]	726.8	934.2	708.5	678.4	450.1
Explo5 V6.05.02					
T_{det} [K][i]	5830	5625	6126	4974	3372
P_{CJ} [kbar][j]	302	410	347	284	357
V_{det} [m s^{-1}][k]	9027	9829	9337	8723	6187
HP	det.	det.	det.	def.	det.
HN	def.	det.	def./det.	dec.	det.
PETN Initiation	neg.	n.d.	pos.	neg.	pos.

[a] Impact sensitivity (BAM drophammer (1 of 6)). [b] Friction sensitivity (BAM friction tester (1 of 6)). [c] Electrostatic discharge device (OZM research). [d] From X-Ray diffraction analysis recalculated to 298 K (* pycnometric measurement). [e] Combined nitrogen and oxygen content. [f] Oxygen balance with respect to CO [g] Decomposition temperature (DTA; $\beta = 5$ °C min^{-1}). [h] Calculated enthalpy of formation. [i] Detonation temperature. [j] Detonation pressure at Chapman-Jouguet point. [k] Detonation velocity; det.: detonation, def: deflagration, dec.: decomposition; neg.: negative; pos.: positive.

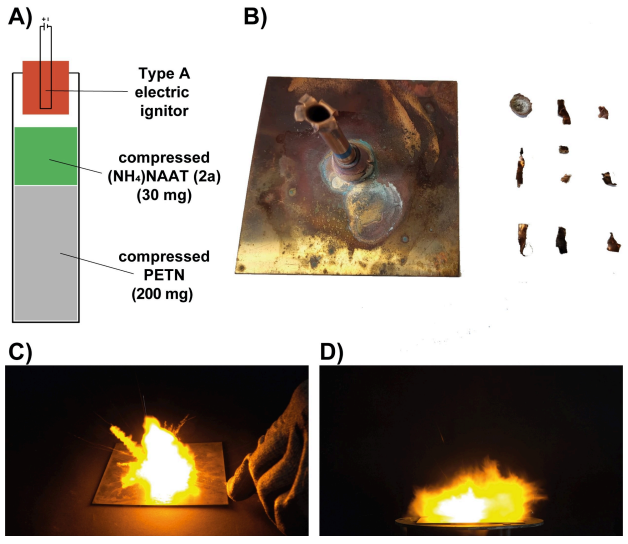


Figure 6. A) Schematic setup of the performed initiation test. B) Result of the initiation test with the shredded copper shell as well as the perforated copper plate. C) Hot Needle Test: Moment of detonation of 10 mg (NH_4)NAAT (**2a**) during hot needle test D) Hot Plate Test: Moment of detonation of 10 mg (NH_4)NAAT (**2a**) during hot plate test.

1-Amino-5-azidotetrazole (**1**) has a higher positive enthalpy of formation than its two-substituted isomer (726.8 kJ mol^{-1} vs. 703.7 kJ mol^{-1}), but the latter has a calculated detonation velocity almost 400 m s^{-1} more than **1** ($V_{det} = 9027$ m s^{-1}), which is mainly due to the large difference in density. The free acid **2** features impressive detonation properties ($P_{CJ} = 410$ kbar; $V_{det} = 9829$ m s^{-1}) and competes with most powerful non-nuclear explosives. Ammonium derivative **2a** has a detonation velocity of 9337 m s^{-1} and is therefore in the same range as HMX, guanidinium derivative **2b** possesses a calculated detonation velocity of 8723 m s^{-1}, which is in the range of RDX and outstanding for a derivative like this.

Hot plate and hot needle tests were performed to find out whether the substances undergo a deflagration to detonation transition (DDT). Both tests allow an initial assessment of whether the compounds could be used as primary explosives.

1-Amino-5-azidotetrazole (**1**) detonates in the hot plate test and deflagrates sharply in the hot-needle test. Ammonium 1-nitrimino-5-azidotetrazole (**2a**) behaved similarly to **1**, with the compound already decomposing close to detonation in the hot needle test (Figure 6 C)–D)). As expected, **2b** deflagrated during the HP test and decomposed without the formation of a flame in the HN test. Due to the promising properties of **1** and **2a** during the heating tests, both compounds were subjected to a classical initiation test toward PETN. The schematic setup and the result are shown in Figure 6 A)-B). PETN (200 mg, <100 µm) was therefore pressed into a copper shell (80 N) and the respective primary explosive (50 mg of **1** or 30 mg **2a**) was filled on top and compressed as well (80 N). After initiation of the primary explosive charge using an electrical ignitor, a negative test result occurred only for **1** but a positive one for **2a**. This was determined by fragmentation of the copper shell and the hole in the copper witness plate. 30 mg of the ammonium derivative **2a** are thus capable of igniting the booster explosive PETN.

To the best of our knowledge, **2a** is the first highly energetic ammonium salt, which was successfully tested as a primary explosive. 30 mg of **2a** were used for the PETN initiation, which demonstrates also its high initiation efficiency. This property is usually possessed mainly by metal salts of energetic azoles, but in very few cases by nitrogen-rich derivatives.

Conclusion

In this study, we described the synthesis and characterization of 1-nitrimino-5-azidotetrazole (**2**) through mixed acid nitration of 1-amino-5-azidotetrazole (**1**). A reaction toward **2** through a selective reaction procedure was not possible. Especially, the ammonium salt **2a**, with a combined nitrogen and oxygen content of 91.5% shows promising properties with a calculated detonation velocity of 9337 m s^{-1}. With the friction sensitivity of 1 N and impact sensitivity of 1 J and the positive hot plate and hot needle test, we considered **2a** as possible primary explosive. The initiation of PETN was positive and therefore our compound is one of the only ammonium derivatives being able to act as primary explosive. Once again, we have been able to demonstrate the potential of energetically substituted tetrazole systems and hope that our

contribution will encourage researchers to intensify their studies in this research area. Nevertheless, it must be noted here that 1-nitrimino-5-azidotetrazole is one of the most energetic mono-heterocycles. Although the taming through the formation of guanidinium or ammonium salt resulted in a significant reduction of the sensitivities, still the compounds are overpowered by the used anion.

Experimental Section

2: Sulfuric acid (96%, 2.0 mL) was cooled to 0 °C and nitric acid (100%, 1.5 mL) was added over 10 min. The mixture was stirred for 10 min and then cooled to −20 °C. 1-Amino-5-azidotetrazole (**1**) (0.20 g, 1.59 mmol, 1.0 eq) dissolved in sulfuric acid (96%, 1.0 mL) was added dropwise keeping the temperature below −15 °C. The mixture was then stirred for 3 h at this temperature and quenched on 50 mL ice water. The mixture was extracted with ethyl acetate (3 x 50 mL) and the combined organic phases were washed with brine (50 mL). The organic phases were dried over anhydrous sodium sulfate and the solvent was evaporated to yield 1-nitrimino-5-azidotetrazole (**2**) (0.15 g, 0.86 mmol, 54%) as slightly yellowish hygroscopic oil.

DTA (5 °C min^{-1}): 85 °C (exo); Sensitivities (liquid): BAM drop hammer: < 1 J, friction tester: 360 N, ESD: -; IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3155(w), 3059(w), 2917(w), 2851(w), 2761(w), 2633(w), 2146(s), 1790(w), 1555(s), 1509(m), 1493(m), 1346(vs), 1194(vs), 1157(vs), 1043(s), 1013(s), 834(vs), 784(s), 742(s), 726(s), 602(s), 529(s), 448(m), 436(m), 419(s), 414(m), 404(s); Elem. Anal. (CHN_9O_2, 171.08 g mol^{-1}) calcd.: C 7.02, H 0.59, N 73.69%. Found: C 6.88, H 0.88, N 72.78%; 1H NMR (DMSO–D6, 400 MHz, ppm) δ = 12.63 (br s, 1H); 13 C NMR (DMSO–D6, 101 MHz, ppm) δ = 150.0; 14 N NMR (DMSO–D6, 29 MHz, ppm) δ = −3, −11, −146; HRMS (ESI) m/z: [M^-] Calcd for CN_9O_2 170.0180, found: 170.0181.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

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[1] H. Gao, J. M. Shreeve, *Chem. Rev.* **2011**, *111*, 7377–7436.
[2] W. Cao, W. Dong, Z. Lu, Y. Bi, Y. Hu, T. Wang, C. Zhang, Z. Li, Q. Yu, J. Zhang, *Chem. Eur. J.* **2021**, *27*, 13807–13818.
[3] Z. Cong, C. Xiang, H. Yongpeng, B. Yang, G. Zhaoqi, F. Daidi, M. Haixia, *RSC Adv.* **2020**, *10*, 36287–36294.
[4] M. A. S. Laidlaw, G. Filippelli, H. Mielke, B. Gulson, A. S. Ball, *Environ. Health* **2017**, *16*, 34.
[5] M. S. Gruhne, T. Lenz, M. Rösch, M. Lommel, M. H. H. Wurzenberger, T. M. Klapötke, J. Stierstorfer, *Dalton Trans.* **2021**, *50*, 10811–10825.
[6] Q. Sun, N. Ding, C. Zhao, Q. Zhang, S. Zhang, S. Li, S. Pang, *Sci. Adv.* **2022**, *8*, eabn3176.
[7] M. Reichel, D. Dosch, T. Klapötke, K. Karaghiosoff, *J. Am. Chem. Soc.* **2019**, *141*, 19911–19916.
[8] O. T. O'Sullivan, M. J. Zdilla, *Chem. Rev.* **2020**, *120*, 5682–5744.
[9] Y.-H. Joo, J. M. Shreeve, *Org. Lett.* **2008**, *10*, 4665–4667.
[10] A. A. Larin, A. V. Shaferov, M. A. Epishina, I. N. Melnikov, N. V. Muravyev, I. V. Ananyev, L. L. Fershtat, N. N. Makhova, *ACS Appl. Energ. Mater.* **2020**, *3*, 7764–7771.
[11] N. Fischer, D. Fischer, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, *J. Mater. Chem.* **2012**, *22*, 20418–20422.
[12] M. I. Eremets, A. G. Gavriliuk, I. A. Trojan, D. A. Dzivenko, R. Boehler, *Nat. Mater.* **2004**, *3*, 558–563.
[13] K. O. Christe, W. W. Wilson, J. A. Sheehy, J. A. Boatz, *Angew. Chem. Int. Ed.* **1999**, *38*, 2004–2009; *Angew. Chem.* **1999**, *111*, 2112–2118.
[14] C. Zhang, C. Sun, B. Hu, C. Yu, M. Lu, *Science* **2017**, *355*, 374–376.
[15] Y. Xu, Q. Wang, C. Shen, Q. Lin, P. Wang, M. Lu, *Nature* **2017**, *549*, 78–81.
[16] T. M. Klapötke, J. Stierstorfer, *J. Am. Chem. Soc.* **2009**, *131*, 1122–1134.
[17] J. Stierstorfer, T. M. Klapötke, A. Hammerl, R. D. Chapman, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1051–1057.
[18] T. M. Klapötke, F. A. Martin, J. Stierstorfer, *Chem. Eur. J.* **2012**, *18*, 1487–1501.
[19] R. Haiges, K. O. Christe, *Inorg. Chem.* **2013**, *52*, 7249–7260.
[20] Y. Hu, X.-J. Wang, W.-S. Dong, Y.-F. Bi, Z.-J. Lu, W.-L. Cao, J.-G. Zhang, Q. Zhang, D. Chen, *Org. Chem. Front.* **2021**, *8*, 2420–2428.
[21] M. Göbel, K. Karaghiosoff, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, *J. Am. Chem. Soc.* **2010**, *132*, 17216–17226.
[22] G. Zhao, C. He, P. Yin, G. H. Imler, D. A. Parrish, J. M. Shreeve, *J. Am. Chem. Soc.* **2018**, *140*, 3560–3563.
[23] P. Yin, D. A. Parrish, J. n. M. Shreeve, *J. Am. Chem. Soc.* **2015**, *137*, 4778–4786.
[24] M. Benz, T. M. Klapötke, J. Stierstorfer, M. Voggenreiter, *J. Am. Chem. Soc.* **2022**, *144*, 6143–6147.
[25] T. M. Klapötke, D. G. Piercey, J. Stierstorfer, *Dalton Trans.* **2012**, *41*, 9451–9459.
[26] T. M. Klapötke, D. G. Piercey, J. Stierstorfer, *Chem. Eur. J.* **2011**, *17*, 13068–13077.
[27] F. Boneberg, A. Kirchner, T. M. Klapötke, D. G. Piercey, M. J. Poller, J. Stierstorfer, *Chem. Asian J.* **2013**, *8*, 148–159.
[28] M. Benz, T. M. Klapötke, T. Lenz, J. Stierstorfer, *Chem. Eur. J.* **2022**, 28, e202200772.
[29] J. Stierstorfer, *Dissertation*, Ludwig-Maximilians-Universität München, **2009**.
[30] D. Fischer, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, *Chem. Eur. J.* **2013**, *19*, 4602–4613.
[31] T. M. Klapötke, B. Krumm, F. A. Martin, J. Stierstorfer, *Chem. Asian J.* **2012**, *7*, 214–224.
[32] L. Liu, C. He, C. Li, Z. Li, *J. Chem. Crystallogr.* **2012**, *42*, 816–823.
[33] R. Da Silva Rodrigues, E. T. Luis, D. L. Marshall, J. C. McMurtrie, K. M. Mullen, *New J. Chem.* **2021**, *45*, 4414–4421.
[34] D. A. Mundal, J. J. Lee, R. J. Thomson, *J. Am. Chem. Soc.* **2008**, *130*, 1148–1149.
[35] M. Benz, T. M. Klapötke, J. Stierstorfer, *Org. Lett.* **2022**, *24*, 1747–1751.
[36] D. Fischer, T. M. Klapötke, J. Stierstorfer, *Angew. Chem. Int. Ed.* **2014**, *53*, 8172–8175; *Angew. Chem.* **2014**, *126*, 8311–8314.

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