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Energetic Materials based on Benzenes, 2,2'-Bisimidazole and 1,2,4,5-Tetrazines

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Erklärung

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Eidesstattliche Versicherung

Diese Dissertation wurde eigenständig und ohne unerlaubte Hilfe erarbeitet.

Andreas Preimesser

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1. Introduction

The research area comprising energetic materials can be subdivided into the following branches: primary and secondary explosives, rocket propellants, propellant powder for ammunition and pyrotechnics. Energetic materials can be detonated thermally, mechanically or electrostatically and do not require any external source of oxygen. They are essentially chemical compounds that combine a fuel and an oxidizer, reacting promptly while releasing energy and gas. This definition is based on the one delivered by the ASTM (American Society for Testing and Materials).[1a,b,c] While explosive materials are able to explode or detonate, propellants are only suitable for deflagration. The difference between deflagration and detonation can be found in the propagation speed of the reaction front within the unreacted material. In the case of a deflagration it lies within the range of subsonic velocity, whereas the propagation speed of a detonation is located above it.[2] Additionally, propellants display a high combustion temperature and a high specific impulse[3], as well as a small molar weight of the resulting combustion gases. Explosives, however, show high detonation pressures and velocities. The detonation velocity shows a linear dependence towards the density of an explosive, the detonation pressure, however, depends squarish.[4] In this case, the decomposition products should be, ideally, gaseous, present in large quantities and have a negative reaction enthalpy. The same criterion applies to flares, which are used in pyrotechnics and in the production of decoy flares.[5a-c] The research goals in the pyrotechnics branch would be, on the one hand, achieving purer colours,[6] and on the other hand, developing more environmentally friendly compounds.[7] Flares can be classified as either NIR (near infrared)[8] or MTV flares. A classic example of an NIR-flare composition would be potassium or caesium nitrate, hexamine, silicon and a suitable binder.[9a-c] MTV flares (Magnesium, Teflon, Viton®), however, display a strong soot production due to the highly exothermic enthalpy of formation of MgF_2. This is particularly useful in order to deviate the trajectory of heat-detecting missiles.[10,11] The mechanism flares rely on is based on the principle of the black body radiator.[12] According to Wien's displacement law, the emitted wavelength is indirectly proportional to the temperature of a black body radiator. The actual research in this area also focuses on the usage of perfluorinated tetrazole derivatives.[13a-c] A further branch, mostly focused on military research, would be the development of propellant powders, which are used to accelerate ammunition through gun barrels by creating gas pressure.[1b] This comprises small caliber up to large caliber artillery ammunition and mortar shells, as well as tank ammunition, depending on the grain size and shape. In this particular case, there is a special need for compounds that are able to generate large volumes of gas. There are three kinds of propellant powders: single-base (only nitrocellulose), double-base (nitrocellulose and nitroglycerin) and triple-base (nitrocellulose, nitroglycerin and

nitroguanidine).[14] These standard mixtures are inexpensive, but only generate moderate amounts of gas while being highly erosive (iron carbide formation). A contemporary example of propellant powder would be the triaminoguanidinium salt of 5,5'-azotetrazole,[15,16] which, having a large proportion of nitrogen (82.3 %), is able to produce a large gas volume. It additionally provides the advantage of a lesser erosion of barrels due to a higher N_2/CO ratio, which leads to a longer shelf life of the weapon system. The research field of rocket propellants is mainly focused on the substitution of ammonium perchlorate (AP) used in solid rocket boosters. This compound is considered harmful because of its ability to replace iodide in the metabolic process regarding the synthesis of thyroxine, which can be attributed to the similar radiuses of iodine and the perchlorate anion.[17-19] It serves as oxidizing agent when generating Al_2O_3. A considerable amount of heat is released by this exothermic reaction, where the oxygen balance, which ensures a complete oxidation of the aluminium, is highly important. The use of ammonium dinitramide (ADN) instead of AP is still investigated nowadays.[20a,b] In the upper stage engine a hypergolic mixture of N_2O_4 and monomethylhydrazine (MMH) is still in use nowadays.[21] Since most hydrazine derivatives are classified as carcinogenic, a substitution of these is essential.[22]

One of the main differences between primary and secondary explosives is their unequal sensitivity towards external stimuli. While primary explosives are substances which are very sensitive towards impact, friction and electrostatic discharge, secondary explosives are only slightly sensitive, if not completely insensitive towards external influences. The task of a primary explosive is the initiation of the secondary explosive through its ignition, which generates a shock wave that travels through the secondary explosive and induces its detonation. In order to achieve this effect, the shockwave must be stable within a specific minimum distance in the secondary explosive, the so called "critical diameter". A few prominent examples of primary explosives are lead azide,[23a,b] mercury fulminate,[24a,b] lead styphnate,[25a,b] tetrazene,[26a,b] 2,4,6-triazidotriazine (TAT)[27a,b] and 2-diazo-4,6-dinitrophenol (DDNP).[28a-d] These substances, which have been majorly used during the past decades due to the inexpensiveness of their production, have, however, significant disadvantages. Primary explosives containing heavy metals have highly adverse effects on both the environment and diverse organisms. Especially on training grounds, a problem regarding the use of lead based substances has arisen, leading to a long term contamination of ground waters.[29a,b] Heavy metal free primary explosives on the other hand often suffer from low thermal stability[30a,b]. Environmental pollution is, as well, a key problem regarding secondary explosives, which are mostly quite corrosive and harm the environment by releasing nitric acid. Secondary explosives can be subdivided into three categories. First there are the traditional explosives like hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)[31a-c], 2,4,6-trinitrotoluene (TNT),[32a,b] pentaerythityltetranitrate (PETN)[33] and 3-nitrotriazol-5-one

(NTO)[34], which are mainly used for military purposes. The second category would be high temperature resistant explosives like 2,2',4,4',6,6'-hexanitrophenylethylen (HNS),[35a-d] 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)[36a-c] and 2,6-dipicrylamino-3,5-dinitropyridine (PYX),[37a-c] which are rather used for civilian purposes like e.g. depth drilling in oil rigs. Also tetranitrodibenzo-1,3a,4,4a-tetraazapentalene[38] and the calcium salt of 5-nitriminotetrazole[39] are being considered for such applications. An overview of the most common commercially available primary and secondary explosives is shown in figure 1.

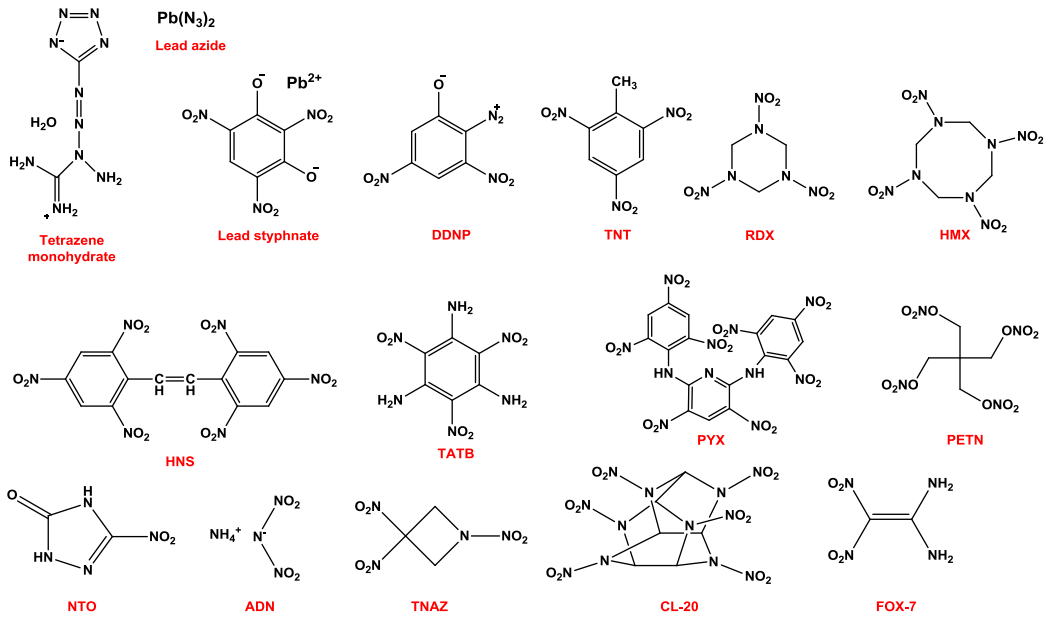

Fig. 1: Overview of commercially used primary and secondary explosives

TNT, for instance, one of the oldest commercially available explosives, has the great advantage of being melt castable. Having a melting point of 80.1 °C, it can be processed easily. A further benefit of its usage would be the inexpensive synthesis with toluene as a starting material. Due to its low density, however, it only delivers a moderate performance. By oxidizing TNT with hypochlorite HNS, which has been the benchmark regarding high temperature resistant ($T_{Dec.}$ = 318 °C) explosives, can be obtained. While being thermally more stable ($T_{Dec.}$ = 370 °C), PYX is only a little bit more expensive in its synthesis than HNS and is tested at the moment.[37c,40] TNAZ would be a viable alternative to TNT being melt castable as well,[41] as it provides a much higher performance than TNT, but is also incredibly expensive to synthesize. TATB is in contrast one of the most expensive but also most insensitive explosives known. It is used among other things to initiate nuclear weapons. A substantially stronger explosive is RDX. Due to its higher density of 1.80 g cm^{-3} it is able to achieve a higher performance than every single compound named above. Its synthesis is quite simple and inexpensive and uses hexamethylentetramine as the starting material. RDX, also known as hexogen, is the most used secondary explosive for military applications. Due

to its toxicity and widespread use, however, it is a major goal to find a replacement. A viable alternative to RDX would be NTO, which has a higher density (1.91 g cm^{-3}) but a slightly lower performance. A further high performance explosive would be the ε-conformer of 2,4,6,8,10,12-hexanitroisowurtzitane (CL-20).[42a-c] Its synthesis requires Pd/C and $NO_2^+BF_4^-$, which leads to a high synthesis cost. In addition to that it has to be noted that only the ε-conformer possesses the required high density (2.08 g cm^{-3}), which must be isolated by selective crystallization.

New secondary explosives should fulfil the following criteria:

- Low costs and high yields in synthesis
- Low toxicity and low water solubility
- Chemical und thermal stability ($T_{Dec.}$ > 200 °C for RDX replacements, $T_{Dec.}$ > 260 °C for 100 h for HNS replacements)
- Insensitivity (IS > 7.5 J, friction > 120 N for RDX replacements, IS > 7.4 J, friction > 235 N for HNS replacements) and high densities
- High performance and compatibility to binders and platizicers

New primary explosives should fulfil the following criteria:

- Fast deflagration to detonation transition (DDT)
- High initiation capability
- Low toxicity (means no Pb, Cd, Hg, N_3^- and ClO_4^-)
- Insensitivity (IS > 1 J, friction sensitivity > 3.5 N)
- Thermal stability > 200 °C
- Low costs and high yields in synthesis

Characterizing secondary explosives in regard to their energetic performance requires a certain amount of physical data. First, the heat of formation ($\Delta_f H°$(s) / kJ mol^{-1}) of the solid must be determined. This can be achieved either via bomb calorimetry, in which the compound is combusted with oxygen, or via the GAUSSIAN computer code. In this thesis all values for $\Delta_f H°$(s) were calculated by using the computational method. All calculations were carried out using the Gaussian G09W (revision A.02) program package. The enthalpies (H) were calculated using the complete basis set (CBS) method of Petersson and coworkers in order to obtain very accurate energies. The CBS models use the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated complete basis set limit. CBS-4 begins with a HF/3-21G(d)

structure optimization; the zero point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy, and a MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. A MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher order contributions. In this study we applied the modified CBS-4M method (M referring to the use of Minimal Population localization) which is a re-parametrized version of the original CBS-4 method and also includes some additional empirical corrections.[43] The enthalpies of the gas-phase species M were computed according to the atomization energy method (eq.1).

$$\Delta_f H°_{(g,\,M,\,298)} = H_{(Molecule,\,298)} - \sum H°_{(Atoms,\,298)} + \sum \Delta_f H°_{(Atoms,\,298)} \quad (1)$$

The gas phase heats of formation are converted to the solid state value by subtracting its sublimation enthalpy calculated with Trouton's rule ($\Delta H_{sub} = 188 \cdot T_m$). Therefore the melting point of the substance is needed. These molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid state energies of formation (ΔU_m) according to equation 2.

$$\Delta U_m = \Delta H_m - \Delta n\, RT \quad (2)$$

(Δn being the change of moles of gaseous components)

After that the EXPLO 5 computer code is used to calculate the detonation parameters of the substance. For the input $\Delta_f H°$(s), the sum formula and the density are required. The density is obtained from the crystal structure mainly measured at 173 K. For all compounds, an Oxford Xcalibur3 diffractometer with a CCD area detector was employed for data collection using Mo-*K*α radiation (λ = 0.71073 Å). By using the CRYSALISPRO software[44] the data collection and reduction were performed. The structures were solved by direct methods (SIR92, [45a] SIR -97[45b] or SHELXS-97[46]) and refined by full-matrix least-squares on *F*2 (SHELXL [46b]) and finally checked using the PLATON software[47] integrated in the WinGX software suite. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The absorptions were corrected by a SCALE3 ABSPACK multiscan method.[48]. All DIAMOND2 and DIAMOND3 plots are shown with thermal ellipsoids at the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. Hydrogen bonds are discussed according the van der Waals radii based on the publication of A. Bondi in 1964.[49]

The density at 173 K can be easily converted into the density at 298 K by using the semi-empirical equation according to Xu et al..[50] The EXPLO 5 computer code calculates the following parameters: the energy of explosion $\Delta_{Ex}U°$ / kJ kg^{-1}, the temperature of explosion T_{det} / K, the detonation pressure P_{CJ} / kbar, the detonation velocity $V_{Det.}$ / m s^{-1}, the volume of gaseous detonation products V_o / L kg^{-1} and the oxygen balance Ω / %.

2. Motivation and goals

In order to synthesize new energetic materials, it is crucial to consider which functional groups are necessary to obtain an explosive and how they affect the thermal stability. In the case of amino-nitrobenzene based explosives, an increasing number of amines neighboring nitro groups increases the thermal stability and the density due to an electronic "push pull system". Therefore those polynitroaniline-based explosives like TATB obtain their explosive potential from their density as well as from the nitro groups. The increase of thermal stability due to the introduction of amino groups into nitrobenzenes is displayed in figure 2.

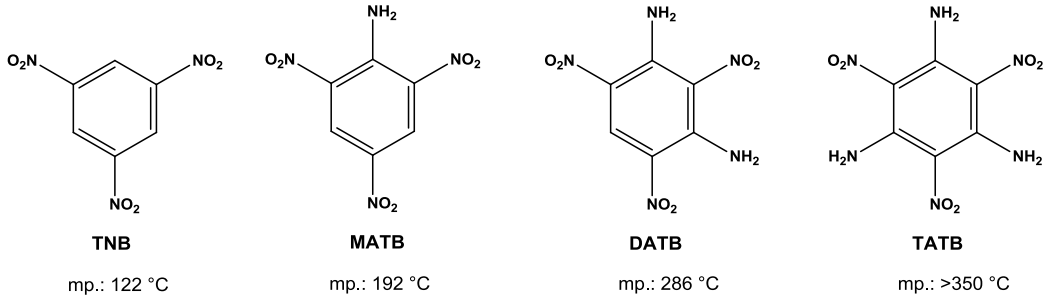

Fig. 2: Thermal stabilities of different aminonitrobenzenes

With growing thermal stability the sensitivity towards external stimuli often decreases. In addition, those explosives are harder to initiate. Another possibility to rise the thermal stability of explosives is the salt-formation of acidic compounds like 5-nitrotetrazole. The introduction of the 3-aminotriazole moiety into a benzene system is also a viable alternative. The heat of formation of explosives is highly dependent on the number of N–N single and double bonds. This can be achieved by using heterocycles containing many nitrogen atoms. For example, 1,2,4,5-tetrazines or tetrazoles derivatives provide many of them. Additionally the formation of primary and secondary nitramine groups rises the heat of formation as well as the oxygen balance significantly.

This doctoral thesis is mainly meant to describe the nitration reactions of inexpensive starting materials in order to synthesize new primary and secondary explosives. Particularly the nitration reactions of 2,2'-bisimidazole and the salt-formation of the resulting 4,4',5,5'-tetranitro-2,2-bisimidazole should provide many new energetic compounds that can be analyzed regarding their energetic properties. Moreover the methylation of the remaining amine functions of the imidazole-moiety should result in a melt-castable secondary explosive (Publication A). The nitration and oxidation reactions of 2-aminobenzimidazole (Publication E) were also researched in detail. A variety of new energetic compounds should be synthesizable depending on the selected nitration conditions. The amines within the imidazole moiety in the case of the obtained nitro-derivatives should be acidic enough to be

deprotonated. Moreover, the behavior of 1,4-disubstituted benzenes towards nitrating conditions, as well as their ability to be converted into diazophenols, were examined (Publication B & F). In addition, the regio-selectivity of those nitration reactions was thoroughly researched. In this case, 4-chloroaniline, 4-aminophenol, 1,4-diaminobenzene, 1,4-dihydro-*p*-quinone and 4-fluorobenzoic acid were the main starting materials. Different nitration techniques were tested on these starting materials. Here it must be discerned whether a certain nitration is suitable for the corresponding precursor. Should this not be the case, suitable protection groups are necessary in order to carry out a successful nitration. Acidic nitration reactions can be carried out by only using nitric acid in different concentrations. Depending on the stability of the substance, as well as the protection group towards the acid, the proper concentration of nitric acid must be determined. 65 %, 82.5 %, 90 % and 99.5 % nitric acid was tested at different temperatures (–40 to 90 °C). The classic "mixed acid" (concentrated sulfuric acid / nitric acid) and its combination with oleum (25 % or 65 % SO_3 by weight) was also used in some reactions. Furthermore a mixture of acetic anhydride and nitric acid, including the *in situ* generation of acetylnitrate, was also tested as a mild nitration method. An additional method would be the use of liquid NO_2, which is a nitration procedure based on a radical mechanism. The downside of this method, however, is the restricted compatibility with some functional groups like primary amines. In this case the use of N_2O_5 in aprotic solvents like dichloromethane or acetonitrile could be an alternative ionic method.

Some of the performed nitration reactions resulted in the formation of new DDNP-derivatives, as mentioned above. Their capability to initiate RDX was tested (Publication F). In addition, new energetic compounds like nitrogen rich salts of 3,6-bishydrazino-1,2,4,5-tetrazine were synthesized and characterized regarding their energetic properties (Publication C). Furthermore, nucleophilic substitution reactions of 3,6-bis(3,5-dimethylpyrazolyl)-1,2,4,5-tetrazine and 3,6-dichloro-1,2,4,5-tetrazine were researched (Publication D). A further goal was the synthesis of 2,3,4,6-tetranitroaniline[51] and 2,3,4,5,6-pentanitroaniline[52a-d] in a 10 g scale. It is possible to synthesize energetic benzofuroxanes and benzodifuroxanes by a nucleophilic substitution of a nitro group using azide as nucleophile and followed by a ring closure reaction.[53] These compounds, which have already been described in the past,[51] were synthesized and analyzed in regard to their sensitivity, thermal stability and energetic performance. All substances that showed theoretically acceptable detonation parameters underwent the so called "Small Scale Shock Reactivity Test" (SSRT), in which a defined volume of the testing substance was pressed into a perforated steel block. This was topped with a commercially available detonator (Orica, DYNADET-C2-0ms). The initiation of the tested explosive resulted in denting a separate aluminium block, which was placed right

underneath the steel block. The volume of the dent was then filled with sand in order to compare the performance of the tested sample with RDX, TNT and HNS.[54a,b]

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3. PUBLICATION A

Energetic Derivatives of 4,4',5,5'-Tetranitro-2,2'-bisimidazole (TNBI)

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Z. Anorg. Allg. Chem. **2012**, *638*, 1278–1286.

3.1 Abstract

4,4',5,5'-Tetranitro-2,2'-bisimidazole (TNBI) was synthesized by nitration of bisimidazole (BI) and recrystallized from acetone to form a crystalline acetone adduct. Its ammonium salt (**1**) was obtained by the reaction with gaseous ammonia. In order to explore new explosives or propellants several energetic nitrogen-rich 2:1 salts such as the hydroxylammonium (**3**), guanidinium (**4**), aminoguanidinium (**5**), diaminoguanidinium (**6**) and triaminoguanidinium (**7**) 4,4',5,5'-tetranitro-2,2'-bisimidazolate were prepared by facile metathesis reactions. In addition, methylated 1,1'-dimethyl-4,4',5,5'-tetranitro-2,2'-bisimidazole (Me_2TNBI, **8**) was synthesized by the reaction of **2** and dimethyl sulfate. Metal salts of TNBI can also be easily synthesized by using the corresponding metal bases. This was proven by the synthesis of pyrotechnically relevant dipotassium 4,4',5,5'-tetranitro-2,2'-bisimidazolate (**2**) which is a brilliant burning component e.g. in near-infrared flares. All compounds were characterized by single crystal X-ray diffraction, NMR and vibrational spectroscopy, elemental analysis and DSC. The sensitivities were determined by BAM methods (drophammer and friction tester). The heats of formation were calculated using CBS-4M electronic enthalpies and the atomization method. With these values and mostly the X-ray densities different detonation parameters were computed by the EXPLO5 computer code. Due to the great thermal stability and calculated energetic properties, especially guanidinium salt (**4**) could be served as a HNS replacement.

3.2 Introduction

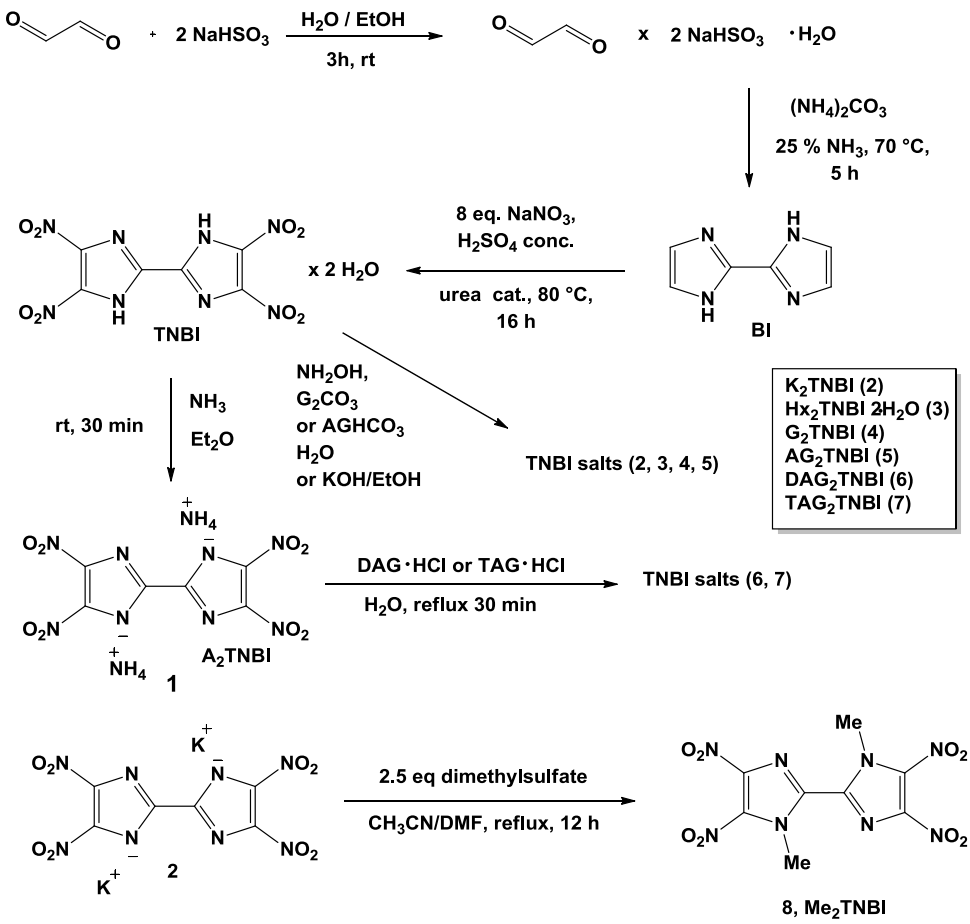
Most commercial secondary explosives like RDX (hexogen) and HNS (hexanitrostilbene) are highly toxic for human and animal. In terms of performance secondary explosives have parameters like a detonation velocity ($V_{Det.}$), detonation pressure (P_{CJ}), heat of detonation ($-\Delta_{Ex}U°$) and a volume of gases (V_0) which is created during their detonation.[1] It is a recent goal to create energetic materials with higher thermostability and lower sensitivity (towards impact (IS), friction (FS), electrostatic discharge (ESD)) and lower toxicity[2] than the current used ones. One approach is the use of azoles in combination with energetic substituents at

the carbon atom(s) like nitro or azide groups. Nitrated imidazoles in general were already investigated by Korean scientists and also in our research group due to their thermal-stabilities and energetic properties.[2,3] For example 1-methyl-2,4,5-trinitroimidazole was investigated, which shows a thermal stability of at least 190 °C.[2,4] In 2007 R. Damavarapu et al. characterized the potassium salt of 2,4,5-trinitroimidazole.[2,4] The synthesis is based upon a alternating nitration/rearrangement strategy starting with commercial available 4-nitroimidazole. Our article reports on derivatives of 4,4',5,5'-tetranitro-2,2'-bisimidazole (TNBI). The connection of two imidazole rings obtaining 2,2'-bisimidazoles follows the trend of generating larger energetic molecules. This mostly results in higher thermal stability and a more positive oxygen balance, which was also observed in the case of the pernitrated species TNBI. The thermal stability can be further improved by deprotonation and the formation of nitrogen rich 2:1 salts. Synthesis of the 2,2'-bisimidazole was already described by Italian researchers in 1981 in two steps *via* an bissulfite adduct. It was used for the investigation of methylated copper and zinc dinitrate complexes due to their interesting electronic spectra and ESR data.[5]. Also 4,4',5,5'-tetranitro-2,2'-bisimidazole (TNBI) was already described by *Cho* et al. in 2005 as a potentially RDX replacement which suffers hygroscopic properties.[6] In 1990 *Cromer* et al. described the crystal structures of TNBI dihydrate and its waterfree bis-ammonium salt.[7,8] In 1999 the 3,6-bishydrazine-1,2,4,5-tetrazinium-TNBI salt was described by *Chavez* et al. showing a thermal stability up to 217 °C.[9] *Oxley* et al. carried out thermochemical studies (isothermal thermolysis) on several tetrazine based salts.[10] We today report on several further nitrogen-rich derivatives of TNBI and on its methylated sister compound and their potential use in explosive formulations. In addition, metal salts like the prepared bispotassium salt **2** could serve as pyrotechnically relevant candidates in near IR or visible flares.

3.3 Results and discussion

3.3.1 Syntheses

An overall synthetic protocol is displayed in Scheme 1.



Scheme 1: Synthesis of TNBI salts **2–7** and 1,1'-dimethyl-4,4',5,5'-tetranitro-2,2'-bisimidazole (**8**)

The synthesis of 2,2'-bisimidazole (BI) was carried out as described by *Bernaducci* et al..[5] The oxidation of glyoxale with sodium-bisulfite leads to a glyoxal-sodium-bisulfite adduct. This adduct is more activated to react with concentrated ammonia in an ammonium bicarbonate buffered solution to yield BI. The synthesis was carried out in a scale of 12 g BI. The nitration was performed in conc. sulfuric acid (96–98 %) using eight equivalents sodium nitrate and a catalytic amount of urea. The nitration worked best by stirring the suspension at 85 °C for 16 hours. The maximum yield was 6 g TNBI · $2H_2O$ when 5 g BI was used. After the nitration is poured onto ice-water TNBI can be easily extracted with diethyl ether. The already known bisammonium 4,4',5,5'-tetranitro-2,2'-bisimidazolate (**1**) is synthesized by the reaction with gaseous ammonia.[9] Compound **1** serves as a valuable starting material to generate several salts because of their lower solubility in aqueous solution. The reaction of TNBI with aqueous potassium hydroxide, hydroxylamine solution, guanidinium carbonate or

aminoguanidinium bicarbonate, respectively, afforded salts **2** (bispotassium TNBI), **3** (bishydroxylammonium TNBI dihydrate), **4** (bisguanidinium TNBI) and **5** (bisaminoguanidinium TNBI) in good yields and high purities. Alternatively, the diethyl ether can be evaporated for the most part and KOH/EtOH is added to yield the bispotassium salt **2**. However, it would also be possible to synthesize salts **2**-**7** directly starting with TNBI and the corresponding bases. Crystalline samples of **2**, **5** and **6** (bis-diamoniguanidinium TNBI) and **7** (bis-triaminoguanidinium TNBI) could be obtained by recrystallization from water. **2** and **6** crystallize without inclusion of water, **3** as a dihydrate. **4** is only soluble in DMSO and crystallizes with two additional DMSO molecules. Salts **6** and **7** were synthesized by heating a suspension of **1** with diaminoguanidinium and triaminoguanidinium chloride, respectively, until a solution is obtained. **6** crystallizes very quickly at approx. 60 °C, **7** crystallizes at 4 °C over night. In general the purity of all salts can be established best via ^{1}H and ^{13}C NMR spectroscopy and elemental analysis.

1,1'-Dimethyl-4,4',5,5'-tetranitro-2,2'-bisimidazole (Me_2TNBI, **8**) was obtained by the reaction of **2** with 2.5 eq of dimethylsulfate in CH_3CN/DMF (9:1). We considered that the lack of hydrogen bonds yields to a low melting point but a high decomposition temperature of **8**. A crystalline sample could be obtained from acetone.

During our syntheses we additionally got single crystals of the TNBI·2 H_2O, potassium-TNBI monohydrate, **4**·DMSO, 1:1 diaminoguanidinium salt (DAGTNBI·H_2O) and **6**, which are all presented in the Supporting Information. Investigations of the alkaline earth metal salts *e.g.* CaTNBI · 8 H_2O and BaTNBI · 3 H_2O will be presented separately with respect to their potential use as pyrotechnic colorants.

3.3.2 Crystal structures

Due to the moderate water solubility, all compounds except of **4** (from DMSO) were recrystallized from water. TNBI can be either recrystallized from water and acetone yielding the corresponding dihydrate or diacetone adduct, respectively. The structures of compounds **2–8** as well as the monoprotonated potassium salt (KTNBI · H_2O) and the 1:1 diaminoguanidinium salt (DAGTNBI · H_2O determined by low temperature (173 K) X–ray diffraction. Selected data and parameters of the X-ray determinations are given in the Supporting Information (Tables S1 and S2). Further crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC-876136 (TNBI · 2H_2O), 876137 (TNBI · 2 acetone), 877533 (**2**), KTNBI · H_2O, 876398 (**3**), 876140 (**4** · 2DMSO), 876143 (**5**), 877534 (**6**), 876141 DAGTNBI · H2O, 876142 (**7**) and 876138 (**8**))[11] The molecular structures of TNBI · 2H_2O, KTNBI·H_2O, **4** · 2DMSO, DAGTNBI · H_2O and **6** are shown in the Supporting Information.) As mentioned in the introduction the

structure of TNBI at room temperature has been described in literature.[8] A redetermination of this structure at 173 K is presented in the Supporting Information. First we would like to present the structure of TNBI with two molecules of acetone (Figure 1), which crystallizes in the monoclinic space group C2/c with four formula units per unit cell and calculated density of 1.581 g cm^{-3}. The structure is similar to that of the dihydrate.[8] Basically, the bis-imidazole backbone is found to be planar in all structures except for **8**. The bond length within the imidazoles are between typical C–N single and C=N double bonds representing the aromatic character. The C–C bond connecting both imidazole rings in all structure is significantly shorter (approx. 1.46 Å) than a typical C–C single bond (1.54 Å). Nitro groups are not co-planar with the imidazole rings to avoid electrostatic repulsion of the nitro oxygen atoms. For example, the torsion angle (in TNBI · 2 acetone) between the atoms O2–N3–N4–O3 is 44°. The acetone molecules are connected to the TNBI molecules by strong NH···O hydrogen bonds (e.g. N1–H1···O5ii: d(D–H) 0.890(18) Å, d(H···A) 1.807(19) Å, d(D···A) 2.6951(16) Å, <(D–H···A) 175.3(16)°.

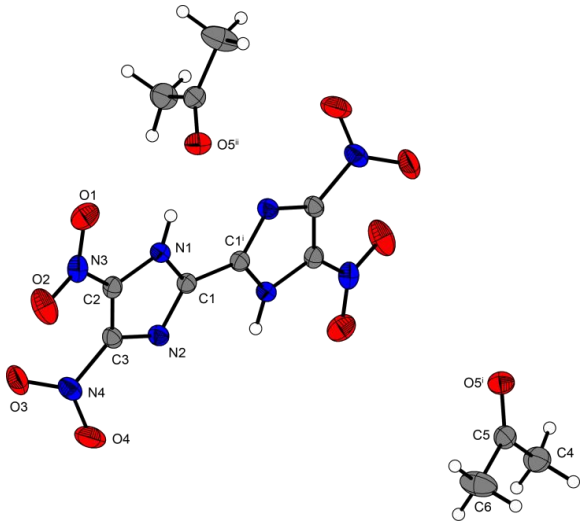


Fig. 1: Molecular structure of TNBI · 2 acetone showing the labeling scheme. The non-hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. Symmetry codes (i) 0.5–x, 1.5–y, –z; (ii) 0.5–x, 0.5+y, 0.5–z. **Selected bond lengths** [Å]: O1–N3 1.2267(17), O2–N3 1.2241(17), O3–N4 1.2234(17), O4–N4 1.2229(17), N1–C1 1.3527(19), N1–C2 1.3584(19), N2–C1 1.3312(18), N2–C3 1.3463(19), N3–C2 1.435(2), N4–C3 1.4555(18), C1–C1i 1.449(3), C2–C3 1.375(2), O5–C5 1.2234(18), C4–C5 1.489(2), C5–C6 1.489(2). **Selected bond angles** [°]: C1–N1–C2 105.92(12), C1–N2–C3 104.21(12), O2–N3–O1 125.22(14), O2–N3–C2 118.06(13), O1–N3–C2 116.69(12), O4–N4–O3 125.16(13), O4–N4–C3 116.74(13), O3–N4–C3 118.09(13), N2–C1–N1 112.76(13), N2–C1–C1 124.25(17), N1–C1–C1i 122.99(16), N1–C2–C3 106.18(13), N1–C2–N3 119.33(13), C3–C2–N3 134.29(13), N2–C3–C2 110.92(12), N2–C3–N4 118.87(13), C2–C3–N4 130.15(14), C4–C5–C6 116.95(16). **Selected torsion angles** [°]: O1–N3–C2–N1 –14.47(19), O2–N3–C2–C3 –10.7(2), O3–N4–C3–N2 149.92(13), O4–N4–C3–N2 –29.1(2), N1–C1–C1i–N2 i –0.1(2).

The potassium salt of TNBI (K_2TNBI **2**) crystallizes in the monoclinic space group $P2_1/c$ with two formula units per unit cell. The calculated density at –100 °C is 2.126 g cm^{-3}. The molecular moiety is displayed in Figure 2.

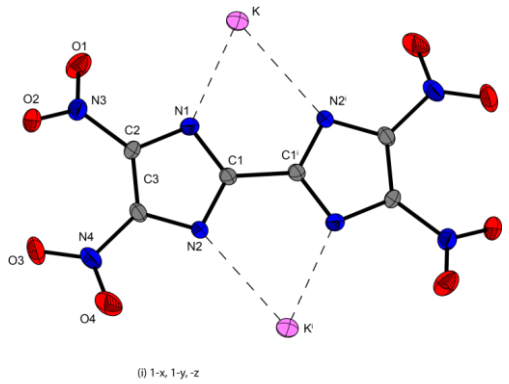


Fig. 2: Molecular structure of K_2TNBI (**2**) showing the labeling scheme. The non-hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. Symmetry code (i) 1–x, 1–y, –z. **Selected bond lengths** [Å]: K–N1 2.8213(19), K–N2i 2.948(10), O1–N3 1.230(2), O2–N3 1.236(2), O3–N4 1.226(2), O4–N4 1.231(2), N1–C2 1.343(3), N1–C1 1.348(3), N2–C3 1.342(3), N2–C1 1.353(3), N3–C2 1.435(3), N4–C3 1.438(3), C1–C1i 1.460, C2–C3 1.390(3). **Selected bond angles** [°]: N1–K–N2i 59.90(5). **Selected torsion angles** [°]: O1–N3–C2–N1 28.3(3), O2–N3–C2–N1 -151.7(2), O3–N4–C3–C2 20.5(4), O4–N4–C3–C2 –160.2(2), N1–C1–C1–N2 1.0(3).

As mentioned before, in the molecular structure of **8** which crystallizes in the triclinic space group *P*–1, the imidazole rings are not co-planar (torsion < N1–C1–C5–N6 = 36.7(4)°). However, the C1–C5 bond length is in the same range observed for the other structures. Since no classical hydrogen bonds can be formed the density of 1.703 g cm^{-3} is lower than that of the solvent free compounds investigated in this work. On the other hand, weak non-classical C–H···O H-bonds as well as nitro-nitro interactions[12] are present. The nitro groups next to the methyl substituents are twisted significantly more out of the ring plane which can be seen in Figure 3.

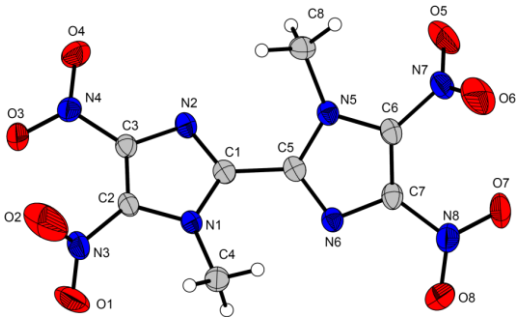
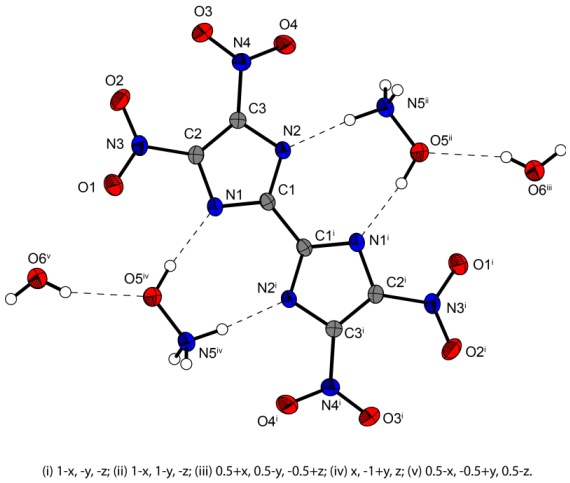


Fig. 3: Molecular structure of Me_2TNBI (8) showing the labeling scheme. The non–hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. **Selected bond lengths** [Å]: O1–N3 1.201(4), O2–N3 1.205(4), O3–N4 1.223(3), O4–N4 1.218(3), O5–N7 1.226(4), O6–N7 1.204(4), O7–N8 1.228(4), O8–N8 1.222(4), N1–C2 1.359(4), N1–C1 1.368(4), N1–C4 1.473(4), N2–C1 1.326(4), N2–C3 1.351(4), N3–C2 1.459(4), N4–C3 1.440(4), N5–C6 1.366(4), N5–C5 1.367(4), N5–C8 1.479(4), N6–C5 1.321(4), N6–C7 1.349(4), N7–C6 1.454(4), N8–C7 1.440(4), C1–C5 1.461(4), C2–C3 1.358(4), C6–C7 1.357(4). **Selected bond angles** [°]: C2–N1–C1 104.9(2), C2–N1–C4 125.7(3), C1–N1–C4 128.9(3), C1–N2–C3 103.9(2), O1–N3–O2 124.8(3), O1–N3–C2 118.4(3), O2–N3–C2 116.8(3), O4–N4–O3 124.9(3), O4–N4–C3 118.8(3), O3–N4–C3 116.4(3), C6–N5–C5 104.8(2), C6–N5–C8 126.3(3), C5–N5–C8 128.6(3), C5–N6– C7 104.1(2), O6–N7–O5 125.6(3), O6–N7–C6 117.9(3), O5–N7–C6 116.5(3), O8–N8–O7 125.2(3), O8–N8–C7 119.0(3), O7–N8–C7 115.9(3), N2–C1–N1 112.9(3), N2–C1–C5 124.9(3), N1–C1–C5 122.0(3), C3–C2–N1 107.0(2), C3–C2–N3 132.2(3), N1–C2–N3 120.7(3), N2–C3–

C2 111.2(3), N2–C3–N4 121.7(3), C2–C3–N4 127.0(3), N6–C5–N5 113.0(3), N6–C5–C1 124.1(3), N5–C5–C1 122.7(3), C7–C6–N5 106.7(3), C7–C6–N7 132.0(3), N5–C6–N7 121.4(3), N6–C7–C6 111.3(3), N6–C7–N8 121.1(3), C6–C7–N8 127.6(3). **Selected torsion angles** [°]: N1–C1–C5–N6 36.7(4), O1–N3–C2–N1 -60.9(4), O2–N3–C2–N1 -119.8(4), O4–N4–C3–N2 -11.0(4), O3–N4–C3–N2 -169.8(3), O6–N7–C6–N5 124.5(3), O5–N7–C6–N5 -54.3(4), O8–N8–C7–N6 -13.6(5), O7–N8–C7–N6 166.3(3).

Compound **3** crystallizes in the monoclinic space group $P2_1/n$ with a cell volume of 763.6(5) $Å^3$ and two formula units per unit cell. The molecular moiety is shown in Figure 4. Its density of 1.810 g cm^{-3} is the highest of the metal-free compounds within this work. Next to the hydroxylammonium cations also the water molecules participate in a strong hydrogen bond network. This may be the reason that it is not possible to dehydrate **3** before decomposition by heating.



(i) 1-x, -y, -z; (ii) 1-x, 1-y, -z; (iii) 0.5+x, 0.5-y, -0.5+z; (iv) x, -1+y, z; (v) 0.5-x, -0.5+y, 0.5-z.

Fig. 4: Molecular structure of bishydroxylammonium tetranitrobisimidazolate dihydrate (**3**) showing the labeling scheme. The non-hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. Symmetry codes (i) 1–x, –y, –z; (ii) 1–x, 1–y, –z; (iii) 0.5+x, 0.5–y, –0.5+z; (iv) x, –1+y, z; (v) 0.5–x, –0.5+y, 0.5–z. **Selected bond lengths** [Å]: O1–N3 1.2269(17), O2–N3 1.2193(17),O3–N4 1.2207(16), O4–N4 1.2256(17), N1–C1 1.3474(18), N1–C2 1.3484(19), N2–C3 1.3409(18), N2–C1 1.3469(19), N3–C2 1.4391(19), N4–C3 1.445(2), C2–C3 1.394(2), O5–N5 1.4141(17); **Selected bond angles** [°]: C1–N1–C2 –103.20(12), C3–N2–C1 103.89(12), O2–N3–O1 123.56(13), O2–N3–C2 119.39(12), O1–N3–C2 117.05(13), O3–N4–O4 123.13(14), O3–N4–C3 119.77(13), O4–N4–C3 117.09(12), N2–C1–N1 114.85(13), N2–C1–C1 122.03(16), N1–C1–C1 123.11(16), N1–C2–C3 109.29(13), N1–C2–N3 117.99(13), C3–C2–N3 132.71(14), N2–C3–C2 108.77(13), N2–C3–N4 117.21(13), C2–C3–N4 134.02(13); **Selected torsion angles** [°]: O2–N3–C2–N1 –174.21(13), O1–N3–C2–N1 5.3(2), O3–N4–C3–N2 –176.41(13), O4–N4–C3–N2 3.3(2), N1–C2–C3–$N2^i$ 0.21(17).

In contrast to compound **4** which could only be obtained crystalline with inclusion of two molecules of dimethylsulfoxide, compound **5** was obtained free of water by recrystallization from water. It crystallizes in the triclinic space group *P*–1 with one formula unit per unit cell and a calculated density of 1.751 g cm^{-3}. All hydrogen atoms of the aminoguanidinium cation participate in hydrogen bonds, a few of them illustrated in Figure 5.

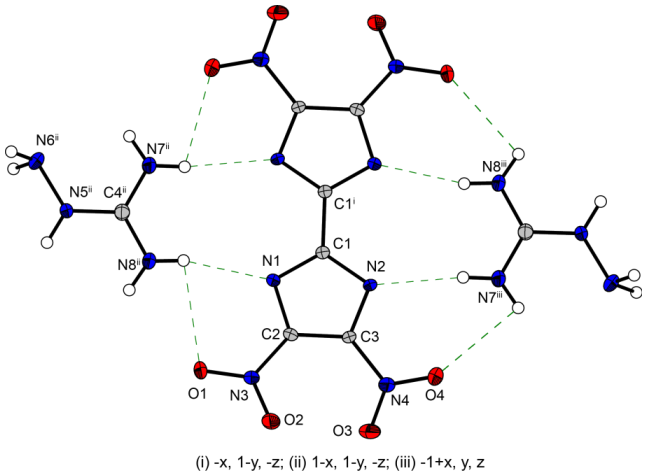


Fig. 5: Molecular structure of bisaminoguanidinium tetranitrobisimidazolate (**4**) showing the labeling scheme. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. Symmetry codes: (i) –x, 1–y, –z; (ii) 1–x, 1–y, –z; (iii) –1+x, y, z., **Selected bond lengths** [Å]: O1–N3 1.2286(19), O2–N3 1.2405(18), O3–N4 1.2281(19), O4–N4 1.2356(19), N1–C1 1.352(2), N1–C2 1.354(2), N2–C3 1.344(2), N2–C1 1.358(2), N3–C2 1.423(2), N4–C3 1.436(2), C1–C1 1.461(3), C2–C3 1.387(2), N5–C4 1.335(2), N5–N6 1.411(2), N7–C4 1.318(2), N8–C4 1.324(2); **Selected bond angles** [°]:C1–N1–C2 102.57(14), C3–N2–C1 102.50(14), O1–N3–O2 122.54(14), O1–N3–C2 119.73(14), O2–N3–C2 117.71(14), O3–N4–O4 123.35(15), O3–N4–C3 119.09(15), O4–N4–C3 117.54(14), N1–C1–N2 115.66(15), N1–C1–C1 122.28(19), N2–C1–C1^{i} 122.06(19), N1–C2–C3 109.34(14), N1–C2–N3 121.10(15), C3–C2–N3 129.26(15), N2–C3–C2 109.94(14), N2–C3–N4 119.58(15), C2–C3–N4 130.38(15), C4–N5–N6 118.05(15), N7–C4–N8 121.32(17), N7–C4–N5 120.12(17), N8–C4–N5 118.56(16); **Selected torsion angles** [°]: O1–N3–C2–N1 18.6(2), O2–N3–C2–N1 –160.03(15), O3–N4–C3–N2 146.31(16), O4–N4–C3–N2 32.0(2), N2–C1–C1^{i}–N1^{i} 0.56 (3).

The triaminoguanidinium salt **7** also crystallizes in the triclinic space group *P*–1 with one formula unit per unit cell. The molecular structure is shown in figure 6. Its calculated crystal density (1.722 g cm^{-3}) is slightly lower than those of **5** (1.806 g cm^{-3}) and **6** (1.758 g cm^{-3}). In the crystal packing the anions and cations are orientated almost perpendicularly to each other.

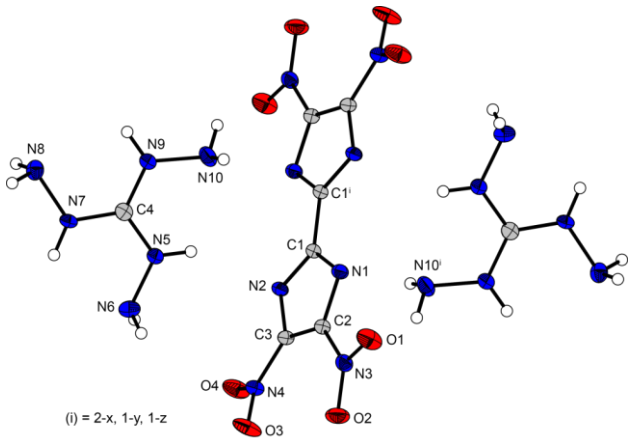


Fig. 6: Molecular structure of bistriaminoguanidinium tetranitrobisimidazolate (**7**) showing the labeling scheme. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. Symmetry codes: (i) 2–x, 1–y, 1–z. **Selected bond lengths** [Å]: O1–N3 1.2313(17), O2–N3 1.2390(17), O3–N4 1.2320(17), O4–N4 1.2258(17), N1–C1 1.3454(19), N1–C2 1.3458(19), N2–C3 1.3467(19), N2–C1 1.3528(19), N3–C2 1.4429(19), N4–C3 1.4384(19), C1–C1i 1.465(3), C2–C3 1.400(2); **Selected bond angles** [°]: C1–N1–C2 102.95(12), C3–N2–C1 103.26(12), O1–N3–O2 123.40(13), O1–N3–C2

117.48(13), O2–N3–C2 119.12(13), O4–N4–O3 122.73(13), O4–N4–C3 118.23(12), O3–N4–C3 119.02(12), N1–C1–N2 115.54(12), N1–C1–C1i 123.04(16), N1–C2–C3 109.58(13), N1–C2–N3 117.98(13), C3–C2–N3 132.40(13), N2–C3–C2 108.67(13), N2–C3–N4 118.20(13), C2–C3–N4 133.12(13); **Selected torsion angles** [°]: O1–N3–C2–N1 12.79(19), O2–N3–C2–N1 –166.49(13), O4–N4–C3–N2 17.5(2), O3–N4–C3–N2 –161.12(14), N1–C1–C1i–N2i 1.2 (2).

3.3.3 Energetic properties

Due to their high combined nitrogen and oxygen content (N+O ≈ 70 %), but low sensitivities (see below) TNBI and its salts are energetic materials which could serve as high-explosives or also propellants. With respect to the thermal stability, compound **4** (without DMSO) shows the highest decomposition temperature ($T_{Dec.}$ = 328 °C) and is a potential HNS replacement ($T_{Dec.}$ = 318 °C[13] but lower explosive performance 7000 ms^{-1}[14]). The other salts show thermal-stabilities between 152 (**7**) and 206 °C (**5**). DSC plots are shown in Figure 7. **8** has an melting area at approx. 236 °C. Unfortunately, the gap between the melting and decomposition point ($T_{Dec.}$ = 258 °C) is too small for being a suitable meltcast explosive (for comparison TNT (2,4,6-trinitrotoluene) melts at 80 °C and decompose not before 310 °C).[12]

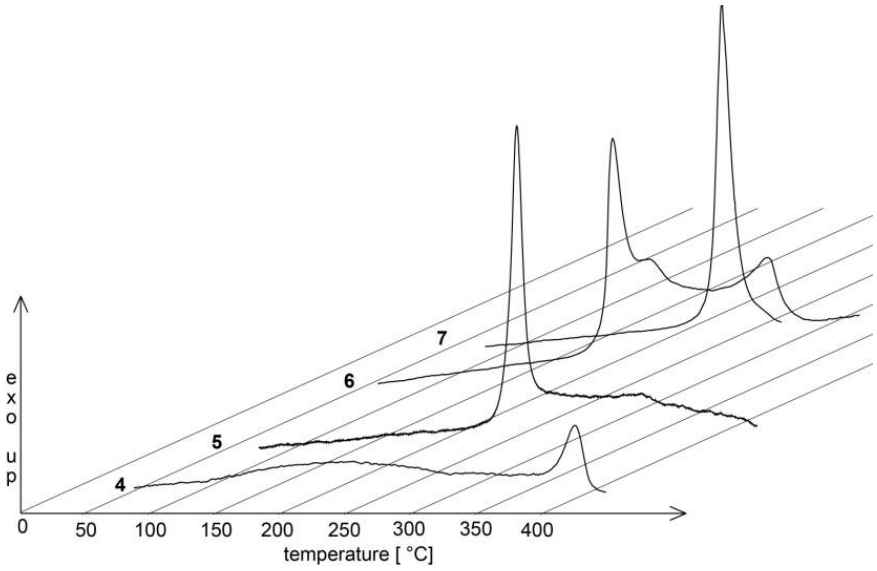


Fig. 7: DSC plots of compounds **4**-**7** measured with a heating rate of 5 °C min^{-1} (exo-up). Onset temperatures: 328 °C (**4**), 206 °C (**5**), 197 °C (**6**), 152 °C (**7**).

For safety issues the sensitivities towards impact, friction and electrostatic discharge were determined by BAM methods (see exp. part) and listed in Table 1. Regarding the impact values, **3** and **7** are the most sensitive (6 J) ones. This value is in the range of those observed for RDX (7 J) and PETN (5 J).[15] According to the "UN recommendations of the transport of dangerous goods"[16] they are classified as sensitive. Compounds **4** and **8** are completely insensitive towards impact (>40 J). Compounds **4** and **5** are insensitive (> 360 N) in terms of their friction sensitivity. Interestingly, salt **6** is the most sensitive one (252 N) which is classified as sensitive. All compounds are not susceptible towards electrical sparks.

Table 1: Energetic properties of compounds **3**-**8**

	3*	**4**	**5**	**6**	**7**	**8**
Formula	$C_6H_{12}N_{10}O_{12}$	$C_8H_{12}N_{14}O_8$	$C_8H_{12}N_{16}O_8$	$C_8H_{16}N_{18}O_8$	$C_8H_{18}N_{20}O_8$	$C_8H_6N_8O_8$
FW / g mol^{-1}	416.22	432.27	462.39	492.33	522.36	342.01
IS / J [a]	> 6	> 40	> 20	> 17	> 6	> 40
	(500 µm)	(500 µm)	(500 µm)	(500 µm)	(500 µm)	(500 µm)
FS / N [b]	> 288	> 360	> 360	> 252	> 288	> 292
	(500 µm)	(500 µm)	(500 µm)	(500 µm)	(500 µm)	(500 µm)
ESD / J [c]	> 0.3	> 1.0	> 1.0	> 0.4	> 0.2	> 0.1
	(500 µm)	(500 µm)	(500 µm)	(500 µm)	(500 µm)	(500 µm)
N / % [d]	33.65	45.36	48.48	51.21	53.63	32.75
Ω / % [e]	–23.06	–51.8	–51.91	–51.99	–52.1	–51.34
$T_{Dec.}$ / °C [f]	186	328	206	197	152	236(T_m),258 (T_{dec})
ρ / g cm^{-3} [g]	1.81	1.80 (pyc.)	1.75	1.76	1.71	1.70
$\Delta_f H_m°$ / kJ mol^{-1} [h]	–515.9	–114.5	171.1	399.3	638.7	145.3
$\Delta_f U°$ / kJ kg^{-1} [i]	–1138.1	–17.0	473.4	916.6	1319.0	504.1
EXPLO5.04 values:						
$-\Delta_{Ex}U°$ / kJ kg^{-1} [j]	5015	4172	4486	4770	5030	4984
T_{Det} / K [k]	3619	3098	3229	3351	3418	3732
P_{CJ} / kbar [l]	311	266	268	286	281	242
$V_{Det.}$ / m s^{-1} [m]	8362	8070	8138	8377	8388	7604
V_o / L kg^{-1} [n]	740	429	750	769	785	624

[a] impact sensitivity (BAM drophammer, 1 of 6); [b] friction sensitivity (BAM friction tester 1 of 6); [c] electrostatic discharge device (OZM); [d] nitrogen content; [e] oxygen balance; [f] decomposition temperature from DSC (β = 5 °C); [g] from X-ray diffraction at 173 K; [h] calculated (CBS-4M) heat of formation; [i] energy of formation; [j] energy of explosion; [k] explosion temperature; [l] detonation pressure; [m] detonation velocity; [n] assuming only gaseous products; ***** all values for dihydrate.

Several detonation parameters of **3**–**8** were calculated by the EXPLO5.04 computer code.[17-19] The program is based on the input of the energy of formation (kJ kg^{-1}) , density (g cm^{-3}) and the sum formula. For all compounds, except for **4**, their maximum X-ray densities at 173 K were used. The density of **4** (1.80 g cm^{-3}) was measured with a Quantachrome helium gas pycnometer. The heats of formation (Table 1) were calculated with the atomization method (equation 1) using CBS-4M enthalpies summarized in Table 2[20,21]. The gas phase enthalpies of formation $\Delta H_m(g)$ were converted into the solid state enthalpies of formation ($\Delta H_m(s)$) either by using the Jenkins' equations for X_2Y salts[22] (for ionic derivatives) or the Trouton rule [23] (**8**).

$$\Delta_f H°_{(g, M, 298)} = H_{(M, 298)} - \sum H°_{(Atoms, 298)} + \sum \Delta_f H°_{(Atoms, 298)} \quad (1)$$

Table 2: CBS-4M calculation results and molecular volumes.

M	$-H^{298}$ / a.u.	$\Delta_f H°$(g,M) / kcal mol^{-1}	V_M / nm^3
Me_2TNBI	1346,195338	57.5	
$TNBI^{2-}$	1266.677508	-8.1	
G^+	205.453192	136.6	
AG^+	260.701802	160.4	
DAG^+	315.949896	184.5	
TAG^+	371.197775	208.8	
NH_4O^+	131.863229	164.1	
3		320.1*	0.333*
4		265.1	0.417
5		312.7	0.439
6		361.0	0.465
7		409.5	0.504

* without crystal water

Lastly, the molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid state energies of formation (ΔU_m) according to equation (2) (Table 2).

$$\Delta U_m = \Delta H_m - \Delta n\, RT \quad (2)$$

(Δn being the change of moles of gaseous components)

The most positive heat of formation (639 kJ mol^{-1}) was achieved for the triaminoguanidinium salt **7**, which has the largest number of N–N single bonds. The hydroxylammonium salt **3** has a negative value (–516 kJ mol^{-1}) due to the inclusion of two molecules of crystal water. Although of this negative value **3** is one of the best compounds investigated in this work in terms of performance (detonation energy, velocity and pressure). The guanidinium salts show the general trend of improving performance with rising number of N–N single bonds in the cations. The highest detonation velocity was calculated for **7**, which is much higher than that of HNS (7000 m s^{-1})[14] and in the range that of PETN (8400 m s^{-1}).[13] Most thermally stable **4** has also a good calculated detonation performance. In order to investigate the ignitability and explosiveness of **4**, a small scale reactivity test (SSRT)[24] was performed. The SSRT was carried out in comparison to HNS in which a defined volume (HNS: 470 mg, density: 1.74 g cm^{-3}, **4**: 485 mg, density: 1.80 g cm^{-3}) was pressed into a perforated steel block (Figure 8). This was topped with a commercially available detonator (Orica, DYNADET-C2–0ms). Initiation of the tested explosive resulted in denting a separate aluminum block, which was placed right underneath the steel block. The volume of the dent was then filled with sand to compare the performance of HNS and **4**. The test showed that HNS is superior

and the dent could be filled with 672 mg sand in comparison to **4** (472 mg). The smaller dent of **4** could be caused by a larger critical diameter of **4**, which should influence the SSRT dramatically.

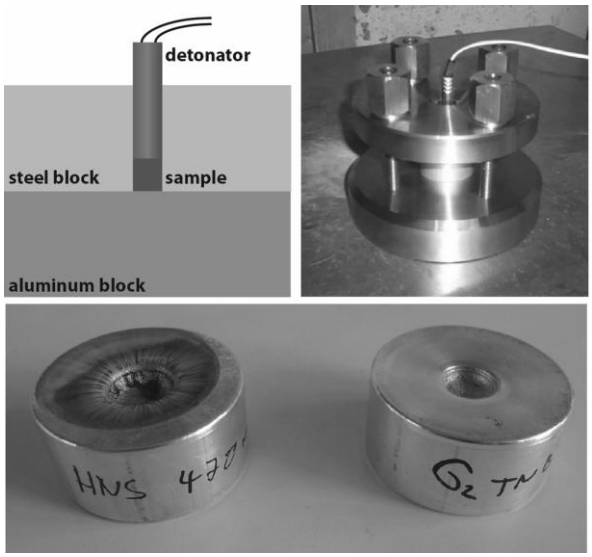


Fig. 7: Dented steel block of HNS (left) and **4** (right)

3.4 Conclusions

From this experimental study the following conclusions can be drawn: TNBI can be synthesized in good yields and purities by nitration of 2,2'-bisimidazole.The bispotassium salt (**2**) crystallizes without crystal water and could be used for near infrared based combustion mixtures. 2:1 salts of TNBI can be synthesized either with corresponding bases (e.g. hydroxides, carbonates) or metathesis reactions using hydrochloride derivatives. Enhanced performance of compounds **3**-**7** correlates with higher sensitivities towards impact, friction and electrostatic discharge. Bis-hydroxylammonium TNBI (**3**) although crystallizing as a dihydrate has the best energetic properties related to secondary explosive applications (highest detonation pressure), highest density (1.81 g cm^{-3}). Bis-guanidinium TNBI (**4**) has a high decomposition temperature (328 °C), low sensitivities and was successfully detonated in a small-scale reactivity test. Me_2TNBI (**8**) cannot be used as a suitable melt castable explosive because of its small melting range. All crystal structures of the herein investigated compounds were determined by low temperature single crystal X-ray diffraction.

3.5 Experimental section

General procedures

Raman spectra were recorded with a Bruker MultiRAM FT–Raman fitted with a liquid nitrogen cooled germanium detector and a Nd:YAG laser (λ = 1064 nm), infrared spectra were measured with a Perkin–Elmer Spectrum BX-FTIR spectrometer equipped with a Smiths DuraSampl*IR* II ATR device. All spectra were recorded at ambient temperature, the samples were solids. NMR spectra were recorded at 25 °C with a JEOL Eclipse 400 ECX instrument, and chemical shifts were determined with respect to external Me_4Si (^1H, 400.2 MHz; ^{13}C, 100.6 MHz), $MeNO_2$ (^{14}N, 29.0 MHz;). Mass spectrometric data were obtained with a JEOL MStation JMS 700 spectrometer (DCI+). Elemental analysis (C/H/N) was performed with a Elementar Vario EL analyzer. Melting points were determined in capillaries with a Büchi Melting Point B–540 instrument and are uncorrected. Decomposition points were determined by Differential Scanning Calorimetry (DSC) measurements with a Linseis DSC–PT10, using a heating rate of 5 °C min^{-1}. Pycnometric measurements were carried out with a Quantachrome helium gas pycnometer. Sensitivity data (impact and friction) were performed using a drophammer and friction tester analog to BAM (Bundesanstalt für Materialforschung und prüfung)[25]. Electrostatic sensitivities were measured with a OZM small scale electrostatic discharge tester.[26] Quantum chemical calculations were performed with the Gaussian09 software.[27]

XRD was performed on an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector using Mo–K_α radiation (λ = 0.71073 Å). The data collection and reduction was carried out using the CrysAlisPro software[28]. The structures were solved either with ShelXS–97 [29] or Sir–92 [30], refined with ShelXL–97[31] and finally checked using the Platon[32] software integrated in the WinGX[33] software suite. The absorptions were corrected with a Scale3 Abspack multi-scan method. Cif files can be obtained free of charge using the CCDC Nos. from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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

Synthesis of 2,2′-Bisimidazole (**BI**)

Sodium bisulfite (36.6 g, 351 mmol) was dissolved in water (180 ml) and ethanol (100 ml) was added. Afterwards, an aqueous glyoxal solution (25.54 g, 176 mmol, 40 % by weight)

was added. The solution was stirred for 1.5 hours at ambient temperature. The white adduct was filtered and washed with ethanol and diethyl ether to yield the glyoxal-sodium bisulfite-hydrate adduct (50.6 g, 175 mmol). The adduct was dissolved in aqueous ammonia (275 ml, 25 %) and ammonium carbonate (10 g) was added. The solution was heated to reflux for 4 hours and cooled down to ambient temperature. After filtration and washing with ethanol and diethyl ether **BI** (2.2 g 40 %) could be obtained. The synthesis can be up-scaled by using the fivefold amount of each reagent yielding 12 g BI. **EA** ($C_6H_6N_4$ 134.14 g mol^{-1}) exp.(calc.): C: 53.50 (53.72), H: 4.16 (4.51), N: 41.54 (41.77) %; **^{1}H NMR** ([D_6]DMSO, 25 °C): δ = 12.58 (s, br, 1H, NH), 7.13 (s, 1 H, $H_{arom.}$), 7.00 (s, 1H, $H_{arom.}$) ppm; **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C): δ = 139.8 (s, 2C, C2/2'), 128.8 (s, 2C, C4/4'), 117.9 (s, 2C, C5/5') ppm.

Synthesis of 4, 4′,5, 5′-tetranitro-2,2′-bisimidazole (**TNBI**)

Sodium nitrate (18 g, 0.2 mol) and urea (0.02 g, 0.33 mmol) were suspended in concentrated sulfuric acid (30 ml) at 0 °C. Afterwards, bisimidazole (5.0 g, 37.0 mmol) was added in small portions. The suspension was stirred for one hour at ambient temperature and was subsequently heated to 85–90 °C for 16 hours. After that the suspension was put onto ice-water (100 ml). The product precipitated immediately. It was filtered off and washed with ice water (4 × 50 ml) to obtain **TNBI · 2H_2O** (6.6 g, 51 %) as a pale yellow powder. **EA** ($C_6H_2N_8O_8 \cdot 2H_2O$, 350.14 g mol^{-1}): exp. (calc.): C: 22.52 (22.58), N: 31.71 (32.00), H: 1.55 (1.73) %; **^{1}H NMR** ([D_6]DMSO, 25 °C): *δ* = 8.95 (2H, N–H) ppm; **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C): *δ* = 138.8 (1C, C–C), 139.1 (1C, C4, C5–NO_2) ppm; **Sensitivities:** IS > 40 J; FS: > 240 N; ESD: > 1.0 J.

Bisammonium-4, 4′,5, 5′-tetranitro-2,2′-bisimidazolate (**1**)

When TNBI was extracted with diethyl ether (starting with 5 g BI) anhydrous ammonia was bubbled through the solution. The ammonium salt precipitated immediately. The solid was filtered and washed with diethyl ether to obtain **1** (6.5 g, 95 %) relating to TNBI. **EA** ($C_6H_8N_{10}O_8$ 348.20 g mol^{-1}) exp. (calc.): C: 19.98 (20.37), N: 39.96 (40.23), H: 2.11 (2.32) %; **^{1}H NMR** ([D_6]DMSO, 25 °C): *δ* = 7.25 (8H, NH_4^+) ppm; **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C): *δ* = 141.0 (1C, C–C), 144.9 (1C, C4, C5–NO_2) ppm; **Raman**: 1/λ [(%)] = 1562 (100),1540 (15), 1496 (10), 1478 (20), 1389 (12), 1344 (19), 1302 (57), 1257 (88), 1026 (19), 867 (21), 771 (8), 758 (10), 688 (2), 432 (3),397 (6) cm^{-1}; **IR**: (ATR) 1/λ = 3262 (m, br), 1492 (s), 1481 (s), 1440 (w), 1390 (s), 1368 (s), 1306 (s), 1246 (s), 1114 (m), 951 (m), 855 (m), 802 (vs), 754 (m), 706 (m) cm^{-1}; **MS** (FAB (–)): m/z = 311.98 (100), 312.99 (10), 313.99 (2); (FAB (+) m/z): 18.03 (100). **Sensitivities:** IS > 9 J; FS : > 240 N; ESD: > 1.0 J.

Bispotassium-4,4′,5,5′-tetranitro-2,2′-bisimidazolate (**2**)

The precipitated TNBI · $2H_2O$ can be purified by extraction with diethyl ether (4 × 100 ml). After evaporation of the solvent until a remaining of 5–10 ml, an excess (approx. 50 ml) KOH/EtOH (0.5 M) was added and the water-free orange bis-potassium salt (**2**) precipitated. To get rid of the precipitated excess KOH, the solid was washed with ice water and EtOH. **EA** ($K_2C_6N_8O_8$ 390.31 g mol^{-1}) exp. (calc.): C: 18.52 (18.46), N: 28.66 (28.71), H: 0.0 (0.0) %; **^{1}H NMR** ([D_6]DMSO, 25 °C): δ = 8.95 (2H, N–H) ppm; **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C): δ = 141.0 (1C, C–C), 144.9 (1C, C4, C5–NO_2) ppm; **Sensitivities:** IS > 40 J; FS: > 240 N; ESD: > 1.0 J.

Synthesis of Bishydroxylammonium 4,4′,5,5′-tetranitro-2,2′-bisimidazolate Dihydrate (**3**)

TNBI · $2H_2O$ (350 mg, 1 mmol) was dissolved in diethyl ether (20 ml). Hydroxylamine-monohydrate (0.25 ml, 50 % by weight) was added and the resulting suspension was stirred for 30 min at ambient temperature. After filtering and washing with diethyl ether, the crude product can be recrystallized from water to yield **3** (300 mg, 72 %). **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 186 °C; **EA** ($C_6H_8N_{10}O_{10}$·$2H_2O$ 416.22 g mol^{-1}) exp. (calc.): C: 17.50 (17.31), N: 33.36 (33.65), H: 2.61 (2.91) %; **^{1}H NMR** ([D_6]DMSO, 25 °C): δ = 10.35 (s, br, 1H, N–OH) ppm; **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C): δ = 140.4 (2C, C2, 2‘), 143.4 (4C, C4, 4‘,5, 5‘ –NO_2) ppm; **^{14}N NMR{^{1}H}** ([D_6]DMSO, 25 °C) δ = –25 (4N, –NO_2), –349 (1N, O–NH_3) ppm; **Raman**: 1/λ [(%)] = 2060 (8), 1603 (19), 1564 (100), 1486 (35), 1388 (22), 1352 (28), 1304 (53), 1266 (64), 1217 (19), 1043 (20), 870 (26), 757 (17), 397 (18) cm^{-1}; **IR** (ATR): 1/λ = 3638 (m, br), 3332 (vw), 3274 (vw), 3216 (vw), 2504 (w), 2086 (vw), 1609 (vw), 1594 (vw), 1509 (s), 1462 (s), 1399 (s), 1348 (m), 1311 (s), 1262 (vs), 1226 (m), 1187 (s), 1115 (m), 996 (w), 966 (w), 927 (vw), 855 (vs), 752 (m), 697 (m), 655 (w),614 (vw) cm^{-1}; **Sensitivities**: IS > 6 J; FS: 288 N; ESD: 0.2 J.

General Procedure for the Syntheses of Compounds **4** and **5**

TNBI dihydrate (350 mg, 1 mmol) was suspended in water (10 ml). Adding guanidinium carbonate (200 mg, 1.1 mmol) or aminoguanidinium bicarbonate (300 mg, 2.2 mmol) resulted in precipitation of the corresponding orange 2:1 salt. Afterwards, the salts could be washed with a lot of water to yield 400 mg of **4** (93 %) and 425 mg of **5** (92 %).

Bisguanidinium-4,4′,5,5′-tetranitro-2,2′-bisimidazolate (**4**): **DSC** (5 °C·min^{-1}): $T_{Dec.}$ = 328 °C; **EA** ($C_8H_{12}N_{14}O_8$ 432.27 g mol^{-1}) exp. (calc.): C:22.38 (22.23); N: 45.09 (45.36); H: 2.67 (2.80) %; **^{1}H NMR** ([D_6]DMSO, 25 °C): δ = 7.12 (s, br, 6H, NH_2) ppm; **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C): δ = 140.8 (2C, C2, 2‘), 144.1 (4C, C4, 4‘,5, 5‘ –NO_2), 158.4 (1C, –(NH_2)

ppm; **^{14}N{^{1}H} NMR** ([D_6]DMSO, 25 °C): δ = –20 (4N, –NO_2) ppm; **MS**: (FAB (–)) m/z = 311.98 (100), 312.99 (10), 313.99 (2); (FAB (+)) m/z = 60.06 (100), 61.06 (2); **Raman**: 1/λ [(%)] = 1551 (100), 1536 (18), 1490 (5), 1465 (19), 1396 (7), 1348 (17), 1303 (42), 1363 (6), 1216 (60), 1111 (3), 1026 (15), 868 (16), 762 (6), 684 (4), 517 (3) cm^{-1}; **IR** (ATR): 1/λ = 3424 (m), 3280 (w), 3116 (m), 1738 (w), 1664 (s), 1650 (s), 1574 (w), 1483 (s), 1460 (s), 1385 (s), 1372 (vs), 1304 (s), 1197 (vs), 1111 (m), 1015 (w), 1015 (w), 945 (w), 858 (m), 820 (vs) cm^{-1}; **Sensitivities**: IS > 40 J; FS: > 240 N; ESD: > 1.0 J.

Bisaminoguanidinium-4,4′,5,5′-tetranitro-2,2′-bisimidazolate (**5**): **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 206 °C; **EA** ($C_8H_{14}N_{16}O_8$ 462.30 g mol^{-1}) exp. (calc.): C: 21.17 (20.48), N: 48.55 (48.48), H: 2.82 (3.05) %; **^{1}H NMR** ([D_6]DMSO, 25 °C): δ = 4.70 (s, 2H, N–NH_2), 7.02 (s, br, 4H,–NH_2), 8.85 (s, br, 1H, C–NH) ppm; **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C): δ = 140, 6 (2C, C2, 2‘), 144.5 (4C, C4, 4‘,5, 5‘ –NO_2), 159.41 (1C, aminoguanidine) ppm; **^{14}N{^{1}H} NMR** ([D_6]DMSO, 25 °C): δ = –25 (4N, –NO_2) ppm, **IR** (ATR): 1/λ = 3423 (m), 3382 (w), 3290 (m), 3109 (m, br), 2649 (w), 2408 (vw), 1666 (s), 1593 (w), 1519 (m), 1464 (vs), 1373 (vs), 1302 (vs), 1258 (m), 1238 (m), 1192 (vs, br), 1111 (vs), 994 (m), 946 (m), 910 (s, br), 856 (s), 811 (vs), 750 (vs), 723 (m), 702 (s) cm^{-1}; **Sensitivities**: IS > 20 J; FS : 360 N; ESD: > 1.0 J.

General Procedure for the Syntheses of Compounds **6** and **7**

Compound **1** (348 mg, 1 mmol) was suspended in water (10 ml). Afterwards, DAG · HCl (260 mg, 1.1 mmol) or TAG · HCl (300 mg, 1.1 mmol), respectively, was added. The corresponding suspension was heated to reflux for 1 h. The DAG_2TNBI precipitated immediately, whereas the TAG_2TNBI crystallized overnight in the fridge at 4 °C. Both compounds can be filtered and washed with ice water to yield 400 mg of **6** (81 %) and 420 mg of **7** (80 %).

Bis-diaminoguanidinium-4,4′,5,5′-tetranitro-2,2′bisimidazolate (**6**): **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 195 °C; **EA** ($C_8H_{16}N_{18}O_8$ 492.33 g mol^{-1}) exp. (calc.): C: 19.82 (19.52), N: 50.56 (51.21), H: 3.14 (3.28) %; **^{1}H NMR** ([D_6]DMSO, 25 °C): δ = 4.48 (s, br, 4H, N–NH_2), 7.12 (s, br, 2H, –NH_2), 8.57 (s, br, 2H, C–NH) ppm; **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C): δ = 140.9 (2C, C2, 2‘), 144.7 (4C, C4, 4‘,5, 5‘ –NO_2), 160.2 (1C, diaminoguanidine) ppm; **^{14}N{^{1}H} NMR** ([D_6]DMSO, 25 °C): δ = –18 (4N, –NO_2) ppm; **MS**: (FAB (–))m/z = 311.98 (100), 312.99 (10), 313.99 (2); (FAB (+) m/z) : 90.08 (100), 91.08 (3); **Raman**: 1/λ [(%)] = 1553 (100), 1542 (43), 1447 (25), 1380 (10), 1346 (18), 1307 (46), 1224 (50), 1182 (18), 1029 (10), 989 (6), 930 (5), 866 (23), 700 (5), 527 (5), 434 (5) cm^{-1}; **IR** (ATR): 1/λ = 3480 (w), 3376 (w), 3348 (w), 3312 (w), 3055 (w, br), 1675 (s), 1562 (w), 1516 (m), 1489 (m), 1443 (s), 1393 (s), 1361 (vs), 1300 (vs),

1264 (w), 1212 (s), 1172 (vs), 986 (s), 962 (vs), 946 (s), 856 (s), 811 (vs), 756 (m), 698 (s), 637 (vs, br) cm^{-1}; **Sensitivities**: IS > 17 J; FS: 252 N; ESD: 0.4 J.

Bis-triaminoguanidinium-4,4′,5,5′-tetranitro-2,2′-bisimidazolate (**7**): **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 152 °C; **EA** ($C_8H_{18}N_{20}O_8$ 522.36 g mol^{-1}) exp. (calc.): C: 18.65 (18.39), N: 53.48 (53.63), H: 3.34 (3.47) %; **^{1}H NMR** ([D_6]DMSO, 25 °C): δ = 4.48 (s, br, 6H, N–NH_2), 8.59 (s, br, 3H, C–NH) ppm; **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C): δ = 141.0 (2C, C2, 2‘), 144.9 (4C, C4, 4‘,5, 5‘ –NO_2), 159, 6 (1C, guanidine) ppm; **^{14}N{^{1}H} NMR** ([D_6]DMSO, 25 °C): δ = –26 (4N, –NO_2) ppm; **MS**:(FAB (+)) m/z = 105.12 (100), 104.12 (3); **Raman**: 1/λ [(%)] = 1557 (100), 1545 (39), 1517 (8), 1451 (17), 1443 (17), 1379 (9), 1340 (14), 1299 (52), 1223 (66), 1145 (4), 1027 (14), 865 (15), 754 (5), 697 (3), 527 (4), 405 (5) cm^{-1}; **IR** (ATR): 1/λ = 3381 (vw), 3340 (w), 3144 (w), 2430 (vw, br), 1670 (m), 1589 (w, br), 1519 (m), 1495 (m), 1445 (m, br), 1389 (s), 1361 (s), 1306 (s), 1219 (s, br), 1108 (m), 1027 (m), 945 (s), 886 (s, br), 854 (vs), 752 (s) 705 (vs) 639 (vs) 606 (s) cm^{-1}; **Sensitivities**: IS > 6 J; FS: 288 N; ESD: 0.2 J.

1,1′-Dimethyl, 4,4′,5,5′-tetranitro-2,2′-bisimidazole (**8**)

Bispotassium-4,4′,5,5′-tetranitro-bisimidazolate (390.1 mg, 1 mmol) was suspended in acetonitrile (20 ml) and dimethylsulfate (0.2 ml, 2 mmol) was added at ambient temperature. The suspension was heated to reflux and DMF (2–3 ml) was added until a solution had been obtained. After heating to reflux for 16 h, all solvents were removed in vacuo. The residue was boiled in water, hot filtered and washed with water to yield bright-shining **8** (212 mg, 62 %) after drying in a 60 °C oven for 12 h. **DSC** (5 °C min^{-1}): $T_{Melt.}$ = 236 °C, $T_{Dec.}$ = 258 °C; **EA** ($C_8H_6N_8O_8$ 342.04 g mol^{-1}): exp.(calc.): C: 27.91 (28.08), N: 32.44 (32.75); H: 1.92 (1.77) %; **^{1}H NMR** ([D_6]DMSO, 25 °C): δ = 4.28 (6H, CH_3) ppm; **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C): δ = 35.7 (2C, C1, C1') 132.2 (2C, C3, C3'), 133.3 (1C, C4–NO_2), 139.6 (1C, C5–NO_2) ppm; **MS**: (EI) m/z = 343.03 (12.94 % MH^+), 342.03 (100 %, M^+), 326.03 (11.45 %MH^+–CH_3), 325.03 (97.67 %), 313.02 (14.07 %, M–2CH_3+1H), 312.02 (61.83 %, M–2CH_3+2H). **IR**: (ATR) 1/λ = 1567 (w), 1534 (s), 1454 (m), 1408 (m), 1384 (m), 1342 (m), 1301 (s), 1164 (w), 1082 (w), 1040 (w), 850 (s), 813 (vs), 744 (m), 687 (m) cm^{-1}; **Raman**: 1/λ [(%)] = 2977 (8), 1584 (100), 1567 (51), 1534 (31), 1490 (4), 1387 (16), 1344 (54), 1312 (56), 1208 (8), 1145 (3), 1054 (8), 874 (3), 817 (9), 778 (5), 764 (6), 742 (6), 292 (4), 240 (3) cm^{-1}. **Sensitivities**: IS > 40 J; FS: 292 N; ESD: 0.1 J.

3.6 References

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3.7 Supporting information

TNBI · 2 H_2O crystallizes in the monoclinic space group $P2_1/n$ with two formula units per unit cell. The calculated density at –100 °C is 1.855 g cm^{-3}.

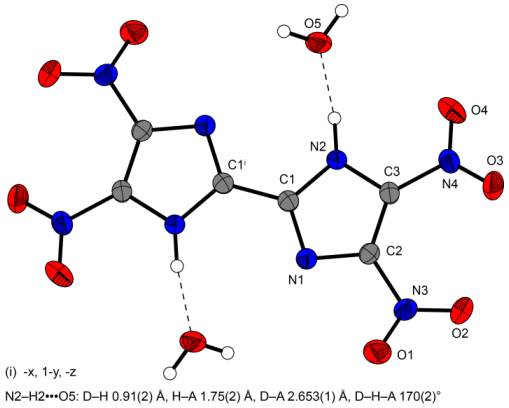


Fig. S1: Molecular structure of TNBI·2 H_2O showing the labeling scheme. The non-hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. Symmetry codes (i) 0.5–x, 1.5–y, –z; (ii) 0.5–x, 0.5+y, 0.5–z. **Selected bond lengths** [Å]: O1–N3 1.2196(13), O2–N3 1.2278(13), O3–N4 1.2259(14), O4–N4 1.2273(13), N1–C1 1.3288(15), N1–C2 1.3413(15), N2–C1 1.3488(15), N2–C3 1.3570(15), N2–H2 0.914(17), N3–C2 1.4522(16), N4–C3 1.4329(15), C1–C1 1.452(2), C2–C3 1.3789(17); **Selected bond angles** [°]:C1–N1–C2 103.85(10), C1–N2–C3 105.91(10), O1–N3–O2 125.41(11), O1–N3–C2 116.86(10), O2–N3–C2 117.72(10), O3–N4–O4 124.71(11), O3–N4–C3 118.53(11), O4–N4–C3 116.75(10), N1–C1–N2 113.18(10), N1–C1–C1 124.08(13), N2–C1–C1 122.74(13), N1–C2–C3 111.27(11), N1–C2–N3 118.85(10), C3–C2–N3 129.85(11), N2–C3–C2 105.78(10), N2–C3–N4 119.18(10), C2–C3–N4 135.00(11); **Selected torsion angles** [°]: O2–N3–C2–N1 156.47(11), O1–N3–C2–C3 159.42(12), O3–N4–C3–N2 160.94(11), O4–N4–C3–N2 –18.04(15), N1–C1–$C1^{i}$–$N2^{i}$ 0.18(18).

KTNBI · H_2O was obtained by attempts to aminate **2** using hydroxylammonium-sulfonic acid. The reaction failed and the monodeprotonated compound was obtained. It crystallizes in the orthorhombic space group *Pbca* with eight formula units per unit cell and a cell volume of 2477.6(7) $Å^3$. Its calculated density is 1.985 g cm^{-3}, which is significantly lower than that of the dipotassium salt **2** (2.126 g cm^{-3}).

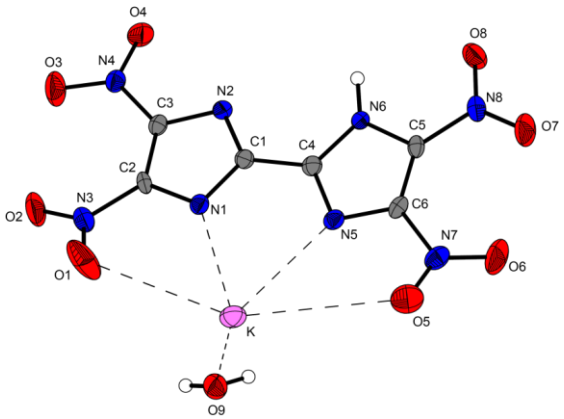


Fig. S2: Molecular structure of KHTNBI · H_2O showing the labeling scheme. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. **Selected bond lengths** [Å]: K–O9 2.838(3), K–N1 2.880(2), K–N5 2.981(2), K–O1 3.015(3), K–O5 3.124(3), O8–N8 1.229(3), N5–C4 1.337(3), N5–C6 1.345(3), N6–C4 1.353(3), N6–C5 1.358(3),

N1–C2–1.335(3), N1–C1 1.351(3), N2–C3 1.343(3), N2–C1 1.346(3), O4–N4 1.228(3), O3–N4 1.225(3), N7–O5 1.212(3), N7–O6 1.213(3), N7–C6 1.459(3), O7–N8 1.213(3), N3–O2 1.205(3), N3–O1 1.216(3), N3–C2 1.449(3), N4–C3 1.433(3), N8–C5 1.442(3), C3–C2 1.399(4), C4–C1 1.452(4), C5–C6 1.366(4); **Selected bond angles** [°]: C4–N5–C6 104.2(2), C4–N6–C5 106.4(2), C2–N1–C1 102.2(2), C3–N2–C1 102.0(2), O5–N7–O6 124.4(2), O5–N7–C6 117.4(2), O6–N7–C6 118.2(2), O2–N3–O1 122.4(2), O2–N3–C2 120.3(2), O1–N3–C2 117.3(2), O3–N4–O4 121.9(2), O3–N4–C3 119.3(2), O4–N4–C3 118.7(2), O7–N8–O8 124.3(2), O7–N8–C5 119.0(2), O8–N8–C5 116.7(2), N2–C3–C2 109.5(2), N2–C3–N4 119.2(2), C2–C3–N4 131.2(2), N5–C4–N6 112.1(2), N5–C4–C1 122.6(2), N6–C4–C1 125.3(2), N6–C5–C6 106.0(2), N6–C5–N8 118.7(2), C6–C5–N8 135.3(2), N2–C1–N1 116.6(2), N2–C1–C4 124.6(2), N1–C1–C4 118.7(2), N1–C2–C3 109.6(2), N1–C2–N3 117.9(2), C3–C2–N3 132.5(2), N5–C6–C5 111.3(2), N5–C6–N7 117.8(2), C5–C6–N7 130.9(2); **Selected torsion angles** [°]:O5–N7–C6–N5 –19.7(4), O6–N7–C6–N5 159.1(3), O2–N3–C2–N1 –167.2(3), O1–N3–C2–N1 14.1(4), O8–N8–C5–C6 174.7(3), O7–N8–C5–N6 175.2(2), O4–N4–C3–C2 –176.2(3), O4–N4–C3–N2 8.2(4), N1–C1–C4–N5 9.6(5).

4 · 2 DMSO was obtained when the solvent free compound (**4**) was dissolved in DMSO and water slowly diffused into the solution. G_2TNBI · 2 DMSO crystallizes in the triclinic space group *P*–1 with two formula units per unit cell. The crystal density was calculated to be 1.558 g cm^{-3}.

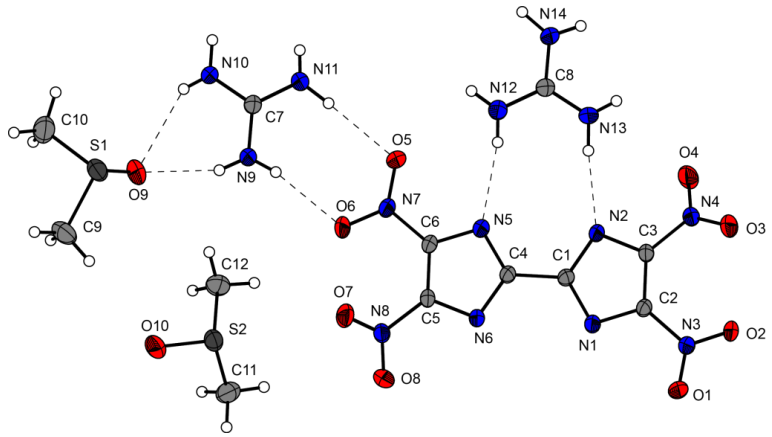


Fig. S3: Molecular structure of **4** · 2 DMSO showing the labeling scheme. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. **Selected bond lengths** [Å]: O1–N3 1.229(3), O2–N3 1.237(3), O3–N4 1.226(3), O4–N4 1.224(3), O5–N7 1.232(3), O6–N7 1.240(3), O7–N8 1.225(3), O8–N8 1.231(3), N1–C1 1.350(3), N1–C2 1.357(3), N2–C3 1.343(3), N2–C1 1.359(3), N3–C2 1.426(3), N4–C3 1.451(3), N5–C4 1.354(3), N5–C6 1.355(3), N6–C5 1.336(3), N6–C4 1.362(3), N7–C6 1.426(3), N8–C5 1.462(3), C1–C4 1.465(3), C2–C3 1.385(3), C5–C6 1.387(3); **Selected bond angles** [°]: C1–N1–C2 102.21(19), C3–N2–C1 102.27(19), O1–N3–O2 123.3(2), O1–N3–C2 119.36(19), O2–N3–C2 117.34(19), O4–N4–O3 123.6(2), O4–N4–C3 118.0(2), O3–N4–C3 118.4(2), C4–N5–C6 102.21(19), C5–N6–C4 102.46(19), O5–N7–O6 123.4(2), O5–N7–C6 119.3(2), O6–N7–C6 117.3(2), O7–N8–O8 124.8(2), O7–N8–C5 118.3(2), O8–N8–C5 116.9(2), N1–C1–N2 116.0(2), N1–C1–C4 122.6(2), N2–C1–C4 121.4(2), N1–C2–C3 109.5(2), N1–C2–N3 121.3(2), C3–C2–N3 129.2(2), N2–C3–C2 110.0(2), N2–C3–N4 118.9(2), C2–C3–N4 130.9(2), N5–C4–N6 115.7(2), N5–C4–C1 122.7(2), N6–C4–C1 121.7(2), N6–C5–C6 110.2(2), N6–C5–N8 119.5(2), C6–C5–N8 130.2(2), N5–C6–C5 109.5(2), N5–C6–N7 121.1(2), C5–C6–N7 129.2(2); **Selected torsion angles** [°]: O1–N3–C2–N1 –19.4(3), O2–N3–C2–N1 159.9(2), O4–N4–C3–N2 –36.1(4), O3–N4–C3–N2 141.7(2), O8–N8–C5–N6 –42.4(3), O7–N8–C5–C6 –40.1(4), O5–N7–C6–N5 –16.3(4), O6–N7–C6.N5 163.6(2), N1–C1–C4–N6 4.16(4).

The procedure to obtain **6** was already described in the experimental section. It crystallizes in the monoclinic space group $P2_1/n$ two formula units per unit cell and a calculated density of 1.758 g cm^{-3}.

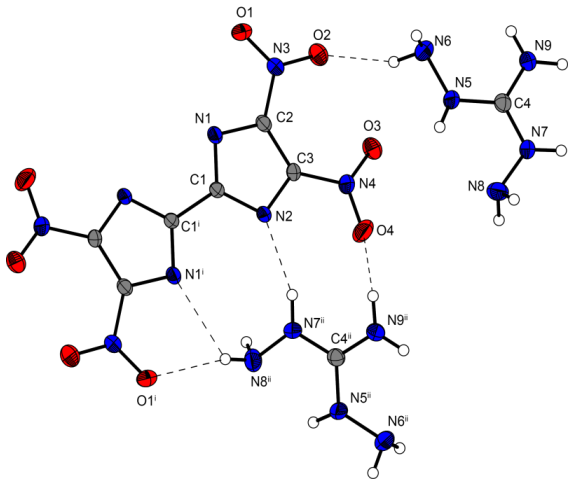


Fig. S4: Molecular structure of DAG_2TNBI showing the labeling scheme. The non–hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. Symmetry codes (i) 0.5–x, 1.5–y, –z; (ii) 0.5–x, 0.5+y, 0.5–z. **Selected bond lengths** [Å]: O1–N3 1.222(3), O2–N3 1.233(3), O3–N4 1.219(3), O4–N4 1.220(3), N3–C2 1.441(3), N4–C3 1.444(3), N1–C2 1.346(3), N1–C1 1.349(3), N2–C3 1.348(3), N2–C1 1.356(3), C3–C2 1.401(3), C1–C1 1.459(5); **Selected bond angles** [°]: O1–N3–O2 122.4(2), O1–N3–C2 117.6(2), O2–N3–C2 120.0(2), O3–N4–O4 123.1(2), O3–N4–C3 119.1(2), O4–N4–C3 117.8(2), C2–N1–C1 103.46(19), C3–N2–C1 103.07(19), N2–C3–C2 109.2(2), N2–C3–N4 117.7(2), C2–C3–N4 133.0(2), N1–C2–C3 109.0(2), N1–C2–N3 117.8(2), C3–C2–N3 133.2(2), N1–C1–N2 115.2(2), N1–C1–C1 122.4(2), N2–C1–C1 122.4(3); **Selected torsion angles** [°]: N2–C1–$C1^{i}$–$N1^{i}$ –0.63(35), N2–C3–N4–O4 4.35(32), N1–C2–N3–O2 –175.4(4), N2–C3–N4–O4 –5.61(33), N2–C3–N4–O3 171.68(22).

The reaction of TNBI with only one equivalent of diaminoguanidinium hydrochloride yielded the 1:1 salt diaminoguanidinium tetranitrobisimidazolate monohydrate in which the diaminoguandium is twice protonated. This compound crystallizes in the triclinic space group *P*–1 with two formula units per unit cell and a calculated density of 1.806 g cm^{-3}. The molecular structure is shown in Figure S5.

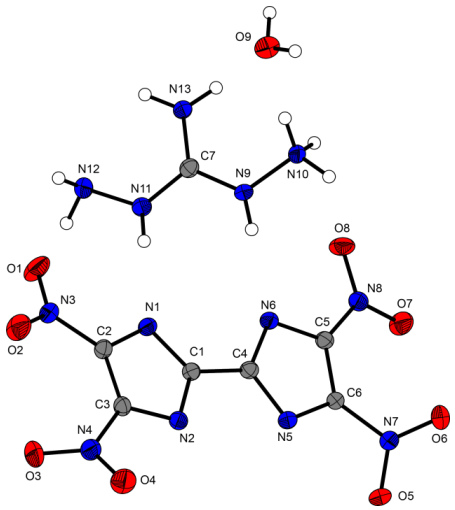


Fig. S5: Molecular structure of diaminoguanidinium tetranitrobisimidazolate showing the labeling scheme. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. **Selected bond lengths** [Å]: O1–N3 1.2281(19), O2–N3 1.223(2), O3–N4 1.225(2), O4–N4 1.234(2), O5–N7 1.237(2), O6–N7 1.2193(19), O7–N8 1.232(2), O8–N8 1.237(2), N1–C1 1.350(2), N1–C2 1.355(2), N2–C3 1.345(2), N2–C1 1.356(2), N3–C2 1.443(2), N4–C3 1.443(2), N5–C6 1.339(2), N5–C4 1.359(2), N7–C6 1.447(2), N8–C5 1.424(2), N6–C4 1.341(2), N6–C5 1.358(2), C1–C4 1.462(2), C2–C3 1.390(2), C5–C6 1.396(2), N11–N12 1.418(2), N13–C7 1.319(2); **Selected bond angles** [°]:C1–N1–C2 102.77(14), C3–N2–C1 103.07(14), O2–

N3–O1 124.23(16), O2–N3–C2 118.33(15), O1–N3–C2 117.42(15), O3–N4–O4–124.07(15), O3–N4–C3 118.69(15), O4–N4–C3 117.22(15), C6–N5–C4 102.74(14), O6–N7–O5, 123.84(15), O6–N7–C6 119.40(14), O5–N7–C6 116.71(14), O7–N8–O8 123.31(15), O7–N8–C5 119.48(14), O8–N8–C5 117.20(14), C4–N6–C5 102.94(14), N1–C1–N2 115.35(15), N1–C1–C4 124.61(15), N2–C1–C4 120.04(15), N1–C2–C3 109.39(15), N1–C2–N3 120.97(15), C3–C2–N3 129.46(15), N2–C3–C2 109.41(15), N2–C3–N4 119.73(15), C2–C3–N4 130.77(16), N6–C4–N5 115.73(15), N6–C4–C1 124.14(15), N5 C4–C1 120.11(15), N6–C5–C6 108.75(15), N6–C5–N8 119.61(15), C6–C5–N8 131.45(15), N5–C6–C5 109.83(15), N5–C6–N7 118.72(15), C5–C6–N7 131.24(15); **Selected torsion angles** [°]: O2–N3–C2–N1 –162.16(16), O1–N3–C2–N1 16.9(2), O3–N4–C3–N2 –143.80(17), O4–N4–C3–N2 34.7(2), O7–N8–C5–N6 –164.58(15), O8–N8–C5–N6 14.3(2), O6–N7–C6–N5 –149.77(16), O5–N7–C6–N5 27.7(2), N1–C1–C4–N6 7.8(3).

Table S1: XRD data and parameters.

	TNBI · 2 H_2O	**TNBI · 2 acetone**	**K_2TNBI (2)**	**KHTNBI · H_2O**	**Hx_2TNBI · 2H_2O (3)**	**G_2TNBI · 2 DMSO (4)**
Formula	$C_6H_6N_8O_{10}$	$C_6H_2N_8O_8$ 2(C_3H_6O)	$K_2C_6N_8O_8$	$KC_6H_3N_8O_9$	$C_6H_{12}N_{10}O_{14}$	$C_{12}H_{24}N_{14}O_{10}S_2$
FW [g mol^{-1}]	350.19	430.31	390.34	370.26	416.26	588.57
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space Group	*P*2_1/*n*	*C*2/*c*	*P*2_1/*c*	*Pbca*	*P*2_1/*n*	*P–1*
Color / Habit	Yellow block	Yellow needle	Orange needle	Orange needle	Beige needle	Orange needle
Size [mm]	0.19 x 0.21 x 0.36	0.10 x 0.18 x 0.20	0.10 x 0.16 x 0.20	0.05 x 0.10 x 0.25	0.19 x 0.23 x 0.34	0.15 x 0.20 x 0.25
a [Å]	5.126(2)	23.703(18)	4.0384(2)	11.3287(18)	5.474(2)	9.7342(8)
b [Å]	8.952(3)	5.482(4)	8.9771(6)	14.194(3)	7.380(2)	10.8737(10)
c [Å]	13.673(6)	15.433(13)	16.9147(1)	15.408(2)	18.918(8)	14.0257(10)
α [°]	90	90	90	90	90	104.134(7)
β [°]	92.28(4)	115.64(1)	95.967(8)	90	92.35(4)	102.017(6)
γ [°]	90	90	90	90	90	112.287(8)
V [$Å^3$]	626.9(4)	1807.9(3)	609.89(5)	2477.6(7)	763.6(5)	1255.0(2)
Z	2	4	2	8	2	2
$\rho_{calc.}$ [g cm^{-3}]	1.855	1.581	2.126	1.985	1.810	1.558
μ [mm^{-1}]	0.177	0.139	0.0848	0.507	0.174	0.289
F(000)	356	888	388	1488	428	612
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	173	173	173
θ Min–Max [°]	4.2, 26.0	4.3, 26.0	4.3, 26.0	4.3, 26.0	4.3, 26.2	4.3, 26.0
Dataset	–6:6; –11:11; –16:16	–28:28; –6:6 ; –13:19	–3:4; –10:11; –20:20	–13:13; –10:17; –18:19	–6:6; –9:8; –23:17	–12:8; –12:13; –16:17
Reflections collected	9013	4416	3723	11979	3924	6521
Independent refl.	1223	1764	1175	2417	1538	4884

R_{int}	0.022	0.020	0.0280	0.068	0.022	0.042
Observed reflections	1011	1764	1175	2417	1538	4884
Parameters	121	164	109	229	151	395
R_1 (obs)	0.0260	0.0339	0.0280	0.0435	0.0329	0.0489
wR_2 (all data)	0.0710	0.0934	0.0548	0.1063	0.0768	0.1318
S^c	1.03	1.03	0.83	1.05	0.98	0.99
Resd. Dens. [e Å^{-3}]	–0.19, 0.27	–0.21, 0.18	–0.28, 0.28	–0.35, 0.43	–0.20, 0.19	–0.43, 0.51
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SHELXS-97	SIR-92	SHELXS-97	SHELXS-97	SIR-92	SIR-97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
CCDC	876136	876137	877533	876139	876398	876140

Table S2: XRD data and parameters.

	AG_2TNBI (5)	**DAG_2TNBI (6)**	**HDAGTNBI · H_2O**	**TAG_2TNBI (7)**	**Me_2TNBI (8)**
Formula	$C_8H_{14}N_{16}O_8$	$C_8H_{16}N_{18}O_8$	$C_7H_{11}N_{13}O_9$	$C_8H_1N_{20}O_8$	$C_8H_6N_8O_8$
FW [g mol^{-1}]	462.35	492.22	421.29	522.42	342.21
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space Group	*P*–1	*P2$_1$/n*	*P*–1	*P–1*	*P–1*
Color / Habit	Orange needle	Orange needle	Orange needle	Orange needle	Orange block
Size [mm]	0.06 x 0.08 x 0.40	0.19 x 0.24 x 0.34	0.05 x 0.10 x 0.25	0.11 x 0.15 x 0.20	0.09 x 0.10 x 0.22
a [Å]	5.2053(4)	3.5846(5)	7.2026(7)	7.6530(6)	8.0210(6)
b [Å]	7.6860(6)	14.6708(13)	10.1327(7)	8.2349(7)	11.8452(7)
c [Å]	11.3598(11)	17.758(2)	11.993(1)	8.6532(6)	14.4535(9)
α [°]	90.344(7)	90	65.271(7)	100.391(6)	90.653(5)
β [°]	98.206(8)	94.999(13)	77.139(8)	91.933(6)	103.543(6)
γ [°]	102.654(7)	90	83.302(7)	109.247(7)	90.188(5)
V [Å^3]	438.58(7)	930.32(19)	774.79(12)	503.86(7)	1334.94(16)
Z	1	2	2	1	2
$\rho_{calc.}$ [g cm^{-3}]	1.751	1.758	1.806	1.722	1.703
μ [mm^{-1}]	0.154	0.154	0.164	0.150	0.154
F(000)	238	508	432	270	696
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	173	173
θ Min–Max [°]	4.2, 26.5	4.3, 26.0	4.3, 26.3	4.1, 27.0	4.3, 26.0
Dataset	–6:6; –9:9;	–3:4;–18:10;–	–8:8;–12:12;–	–9:9;–10:10;–	–9:9;–14:10;–

	–14:14	21:11	14:14	11:11	17:17
Reflections collected	4601	2529	7941	5442	6936
Independent refl.	1815	1679	3106	2176	5190
R_{int}	0.033	0.032	0.031	0.023	0.019
Observed reflections	1815	1679	3106	2176	4340
Parameters	173	186	306	215	481
R_1 (obs)	0.0388	0.0475	0.0371	0.0370	0.0594
wR_2 (all data)	0.0999	0.1227	0.0977	0.0992	0.1437
S^c	1.07	1.03	1.02	1.03	1.13
Resd. Dens. [e Å^{-3}]	–0.28, 0.28	–0.23, 0.23	–0.22, 0.36	–0.48, 0.46	–0.29, 0.34
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-97	SHELXS-97	SIR-92	SHELXS-97	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
CCDC	876143	877534	876141	876142	876138

4. PUBLICATION B

Syntheses and Energetic Properties of 4-Diazo-2,6-dinitrophenol and 6-Diazo-3-hydroxy-2,4-dinitrophenol

T. M. Klapötke, A. Preimesser, J. Stierstorfer,

Eur. J. Org. Chem. **2015**, 4311–4315.

4.1 Abstract

4-Amino-3,5-dinitroaniline (**3**) was synthesized by fluorine/amine exchange of 4-fluoro-3,5-dinitroaniline in ethanol. 4-Diazo-2,6-dinitrophenol (Iso-DDNP, **4**) was obtained after nitration in HNO_3 (100%) and acetic anhydrid. 4-Amino-2,3,5-trinitrophenol (**7**) was gained *by* nitration of *N*-(4-acetoxyphenyl)acetamide and deprotection of the amine. Further nitration resulted in 6-diazo-3-hydroxy-2,4-dinitrophenol (**8**). The thermal stability and sensitivity of **4** and **8** toward impact and friction was compared to commercially used DDNP (2-diazo-4,6-dinitrophenol). All target compounds were characterized by single crystal X-ray diffraction, NMR and elemental analysis and DSC. The sensitivities were determined by BAM methods (drophammer and friction tester). The heats of formation were calculated using CBS-4M electronic enthalpies and the atomization method. Various detonation parameters such as detonation velocity and pressure were computed using the EXPLO5 computer code V6.01.

4.2 Introduction

Synthesis of energetic materials based on a benzene backbone has a long tradition since the discovery of trinitrotoluene (TNT) in 1863.[1] Because of its important property as a melt-castable explosive it is still in use nowadays, even though it is highly toxic for the environment.[2] 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) was synthesized in 1888. It is a well-known insensitive explosive with a high melting point (T_{melt} > 350 °C) due to its strong intramolecular hydrogen bonds between alternation of amino and nitro groups.[3,4] This leads to a high density of (ρ = 1.937 g cm^{-3} at 298 K) which was confirmed by its crystal structure[5] in 1965. For many applications TATB shows a meager performance and is too insensitive to detonate, therefore alternatives with a better performance, less toxic properties and lower sensitivities towards external stimuli like impact, friction and electrostatic discharge, are desired. Originally, our research goals had been the synthesis of 4-amino-2,3,5,6-tetranitrophenol and 1,4-diamino-2,3,5,6-tetranitrobenzene. In order to obtain the latter, 4-

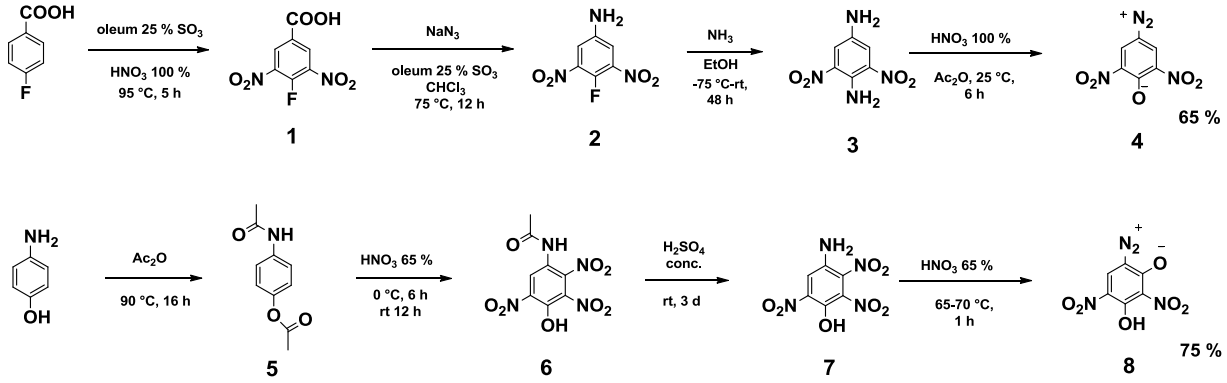
amino-3,5-dinitroaniline (**3**) seemed to be a promising starting material. Its synthesis was already mentioned by Chu and Griffiths.[6] They reported on the nitration of *N,N'*-bis-(phenylsulfonyl)-*p*-phenylenediamine and received three different *C*-nitrated dinitro-isomers, which were separated by column chromatography after the cleavage of the sulfonamide in concentrated sulfuric acid. However, for synthesis in larger scales, this reaction is useless and a proper synthesis had to be developed. Alternatively, the substitution of the chlorine atom or the methoxy group of 4-chloro-2,6-dinitroaniline,[7] as well as its 4-methoxy derivative,[8] failed. Even the use of ammonia in high-pressure vessels did not result in any notable conversion. Finally, **3** could be synthesized by fluorine/amine exchange of 4-fluoro-3,5-dinitroaniline in ethanol. A further approach was the nitration of 4-aminophenol, however, all nitration attempts finally resulted in the formation of highly energetic diazophenols. These species represent a very interesting group of energetic zwitterionic molecules. A paper discussing the increased-valence bond structure of DDNP, as opposed to the zwitterionic approach, was published in 2003.[10] The mechanism of formation of *ortho*-diazophenols was described in detail by Atkins and Wilson in 1986[9]. Most compounds containing a nitro group in *ortho*-position to a nitramine functionality eliminate nitric acid during the nitration reaction or boiling process in organic solvents. Including a cyclic transition state, this rearrangement results in the formation of *ortho*-diazophenols. DDNP (2-diazo-4,6-dinitrophenol) was synthesized for the first time by Griess in 1858.[11] It is an extremely sensitive primary explosive, which is commercially used in stab detonators.[12] Sensitization of lead azide using DDNP as an energetic additive was intensively studied by Spear and Elischer in 1982.[13]. This study provides a comparison (*e.g.* sensitivities, thermal behavior) of the two title diazophenols to DDNP is given. While the synthesis of DDNP by oxidation of the primary aromatic amine of picramic acid (2-amino-4,6-dinitrophenol) has been published,[14] the formation of *para*-diazophenols is only rarely described.[9]

4.3 Results and discussion

4.3.1 Syntheses

An overall synthetic protocol is displayed in Scheme 1. 4-Fluoro-3,5-dinitroaniline (**2**) was synthesized as described by Nielsen et al.[15] Compound **3** was obtained by reaction of **2** with ammonia in ethanol. Any further attempts to synthesize a tri- or tetranitro derivative of 1,4-diaminobenzene by various nitration conditions resulted in the formation of 4-diazo-2,6-dinitrophenol (**4**). Even if the amine in C1 position was protected with an acetyl or methylsulfonyl group, no other product but **4** was obtained, indicating that the protection group was cleaved quickly in nitrating media. Compound **5** was easily synthesized by using acetic anhydride both as acetylating reagent and solvent. Nitration of **5** using 65% nitric acid yielded compound **6** in moderate quantities. To obtain compound **7** in high purity, **6** must be

stirred in concentrated sulfuric acid for at least three days, which indicates that the amide cleavage of **6** only works very slowly. Compound **7** could easily purified by recrystallization from benzene. Further nitration attempts of **7** always resulted in decomposition or the formation of compound **8**, which is 6-diazo-3-hydroxy-2,4-dinitrophenol.



Scheme 1: Synthesis protocol of compounds **1**-**8**.

4.3.2 Crystal structures and ^{15}N spectra

All target compounds and intermediates were characterized extensively. Single crystals of **3**, **4**, **7** and **8** could be grown from organic solvents (**3** and **8**: acetone, **4**: ethanol, **7**: benzene) and their structures determined by low-temperature X-ray diffraction (details are given in the Supporting Information). Figures 1 and 2 show the molecular structures of **3**, **4**, **7** and **8**. They crystallizes in the monoclinic or orthorhombic crystal system in common space groups (**3:** $P2_1/c$, **4**: $P2_12_12_1$, **7** and **8:** *Pbca)*.

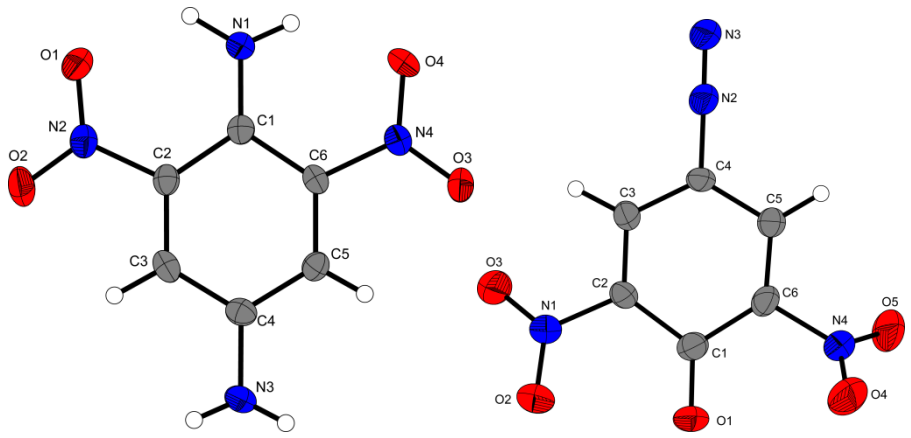


Figure 1: Molecular structure of **3** (left) and 4-diazo-2,6-dinitrophenol (**4**, right).. Ellipsoids of non-hydrogen atoms in all structures are drawn at the 50% probability level.

The X-ray densities at 173 K increase with the number of nitro groups [1.742 (**3**) < 1.824 (**4**) < 1.837 (**8**) < 1.839 g cm^{-3} (**7**)]. In the case of **3** a nearly planar system is formed. Both nitro groups lie within the ring plane fixed by the intermolecular hydrogen bonds N1–H···O1 and N1–H···O4.

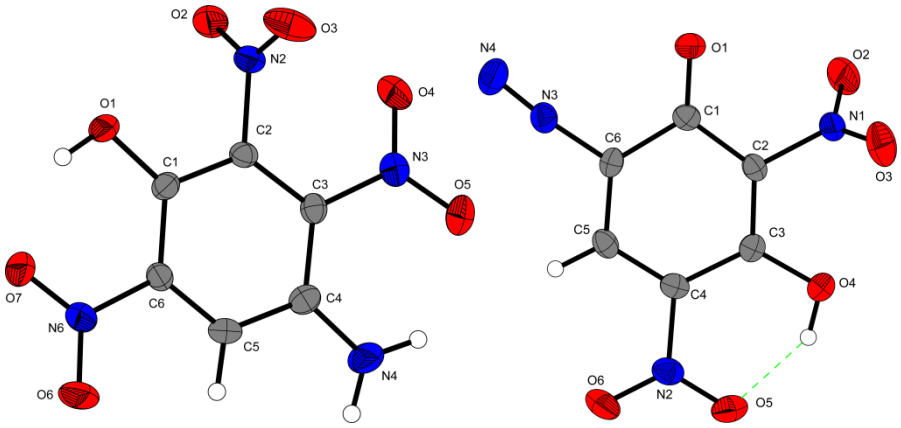


Figure 2: Molecular structure of 4-amino-2,3,6-trinitrophenol (**7**, left) and 6-diazo-3-hydroxy-2,4-dinitrophenol (**8**, right).

Proton-coupled ^{15}N NMR spectra of compounds **4**, **7** and **8** were recorded and are displayed in Figure 3. All four nitrogen atoms of **4** could be assigned. N_{α} is the only nitrogen atom, which shows a singlet at δ = –21.7 ppm. The N_{δ} and N_{β} signals appear as doublets at δ = −17.2 ($^3J_{N,H}$ = 2.9 Hz) and −19.9 ppm ($^4J_{N,H}$ = 1.2 Hz). Even the nitrogen-proton coupling ($^3J_{N,H}$ = 2.4 Hz) of the amine could be observed. In the ^{15}N NMR spectrum of compound **7** three signals could be detected. N_{β} of the diazo group shows a singlet at δ = −45.0 ppm. N_{α} shows a first order triplet at δ = −139.3 ppm (t, $^3J_{N,H}$ = 2.4 Hz). In contrast for N_{γ} a deceptively simple triplet is observed. In fact the ^{15}N NMR signal of N_{γ} represents the X part of a AA'X spectrum, from which $N = |^3J_{N,H} + {}^5J_{N,H}|$ = 3.0 Hz is determined. The coupling constant $^5J_{N,H}$ is expected to be very small, and thus the value of N observed corresponds roughly to $^3J_{N,H}$. In the ^{15}N NMR spectrum of compound **8** four signals could be observed. N_{β} of the diazo group shows a singlet at δ = −33.2 ppm. N_{α} shows a doublet at δ = −134.9 ppm ($^3J_{N,H}$ = 1.8 Hz). N_{γ} appears as singlet and N_{δ} and a doublet ($^3J_{N,H}$ = 2.8 Hz).

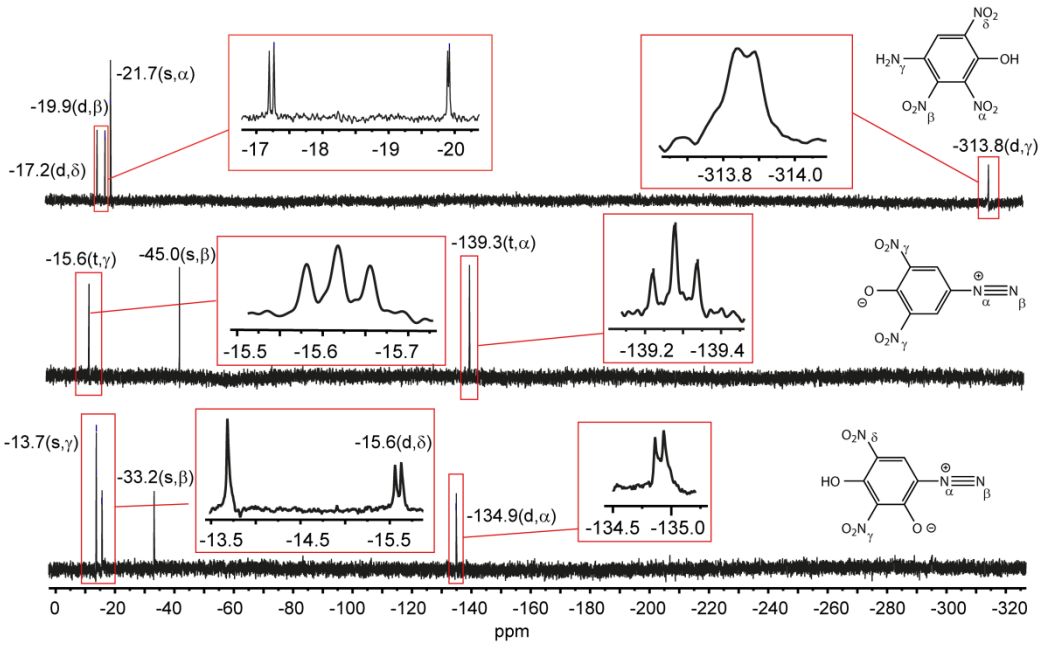


Figure 3: ^{15}N NMR spectra of **4** (top), **7** (middle) and **8** below).

4.3.3 Energetic properties

Energetic properties of compounds **4** and **8** in comparison to DDNP are displayed in Table 1. The impact sensitivity of all three compounds is 1 J, typically for primary explosives. *Therefore handling of these compounds should only be carried out only with proper safety measures!* Interestingly, compounds **4** and **8** are also very sensitive toward friction but slightly less than DDNP is, what makes them safer for handling. In addition they are slightly better (ca. 10–12° C) in thermal stability. Due to the higher densities of **4** and **8** in comparison to DDNP higher detonation parameters were calculated by using the EXPLO5 V6.01 computer code. Statistically, detonation pressure and velocity of **4** and **8** are ca. 5 % higher than those of DDNP. An empirical confirmation of these values has to be further researched in order to determine the relevance, as well as the benefits of those compounds. For selected applications like initiation of secondary explosives, these advantages could surpass the detriment of an increased number of synthetic steps to produce **4** and **8**.

Table 1: Energetic properties of compounds **4** and **8** in comparison to DDNP.

	4	**8**	**DDNP**[a]
Formula	$C_6H_2N_4O_5$	$C_6H_2N_4O_6$	$C_6H_2N_4O_5$
FW / g mol^{-1}	210.10	226.10	210.10
IS / J [b]	1(<100 µm)	1(<100 µm)	1(<100-500 µm)
FS / N [c]	40(<100 µm)	16(<100 µm)	5(<100-500 µm)

	4	**8**	**DDNP**[a]
N / % [d]	26.67	24.78	26.67
$T_{Dec.}$ / °C [e]	168	170	158[16]
ρ / g cm^{-3} [f]	1.790[g]	1.803[g]	1.727[16]
$\Delta_f H_m°$ / kJ mol^{-1} [h]	184.1	–42.0	142.4[16]
$\Delta_f U°$ / kJ kg^{-1} [i]	941.0	–120.0	742.6[16]
Ω / % [j]	–60.9	–49.5	–60.9
EXPLO 6.01 values:[k]			
$-\Delta_{Ex}U°$ / kJ kg^{-1} [l]	5241	4755	5009
T_{Det} / K [m]	3816	3579	3737
P_{CJ} / kbar [n]	269	263	241
$V_{Det.}$ / m s^{-1} [o]	7978	7900	7685
V_o / L kg^{-1} [p]	620	627	632

[a] DDNP sample of high purity was provided by another group member.[16] [b] Impact sensitivity (BAM drophammer, 1 of 6). [c] Friction sensitivity (BAM friction tester 1 of 6). [d] Nitrogen content. [e] Decomposition temperature from DSC (β = 5 °C). [f] From X-ray diffraction. [g] Density at 298 K was calculated using the formula $\rho_{298K} = \rho_T/1+\alpha_v(298-T_0)$ with $\alpha = 1.50 \cdot 10^{-4}$ K^{-1} and T_0 = 173 K[8,17]. [h] Calculated (CBS-4M) heat of formation. [i] Energy of formation. [j] Oxygen balance. [k]Values have been calculated by using room-temperature densities. [l] Energy of explosion. [m] explosion temperature. [n] Detonation pressure. [o] Detonation velocity. [p] Assuming only gaseous products.

4.4 Conclusions

From this experimental study the following conclusions can be drawn: 4-Amino-3,5-dinitroaniline (**3**) can be synthesized in three synthetic steps in high purity and large scales (> 20g). 4-Amino-2,3,6-trinitrophenol (**7**) can also be synthesized in a three step protocol in good yields. Unfortunately **7** is only stable up to 119 °C and therefore not of interest for any explosive-based applications. Further nitration of compounds **3** and **7** resulted in the formation of the very sensitive diazophenol derivatives **4** (4-diazo-2,6-dinitrophenol) and **8** (6-diazo-3-hydroxy-2,4-dinitrophenol). The molecular structures of **3**, **4**, **7** and **8** were determined by single-crystal X-ray diffraction. The sensitivities of **4** and **8** are in the range of DDNP's values, while the thermal stability and calculated performance are slightly better from a statistical point of view.

4.5 Experimental section

4-Fluoro-3,5-dinitrobenzoic acid (**1**):

To oleum (25 % SO_3 by weight, 175 ml) was added nitric acid (100 %, 50 ml) under cooling. 4-Fluorobenzoic acid (25.0 g, 178 mmol) was dissolved in this solution portionwise. After complete dissolution, the mixture was heated slowly to 95 °C. This temperature was kept for 5 h. Compound **1** slowly started to precipitate. After cooling, the suspension was poured onto crushed ice (600 g). The product was filtered and washed three times with of ice-cold water (3 × 100 ml) to remove the acid. Compound **1** was obtained as a bright-shining colorless powder (32 g, 78 %). **EA** ($C_7H_3FN_2O_6$ 230.11 g mol^{-1}): calcd. C 36.54, H 1.31, N 12.17; found C 36.58, H 1.24, N 12.44. **^{1}H NMR** (400.1 MHz, [D_6]acetone): δ = 8.94 [d, $^4J_{H,F}$ = 6.3 Hz, 2 H, CH], 11.59 (br. s, 1 H, COOH) ppm. **^{13}C NMR** (100.6 MHz, [D_6]acetone): δ = 127.4 (d, $^4J_{C,F}$ = 5.8 Hz, 1 C, *C*-COOH), 131.6 (s, 2 C, C-H), 139.2 (d, $^2J_{C,F}$ = 6.7 Hz, 2 C, C-NO_2), 152.0 (d, $^1J_{C,F}$ = 283.7 Hz, 1 C, C-F), 162.8 (s, 1 C, COOH) ppm. **^{19}F NMR** (376.5 MHz, [D_6]acetone): δ = –121.0 (t, $^4J_{H,F}$ = 6.5 Hz, 1 F) ppm.

4-Fluoro-3,5-dinitroaniline (**2**):

Compound **1** (10 g, 43.5 mmol) was dissolved in oleum (25 % SO_3 by weight, 25 ml). Afterwards, chloroform (40 ml) was added. Then the suspension was heated to 45 °C, and sodium azide (4.80 g, 73.8 mmol) was added portionwise so that the temperature did not exceed 55 °C. After that, the suspension was stirred for 1 h and then heated to reflux (75 °C) for 16 h. After cooling, the mixture was poured onto crushed ice (500 g), and **2** precipitated as a yellow-brownish powder (7.7 g, 88 %). **EA** ($C_6H_4FN_3O_4$ 201.11 g mol^{-1}): calcd. C 35.83, H , N 20.89; found C 35.68, H 2.20, N 20.96. **^{1}H NMR** (400.2 MHz, [D_6]acetone): δ = 5.40 (br. s, 2 H, NH_2), 7.63 (d, $^4J_{H,F}$ = 5.5 Hz, 2 H, C-H) ppm. **^{13}C NMR** (100.6 MHz, [D_6]acetone): δ = 121.3 (d, $^3J_{C,F}$ = 27.8 Hz, 2 C, C-H), 134.9 (d, $^4J_{C,F}$ = 7.7 Hz, 1 C, C-NH_2), 139.1 (s, 2 C, C-NO_2), 149.5 (d, $^1J_{C,F}$ = 237.7 Hz, 1 C, C-F) ppm. ^{19}F NMR (376.5 MHz, [D_6]acetone): δ = –147.5 (t, $^4J_{H,F}$ = 4.3 Hz, 1 F) ppm. **^{14}N NMR** (29.0 MHz, [D_6]acetone): δ = –14 (s, 2 N, NO_2), –308 (br. s, 1 N, NH_2) ppm.

4-Amino-3,5-dinitroaniline (**3**):

Ethanol (300 ml) was placed into a three-neck flask and cooled to –75 °C by using a CO_2/ethanol cooling bath. Then gaseous ammonia was bubbled through the mixture for ca. 30 min. Then **2** (20.0 g, 99.5 mmol) was suspended in this solution. The color of the suspension turned deep red relatively quickly. The temperature was kept at –45 °C for at least 6 h, and then the suspension was further stirred at ambient temperature for ca. 2 d.

After removal of the ethanol, the dark brown precipitate was washed several times with ice-cold water to remove the ammonium fluoride. Compound **3** was obtained as a "dark red-black" powder (17.4 g, 88 %). **EA** ($C_6H_6N_4O_4$ 198.14 g mol^{-1}): calcd. C 36.37, H 3.05, N 28.28; found C 36.48, H 2.98, N 27.96. **^{1}H NMR** (400.2 MHz, [D_6]DMSO): δ = 5.40 (br. s, 2 H, NH_2), 7.85 (br. s, 2 H, NH_2), 7.89 (s, 2 H, C-H) ppm. **^{13}C NMR** (100.6 MHz, [D_6]DMSO): δ = 119.5 (s, 2 C, C-H), 134.3 (s, 1 C, C-NH_2), 135.3 (s, 2 C, C-NH_2), 137.6 (s, 2 C, C-NO_2) ppm. **IR** (ATR): *1/λ* = 3443, 3361, 3298, 3099, 1614, 1578, 1521, 1506, 1420, 1251, 1231, 1114, 1022, 988, 896, 878, 803, 766 (m) cm^{-1}.

4-Diazo-2,6-dinitrophenol (**4**):

Acetic anhydride (10 ml) was cooled to –10 °C, and nitric acid (100 %, 1 ml) was added slowly. After stirring for 1 h, **3** (500 mg, 2.52 mmol) was added. The solution was stirred at 0 °C for 3 h and further at ambient temperature for 16 h. As soon as 24 °C was reached, **4** started to precipitate slowly from the solution. Afterwards, the suspension was poured onto crushed ice (50 g). A beige precipitate of **4** (344 mg, 65 %) was obtained. It was filtered and washed with cold water and twice with ice-cold ethanol (20 mL). **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 168 °C. **EA** ($C_6H_2N_4O_5$ 210.10 g mol^{-1}): calcd. C 34.30, H 0.96, N 26.67; found C 34.40, H 0.89, N 26.52. **^{1}H NMR** (400.2 MHz, [D_6]acetone/[D_6]DMSO, 5:1): δ = 9.01 (s, 2 H, C-H) ppm. **^{13}C NMR** (100.6 MHz, [D_6]acetone/[D_6]DMSO, 5:1): δ = 80.9 (s, 1 C, C-N_2) 132.6 (s, 2 C, C-H), 143.9 (s, 2 C, C-NO_2), 161.8 (s, 1 C, C-O) ppm. **^{15}N NMR** (40.6 MHz, [D_6]DMSO): δ = –15.6 (t, $N = |^3J_{N,H} + {}^5J_{N,H}|$ = 3.0 Hz, 2 N, NO_2), –45.0 (s, 1 N, N_2), –139.3 (t, $^3J_{N,H}$ = 2.4 Hz, 1 N, N_2) ppm. **IR** (ATR): *1/λ* = 3033, 2204, 2186, 1639, 1616, 1522, 1504, 1355, 1339, 1291, 1168, 1086, 938, 908, 900, 783, 706 cm^{-1}.

N-(4-Acetoxyphenyl)acetamide (**5**):

4-Aminophenol (35 g, 320.7 mmol) was dissolved in acetic anhydride (250 ml). Afterwards the solution was stirred until a precipitate formed (typically after 20–25 min). The suspension was heated to 95 °C for 16 h. Then the suspension was poured on crushed ice (1 kg) and stirred until all acetic anhydride was hydrolyzed. Compound **5** was obtained as a white crystalline powder (50 g, 81 %). **EA** ($C_{10}H_{11}NO_3$ 193.20 g mol^{-1}): calcd. C 62.17, H 5.74, N 7.25; found C 62.01, H 5.80, N 6.96.

N-(4-Hydroxy-3,5,6-trinitrophenyl)acetamide (**6**):

Compound **5** (12 g, 62.1 mmol) was dissolved in nitric acid (100 ml, 65 %) at 0 °C. This temperature was kept for 5 h, and then the solution's temperature was slowly risen to ambient temperature (6–8 h) and stirring continued for further 12 h. A yellow precipitate was formed. The suspension was poured on crushed ice (500 g). After the ice was molten, the

suspension was filtered and washed with only small amounts of ice-cold water to remove the nitric acid. Compound **6** was obtained as a bright-shining yellow powder (10 g, 56 %). **EA** ($C_8H_6N_4O_8$ 286.16 g mol^{-1}): calcd. C 33.58, H 2.11, N 19.58; found C 33.41, H 2.30, N 19.76. **^{1}H NMR** (400.1 MHz, [D$_6$]acetone): δ = 2.19 (s, 3 H, CH_3), 8.84 (s, 1 H, C-H), 9.58 (br. s, 1 H, N-H), 11.08 (br. s, 1 H, OH) ppm. **^{13}C NMR** (100.6 MHz, [D$_6$]acetone): δ = 22.6 (s, 1 C, CH_3) 123.3 (s, 1 C, C-NH), 124.7 (s, 1 C, C-H), 135.8 (s, 1 C, C-NO_2), 137.5 (s, 1 C, C-NO_2), 139.7 (s, 1 C, C-NO_2), 143.4 (s, 1 C, C-OH), 169.2 (s, 1 C, C=O) ppm.

4-Amino-2,3,6-trinitrophenol (**7**):

Compound **6** (11.0 g, 38.4 mmol) was dissolved in concentrated sulfuric acid (100 ml) at 0 °C. The yellow solution was stirred at ambient temperature in an open flask for at least 3 d. Afterwards it was poured onto crushed ice (400 g), and a deep dark-reddish powder precipitated. After filtration and subsequent washing with ice-cold water, **7** was obtained as a dark powder (7.14 g, 76 %). **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 119 °C. **EA** ($C_6H_4N_4O_7$ 244.12 g mol^{-1}): calcd. C 29.52, H 1.65, N 22.95; found C 29.40, H 1.39, N 23.10. **^{1}H NMR** (400.1 MHz, [D$_6$]acetone): δ = 6.60 (br. s, 2 H, NH_2), 8.13 (s, 1 H, C-H), 9.82 (br. s, 1 H, O-H) ppm. **^{13}C NMR** (100.6 MHz, [D$_6$]acetone): δ = 117.7 (s, 1 C, C-H) 127.1 (s, 1 C, C-NH_2), 135.1 (s, 1 C, C-NO_2), 136.7 (s, 1 C, C-NO_2), 138.6 (s, 1 C, C-NO_2), 140.9 (s, 1 C, C-OH) ppm. **^{15}N NMR** (40.6 MHz, [D$_6$]acetone): δ = –17.2 (d, $^3J_{N,H}$ = 2.9 Hz, 1 N, NO_2), –19.9 (d, $^4J_{N,H}$ = 1.2 Hz, 1 N, NO_2), –21.7 (s, 1 N, NO_2), –313.8 (d, $^3J_{N,H}$ = 2.4 Hz, 1 N, NH_2) ppm. **IR** (ATR): *1/λ* = 3500, 3385, 3286, 3095, 1602, 1577, 1544, 1508, 1479, 1430, 1372, 1340, 1320, 1262, 1240, 1154, 1043, 903, 893, 806, 758, 736 cm^{-1}.

6-Diazo-3-hydroxy-2,4-dinitrophenol (**8**):

Compound 7 (1.00 g, 4.10 mmol) was dissolved in nitric acid (15 ml, 65 %) at 65 °C. The solution was stirred at 65–70 °C for 2 h. Afterwards it was poured onto crushed ice (100 g). After a few minutes, **8** precipitated as a bright yellow powder (695 mg, 75 %). **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 170 °C. **EA** ($C_6H_2N_4O_6$ 226.10 g mol^{-1}): calcd. C 31.87, H 0.89, N 24.28; found C 31.96, H 1.05, N 24.51. **^{1}H NMR** (400.1 MHz, [D$_6$]acetone): δ = 9.28 (s, 1 H, C-H), 11.37 (br. s, 1 H, O-H) ppm. **^{13}C NMR** (100.6 MHz, [D$_6$]acetone): δ = 90.9 (s, 1 C, C-N_2) 123.8 (s, 1 C, C-NO_2), 132.3 (s, 1 C, C-NO_2), 133.7 (s, 1 C, C-H), 154.1 (s, 1 C, C-OH), 164.6 (s, 1 C, C-O) ppm. **^{15}N NMR** (40.6 MHz, [D$_6$]DMSO): δ = –13.7 (s, 1 N, NO_2), –15.6 (d, $^3J_{N,H}$ = 2.8 Hz, 1 N, NO_2), –33.2 (s, 1 N, N_2), –134.9 (d, $^3J_{N,H}$ = 1.8 Hz, 1 N, N_2) ppm. **IR** (ATR): *1/λ* = 3075, 2192, 1638, 1606, 1516, 1492, 1449, 1368, 1304, 1215, 1172, 1084, 932, 915, 798, 770, 743, 706 cm^{-1}.

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4.7 Supporting information

Syntheses and Energetic Properties of 4-Diazo-2,6-dinitrophenol and 6-Diazo-3-hydroxy-2,4-dinitrophenol

4.7.1 X-ray diffraction

For all compounds, an Oxford Xcalibur3 diffractometer with a CCD area detector was employed for data collection using Mo-*K*α radiation (*λ* = 0.71073 Å). By using the CRYSALISPRO software[S1] the data collection and reduction were performed. The structures were solved by direct methods (SIR92, [S3] SIR -97[S3] or SHELXS-97[S4]) and refined by full-matrix least-squares on *F*2 (SHELXL [S4]) and finally checked using the PLATON software [S5] integrated in the WinGX software suite. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The absorptions were corrected by a SCALE3 ABSPACK multiscan method.[S6]. All DIAMOND2 plots are shown with thermal ellipsoids at the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius.

Table S1: Crystallographic data and refinement parameters of compounds **3, 4, 7** and **8**.

Compound	**3**	**4**	**7**	**8**
Formula	$C_6H_6N_4O_4$	$C_6H_2N_4O_5$	$C_6H_4N_4O_7$	$C_6H_2N_4O_6$
FW [gmol^{-1}]	198.14	210.10	244.13	226.10
Color, habit	red plate	colorless needle	dark-red rod	yellow plate
Size [mm]	0.57x0.15x0.02	0.25x0.09x0.02	0.33x0.07x0.04	0.39x0.32x0.08
Crystal system	monoclinic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$	*Pbca*	*Pbca*
a [Å]	5.1323(4)	7.7319(7)	12.5540(10)	11.3036(4)
b [Å]	14.2678(9)	12.8856(10)	10.3306(8)	9.3770(4)
c [Å]	10.4372(9)	15.3606(12)	13.5974(9)	15.4235(5)
α [°]	90	90	90	90
β [°]	98.642(7)	90	90	90
γ [°]	90	90	90	90
V [Å^3]	755.60(10)	1530.4(2)	1763.5(2)	1634.80(10)
Z	4	8	8	8
ρ_{calc} [g cm^{-3}]	1.742	1.824	1.839	1.837
μ [mm^{-1}]	0.149	0.163	0.171	0.168
Irridiation [nm]	MoK$_\alpha$ 0.071073	MoK$_\alpha$ 0.071073	MoK$_\alpha$ 0.071073	MoK$_\alpha$ 0.071073
F(000)	408	848	992	912
Θ-Bereich [°]	4.20-26.49	4.33-21.73	4.38-25.15	4.21-26.50
T [K]	173(2)	173(2)	173(2)	173(2)
Dataset h	$-6 \le h \le 5$	$-9 \le h \le 9$	$-15 \le h \le 13$	$-14 \le h \le 13$
Dataset k	$-16 \le k \le 17$	$-11 \le k \le 16$	$-12 \le k \le 12$	$-11 \le k \le 10$
Dataset l	$-13 \le l \le 13$	$-19 \le l \le 19$	$-16 \le l \le 15$	$-17 \le l \le 19$
Reflecions coll.	3151	11859	12024	12398
Independent refl.	1566	1918	1793	1697
Observed refl.	1288	1242	1317	1438
Parameters	151	244	167	153
R (int)	0.0180	0.1053	0.0523	0.0306
GOOF	1.038	1.023	1.055	1.071
R_1, wR_2 ($I>\sigma I_0$)	0.0354, 0.0876	0.0571, 0.1063	0.0371, 0.0785	0.0334, 0.0818
R_1, wR_2 (all data)	0.0455, 0.0957	0.1055, 0.1286	0.0591, 0.0853	0.0405, 0.0869
Remaining density [e	−0.201, 0.233	−0.270, 0.266	−0.236, 0.234	−0.257, 0.286

· A-^{3}]				
Device type	Oxford XCalibur3 CCD	Oxford XCalibur3 CCD	Oxford XCalibur3 CCD	Oxford XCalibur3 CCD
Solution	SIR-92	SIR-92	SHELXS-97	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-2013	SHELXL-97
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
CCDC No.	1057558	1057560	1057559	1057561

4.7.2 Heat of formation calculations

All calculations were carried out using the Gaussian G09W (revision A.02) program package. The enthalpies (H), listed in Table S3, were calculated using the complete basis set (CBS) method of Petersson and coworkers in order to obtain very accurate energies. The CBS models use the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated complete basis set limit. CBS-4 begins with a HF/3-21G(d) geometry optimization; the zero point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy, and a MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. A MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher order contributions. In this study we applied the modified CBS-4M method (M referring to the use of Minimal Population localization) which is a re-parametrized version of the original CBS-4 method and also includes some additional empirical corrections.[S7] The enthalpies of the gas-phase species M were computed according to the atomization energy method (eq.1).

$$\Delta_f H°_{(g,\,M,\,298)} = H_{(Molecule,\,298)} - \sum H°_{(Atoms,\,298)} + \sum \Delta_f H°_{(Atoms,\,298)} \quad (1)$$

Table S2: CBS-4M results and calculated gas-phase enthalpies

	M	$-H^{298}$ / a.u.	$\Delta_f H°$(g,M) / kcal mol^{-1}	ΔH_{sub} / kcal mol^{-1}
4	$C_6H_2N_4O_5$	823.662302	63.8	19.8
7	$C_6H_4N_4O_7$	975.148750	-27.9	17.6
8	$C_6H_2N_4O_6$	898.834400	9.9	19.9

Table S3: CBS-4M values and literature values for atomic $\Delta H°_f^{298}$ / kcal mol^{-1}

	$-H^{298}$ / a.u.	NIST [S8] / $\Delta H°_f^{298}$
H	0.500991	52.1
C	37.786156	171.3

N	54.522462	113.0
O	74.991202	59.6

The gas phase heats of formation of **4**, **7** and **8** are converted to the solid state value by subtracting its sublimation enthalpy calculated with Trouton's rule ($\Delta H_{sub} = 188 \cdot T_m$) These molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid state energies of formation (ΔU_m) according to equation 2.

$$\Delta U_m = \Delta H_m - \Delta n\, RT \quad \textbf{(2)}$$

(Δn being the change of moles of gaseous components)

Table S4: Solid state energies of formation ($\Delta_f U°$)

	$\Delta_f H°$(s) / kcal mol^{-1}	$\Delta_f H°$(s) / kJ mol^{-1}	Δn	$\Delta_f U°$(s) / kJ mol^{-1}	M / g mol^{-1}	$\Delta_f U°$(s) / kJ kg^{-1}
4	44.0	184.1	5.5	197.7	210.12	941.0
7	-45.5	-190.4	7.5	-171.8	244.14	-703.8
8	-10.0	-42.0	6	-27.1	226.12	-120.0

4.8 Experimental methods

Infrared spectra were measured with a Perkin–Elmer Spectrum BX-FTIR spectrometer equipped with a Smiths DuraSamplIR II ATR device. All spectra were recorded at ambient temperature; the samples were neat solids. NMR spectra were recorded with a JEOL Eclipse 400 ECX and a BRUKER AVANCE III HD instrument. All samples were measured at 25 °C. C/H/N analysis was carried out by the department's internal micro analytical laboratory on a *Elementar Vario el* by pyrolysis of the sample and subsequent analysis of the formed gases. Differential Scanning Calorimetry (DSC) was performed on a *LINSEIS DSC PT10* with about 1 mg substance in a perforated aluminum vessel and a heating rate of 5 K min^{-1} and a nitrogen steam of 5 L h^{-1}. Melting points were determined in the same way. The sensitivities of the compounds were determined according to the BAM (German: Bundesanstalt für Materialforschung und Prüfung) standard for friction and impact. [S9] The impact sensitivities were tested according to STANAG 4489 modified instruction using a BAM drophammer. The friction sensitivities were tested according to STANAG 4487 modified instructions using a BAM friction tester. The tested compounds were classified from the results by the "UN Recommendations on the Transport of Dangerous Goods". Energetic properties have been calculated with the EXPLO5 6.01 computer [S10] code using the to RT converted X-ray density and calculated solid state heats of formation. These were computed by the atomization

method as described in recently published papers. Electronic enthalpies were calculated with the Gaussian09 software [S11] suite using the CBS-4M method.

4.9 References

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4.10 ^{1}H and ^{13}C NMR spectra of key intermediates and final products

In this chapter the ^{1}H and ^{13}NMR spectra of following compounds are displayed:

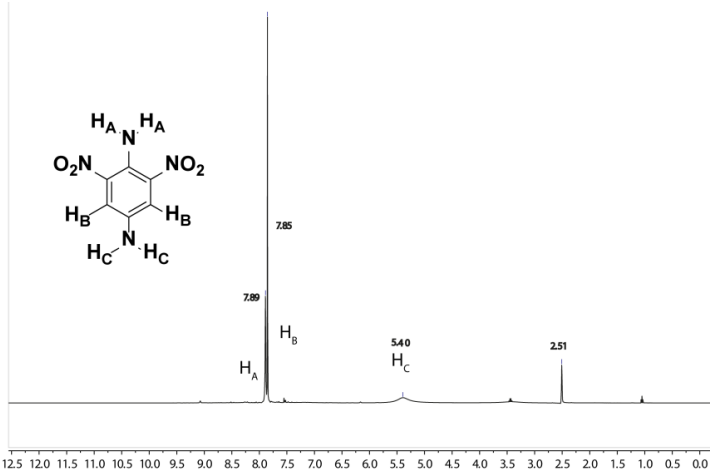
Key intermediates

4-amino-3,5-dinitroaniline (**3**), *N*-(4-Hydroxy-3,5,6-trinitrophenyl)-acetamide (**6**) and 4-Amino-2,3,6-trinitrophenol (**7**).

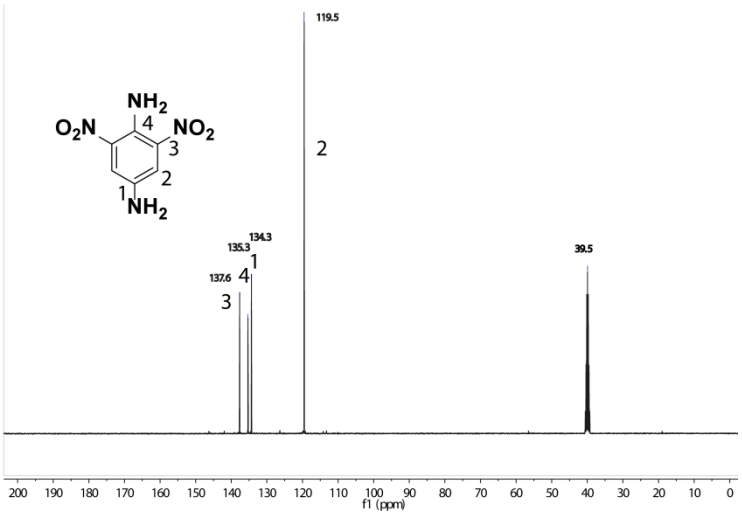
Final products

4-Diazo-2,6-dinitrophenol (**4**) and 6-Diazo-3-hydroxy-2,4-dinitrophenol (**8**)

4-amino-3,5-dinitroaniline (3)

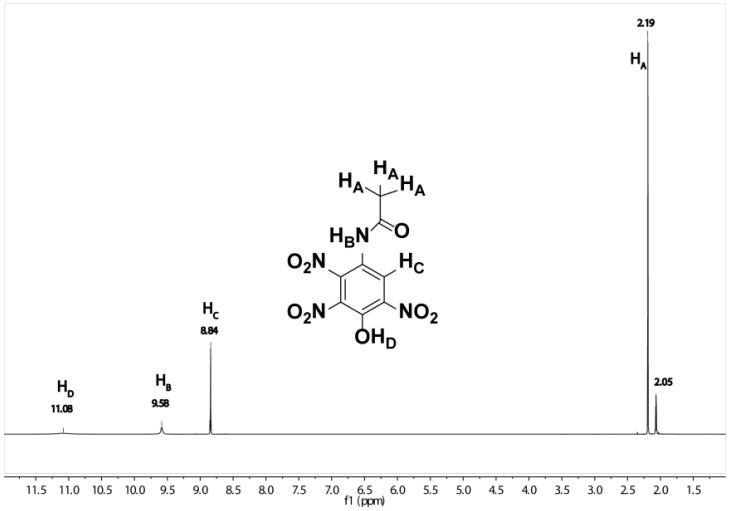


^{1}H NMR spectrum of compound 3 measured in d_6-DMSO

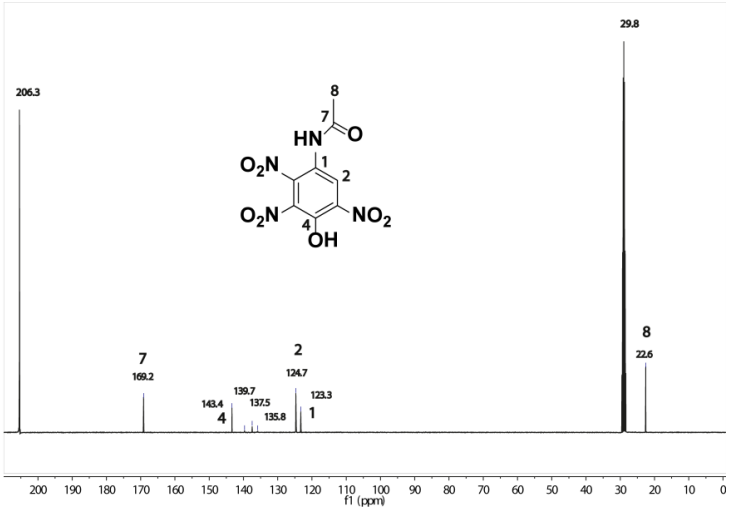


^{13}C NMR spectrum of compound 3 measured in d_6-DMSO

N-(4-Hydroxy-3,5,6-trinitrophenyl)-acetamide (**6**)

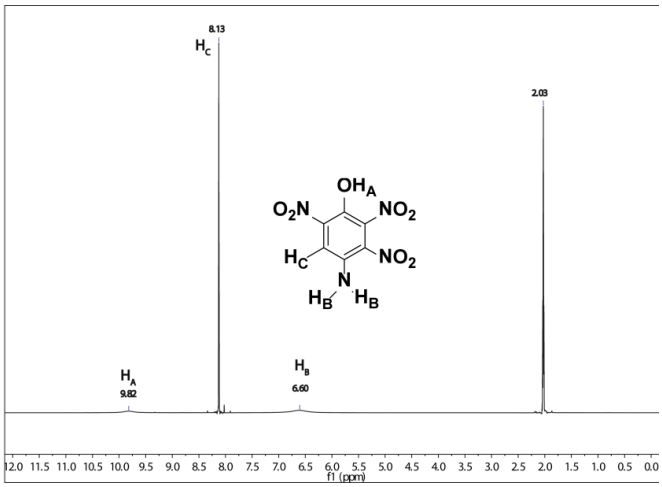


^{1}H NMR spectrum of compound 6 measured in d_6-acetone

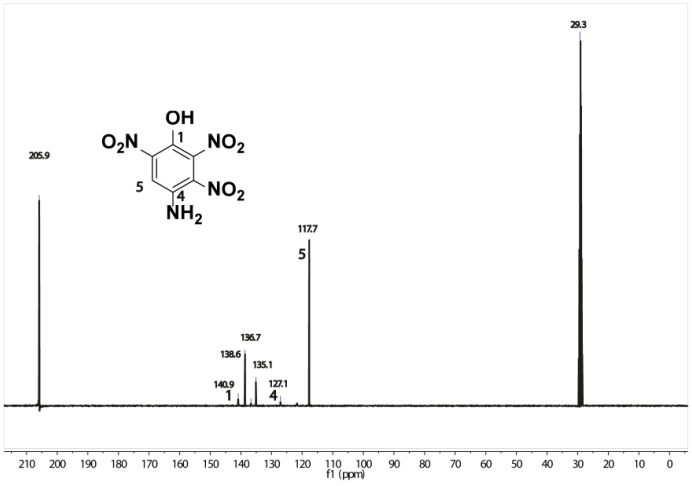


^{13}C NMR spectrum of compound 6 measured in d_6-acetone

4-amino-2,3,6-trinitrophenol (7)



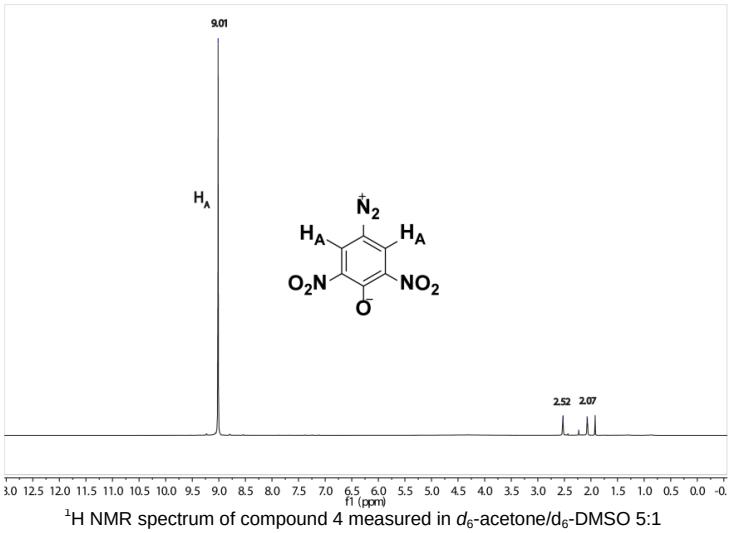
^{1}H NMR spectrum of compound 7 measured in d_6-acetone



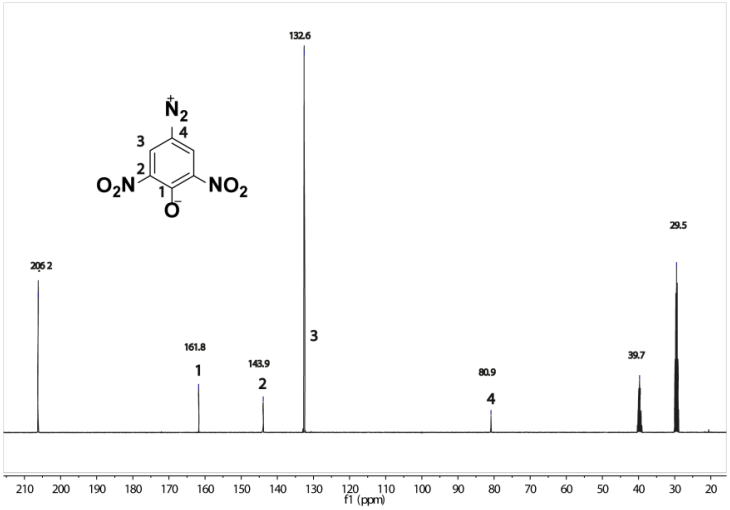
^{13}C NMR spectrum of compound 7 measured in d_6-acetone

Final products

4-diazo-2,6-dinitrophenol (4)

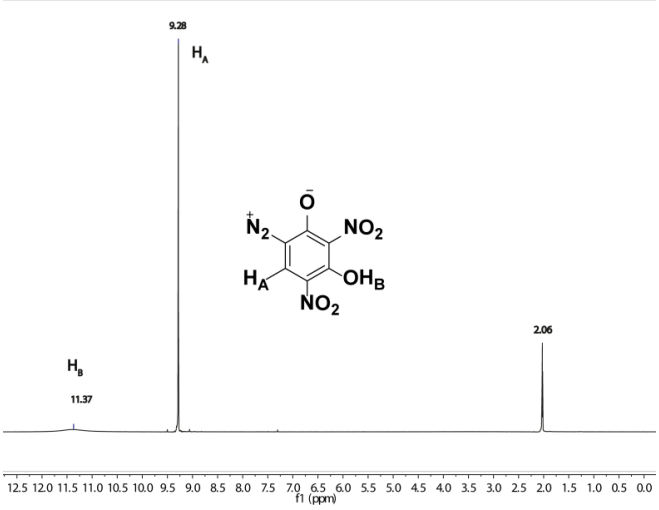


^{1}H NMR spectrum of compound 4 measured in d_6-acetone/d_6-DMSO 5:1

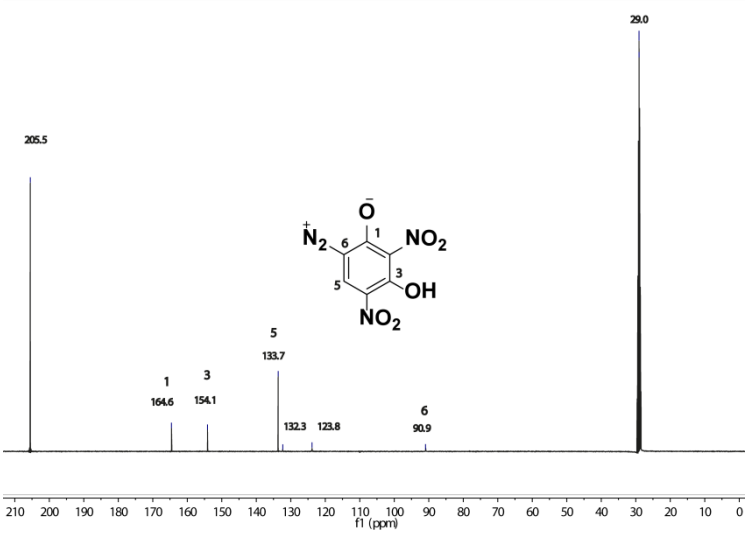


^{13}C NMR spectrum of compound 4 measured in d_6-acetone/d_6-DMSO 5:1

6-Diazo-3-hydroxy-2,4-dinitrophenol (**8**)



^{1}H NMR spectrum of compound 8 measured in d_6-acetone



^{13}C NMR spectrum of compound 8 measured in d_6-acetone

5. PUBLICATION C

Highly Energetic Salts of 3,6-Bishydrazino-1,2,4,5-tetrazine

T. M. Klapötke, A. Preimesser, S. Schedlbauer and J. Stierstorfer,

Cent. Eur. J. Energ. Mat. **2013**, *10*, 151–170.

5.1 Abstract

3,6-Bishydrazino-1,2,4,5-tetrazine was synthesized as described byhydrazinolysis of 3,6-bis-(3,5-dimethylpyrazolyl)-1,2,4,5-tetrazine. Doubly protonated 1:1 and 1:2 salts of the highly energetic anions were synthesized. These are bishydrazinium-tetrazine dichloride dihydrate (1:2) (BHT · 2HCl · $2H_2O$) (**2**), bishydrazinium-tetrazine (5,5´-azotetrazolate) dihydrate (1:1) (BHT-ATz·$2H_2O$) (**3**), bishydrazinium-tetrazine bis (3,5-dinitrotriazolate) dihydrate (1:2) (BHT-$(DNT)_2$ · $2H_2O$) (**4**), bishydrazinium-tetrazine bis (5-nitrotetrazolate) (1:2) (BHT-$(NT)_2$) (**5**), bishydrazinium-tetrazine (5,5´-bistetrazolate) dihydrate (1:1) (BHTBT · $2H_2O$) (**6**), bishydrazinium-tetrazine bistetrazolylamine (1:1) (BHT-BTA) (**7**), bishydrazinium-tetrazine bis (3-amino-5-nitrotriazolate) (1:2) (BHT-$(ANTA)_2$) (**8**) and bishydrazinium-tetrazine 4,4´,5,5´-tetranitro-2,2´-bisimidazolate (1:1) (**9**). Compounds **2**-**6** could be characterized by low temperature X-ray diffraction. All of the compounds were sufficiently analyzed by ^{1}H and $\{1H\}^{13}C$ and ^{14}N NMR spectroscopy, elemental analysis (CHN), mass spectroscopy (FAB)) and vibrational spectroscopy (IR and Raman). The detonation parameters of the most promising candidates **5** and **9** in terms of energetic applications were calculated using the EXPLO5 V5.05 computer code. The energies of formation were calculated using CBS-4M electronic enthalpies and the atomization method. Furthermore, since all of the compounds are energetic materials, sensitivity tests towards impact (IS), friction (FS) and electrostatical discharge (ESD) were carried out. In addition their thermal stabilities were determined using a differential scanning calorimeter with a heating rate of 5 °C min^{-1}.

5.2 Introduction

Most commercial secondary explosives like RDX (hexogen) and HNS (hexanitrostilbene) are very toxic for human and animal organisms.[1] In terms of performance, secondary explosives are characterized by parameters like the detonation velocity ($V_{Det.}$), detonation pressure (P_{CJ}), heat of detonation ($\Delta_{Ex}U°$) and the volume of detonation gases (V_0) which is created during their detonation.[2] It is a recent project to forge energetic materials and compositions[3]

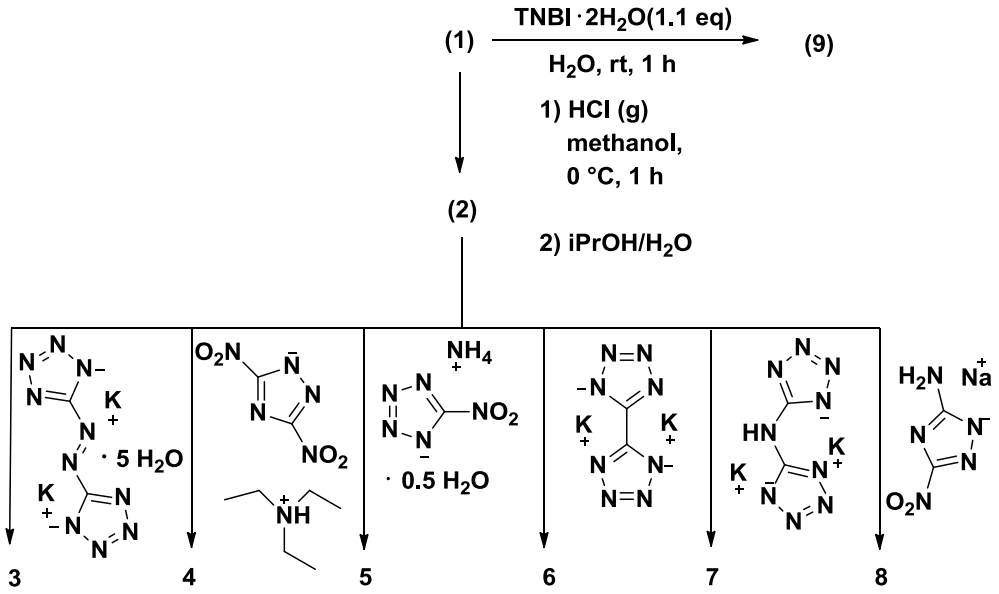
with higher thermal stability, lower sensitivity (towards impact (*IS*), friction (*FS*), electrostatic discharge (*ESD*)) and lower toxicity than the currently used ones. One approach is the use of azoles in combination with energetic substituents like nitro or azide groups at the carbon atom(s).[4] High positive heats of formation, which are strongly desired, are also found in 1,2,4,5-tetrazines.[5] 3,6-Bishydrazino-1,2,4,5-tetrazine (**BHT**, **1**) is a highly energetic molecule with a highly positive enthalpy of formation (577.0 kJ mol^{-1})[6], due to the N–N single bonds of the hydrazine moiety and the aromatic N–N bonds of the 1,2,4,5 tetrazine. It can serve as a doubly charged cation to create 1:2 or 1:1 salts. This was already investigated by Hiskey *et al.* in the 1990's with respect to propellant ingredients.[7] They synthesized 1:1 and 1:2 salts by direct protonation of BHT using nitric acid, perchloric acid, ammonium dinitramide and 4,4´,5,5´-tetranitro-2,2´-bisimidazole (TNBI) as acids and characterized their sensitivity towards impact as well as their thermal stability. Additionally, the 1:1 5,5´-bistetrazolate and the bis-tetrazolyl amine salts were investigated with respect to low smoke producing pyrotechnic compositions. However their structures were not yet determined.[8] Herein we report on the syntheses and potential use as ionic explosives of various energetic BHT 1:1 and 1:2 salts. The compounds were synthesized by salt metathesis or direct acid/base reaction in good yields and purity.

5.3 Results and discussion

5.3.1 Syntheses

3,6-Bishydrazino-1,2,4,5-tetrazine (**1**) was synthesized as described in the literature[9–12] in four steps *via* triaminoguanidinium chloride and acetyl acetone, followed by oxidation with liquid NO_2 in NMP or $NaNO_2$ in CH_2Cl_2/glacial acid and substitution with hydrazine. An overall synthetic protocol is displayed in Scheme 1. 3,6-Bishydrazino-1,2,4,5-tetrazine (**1**) and the corresponding 4,4´,5,5´-tetranitro-2,2´-bisimidazolate (**9**) were also synthesized as described in the literature.[7,9] The reaction of gaseous HCl with **1** suspended in methanol at 0 °C yielded the 3,6-bishydrazinium-tetrazine dichloride dihydrate (BHT · 2HCl·2 H_2O, **2**) in high yield after recrystallization from i-PrOH/H_2O. By metathesis reactions with alkaline metal salts of highly energetic anions, 1:1 and 1:2 salts of **BHT** were synthesized. These are bishydrazinium-tetrazine (5,5´-azotetrazolate) dihydrate (1:1) (BHT-ATz · 2 H_2O) (**3**), bishydrazinium-tetrazine bis (3,5-dinitrotriazolate) dihydrate (1:2) (BHT-$(DNT)_2$ · 2 H_2O) (**4**), bishydrazinium-tetrazine bis (5-nitrotetrazolate) (1:2) (BHT-$(NT)_2$) (**5**), bishydrazinium-tetrazine (5,5'-bistetrazolate) dihydrate (1:1) (BHT-BT · 2 H_2O) (**6**), bishydrazinium-tetrazine bistetrazolylamine (1:1) (BHT-BTA) (**7**) and bishydrazinium-tetrazine bis (3-amino-5-nitrotriazolate) (1:2) (BHT-$(ANTA)_2$) (**8**). All of these specified anions were synthesized as

described in the literature.[13-18] Furthermore we tried to use *N*-oxides as potentially energetic anions, namely 5-nitrotetrazole-1-oxide and 5,5'-azotetrazole-1,1'-dioxide. Unfortunately BHT seems to be incompatible with these *N*-oxide species and decomposition due to oxidation reactions of the hydrazine moiety occurs.



Scheme 1: Overall syntheses scheme of compound **2**-**9**; reaction conditions: ambient temperature 2 h for each compound (**3**-**9**), 1:1 or 1:2 stoichiometry.

5.3.2 Crystal structures

The single crystal X-ray diffraction data were collected using an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collections were undertaken using the CrysAlis CCD software[19] and the data reductions were performed with the CrysAlis Red software.[20] The structures were solved with Sir-92[21], refined with Shelxl-97[22] and finally checked using Platon[23]. In all of the structures the hydrogen atoms were located and refined. The absorptions of the structures were corrected using the Scale3 Abspack multi-scan method.[24] Selected data and parameters from the X-ray data collection and refinements are given in Table 1. Further information regarding the crystal-structure determinations have been deposited with the Cambridge Crystallographic Data Centre[25] as supplementary publication Nos. 926094 (**2**), 926097 (**3**), 926095 (**4**), 926096 (**5**) and 926098 (**6**).

Table 1: XRD data and parameters.

Compound	BHT·2 HCl ·2 H_2O (**2**)	BHT(ATZ) ·2·H_2O (**3**)	$BHT(DNT)_2$ ·2 H_2O (**4**)	$BHT(NT)_2$ (**5**)	BHT(BT) ·2 H_2O (**6**)
Formula	$C_2H_{12}Cl_2N_8O_2$	$C_4H_{12}N_{18}O_2$	$C_6H_{12}N_{18}O_{10}$	$C_4H_8N_{18}O_4$	$C_4H_{12}N_{16}O_2$
FW [g mol^{-1}]	251.08	344.24	496.27	372.22	316.13
Crystal system	triclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	*P*–1	$P2_1/c$	$P2_1/n$	*P*–1	*P*–1
Habitus	orange needle	red needle	orange needle	yellow needle	orange needle
Crystal Size [mm]	0.18 x 0.21 x 0.28	0.11 x 0.13 x 0.24	0.20 x 0.29 x 0.34	0.20 x 0.22 x 0.29	0.13 x 0.18 x 0.24
a [nm]	0.63094(6)	0.43434(7)	1.07777(18)	0.64465(6)	0.77949(8)
b [nm]	0.69132(6)	1.20583(16)	0.61512(15)	0.71755(7)	0.92606(10)
c [nm]	0.74141(7)	1.29592(17)	1.3668(3)	0.80547(7)	0.99301(12)
α [°]	114.060(9)	90.00	90.00	99.369(8)	117.382(12)
β [°]	97.162(7)	91.900(14)	93.110(18)	103.574(8)	90.858(9)
γ [°]	112.699(9)	90.00	90.00	96.879(8)	97.500(9)
V [nm^3]	0.25670(4)	0.67835(17)	0.9048(3)	0.35247(6)	0.62876(12)
Z	1	2	4	1	2
$\rho_{calc.}$ [g cm^{-3}]	1.624	1.686	1.822	1.754	1.671
μ [mm^{-1}]	0.627	0.139	0.167	0.151	0.137
F(000)	130	356	508	190	328
$\lambda_{MoK\alpha}$ [nm]	0.071073	0.071073	0.071073	0.071073	0.071073
T [K]	173	173	173	173	173
θ Min–Max [°]	4.54, 25.98	4.62, 26.25	4.13, 26.48	4.32, 26.00	4.13, 25.00
Dataset	–7:7; –8:8; –9:9	–5:5; –14:14; –15:16	–13:13; –5:7; –16:17	–7:7; –8:8; –9:9	–9:8; –10:10; –11:11
Reflections collected	2597	3485	4666	3546	2647
Independent refl.	997	1362	1870	1373	2103
R_{int}	0.025	0.048	0.027	0.028	0.020
Observed reflections	879	737	1357	1004	1750
Parameters	88	133	192	134	247
R_1 (obs)	0.0209	0.0361	0.0320	0.0321	0.0394
wR_2 (all data)	0.0590	0.0542	0.0737	0.0782	0.0998
S^c	1.015	0.752	0.970	0.924	1.081
Min. and Max. Resd. Dens. [e/(10^{-3} nm^3)]	–0.204, 0.206	–0.281, 0.246	–0.177, 0.186	–0.222, 0.195	–0.187, 0.503
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SIR-92	SiR-92	SiR-92	SiR-97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
CCDC	926094	926097	926095	926096	926098

2 crystallizes in the triclinic space group *P–1* with 2 formula units per unit cell and a density of 1.624 g cm^{-3} at 173 K. The generally planar structure of the dication (trans arrangement of the hydrazinium moieties) is in agreement with a previously published tetrazolate derivative.[26]

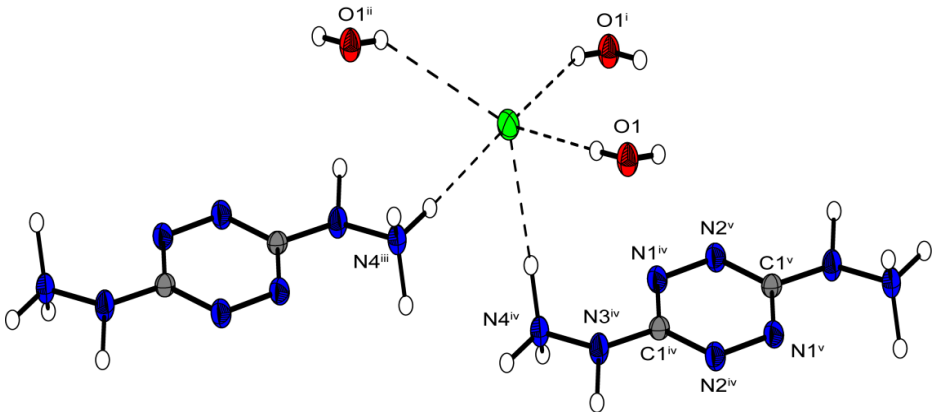


Fig. 1: View on the coordination sphere of one chloride anion in the crystal structure of **2** showing the labeling scheme. The non-hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. **Selected bond lengths** [nm]: $N1^{iv}$–$C1^{iv}$ 0.1341(2), $N2^{iv}$–$N1^{v}$ 0.1323(2), $N2^{iv}$–$C1^{iv}$ 0.1338(2), $N3^{iv}$–$C1^{iv}$ 0.1376(2), $N3^{iv}$–$N4^{iv}$ 0.1427(2); Cl1–O1 0.3142(5); **Selected bond angles** [°]: $N2^{iv}$–$N1^{iv}$–$C1^{iv}$ 117.4(1), $C1^{iv}$–$N3^{iv}$–$N4^{iv}$ 115.4(1), $N2^{iv}$–$C1^{iv}$–$N1^{iv}$ 126.1(1), $N1^{iv}$–$C1^{iv}$–$N3^{iv}$ 118.1(1); **Selected torsion angles** [°]: $N4^{iv}$–$N3^{iv}$–$C1^{iv}$–$N2^{iv}$ 171.1(1), $N4^{iv}$–$N3^{iv}$–$C1^{iv}$–$N1^{iv}$ -11.2(2), $N3^{iv}$–$C1^{iv}$–$N2^{iv}$–$N1^{iv}$ 177.9(1); Illustrated hydrogen bond [nm]: $N4^{iv}$–$H2B^{iv}$···Cl1, D–H 0.094(2), H···A 0.228(2), D···A 0.3158(1), <D–H···A 155.0 (2)°; $N4^{iii}$–$H2B^{iii}$···Cl1, 0.090(2), 0.218(2), 0.3078(1), 176.7(17)°; symmetry codes: (i) -x, 2-y, 2-z; (ii) 1+x, y, z; (iii) x, y, -1+z; (iv) -x, 1-y, 2-z; (v) -1+x, y, z; selected crystal data: *a* 0.63094(6) nm, *b* 0.69132(6) nm, *c* 0.74141(7) nm, *α* 114.060(9)°, *β* 97.162(7)°, *γ* 112.699(9)°, V 0.25670(4) nm^3.

Single crystals of compound **5** could be obtained in the anhydrous form. **5** crystallizes in the triclinic space group *P*–1 with one formula unit per unit cell and a density of 1.754 g cm^{-3} at 173 K. The nitrotetrazolate anions also follow the planar structure described previously for *e.g.* ammonium 5-nitrotetrazolate.[27]

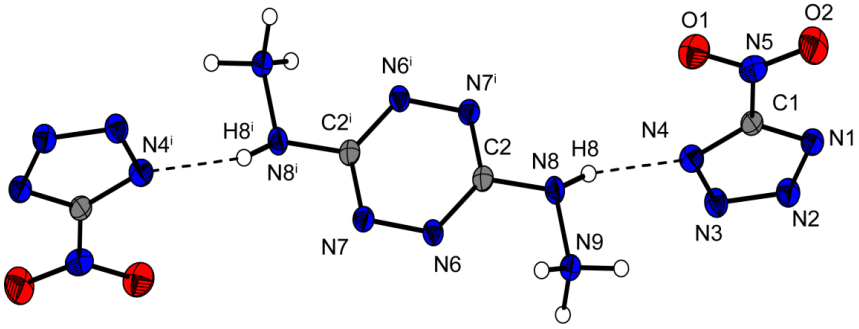


Fig. 2: View on the coordination sphere of one BHT cation in compund **5** showing the labeling scheme. The non-hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. **Selected bond lengths** [nm]: C2–N7 0.1334(2), O1–N5 0.1225(2), N6–N7 0.1325(2), N6–C2 0.1340(2), N7–C2 0.1334(2), N8–C2 0.1377(2), N8–N9 0.1428(2); **Selected bond angles** [°]: O1–N5–O2 125.7(1), O1–N5–C1 116.7(1), O2–N5–C1 117.4(1), N6–N7–C2 116.2(1), C2–N8–N9 115.6(1), C2–N8–H8 116.4(12), N9–N8–H8 114.3(12) N7–C2–N8 116.5(1), N6–C2–N8 117.5(1), C1–N1–N2 103.2(1), N3–N2–N1 109.5(1), N2–N3–N4 109.7(1); **Selected torsion angles** [°]: O1–N5–C1–N1 176.1(1), O2–N5–C1–N4 173.9(1), N9–N8–C2–N6 11.7(2), N2–N1–C1–N5 179.2(1); Illustrated hydrogen bond [nm]: N8–H8···N4, D–H 0.088(2), H···A 0.216(2), D···A 0.3008(2), <D–H···A 162.5(16)°; symmetry codes: (i) –x, 2–y, –z; selected crystal data: *a* 0.64465(6) nm, *b* 0.71755(7) nm, *c* 0.80547(7) nm, *α* 99.369(8)°, *β* 103.574(8)°, *γ* 96.879(8)°, V 0.35247(6) nm^3.

BHT-ATZ · 2 H_2O crystallizes in the monoclinic space group $P2_1/c$ with 2 formula units per unit cell. The unit cell has the dimension of *a* = 0.43434(7) nm, *b* = 1.20583(16) nm,

c = 1.29592(17) nm, β = 91.900(14)°. It crystallizes with a cell volume of 0.67835(17) nm^3 and a density of 1.686 g cm^{-3} at a temperature of 173 K.

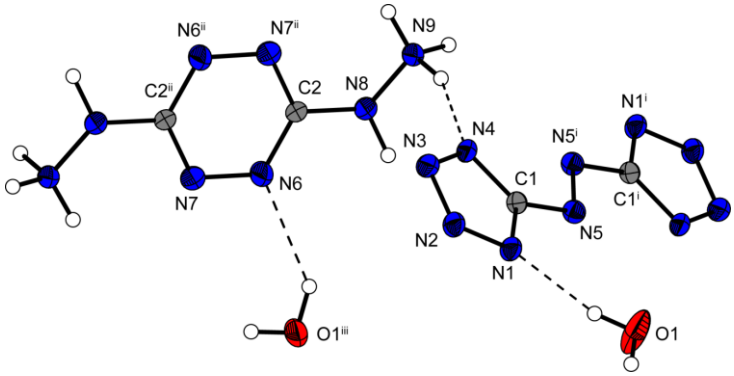


Figure 3: Molecular unit of **3**; the non-hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. **Selected bond lengths** [nm]: C1—N1 0.1329(2), C1—N4 0.1335(2), C1—N5 0.1414(2), N4—N3 0.1342(2), N8—C2 0.1377(2), N8—N9 0.1436(2), N3—N2 0.1331(2), N1—N2 0.1345(2); **Selected bond angles** [°]: N1—C1—N4 112.8(2), N1—C1—N5 119.2(2), N4—C1—N5 128.0(2), C1—N4—N3 104.0(2), C2—N8—N9 117.5(2), N9—N8—H8 110.7(1), N2—N3—N4 109.9(1),C1—N1—N2 104.7(2), N3—N2—N1 108.7(2), N8—N9—H9A 106.8(2), N8—N9—H9B 112.5(2); **Selected torsion angles** [°]: N7—N6—C2—N8 -175.9(2), N1—C1—N5—N5^i 179.9(2), N6—C2—N8—N9 -162.0(2); selected hydrogen bonds [nm]: O1—H1A···N1 (0.083(2), 0.196(3), 0.2781(2) nm, 167.3(2)°, N9—H9C···N4 (0.110(3), 0.183(3), 0.2865(2), 156.(2)°), O1^{iii}—H1B^{iii}···N6^v (0.90(3), 2.37(3), 3.116(2) Å, 140.7(19)°); symmetry codes: (i) -x, -1-y, 1-z; (ii) -x, -1-y, -z; (iii) -1+x, -0.5-y, -0.5+z.

BHT-(DNT)$_2$ · 2 H_2O crystallizes in the monoclinic space group $P2_1/n$ with 4 formula units per unit cell. It crystallizes with a cell volume of 0.9048(3) nm^3 and the density was calculated to 1.822 g cm^{-3} at a temperature of 173 K.

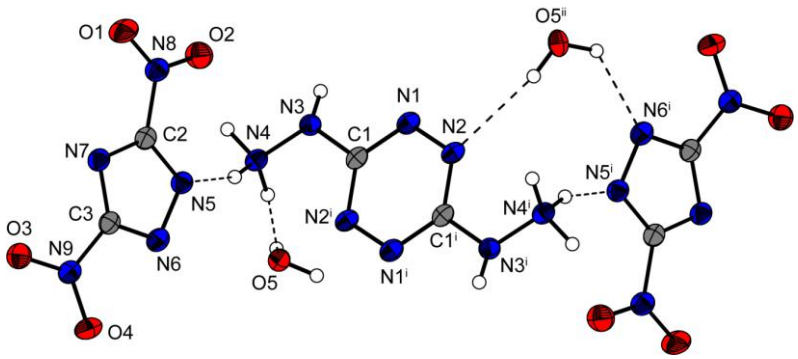


Figure 4: Molecular unit of **4**; the non-hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. **Selected bond lengths** [nm]: O1—N8 0.1224(2), O2—N8 0.1224(2), O3—N9 0.1227(2), O4—N9 0.1230(2), N5—C2 0.1335(2), N5—N6 0.1352(2), N6—C3 0.1336(2), N7—C2 0.1326(2); **Selected bond angles** [°]: C2—N5—N6 104.4(1), C3—N6—N5 103.8(1), O1—N8—O2 124.9(1), O1—N8—C2 117.7(1), O2—N8—C2 117.4(1), O3—N9—O4 124.0(1), O4—N9—C3 116.9(1), N7—C2—N5 116.9(1), N5—C2—N8 120.2(1); **Selected torsion angles** [°]: C2—N5—N6—C3 0.5(1), C3—N7—C2—N5 0.7(2), C3—N7—C2—N8 179.2(1), N6—N5—C2—N7 -0.8(2), N6—N5—C2—N8 179.4(1), O1—N8—C2—N7 3.4(2), O2—N8—C2—N7 -175.7(1); selected hydrogen bonds: symmetry codes: (i) 1-x, -y, -z ; (ii) 0.5+x, 0.5-y, -0.5+z.

BHT-(BT) 2 H_2O crystallizes in the triclinic space group P–1 with 2 formula units per unit cell. The unit cell has the dimension of a = 0.77949(8) nm, b = 0.92606(10) nm,

c = 0.99301(12) nm, α = 117.382(12)°, β = 90.858(9)° and γ = 97.500(9)°. It crystallizes with a cell volume of 0.62876(12) nm^3 and a density of 1.671 g cm^{-3} at a temperature of 173 K.

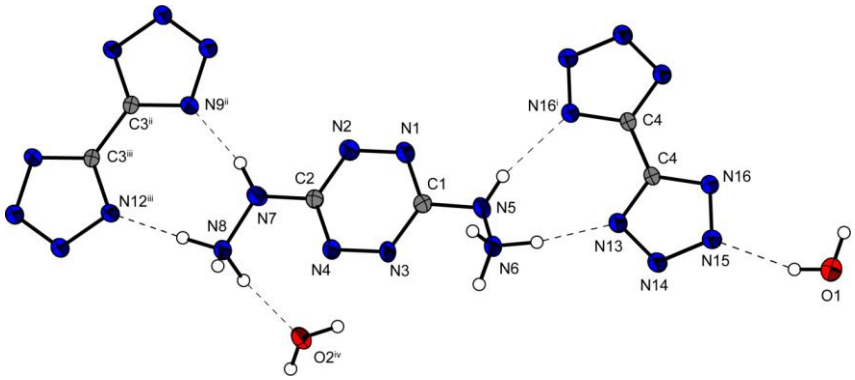


Figure 5: Molecular unit of **6**; the non-hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. **Selected bond lengths** [nm]: N1—N2 0.1328(2), N1—C1 0.1350(3), N2—C2 0.1348(3), N4—N3 0.1324(2), N4—C2 0.1343(3), N3—C1 0.1338(3), N5—C1 0.1369(3), N5—N6 0.1438(3); **Selected bond angles** [°]: N2—N1—C1 117.6(12), N1—N2—C2 116.6(2), N3—N4—C2 117.4(2), N4—N3—C1 117.4(2), C1—N5—N6 114.6(2), N6—N5—H5 109.1(2), N5—N6—H6C 102.4(2), N5—N6—H6B 110.7(2), H6C—N6—H6B 116.3(2), N5—N6—H6A 108.7(2); **Selected torsion angles** [°]: C1—N1—N2—C2 0.8(3), C2—N4—N3—C1 0.3(3), N4—N3—C1—N1 1.1(3), N2—N1—C1—N5 174.3(2), N6—N5—C1—N3 -31.0(3), N6—N5—C1—N1 152.7(2), N3—N4—C2—N2 -1.0(3), N1—N2—C2—N4 0.5(3), N8—N7—C2—N4 -13.8(3), N8—N7—C2—N2 167.8(2); selected hydrogen bonds: O1—H12···N15 (0.084(5), 0.210(4), 0.2902(3) nm, 159.0(4)°); N5—H5···N16^{i} (0.085(3), 0.205(3), 0.2874(3) nm, 165.0(3)°; N6—H6C···N13 (0.099(3), 0.186(3), 0.2836(4) nm, 172.0(3)°; symmetry codes: (i) 1-x, 1-y, 1-z; (ii) x, 1+y, z; (iii) 1-x, 2-y, -z; (iv) 1-x, 1-y, -z.

5.4 Thermodynamics and energetic properties

5.4.1 Sensitivity data and thermal stabilities

Differential scanning calorimetric measurements to determine the decomposition temperatures ($T_{Dec.}$) of **1**-**9** were performed in sealed Al-containers, with a hole (0.1 mm) for gas release, with a nitrogen flow of 20 ml min^{-1} on a Linseis PT-10 DSC calibrated with standard pure indium and zinc at a heating rate of 5 K min^{-1}. Compounds **1**-**9** were also tested for their sensitivities towards impact (IS), friction (FS) and electrostatical discharge (ESD). The sensitivity data of compounds **1**-**9** and their thermal stabilities are shown in Table 2.

Table 2: Sensitivity data and thermostability of compound **1**-**9**

	IS [J] [a]	*FS [N]* [b]	*ESD [J]* [c]	$T_{dec.}$ *[°C]* [d]
1	30	>360	>1.0	140
2	35	>360	0.80	170
3	4	120	0.10	104

	IS [J] [a]	*FS [N]* [b]	*ESD [J]* [c]	$T_{dec.}$ *[°C]* [d]
1	30	>360	>1.0	140
2	35	>360	0.80	170
4	10	96	0.10	165
5	2	24	0.10	176
6	15	360	0.40	126
7	10	260	0.40	145
8	20	>360	0.50	150
9	8	252	0.15	217
RDX[21]	7.5	160	0.1	210

[a] impact sensitivity (BAM drophammer, 1 of 6); [b] friction sensitivity (BAM friction tester 1 of 6); [c] electrostatic discharge device, [d] decomposition temperature [°C]

The thermal stabilities of compounds **2**-**9** strongly depend on the acidity of the corresponding acid. When strong acids are used the thermal stabilities are enhanced (**2**, **4**, **5**, **9**). Interestingly compounds **3**, **6** and **7** suffer from low thermal stability. **5** is the most sensitive compound towards external stimuli (IS 2 J, FS 24 N). Due to their crystallization without crystal water, only the detonation parameters of **5** and **9** were calculated using the EXPLO5 V.5.05 code and the measured low temperature X-ray densities. The energies of formation, which are needed for the EXPLO5 input, were calculated to be 2058 $kJ \cdot kg^{-1}$ (**5**) and 582 $kJ \cdot kg^{-1}$ (**9**). Table 3 shows the CBS-4M calculation results and the molecular volumes, and Table 4 shows the detonation parameters of **5** and **9** in comparison to RDX. Although **5** has a quite high enthalpy of formation ($\Delta_f Hm°$), the detonation pressure of **5** is ~20% lower than that of RDX. Its detonation velocity is only 5% lower. Nevertheless **5** is too sensitive and its thermal stability is not high enough to be considered as a potential RDX replacement. **9**, which is the most stable BHT salt mentioned here, has the highest density. Unfortunately its detonation parameters are lower in comparison to RDX, due to its low heat of formation.

5.4.2 Heats of formation and detonation parameters

Solid state heats of formation ($\Delta_f H°(s,M)$) were calculated with the atomization method (Equation 1) using CBS-4M enthalpies (computed by Gaussian09W.A.02[28]) and summarized in Table 3.[29] The gas phase enthalpies of formation $\Delta H_m(g)$ were converted into the solid state enthalpies of formation ($\Delta H_m(s)$) either by using Jenkins' equations for X2+Y2- and X2+Y2- salts [30] (for ionic derivatives) or Trouton's rule [31] (Equation 1).

$$\Delta_f H°(g, M, 298) = H(M, 298) - \Sigma H°(Atoms, 298) + \Sigma \Delta_f H°(Atoms, 298) \quad (1)$$

Table 3: CBS-4M calculation results and molecular volumes.

M	$-H^{298}$ / a.u.	$\Delta_f H°$(g,M) / kJ mol^{-1}	V_M / nm^3	$\Delta_f H°$(s,M) / kJ mol^{-1}
BHT	516.99351	654.7		577.0
$BHTI^{2+}$	517.532665	101.6		
NT^-	461.705513	2307.0		
$TNBI^{2-}$	1266.677508	–33.9		
5		2268.7	0.352	762.3
9		2031.5	0.454*	353.0

* recalculated from K_2TNBI and $BHT \cdot 2HCl \cdot 2H_2O$ ($V_m(Cl^-)$=0.028 nm^3, $V_m(H_2O)$=0.024 nm^3, $V_m(K^+)$=0.01 nm^3)[30a].

Lastly, the molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid state energies of formation (ΔU_m) according to equation (2) (Table 2).

$$\Delta U_m = \Delta H_m - \Delta n\, RT \quad (2)$$

(Δn being the change of moles of gaseous components)

Table 4: Energetic properties of compounds **5** and **9** in comparison to RDX.

	5	**9**	**RDX**
Formula	$C_4H_8N_{18}O_4$	$C_8H_8N_{16}O_8$	$C_3H_6N_6O_6$
FW / g mol^{-1}	372.10	456.07	222.12
IS / J [a]	2	8	7.5
FS / N [b]	24	252	120
ESD / J [c]	0.10	0.15	0.1-0.2
N / % [d]	67.73	49.12	37.8
Ω / % [e]	–34.38	–42.08	–21.6
$T_{Dec.}$ / °C [f]	176	217	210
ρ / g cm^{-3} [g]	1.75 (X-ray), 1.722 [o]	1.84 (pyc.)	1.80 [32]
$\Delta_f H_m°$ / kJ mol^{-1} [h]	762.3	353.0	70.0 [32]
$\Delta_f U°$ / kJ kg^{-1} [i]	2057.9	860.6	410.0
EXPLO5.05 values:			
$-\Delta_{Ex}U°$ / kJ kg^{-1} [j]	4601, 4599 [p]	4594	6125

T_{Det} / K [k]	3519, 3540 [p]	3515	4236
P_{CJ} / kbar [l]	290, 279 [p]	295	349
$V_{Det.}$ / m s^{-1} [m]	8409, 8300 [p]	8257	8748
V_o / L kg^{-1} [n]	779, 779 [p]	685	739

[a] impact sensitivity (BAM drophammer, 1 of 6); [b] friction sensitivity (BAM friction tester 1 of 6); [c] electrostatic discharge device, [d] nitrogen content; [e] oxygen balance; [f] decomposition temperature from DSC (β = 5°°C/min); [g] from X-ray diffraction; [h] calculated heat of formation; [i] energy of formation; [j] energy of Explosion; [k] explosion temperature; [l] detonation pressure; [m] detonation velocity; [n] assuming only gaseous products, [o] extrapolated to RT by the formula, $\rho_{298K} = \rho_{T(0)} / [1+\alpha_v(298-T_0)]$, $\alpha_v = 1.50 \cdot 10^{-4}$ K^{-1}.[33]; [p] RT values.

5.5 Experimental section

Raman spectra were recorded with a Bruker MultiRAM FT-Raman fitted with a liquid nitrogen cooled, germanium detector and a Nd:YAG laser (λ = 1064 nm), and infrared spectra were measured with a Perkin-Elmer Spectrum BX-FTIR spectrometer equipped with a Smiths DuraSampl*IR* II ATR device. All spectra were recorded at ambient temperature, the samples being in the solid state. ^{1}H decoupled ({^{1}H}) NMR spectra were recorded at 25 °C with a JEOL Eclipse 400 ECX instrument, and chemical shifts were determined with respect to external Me4Si (^{1}H, 400.2 MHz; ^{13}C, 100.6 MHz), $MeNO_2$ (^{14}N, 29.0 MHz). Mass spectrometric data were obtained with a JEOL MStation JMS 700 spectrometer (FAB+/FAB-) using glycerol as the matrix. Elemental analyses (C/H/N) were performed with an Elementar Vario EL analyzer. Melting points were determined in capillaries with a Büchi Melting Point B-540 instrument and are uncorrected. Decomposition points were determined by Differential Scanning Calorimetry (DSC) measurements with a Linseis DSC-PT10, using a heating rate of 5 °C·min^{-1}. Pycnometric measurements were carried out with a Quantachrome helium gas pycnometer. Quantum chemical calculations were performed with the Gaussian09 software. Sensitivity data (impact and friction) were performed using a drophammer and friction tester analogous to BAM (Bundesanstalt für Materialforschung und Prüfung). Electrostatic sensitivities were measured with an OZM small scale electrostatic discharge tester.[34-42]

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

3,6-bishydrazino-1,2,4,5-tetrazinium dichloride dihydrate (BHT · 2 HCl · 2 H_2O) (**2**):

1 (14.2 g, 100 mmol) was suspended in 150 ml methanol and hydrochloric gas was bubbled through the suspension at 0 °C until a solution was obtained. Additional 10 min of HCl

injection results in precipitation of anhydrous **2**. Subsequently, the mixture was stirred for 1 h at 0 °C. The precipitate was filtered and washed with methanol. Afterwards **2** was recrystallized out of 2-propanol/water under reflux. Subsequently the solution was left to stand overnight at 4 °C in the fridge and single crystals of **2** could be isolated. **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 170 °C; **EA** found (calc): C 9.52 (9.57), H 4.56 (4.82), N 44.90 (44.63); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 6.75 (s, br, 6H, NH_3), 10.75 (s, 2H, NH);**{^{1}H}^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ = 162.8 (2C, C_q tetrazine), **Sensitivities**: **IS**: > 35.00 J; **FS**: > 360 N; **ESD**: 0.80 J.

3,6-bishydrazino-1,2,4,5-tetrazinium 5,5‘-azotetrazolate dihydrate (BHT(ATZ) · 2 H_2O) (**3**):

Bis-potassium 5,5’-azotetrazolate pentahydrate (1.32 g, 3.98 mmol) was dissolved in 20.0 ml water. This solution was added to a stirring solution of 3,6-bishydrazinium-1,2,4,5-tetrazine dichloride dihydrate (1.00 g, 3.98 mmol) in 20.0 ml water. The mixture was stirred at ambient temperature and stored at 5 °C over night. Afterwards the crystals were filtered off and dried, yielding (1.17 g 90 %) light red needles of (**3**). **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 104 °C; **EA** found (calc)**:** C 13.62 (13.96), H 3.46 (3.51), N 72.93 (73.24); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 6.71 (s, br, 6H, NH_3), 10.70 (s, 2H, NH); **{^{1}H}^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ = 162.8 (2C, C_q tetrazine), 171.0 (2C, C_q azotetrazolate); **Raman** [cm^{-1}]: $\tilde{\nu}$ = 1491 (49), 1423 (9), 1393 (100), 1100 (36), 1078 (6), 917 (5); **IR** (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3554 (m), 3166 (br, m), 1644 (s), 1567 (s), 1526 (s), 1430 (s), 1400 (vs), 1314 (s), 1254 (m), 1210 (s), 1180 (s), 1166 (w), 1087 (s), 1042 (vs), 926 (vs), 875 (s), 776 (s), 740 (vs), 682 (vs); **Mass spec**.: (FAB (-) m/z): 165.2 (12) [$C_2HN_{10}^-$], 257.4 (10) [$(Gly)_1 + C_2H_2N_{10}$], 349.5 (5) [$(Gly)_3 + C_2N_{10}^{2-}$]; **Sensitivities**: **IS**: > 4.00 J; **FS**: > 120 N; **ESD**: 0.10 J.

3,6-bishydrazino-1,2,4,5-tetrazinium bis-(3,5-dinitro-triazolate) dihydrate (BHT-(DNT)$_2$ · 2 H_2O) (**4**):

Triethylammonium 3,5-dinitro-1,2,4-triazolate (2.07 g, 7.98 mmol) was dissolved in 20.0 ml water. This solution was added to a stirring solution of 3,6-bishydrazinium-1,2,4,5-tetrazine dichloride dihydrate (1.00 g, 3.98 mmol) in 20.0 ml water. The mixture was stirred at ambient temperature and stored at 5 °C over night. Afterwards the crystals were filtered off and dried, yielding (1.78 g 90 %) dark orange needles of **4**. **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 165 °C; **EA** found (calc): C 14.76 (14.52), H 2.39 (2.44), N 50.19 (50.80); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 6.65 (s, br, 6H, NH_3), 10.68 (s, 2H, NH); **{^{1}H}^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ =161.7 (2C, C-NO_2), 163.3 (. 2C, C_q tetrazine); **^{14}N NMR** ([D_6]DMSO, 25 °C, ppm): δ = – 22 (2N, -NO_2); **Raman** [cm^{-1}]: $\tilde{\nu}$ = 1544 (4), 1493 (3), 1405 (100), 1354 (14), 1312 (2), 1303 (2), 1139 (63), 1022 (5), 872 (7), 833 (7), 770 (3), 685 (2), 299 (3); **IR (**ATR, cm^{-1}): $\tilde{\nu}$ = 3467 (m), 3246 (w), 1675 (w), 1604 (br, s), 1554 (s), 1528 (s), 1492 (vs), 1428 (s), 1385 (vs), 1350 (s), 1311

(m), 1301 (s), 1257 (m), 1142 (s), 1056 (s), 945 (s), 848 (vs), 832 (s), 756 (m); **Mass spec**.: (FAB (-) m/z): 142.0 (10) [$C_2N_5O_3^-$], 158.0 (86) [$C_2N_5O_4^-$], 250.0 (14) [$(Gly)_1$ + $C_2HN_5O_4$], 311.0 (15) [$(Gly)_{1.7}$ + $C_2N_5O_4^-$], 342.0 (3) [$(Gly)_2$ + $C_2HN_5O_4$], 463.0 (3) [$(Gly)_{3.3}$ + $C_2N_5O_4^-$]; **Sensitivities: IS**: > 10.0 J; **FS**: > 96.0 N; **ESD**: 0.10 J. 2C, C_q tetrazine.

3,6 Bishydrazino 1,2,4,5-tetrazinium bis-(5-nitrotetrazolate) (BHT-$(NT)_2$) (**5**):

Ammonium 5-nitrotetrazolate · 0.5 H_2O (1.12 g, 7.97 mmol) was dissolved in 20.0 ml water. This solution was added to a stirring solution of 3,6-bishydrazinium-1,2,4,5-tetrazine dichloride dihydrate (1.00 g, 3.98 mmol) in 20.0 ml water. The mixture was stirred at ambient temperature and stored at 5 °C over night. Afterwards the crystals were filtered off and dried, yielding (1.26 g 85 %) yellow needles of **5**. **DSC** (5 °C min^{-1}): T_{Dec} = 176 °C; **EA** found (calc): C 13.26 (12.91), H 2.19 (2.17), N 66.79 (67.73); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 6.76 (s, br, 6H, NH_3), 10.73 (s, 2H, NH); **{^{1}H}^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ =162.7 (2C, C_q tetrazine), 169.2 (2C, C-NO_2); **Raman** [cm^{-1}]: $\tilde{\nu}$ = 1914 (7), 1772 (7), 1627 (7), 1559 (9), 1495 (9), 1464 (5), 1422 (95), 1327 (8), 1072 (63), 876 (24), 835 (12), 774 (10), 459 (11), 314 (8); **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 3194 (w), 3140 (w), 1566 (s), 1546 (vs), 1506 (w), 1452 (s), 1422 (vs), 1340 (m), 1318 (vs), 1238 (w), 1211 (m), 1189 (m), 1176 (m), 1107 (m), 1060 (s), 945 (s), 835 (vs), 774 (w), 731 (w), 664 (s); **Mass spec**.: (FAB (–) m/z): 114.2 (26) [$CN_5O_2^-$], 206.4 (12) [$(Gly)_1$ + CHN_5O_2]; **Sensitivities**: **IS**: > 2.00 J; **FS**: > 24 N; **ESD**: 0.10 J.

3,6-bishydrazino-1,2,4,5-tetrazinium 5,5'-bistetrazolate dihydrate (BHT(BT)·2 H_2O) (**6**):

Bis-potassium 5,5'-bistetrazolate (0.96 g, 3.98 mmol) was dissolved in 20.0 ml water. This solution was added to a stirring solution of 3,6-bishydrazinium-1,2,4,5-tetrazine dichloride dihydrate (1.00 g, 3.98 mmol) in 20.0 ml water. The mixture was stirred at ambient temperature and was stored at 5 °C over night. Afterwards the crystals were filtered off and dried, yielding (1.01 g 80 %) dark red needles of 3,6-bishydrazinium-1,2,4,5-tetrazine 5,5'-bistetrazolate dihydrate. **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 126 °C; **EA** found (calc): C 15.65 (15.29), H 3.71 (3.82), N 70.14 (70.87); **^{1}H NMR**([D_6] DMSO, 25 °C, ppm): δ = 6.93 (br, s, 6H, NH_3), 10.59 (s, 2H, NH); **{^{1}H}^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ = 150.6 (2C, C_q tetrazolate), 162.6 (2C, C_q tetrazine) ; **Raman** [cm^{-1}]: $\tilde{\nu}$ = 1587 (99), 1490 (20), 1221 (12), 1120 (25), 1095 (14), 865 (30), 417 (8); **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 3544 (m), 3313 (br, m), 3150 (br, m), 1542 (s), 1471 (s), 1408 (s), 1327 (s), 1306 (s), 1269 (m), 1202 (m), 1188 (m), 1142 (m), 1112 (w), 1086 (vw), 1051 (s), 1027 (s), 950 (vs), 853 (br, m), 804 (w), 732 (s), 665 (vs); **Mass spec**.: (FAB (+) m/z): 143 (5) [$C_2H_7N_8^+$]; (FAB (–) m/z): 137.2 (68) [$C_2HN_8^-$], 275.4 (16) [(2 $C_2H_2N_8$]; **Sensitivities**: **IS**: > 15 J; **FS**: > 360 N; **ESD**: 0.40 J.

3,6-bishydrazino-1,2,4,5-tetrazinium 5,5'bis-tetrazolyl-amine (BHT-BTA) (**7**):

Bis-potassium 5,5'-bistetrazolyl-amine (0.91 g, 3.98 mmol) was dissolved in 20.0 ml water. This solution was added to a stirring solution of 3,6-bishydrazinium-1,2,4,5-tetrazine dichloride dihydrate (1.00 g, 3.98 mmol) in 20.0 ml water. While stirring of the mixture at ambient temperature (**13**) already precipitated as pale-orange powder. Afterwards the powder was filtered off, washed with cold water and dried, yielding (0.96 g 82 %) light orange needles of 3,6-bishydrazinium-1,2,4,5-tetrazine 5,5'bis-tetrazolyl-amine. **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 145 °C; **EA** found (calc): C 16.15 (16.27), H 3.32 (3.07), N 78.55 (80.55); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 6.84 (br, s, 6H, NH_3), 10.64 (s, 2H, NH); **{^{1}H}^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ =154.9 (2C, C_q tetrazole), 163.7 (2C, C_q tetrazine); **Raman** [cm^{-1}]: $\tilde{\nu}$ = 3197 (25), 1574 (15), 1512 (91), 1331 (22), 1122 (14), 1075 (33), 862 (73), 803 (13), 673 (22), 633 (13), 458 (51), 411 (22), 308 (18); **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 3376 (br, m), 3312 (w), 1626 (s), 1561 (m), 1501 (vs), 1418 (s), 1344 (m), 1324 (m), 1278 (w), 1260 (w), 1167 (w), 1138 (m), 1103 (w), 1051 (s), 947 (s), 875 (m), 792 (m), 730 (m), 683 (m); **Mass spec**.: (FAB (–) m/z): 152.2 (18) [$C_2H_2N_9^-$], 244.4 (9) [$(Gly)_1$ + $C_2H_3N_9$],336.5 (4) [$(Gly)_2$ + $C_2H_3N_9$], 428.7 (3) [$(Gly)_3$ + $C_2H_3N_9$]; **Sensitivities**: **IS**: > 10.0 J; **FS**: > 260 N; **ESD**: 0.40 J.

3,6-bishydrazino-1,2,4,5-tetrazinium bis-(3-amino-5-nitro-1,2,4-triazolate) BHT-$(ANTA)_2$ (**8**):

Sodium 3-amino-5-nitro-triazolate (1.20 g, 7.97 mmol) was dissolved in 20.0 ml water. This solution was added to a stirring solution of 3,6-bishydrazinium-1,2,4,5-tetrazine dichloride dihydrate (1.00 g, 3.98 mmol) in 20.0 ml water. While stirring of the mixture at ambient temperature **8** already precipitated as a red solid. Afterwards the crystals were filtered off, washed with cold water and dried, yielding 1.39 g (3.46 mmol, 87 %) a red powder of **8**. **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 150 °C; **EA** found (calc): C 18.27 (18.00), H 3.01 (3.02), N 63.06 (62.99); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 4.60 (s, br, 2H, NH_2), 6.76 (s, 6H, NH_3), 10.53 (s, 2H, NH); **{^{1}H}^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ = 157.9 (2C, C-NH_2) , 161.4 (2C, C-NO_2), 163.9 (2C, C_q tetrazine); **Raman** [cm^{-1}]: $\tilde{\nu}$ = 3235 (5), 3218 (16), 1653 (14), 1553 (12), 1518 (27), 1426 (15), 1381 (100), 1305 (17), 1136 (23), 1019 (18), 870 (37), 449 (10); **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 3396 (s), 3346 (s), 3316 (s), 3259 (w), 3230 (m), 3209 (m), 1590 (s), 1558 (s), 1536 (w), 1518 (vs), 1464 (w), 1422 (s), 1379 (s), 1305 (vs), 1281 (m), 1160 (s), 1133 (s), 1089 (m), 1064 (m), 1025 (w), 1003 (s), 946 (vs), 850 (m), 837 (s), 758 (w), 751 (s), 724 (vs); **Mass spec**.: (FAB (–) m/z): 128.0 (9) [$C_2H_2N_5O_2^-$], 220.3 (7) [$(Gly)_1$ + $C_2H_3N_5O_2$], 282.0 (5) [$(Gly)_{1.7}$ + $C_2H_3N_5O_2$] 312.6 (4) [$(Gly)_2$ + $C_2H_3N_5O_2$]; **Sensitivities**: **IS**: > 20.0 J; **FS**: > 360 N; **ESD**: 0.50 J.

3,6-bishydrazino-1,2,4,5-tetrazinium 4,4‘,5,5‘-tetranitro-2,2‘-bisimidazolate BHT-TNBI (**9**):

4,4',5,5'-tetranitro-2,2'-bisimidazole dihydrate (1.39 g, 3.98 mmol) was dissolved in 20.0 ml water. This solution was added to a stirring solution of 3,6-bishydrazino-1,2,4,5-tetrazine (0.57 g, 3.98 mmol) in 20.0 ml water. While stirring of the mixture at ambient temperature **9** already precipitated as orange powder. Afterwards **(9)** was filtered off, washed with cold water and dried, yielding 1.69 g (3.70 mmol, 93 %) orange powder of 3,6-bishydrazinium-1,2,4,5-tetrazine 4,4‘,5,5‘-tetranitro-2,2‘-bisimidazolate. **DSC** (5 °C min^{-1}): T_{Dec} = 217 °C; **EA** found (calc): C 21.24 (21.06), H 1.54 (1.77), N 48.04 (49.12); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 6.89 (s, br, 6H, NH_3), 10.50 (s, br, 2H, NH); **{^{1}H}^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ =139.9 (2C, C_q TNBI), 142.3 (4C, C-NO_2), 162.9 (2C, C_q tetrazine); **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 3204 (m), 3128 (w), 1593 (m), 1544 (s), 1494 (s) 1464 (s), 1392 (vs), 1362 (br, s), 1311 (vs), 1273 (s), 1226 (br, vs), 1117 (s) 1092 (m), 1050 (s), 942 (s), 854 (s), 839 (w), 810 (vs), 754 (s), 700 (s); **Sensitivities**: **IS**: > 8.00 J; **FS**: > 252 N; **ESD**: 0.15 J.

5.6 Conclusions

- Highly energetic salts using BHT as two times charged cation can be synthesized in high yields.
- Crystal structures of compound **2**,**3**,**4**,**5**,**6** could be determined by low temperature X-ray diffraction
- All here mentioned compounds were fully characterized towards thermostability and sensitivities towards impact, friction and electrostatical discharge
- BHT bis-(5-nitrotetrazolate) (**5**) shows the best calculated detonation parameters (e.g. V_{det} = 8409 m s^{-1}) but is too sensitive and decomposes already at 176 °C
- BHT tetranitrobisimidazolate (**9**) has the highest thermo stability (217 °C) but shows much lower calculated detonation parameters (V_{det} = 8257 m s^{-1}) in comparison to RDX.

5.7 References

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6. PUBLICATION D

Thermally Stable 3,6-Disubstituted 1,2,4,5-Tetrazines

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Z. Naturforsch. **2013**, *68B*, 1310–1320.

6.1 Abstract

Several 3,6-disubstituted 1,2,4,5-tetrazines were synthesized by nucleophilic substitution using 3,6-bis-(3,5-dimethyl-pyrazol-1-yl)-1,2,4,5-tetrazine and 3,6-dichloro-1,2,4,5-tetrazine as electrophiles. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR and vibrational spectroscopy, mass spectrometry and elemental analysis (C,H,N). For analysis of the thermostabilty, differential scanning calorimetry (DSC) was used. Especially, the symmetrically bis-3,5-diamino-1,2,4-triazolyl-substituted derivative shows a very high thermal stability up to 370 °C. Therefore its energetic properties were determined and compared with thoses of hexanitrostilbene (HNS). The crystal structures of 3,6-bishydrazino-1,2,4,5-tetrazine, 3,6-dichloro-1,2,4,5-tetrazine and 3-amino-6-(3,5-diamino-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine dihydrate have been determined by low-temperature X-ray-diffraction.

6.2 Introduction

1,2,4,5-Tetrazines, also known as *s*-tetrazines, have been first synthesized by Pinner in 1893.[1] They have attracted attention of scientists in various fields of research: theoretical chemistry,[2] coordination chemistry,[3] pharmaceutical chemistry,[4] and natural products chemistry[5] amongst others. Research for special applications of this compound class includes anti-corrosion agents[6] and sensors.[7,8] A detailed review of the recent advantages and applications of *s*-tetrazine chemistry in general is given by Saracoglu *et al.*.[9] The properties of *s*-tetrazines are directly related to their electronic structure. Waluk *et al.*[10] have provided a simple model for the qualitative MO-analysis of *s*-tetrazines. A further interesting field of research are the energetic properties of 1,2,4,5-tetrazines, namely for secondary explosives, propellants and low smoke pyrotechnical fuels. Especially gun powder mixtures benefit from nitrogen-rich compounds. To get rid of the widely known problems of barrel corrosion in gun and rocket propellant systems, thermally stable compounds with low carbon and high nitrogen content are of great interest.[11,12] The main contributors to the chemistry of energetic *s*-tetrazines have been Chavez and Hiskey from the Los Alamos National Laboratory in New Mexico, USA.[13-16] Thermally stable secondary explosives are widely

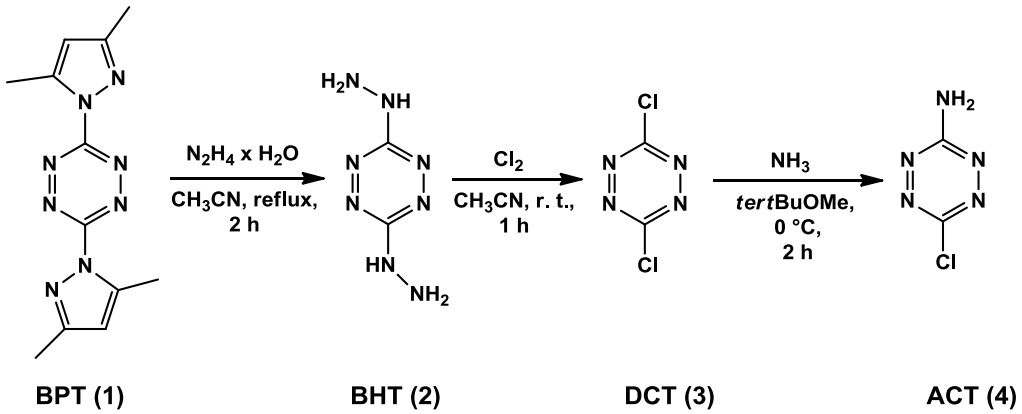
needed for special applications such as drilling deep oil-wells and space exploration. The research on heat-resistant explosives was reviewed e. g. by Urbanski and Vasudeva,[17] Agrawal[18] and Sikder.[19] The state of the art reference in these applications is HNS (hexanitrostilbene), which is easily synthesized by oxidation of TNT (2,4,6-trinitro-toluene) and is stable up to 318 °C.

In the work reported herein, further nitrogen-rich substituted 1,2,4,5-tetrazines were investigated. Especially the 3,6-bis-(3,5-diamino-triazol-1-yl)-1,2,4,5-tetrazine derivative (**8**) is of great interest because of its high thermostability and high weight percentage of nitrogen content. The detonation parameters of **8** were determined using the EXPLO5 V.5.05 and V 6.01 computer code and compared with those calculated for HNS. Crystal structures of 3,6-bishydrazino-1,2,4,5-tetrazine (**2**), 3,6-dichloro-1,2,4,5-tetrazine (**3**) and 3-amino-6-(3,5-diamino-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (**9**) were determined by low-temperature X-ray diffraction.

6.3 Results and discussion

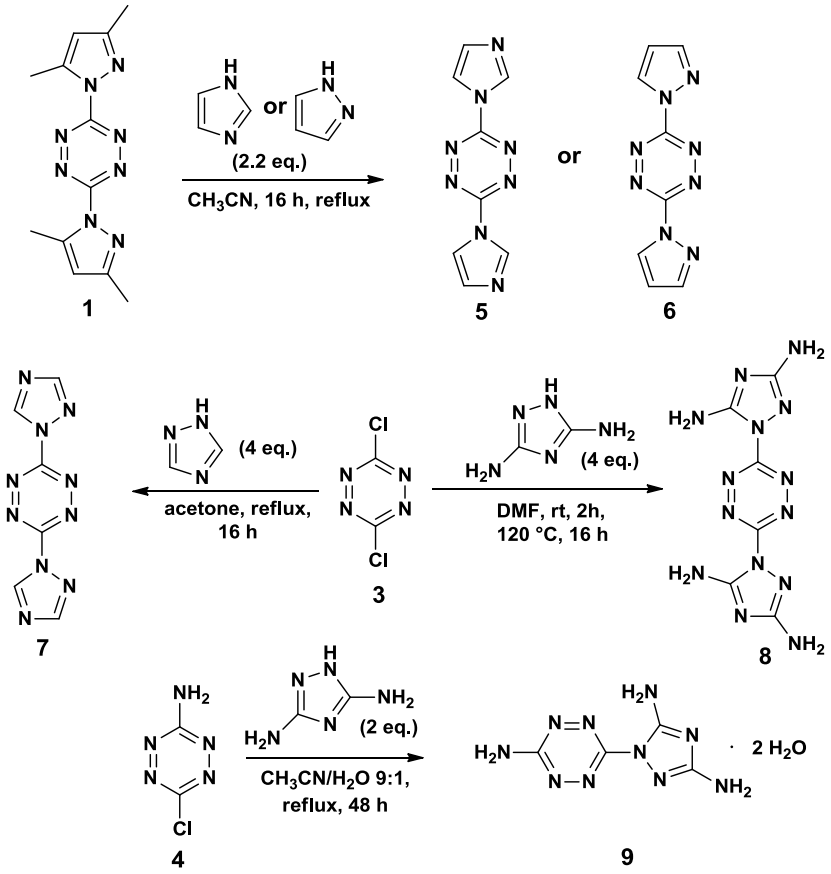
6.3.1 Syntheses

Scheme 1 illustrates already known syntheses of the commonly used 1,2,4,5-tetrazines, on which nucleophilic substitution reactions were carried out.[13-16]



Scheme 1: Known syntheses of 1,2,4,5-tetrazines **1**-**4**.

After preparing these four precursors (**1**-**4**), as described in literature, we tested nucleophilic substitutions using imidazole, pyrazole, triazole, and 3,5-diamino-triazole. Compound **3** is not long time stable on air. However, solutions in acetonitrile (0.6 M) proved to be stable at 4 °C for about one month. The purity of this solution was established by ^{13}C NMR in $CDCl_3$, in which only one signal at 168.4 ppm of (**3**) and those of acetonitrile (1.9 and 117.6 ppm) occured. The investigated substitution reactions are illustrated in Scheme 2.



Scheme 2: Nucleophilic substitutions on 1,2,4,5-tetrazine precursors.

The reaction of **1** with imidazole yielded **5**, carried out already by Russian researchers.[20] Pyrazole has not been used yet, so we successfully obtained **6** using the same reaction conditions. Remarkably, no reaction occurred when triazole was used as the nucleophile in this reaction. In contrast to this result, when **3** is used as electrophile the yield of compound **7** is about 80 %. For this reaction the choice of the solvent is important. If only acetonitrile is used, no reaction occurs at all. Therefore an excess of acetone (10:1) was used in this reaction. All three compounds **5**, **6** and **7** precipitated during the reaction as fine orange powders. To enhance the thermostability of these symmetrically 3,6-disubstituted 1,2,4,5-tetrazine derivatives we also repeated the reaction with 3,5-diamino-1,2,4-triazole as nucleophile. Using **1** as electrophile only the mono-substituted product was obtained, which is not interesting for our applications, because of its high carbon content. The reactivity of 1,2,4,5-tetrazines in this type of processes was investigated comprehensively by Hungarian researchers in 2003.[21] The reaction of **3** with 3,5-diamino-1,2,4-triazole results only in the disubstituted product **8**. We also tried the reaction of 3,5-diamino-triazole with 3-amino-6-chloro-tetrazine (**4**) as electrophile. This reaction gave compound **9** in 72 % yield. We always used four equivalents of the nucleophile, if **3** was used as electrophile. Chavez *et al.* already described that the reaction of **3** with four equivalents 3-azido-1,2,4-triazole gave two equivalents of 3-azido-1,2,4-triazolium hydrochloride as a side product. That means that two

molecules HCl are intercepted by the nucleophile used itself.[22] This hydrochloride species of the used nucleophile also precipitated in the reaction but could be removed by washing the crude compound with an excess of water. We also used more electron deficient nucleophiles like 3-nitro-1,2,4-triazole, 3,5-dinitro-1,2,4-triazole and 5-nitro-tetrazole, but none of these reacted with 1,2,4,5-tetrazines as electrophiles. The crystal structures of compounds **2**, **3** and **9** were determined by low-temperature X-ray diffraction.

6.3.2 Crystal structures

Single crystals suitable for XRD were obtained of **2**, **3** and **9**. Selected data and parameters from the low-temperature (173 K) X-ray data collection and refinements are given in Table 1. Further information regarding the crystal structure determinations have been deposited with the Cambridge Crystallographic Data Centre[23] as supplementary publication nos. 948331 (**2**), 948330 (**3**), 948329 (**9**).

Table 1: Crystallographic data of compounds **2**, **3** and **9**.

Compound	**2**	**3**	**9**·2 H_2O
Formula	$C_2H_6N_8$	$C_2Cl_2N_4$	$C_4H_{10}N_{10}O_2$
M_r, g mol^{-1}	142.15	150.95	230.19
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/c$	*Pbca*	*Pbca*
Color, habitus	red block	orange block	red needle
Crystal Size mm	0.2 × 0.1 × 0.05	0.19 × 0.22 × 0.23	0.14 × 0.18 × 0.30
a, *b*, *c* Å	4.0439(6), 5.6448(7), 12.129(2)	6.4884(7), 5.6381(7), 14.0048(14)	16.175(3), 6.6357(15), 17.625(3)
β, deg	99.124(15)	90	90
V, Å^3	272.91(7)	512.33(10)	1891.8(7)
Z	2	4	8
$\rho_{calc.}$, g cm^{-3}	1.73	1.96	1.62
μ, mm^{-1}	0.1	1.1	0.1
F(000), e	148	296	960
$\lambda_{MoK\alpha}$, Å	0.71073	0.71073	0.71073
T, K	173	173	173
θ Min–Max, deg	4.95; 33.34	4.28, 26.00	4.43, 26.00
Dataset	−5:5; −7:6; −15:10	−8:7; −6:6; −9:17	−18:19; −8:8; −19:21
Reflections collected	1459	2336	8937
Independent refl.	594	501	1851
R_{int}	0.068	0.037	0.066
Observed reflections	390	361	1327
Parameters	59	37	185
R_1 (obs.)	0.0435	0.0259	0.0717
wR_2 (all data)	0.1038	0.0627	0.1013
S	0.887	0.881	1.033
Resd. dens., e Å^{-3}	–0.24, 0.28	–0.12, 0.24	–0.24, 0.20
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan	multi-scan
CCDC number	948331	948330	948329

Single crystals of **2** in the form of small red blocks were grown from an acetonitrile/water mixture. The compound crystallizes in the monoclinic space group $P2_1/c$ with 2 formula units per unit cell and a density of 1.730 g cm^{-3}. Fig. 1 shows the molecular unit of compound (**2**) with its center of inversion in the middle of the tetrazine moiety. The packing of the molecules is directed by three N–H hydrogen bonds involving all of the hydrogen atoms of the hydrazine groups, the strongest being observed between N3 and N4^{ii} (N3–H3···N4^{ii}, 0.88(3) Å, 2.12(3) Å, 2.980(2) Å, 165.3(19)°; (ii) 1−*x*, 0.5+*y*, 0.5−*z*.).

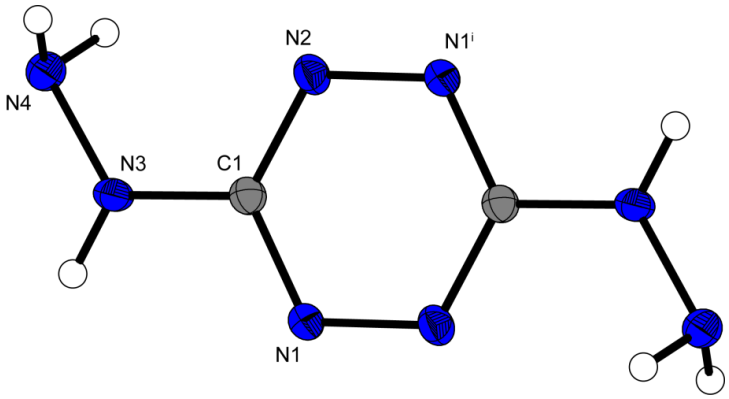


Fig 1: Molecular unit of **2**. The non-hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. **Selected bond lengths** [Å] : N1–N2^{i} 1.328(2), C1–N1 1.352(3), C1–N2 1.344(2), C1–N3 1.355(3), N3–N4 1.418(2); **Selected bond angles** [°]: N2^{i}–N1–C1 117.3(2), N1–C1–N3 116.2(2), N1–C1–N2 124.9(2), C1–N3–N4 121.9(2). Symmetry code: (i) 2−*x*, 2−*y*, −*z*.

Single crystals of **3** were obtained by slow evaporation of a 0.6 M solution in acetonitrile and used for all experiments. **3** crystallizes in the orthorhombic space group *Pbca* with 4 formula units per unit cell and a high density of 1.957 g cm^{-3} at a temperature of 173 K. Again the molecular unit, which is shown in Fig. 2, features a center of inversion.

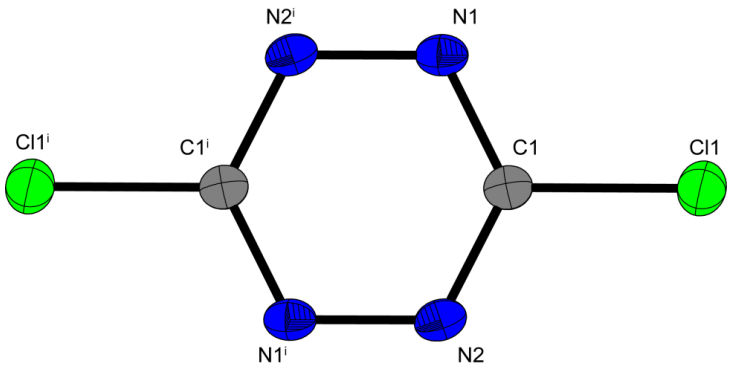


Fig.2: Molecular unit of 3 showing the labeling scheme. Non-hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. **Selected bond lengths** [Å]: Cl1–C1 1.702 (2), N1–N2^{i} 1.324 (2), N1–C1 1.327 (3), N2–C1 1.332 (2); **Selected bond angles** [°]: N1^{i}–N2–C1 116.4(2), N1–C1–N2 127.4(2), N1–C1–Cl1 116.3(2), N2–C1–Cl1 116.3(2). Symmetry code: (i) 1−*x*, 1−*y*, −*z*.

Molecules of **3** are stacked in alternating AB layers (Figure 3A). In these layers A and B the molecules have different orientations. Figure 3B shows a larger section of the wave-like layer structure along the *c* axis. The distance between two molecules lying upon another along the *a* axis is 6.488(3) Å.

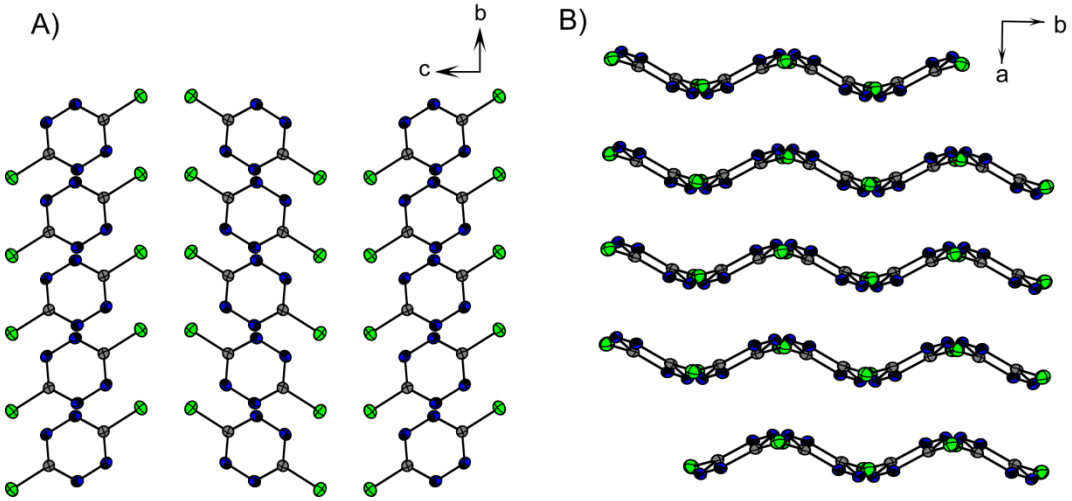


Fig. 3: View on the crystal structure of **3**, A) along the *a* axis, and B) along the *c* axis.

Single crystals of the dihydrate of **9** suitable for XRD were obtained from water. After a concentrated solution was cooled to 4 °C, red needles slowly started to crystallize. Compound **9** crystallizes in the orthorhombic space group *Pbca* with 8 formula units in the unit cell and a density of 1.617 g cm^{-3} (at 173 K). Figure 4 shows an excerpt of four molecules of **9** with respect to the intermolecular hydrogen bond interactions. The corresponding data are presented in Table 2. Combinations of all common (N–H···N, N–H···O, O–H···N and O–H···O) hydrogen donor-acceptor interactions can be observed. Either the amino groups of the triazole and the tetrazine, or the nitrogen atoms of the rings participate in the hydrogen bonding network. In total a wave-like layer structure of the tetrazine molecules is formed. Between the layers of molecules, the water molecules form strong H-bonds, between themselves and the triazole moieties, stabilizing the structure.

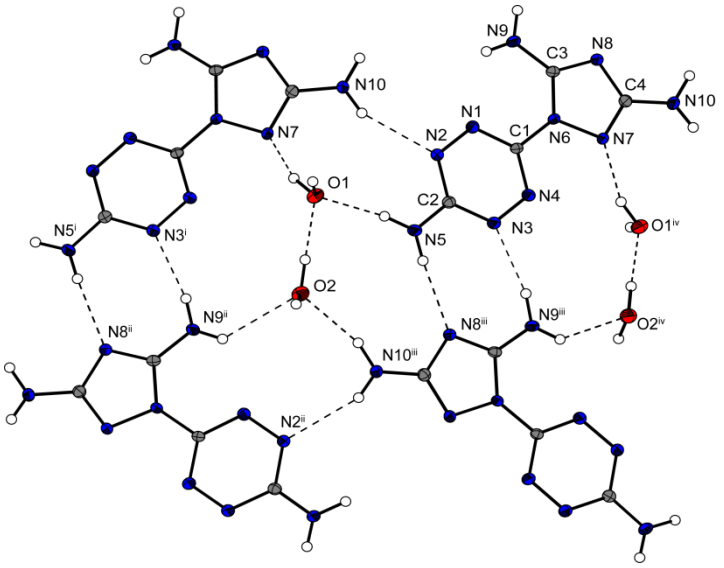


Fig. 4: Intermolecular hydrogen bond interactions in the solid state of **9**. Symmetry codes: (i) *x*, 0.5−*y*, 0.5+*z*; (ii) −0.5+*x*, *y*, 0.5−*z*; (iii) −0.5+*x*, 0.5−*y*, 1−*z*; (iv) *x*, 0.5−*y*, 0.5+*z*.

Table 2: Hydrogen bond interactions in compound **9**[a].

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(D–H···A) (°)
N10^{i}–H10B^{i}···N2	0.87(3)	2.28(3)	3.085(3)	154.(2)
N5–H5B···N8^{iii}	0.87(3)	2.17(3)	3.039(3)	175.(2)
O1–H1A···N7^{i}	0.90(4)	1.97(4)	2.832(2)	162.(3)
N10^{iii}–H10A^{iii}···O2	0.92(2)	2.02(2)	2.909(3)	162.(2)
N9^{iii}–H9A^{iii}···N3	0.92(3)	2.13(3)	3.036(3)	167.(2)
N5–H5A···O1	0.94(3)	2.03(3)	2.969(3)	172.(2)
N9–H9A···N1	0.84(3)	2.25(3)	2.828(3)	126.(2)
N9^{ii}–H9B^{ii}···O2	0.84(3)	2.51(3)	3.136(3)	132.(2)
O2–H2A···O1	0.95(4)	1.80(4)	2.741(3)	171.(3)

[a] Symmetry codes: (i) *x*, 0.5−*y*, 0.5+*z*; (ii) −0.5+*x*, *y*, 0.5−*z*; (iii) −0.5+*x*, 0.5−*y*, 1−*z*.

6.4 Energetic properties and thermal stabilities

6.4.1 Thermal stabilities

Fig. 5 shows the curves of the DSC (differential scanning calorimetry) measurements of compounds **5**-**9** with a heating rate of 5 K/min. In Table 3 the decomposition temperatures are listed in °C. The *1H*-triazole substituted 1,2,4,5-tetrazine (**7**) is about 45 °C more stable than the imidazole derivative **5**. Compound **6** is the only one which decomposes after melting. A significant increase in thermostability can be accomplished by using 3,5-diamino-

1,2,4-triazole as substituent. Both compounds **8** and **9** show a significant increase in thermostability in comparison to all other investigated compounds. Compound **9** is the thermally most stable 1,2,4,5-tetrazine derivative known in the literature. In comparison to the 3,6-bis-(3-amino-5-nitro)-1,2,4,5-tetrazine, synthesized by Coburn *et al.* in 1991, **8** is about 109 °C more stable.[24]

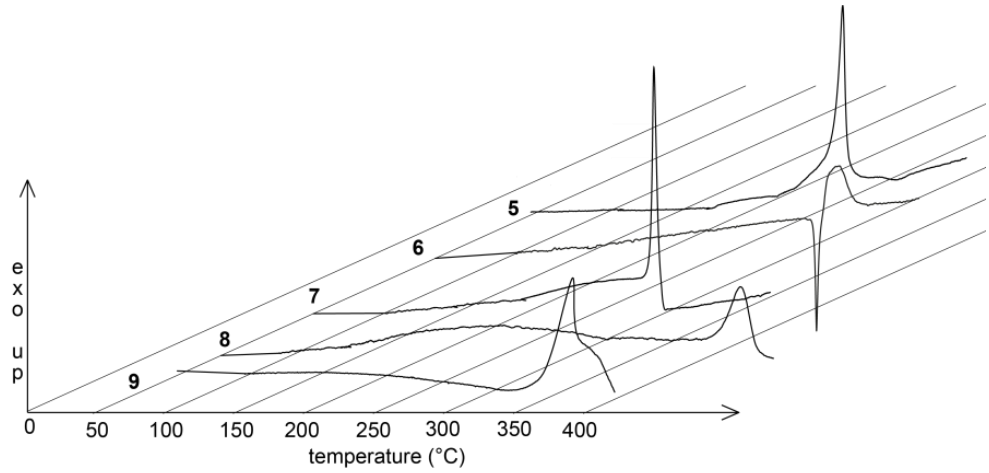


Fig. 5: DSC curves of compounds **5**-**9**.

Table 3: Thermostability data of compounds **5**-**9**.

Compound	$T_{dec.}$ (°C)[a]
3,6-Bis-(1,3-imidazol-1-yl)-1,2,4,5-tetrazine (**5**)	200
3,6-Bis-(1,2-pyrazol-1-yl)-1,2,4,5-tetrazine (**6**)	260
3,6-Bis-(1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (**7**)	245
3,6-Bis-(3,5-diamino-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (**8**)	370
3-Amino-6-(3,5-diamino-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (**9**)	314

a: Onset decomposition temperature at a heating rate of β = 5 K min^{-1}

6.4.2 Energetic properties

Because of the high decomposition temperature of **8** we calculated the enthalpy ($\Delta_f H°$) and energy of formation ($\Delta_f U°$) using the CBS-4M method. Gas phase heats of formation [$\Delta_f H°$(g,M)] were calculated with the atomization method (Eq. 1) using CBS-4M enthalpies (computed by GAUSSIAN09W.A.02.[25–30] The gas phase enthalpies of formation ΔH_m(g) were converted into the solid-state enthalpies of formation [ΔH_m(s)] by using the Trouton rule (**1**).[31, 32]

$$\Delta_f H°_{(g, M, 298)} = H_{(M, 298)} - \sum H°_{(Atoms, 298)} + \sum \Delta_f H°_{(Atoms, 298)} \quad (1)$$

From these values it is possible to calculate the detonation parameters of compound **8** in comparison to HNS, using EXPLO5 V.5.05 and the most recent version V.6.01.[33-35] For this calculation the density of compound **8** (ρ = 1.75 g cm^{-3}) was obtained by pycnometric density measurements. An overview of the energetic properties of compound **8** in comparison to HNS is given in Table 4.

Table 4: Energetic properties of compound **8** in comparison to HNS.

	8	HNS
Formula	$C_4H_8N_{14}$	$C_{14}H_6N_6O_{12}$
M_r, g mol^{-1}	276.24	450.24
IS, J [a]	> 40	5
FS, N [b]	> 360	> 360
ESD, J [c]	> 1	0.3
N, % [d]	70.99	18.67
Ω, % [e]	–92.70	–67.52
$T_{Dec.}$, °C [f]	370	318
ρ, g cm^{-3}	1.75[g]	1.74
$\Delta_f H_m°$, kJ mol^{-1} [h]	707.5	78.3
$\Delta_f U°$, kJ kg^{-1} [i]	2659.4	240.6
EXPLO5 5.05 and 6.01 values		
$-\Delta_{Ex} U°$, kJ kg^{-1} [j]	3039(3052)	5474(5143)
T_{Det}, K [k]	2382(2237)	3982(3681)
P_{CJ}, kbar [l]	227(225)	242(244)
$V_{Det.}$, m s^{-1} [m]	7733(8035)	7446(7612)
V_o, L kg^{-1} [n]	680(740)	530(602)

[a] impact sensitivity (BAM drophammer, 1 of 6); [b] friction sensitivity (BAM friction tester 1 of 6); [c] electrostatic discharge device, [d] nitrogen content; [e] oxygen balance, [f] decomposition temperature from DSC (β = 5°°C / min); [g] from pycnometric measurements at 25 °C and 1 bar; [h] calculated heat of formation; [i] energy of formation; [j] energy of Explosion; [k] explosion temperature; [l] detonation pressure; [m] detonation velocity; [n] assuming only gaseous products.

As can be seen from Table 4 compound **8** has a much higher heat of formation than HNS. This is related to the high content of endothermic N=N and C=N double bonds. HNS, however, consists of six exothermic nitro groups and two benzene moieties with high aromaticity. The densities of **8** and HNS are in the same range. Whereas the two compounds

are insensitive towards friction, HNS decomposes in the BAM drophammer test when impact energies larger than 5 Joules are used. Tetrazine **8** is insensitive towards impact stimulus. Regarding the detonation parameters one can assume that HNS is superior relating to the explosion energy ($\Delta_{Ex}U°$). The most significant values for secondary explosives are the detonation pressure (P_{CJ}), the detonation velocity ($V_{Det.}$), the thermostability ($T_{Dec.}$) and the sensitivities towards external stimuli, as described above. Regarding $V_{Det.}$, P_{CJ} and $T_{Dec.}$, one can assume that compound **8** is superior to HNS.

Low combustion temperatures ($T_{Comb.}$) and a high N_2/CO ratio in the combustion gases are desirable in order to reduce gun barrel erosion problems caused by the formation of iron carbide.[36] State of the art gun propellants are nitrocellulose, mixtures of nitrocellulose and nitroguanidine, and nitroglycerine. Nitrocellulose (12 % nitrogen content) has a combustion temperature of 2310 K but a high content of carbon, what accelerates the wear of gun barrels. Compound **8** has a nitrogen content of 71 % but does not burn completely without residue in the flame. Compound **8** can be used as additive in mixtures with nitroguanidine or nitroglycerine to enhance the nitrogen content of the whole composition.

6.4.3 Small scale shock reactivity test (SSRT)

The SSRT of compound **8** was carried out in comparison to HNS. A defined volume (HNS: 470 mg, density:1.74 g cm^{-3}, **8**: 473 mg, density: 1.75 g cm^{-3}) was pressed into a perforated steel block.[37] This was topped with a commercially available detonator (Orica, DYNADET-C2–0ms). Initiation of the tested explosive resulted in denting a separate aluminum block, which was placed right underneath the steel block. The volume of the dent was then filled with sand to compare the performance of HNS and **8**. The test showed that HNS is superior and the dent could be filled with 672 mg sand in comparison to **8** where only a very small dent was detected, which is caused by the used detonator. The non-initiation of compound **8** could be explained by the assumption that the critical diameter, which could not be determined at the time, is too high.

6.5 Conclusions

- The crystal structures of 3,6-bis-hydrazino-1,2,4,5-tetrazine, 3,6-dichloro-1,2,4,5-tetrazine and 3-amino-6-(3,5-diamino-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine could be determined by low-temperature x-ray diffraction.
- The disubstituted products, using imidazole, pyrazole and 1,2,4-triazole as nucleophiles, could be synthesized in high yields.
- Synthesizing 3,6-bis-(1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (**7**) requires different solvent combinations and 3,6-dichloro-1,2,4,5-tetrazine as a strong electrophile in comparison to

compounds **5** and **6**, which are accessible using 3,6-bis(3,5-dimethyl-pyrazol-1-yl)-1,2,4,5-tetrazine as electrophile.

- When 3,5-diamino-1,2,4-triazole is used as nucleophile the resulting products **8** and **9** show very high thermal stability.
- Compound **8** appears to be the thermally most stable 1,2,4,5-tetrazine compound known in the literature so far.
- Compound **8** could not be initiated in a SSRT setup. A potential explanation could be the fixed diameter of the test setup (predefined volume), which was possibly below the critical diameter of **8**.

6.6 Experimental section

Synthesis of 3,6-bis-(1,3-imidazol-1-yl)-1,2,4,5-tetrazine (**5**):

3,6-Bis-(3,5-dimethyl-pyrazol-1-yl)-1,2,4,5-tetrazine (**1**) (4.05 g, 15.0 mmol) and 1*H*-imidazole (2.35 g, 35.0 mmol) were suspended in 25 ml acetonitrile and the mixture refluxed for 3 h. After cooling, the resulting precipitate was filtered and washed with large amounts of water (1 l), followed by acetonitrile and dichloromethane. (2.69 g, 84 %) of **5** was isolated as an orange powder. **3,6-Bis-(1,3-imidazol-1-yl)-1,2,4,5-tetrazine** (**5**) ($C_8H_6N_8$, 214.19 g mol^{-1}): **EA** exp. (calcd.) in %: C 44.90 (44.86), N 52.03 (52.32), H 2.90 (2.82). **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 200 °C (onset). **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 7.35 (m, 1H, C-H), 8.16 (m, 1H, C-H), 8.81 (m, 1H, C-H). **^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ = 117.1 (1C), 121.5 (1C), 132.4 (1C), 153.1 (1C). **Raman** (cm^{-1}): $\tilde{\nu}$ = 3158 (10), 3126 (5), 3113 (10), 1912 (5), 1537 (7), 1500 (8), 1490 (100), 1407 (13), 1372 (2), 1318 (13), 1282 (7), 1254 (2), 1129 (5), 1091 (16), 1048 (4), 962 (54), 895 (5), 858 (3), 801 (33), 747 (2), 665 (3), 613 (2). **IR** (25 °C, ATR): $\tilde{\nu}$ (cm^{-1}) = 3155 (w), 3122 (w), 3110 (w), 1775 (vw), 1702 (vw), 1648 (vw), 1614 (vw), 1531 (w), 1522 (w), 1475 (s), 1366 (w), 1321 (s), 1301 (m), 1260 (m), 1233 (w), 1214 (m), 1153 (w), 1104 (m), 1068 (m), 1038 (vs), 971 (s), 946 (s), 926 (m), 898 (s), 854 (vs), 762 (vs), 693 (w).

Synthesis of 3,6-bis-(1,2-pyrazol-1-yl)-1,2,4,5-tetrazine (**6**):

3,6-Bis-(3,5-dimethyl-pyrazol-1-yl)-1,2,4,5-tetrazine (5.4 g, 20 mmol) (**1**) and 1*H*-pyrazole (3.4 g, 50 mmol) were suspended in 30 ml acetonitrile and the mixture refluxed for 2 h. After cooling the resulting precipitate was filtered and washed with large amounts (1 l) of water, followed by acetonitrile and diethyl-ether. (2.2 g, 50 %) of **6** was isolated as an orange powder. **3,6-Bis(pyrazol-1-yl)-1,2,4,5-tetrazine** (**6**) ($C_8H_6N_8$, 214.19 g mol^{-1}): **EA** exp.(calcd.) in %: C 44.87 (44.86), N 51.53 (52.32), H 2.71 (2.82). DSC (5 °C min^{-1}): $T_{Dec.}$ =

$T_{Melt.}$ = 260 °C (onset). **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 6.80 (dd, 1H, C-H, $^{3}J_{H-H}$ = 2.6 Hz, $^{3}J_{H-H}$ = 1.5 Hz), 8.10 (d, 1H, C-H, $^{3}J_{H-H}$ = 1.5 Hz), 8.87 (d, 1H, C-H, $^{3}J_{H-H}$ = 2.6 Hz). **^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ = 111.1 (1C), 130.8 (1C), 145.8 (1C), 158.9 (1C). **Raman** (cm^{-1}): $\tilde{\nu}$ = 3149 (21), 3131 (14), 3104 (13), 1926 (4), 1541 (4), 1503 (65), 1483 (100), 1407 (4), 1400 (22), 1379 (3), 1352 (18), 1206 (2), 1115 (15), 1036 (8), 926 (41), 908 (6), 883 (2), 801 (22), 741 (3), 661 (2). **IR** (25 °C, ATR): $\tilde{\nu}$ (cm^{-1}) = 3145 (w), 3127 (w), 3102 (w), 1834 (vw), 1797 (vw), 1759 (vw), 1661 (vw), 1522 (m), 1479 (s), 1398 (s), 1376 (m), 1254 (m), 1213 (w); 1184 (m), 1164 (m), 1075 (m), 1042 (w), 1026 (s), 953 (m), 918 (vs), 888 (m), 775 (vs).

Synthesis of 3,6-bis-(1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (**7**):

1,2,4-Triazole (3.5 g, 50 mmol) was dissolved in 200 ml acetone and 20 ml (12 mmol) of a 0.6 M solution of 3,6-dichloro-tetrazine in acetonitrile was added. The solution was refluxed for 20 h. After cooling the resulting precipitate was washed with water and acetone. (2.1 g, 83 %) of (**7**) was isolated as an orange powder. **3,6-Bis(1,2,4-triazol-1-yl)-1,2,4,5-tetrazine** (**7**) ($C_6H_4N_{10}$, 212.21 g mol^{-1}): **EA** exp.(calcd.) [%]: C 33.43 (33.34), N 64.33 (64.80), H 1.87 (1.87). **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 245 °C (onset); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 8.34 (s, 1H, C-H), 9.46 (s, 1H, C-H). **^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ = 144.9 (1C), 147.2 (1C), 154.2 (1C). **MS**: (DEI+) m/z = 216 [M^+] (50), 94 (100), 67 (92). **Raman** (cm^{-1}): $\tilde{\nu}$ = 3139 (8), 3124 (12), 1912 (2), 1557 (2), 1511 (63), 1483 (100), 1426 (4), 1379 (21), 1336 (2), 1293 (2), 1264 (12), 1135 (19), 980 (43), 947 (5), 813 (20), 662 (2). **IR** (25 °C, ATR): $\tilde{\nu}$ (cm^{-1}) = 3135 (w), 3120 (w), 1813 (vw), 1755 (vw), 1551 (vw), 1514 (s), 1480 (vs), 1384 (m), 1365 (m), 1337 (w), 1293 (vs), 1266 (m), 1196 (s), 1170 (vw), 1155 (s), 1116 (s), 1112 (s), 1054 (s), 976 (vs), 953 (m), 939 (m), 910 (m), 880 (m), 672 (vs).

Synthesis of 3,6-bis-(3,5-diamino-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (**8**):

3,5-Diamino-1,2,4-triazole (2.40 g, 24.2 mmol) was dissolved in 50 ml DMF at ambient temperature and 10 ml (6 mmol) of a 0.6 M solution of dichlorotetrazine in acetonitrile was added *via* a dropping funnel. The solution was stirred for 2 h at ambient temperature. The product started to precipitate rather quickly. The suspension was heated to 120 °C for 16 h. After filtration the product was successively washed with large amounts of DMF, water and acetonitrile to gain (1.40 g, 85 %) of **8** as a brownish-red powder. **3,6-Bis(3,5-diamino-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine** (**8**) ($C_6H_8N_{14}$, 276.22 g mol^{-1}): **EA** exp. (calcd.) in %: C 26.25 (26.09), N 69.99 (70.99), H 2.90 (2.92). DSC (5 °C min^{-1}): $T_{Dec.}$ = 370 °C (onset). **^{1}H NMR** ([D_6]DMSO, 80 °C, ppm): δ = 7.34 (2H, NH_2), 5.66 (2H, NH_2). **^{13}C NMR** ([D_6]DMSO, 80 °C, ppm): δ = 162.5 (1C), 155.5 (1C), 152.6 (1C); **MS**: (DEI+): m/z = 276 [M] (23), 99 [$C_2H_5N_5$] (100), 124 [$C_2N_5H_4$-CN] (21). **Raman** (cm^{-1}): $\tilde{\nu}$ = 1931 (6), 1643 (4), 1622 (9), 1560 (2), 1546

(12), 1498 (100), 1420 (15), 1368 (12), 1166 (17), 1058 (4), 844 (45), 797 (2), 780 (29), 746 (3), 658 (2), 591 (2), 478 (3), 415 (8), 372 (2). **IR** (25 °C, ATR): $\tilde{\nu}$ (cm^{-1}) = 3416 (w), 3383 (w), 3272 (w), 3214 (w), 3131 (w, br), 1620 (s), 1554 (m), 1474 (s), 1448 (vs), 1388 (m), 1331 (w), 1151 (m), 1134 (m), 1083 (w), 1054 (m), 1028 (m), 956 (m), 828 (m), 758 (m), 704 (m), 669 (m), 655 (vw). Density: ρ ($g\ cm^{-3}$): 1.75. **Sensitivity-data**: IS: > 40 J; FS: > 360 N; ESD: > 1 J.

Synthesis of 3-amino-6-(3,5-diamino-1,2,4-triazol-1-yl-)-1,2,4,5-tetrazine dihydrate (**9**):

3-Amino-6-chloro-1,2,4,5-tetrazine (**4**) (1.00 g, 7.60 mmol) was dissolved in a solution of 16.0 ml acetonitrile and 2.00 ml water. To the stirred solution 3,5-diamino-1,2,4-triazole (1.51 g, 15.2 mmol) was added. The mixture was heated to 90 °C and refluxed for 16 h. The precipitate was filtered and washed with water and acetonitrile. The product, (**9**) was recrystallized from water. After standing overnight at ambient temperature, the crystals were filtered and dried. (1.33 g, 76 %) red needles of (**9**) were yielded**. 3-amino-6-(3,5-diaminotriazolyl)-1,2,4,5-tetrazine dihydrate** (**9**) ($C_4H_{10}N_{10}O_2$ 230.19 g mol^{-1})*:* **EA** exp (calcd.) [%]: C 20.62 (20.87); H 4.18 (4.38); N 60.37 (60.85); **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 314 °C. **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 5.38 (s, 2H, NH_2 triazole), 6.94 (s, 2H, NH_2 triazole), 7.83 (s, 2H, NH_2 tetrazine); **^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ = 155.5 (1C, C-NH_2 triazole), 156.3 (1C, C-NH_2 triazole), 162.7 (1C, C-tetrazine), 162.9 (1C, C-tetrazine). **MS**: (DEI +): m/z = 194.1 (100) [$C_4H_6N_{10}$+], 124.1 (43) [$C_3H_4N_6$+], 99.1 (5) [$C_2H_5N_2$+], 82.1 (19) [$C_2H_2N_5$+]. **Raman** (cm^{-1}): $\tilde{\nu}$ = 3250 (2), 3184 (5), 1648 (7), 1570 (5), 1555 (12), 1526 (5), 1477 (90), 1399 (4), 1371 (8), 1335 (6), 1158 (10), 1027 (18), 866 (100), 828 (4), 669 (7), 580 (9), 456 (5), 356 (4), 345 (7), 321 (6). **Sensitivity-data**: IS: > 40 J; FS: > 360 N; ESD: > 1 J.

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7. PUBLICATION E

Energetic Derivatives of 2-Nitrimino-5,6-dinitro-benzimidazole

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7.1 Abstract

2-Nitrimino-5,6-dinitrobenzimidazole (**1**) was synthesized by nitration of 2-aminobenzimidazole at ambient temperature in good yield. In order to explore new insensitive explosives four energetic nitrogen-rich 1:1 salts such as the guanidinium (**1a**), aminoguanidinium (**1b**), triaminoguanidinium (**1c**) and hydroxylammonium (**1d**) were synthesized either by facile acid/base or *in situ* metathesis reaction. In addition 2-nitrobenzimidazole (**2**) was synthesized by the reaction of 2-aminobenzimidazole using potassium hyperoxide in THF. Different nitration methods were tested to obtain a theoretically 2,4,5,6,7-pentanitrobenzimidazole but only the already known 4,5,6,7-tetranitrobenzimidazol-2-one (**3**) could be isolated. All synthesized compounds were characterized especially by low temperature X-ray diffraction, CHN elemental analysis and ^{1}H and ^{13}C NMR. The heat of formation of all new synthesized compounds was calculated using CBS-4M electronic enthalpies in combination with the atomization method to calculate their detonation parameters with the EXPLO 5 V5.05 computer code.

7.2 Introduction

Most commercially secondary explosives like RDX (hexogen) and HNS (hexanitrostilbene) are toxic for human and animal organisms.[1] Therefore it is a main goal to substitute these toxic compounds. Another goal is to enhance the performance of secondary explosives which is defined by parameters like the detonation velocity ($V_{Det.}$), detonation pressure (P_{CJ}), heat of detonation ($\Delta_{Ex}U°$) and volume of detonation gases (V_0) generated during their detonation.[2] It is a recent task to investigate energetic materials and compositions[3] with higher performance and thermostability and lower sensitivity (towards impact (*IS*), friction (*FS*), electrostatic discharge (*ESD*)) and also lower toxicity than the current used ones. One approach is the use of azoles in combination with energetic substituents at the carbon atom(s) like nitro or azide groups.[4] Benzimidazole and especially 2-aminobenzimidazole are commercially available substances, which are poorly characterized with respect to their polynitro-derivatives. The probably most common derivative of this class of substances is 4,5,6,7-tetranitro-benzimidazol-2-one (**3**, Scheme 1), which was synthesized by Schindlbauer

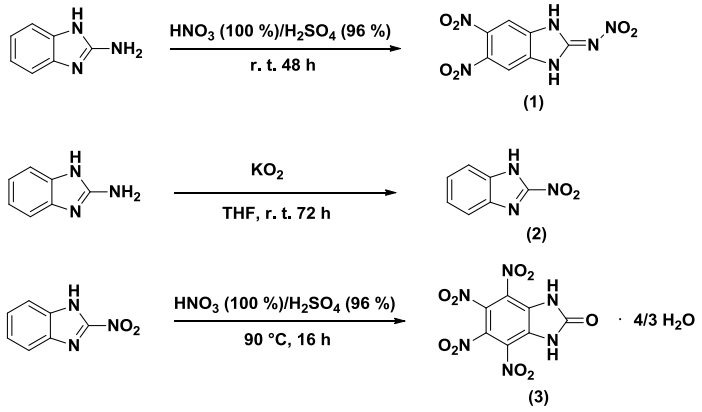
et al. in 1976 by direct nitration of benzimidazol-2-one.[5] Furthermore Sizov et al. forced the research of thermal rearrangement of N-nitrobenzimidazol-2-one in different organic solvents.[6] Investigations regarding enzymatic reactions and cytotoxicity of different nitrobenzimidazoles were made by Cenas et al. in 1997.[7] All reported syntheses of **3** were carried out under thermodynamical conditions; this means the nitration mixtures were heated over a longer period of time. So far no one reported about 2-nitrimino-5,6-dinitrobenzimidazole (**1**), which is formed at ambient temperature using 2-aminobenzimidazole as starting material, and its high-nitrogen containing salts (**1a**–**1d**). Furthermore we report on the oxidation of 2-aminobenzimidazole yielding 2-nitrobenzimidazole (**2**) by using potassium hyperoxide in THF. This method was used by Schmitzer et al. for oxidation of 1,4-diaminobenzene, yielding the corresponding 1,1'-diamino-4,4'-azobenzene.[8] The nitration of **2** was also investigated by us.

7.3 Results and discussion

7.3.1 Syntheses

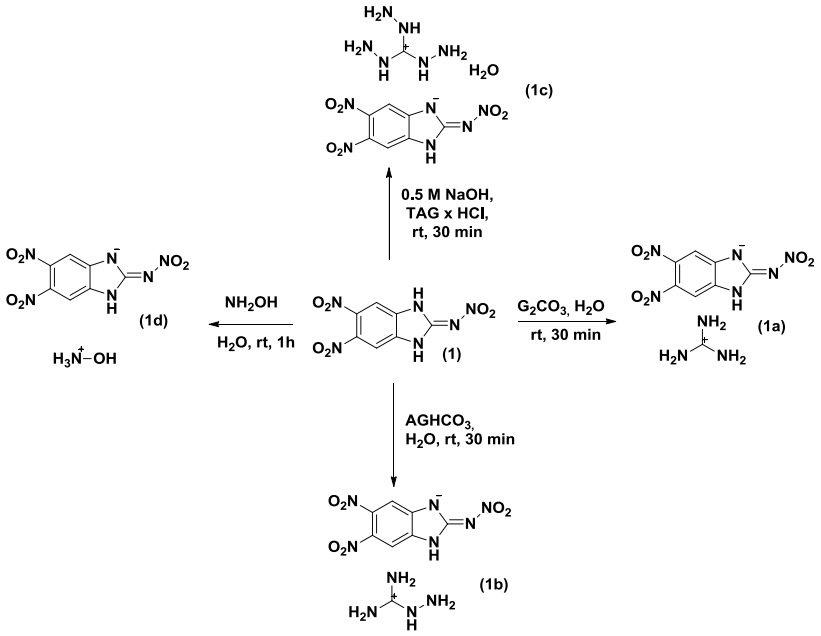
2-Nitrimino-5,6-dinitrobenzimidazole (**1**) was synthesized by nitration, using 100% HNO_3 and concentrated sulfuric acid (96–98 %) at ambient temperature. We have tested different reaction durations (12–48 h) and found that a reaction time of 48 h seems to be the optimum. Yields of **1** varied between 45 and 50 %, depending on the amount of water, which was used to wash **1** free of acid after filtration. We think that firstly the nitrimino group is formed at 0 °C, because the amino group is kinetically favored to be nitrated first. In the second step the benzene ring is nitrated selectively at carbon atoms C5 and C6 at ambient temperature because the nitrimino group decreases the electron density at atoms C4 and C7. Afterwards we tried to chlorinate **1** in C4 and C7 position using either chlorine gas in different aprotic solvents or N-chloro-succinimide in acetonitrile but no reaction occurred. Since **1** is stable up to 250°C it might become suitable for secondary explosive applications. We additionally synthesized four different nitrogen-rich salts, the guanidinium (**1a**), the aminoguanidinium (**1b**), the triaminoguanidinium (**1c**) and hydroxylammonium (**1d**) salt. The synthesis of these corresponding salts is depicted in Scheme 2. The oxidation reaction of 2-aminobenzimidazole with potassium hyperoxide (KO_2) yields 2-nitrobenzimidazole (**2**). Byproducts like different azo-coupled species, which could be detected in the mass spectra was removed by recrystallization of the raw material from acetone. Various attempts to synthesize a pentanitro-benzimidazole using harsh nitration conditions were carried out. The amount of sulfuric acid was varied as well as additional SO_3 (10-65 % by weight). However, **2**

seems to be incompatible with H_2SO_4/SO_3 mixtures. Use of concentrated sulfuric acid and 100 % HNO_3 resulted in the formation of compound **3**. We conclude that firstly the benzene ring has been nitrated four times. The electron deficit was increased in that way that hydrolysis in C2 position specifically leading to the much more stable urea derivative **3**.



Scheme 1: Synthetic protocol towards compounds **1**, **2** and **3**.

Scheme 2 shows typical deprotonation reactions in order to synthesize the high-nitrogen salts **1a**–**d**. Wheras the syntheses of **1a**, **1b** and **1d** are typical acid/base reactions, the synthesis of **1c** represents an *in situ* salt metathesis, in which the sodium salt is formed and triaminoguanidinium chloride is added afterwards. All salts (**1a**–**d**) can be synthesized in high yields and their perfect purity was confirmed by CHN elemental analysis.



Scheme 2 Syntheses of nitrogen-rich salts (**1a**–**1d**)

7.3.2 Crystal structures

Single crystals for XRD of compounds **1**, **1a**-**d**, **2**, and **3** · 4/3 H_2O could be obtained during this work. Single crystals of **1** were obtained out of acetone, whereas all corresponding salts crystallized from EtOH/H_2O mixture. 2-Nitrobenzimidazole (**2**) and 4,5,6,7-tetranitrobenzimidazole · 4/3 hydrate (**3**) crystallized from water/acetone. Crystallographic data and parameters are given in Table S1 in the supplementary information. The cif files were deposited at the Cambridge Crystallographic Data Centre (CCDC) and can be obtained free of charge by the numbers 986185 (**1**), 986187 (**1a**), 986186 (**1b**), 986189 (**1c**), 986190 (**1d**), 986191 (**2**), 986188 (**3**). 2-Nitrimino-5,6-dinitrobenzimidazole (**1**) crystallizes in the monoclinic space group *P*2_1*/n* with four molecules in the unit cell. The molecular unit is shown in Figure 1. It is the first 2-nitramino-benzimidazole derivative which is characterized by XRD. Its calculated density of 1.850 g cm^{-3} (at 100 K) is higher than those of its salts **1a**-**1d**. Both acidic protons (located on the imidazole nitrogen atoms) participate in strong hydrogen bonds e.g. intramolecular: N2–H2···O1 840(30) ppm, 217(3), 264.2(2) 116(2)°; intermolecular: N2–H2···O2^{i} 840(30), 203(3), 284.4(2) ppm, 163(3)°, N1–H1···O2^{ii} 89(2) ppm, 208(3), 293.3(2), 162(2)° (symmetry codes: (i) 1.5−x, −0.5+y, 1.5−z; (ii) 1−x, 1−y, 1−z). Except for the oxygen atoms of the nitro group at carbon atom C5 all atoms are almost planar to each other. The investigated salts of **1** crystallize in monoclinic (*P*2_1*/c:* **1a**, **1d,** *P*2_1*/n:* **1b**,) and triclinic (*P–1*: **1c**) space groups. The densities decrease in the following (expected) order: 1.835 g cm^{-3} (**1d** at 173 K) >1.743 g cm^{-3} (**1a** at 100 K) > 1.735 g cm^{-3} (**1c** at 123 K) > 1.706 g cm^{-3} (**1b** at 100 K).

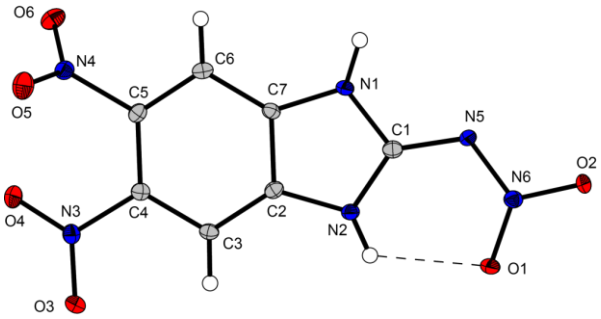


Fig. 1: Molecular unit of **1**. Thermal ellipsoids are drawn at the 50% probability level.

It oftentimes has been observed that hydroxylammonium salts show higher densities than other corresponding ammonium, hydrazinium and guanidinium salts. The triaminoguanidinium salt **1c** is the only salt synthesized which includes a molecule of crystal water. A view on the molecular units is given in Figures 2–5. All structures are dominated by strong hydrogen bond interactions. As a general trend in all salts the intramolecular hydrogen

bridge (graph set R6(1,1)) between the nitramine oxygen atom and the remaining imidazole N–H functionality can be observed.

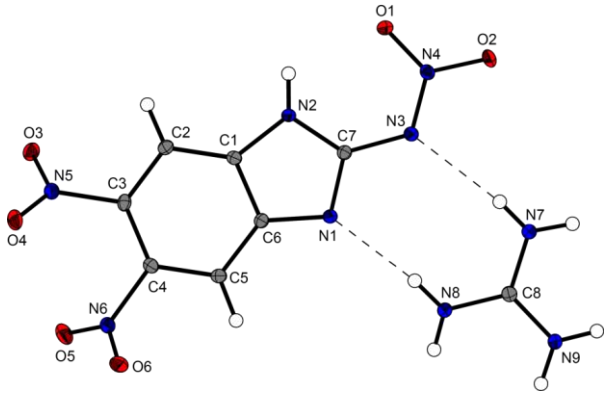


Fig. 2: Molecular unit of **1a**. Thermal ellipsoids are drawn at the 50% probability level.

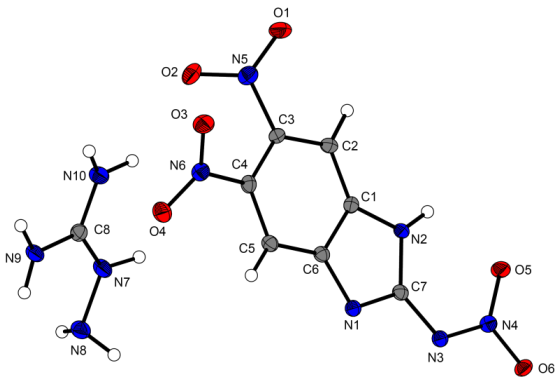


Fig. 3: Molecular unit of **1b**. Thermal ellipsoids are drawn at the 50% probability level.

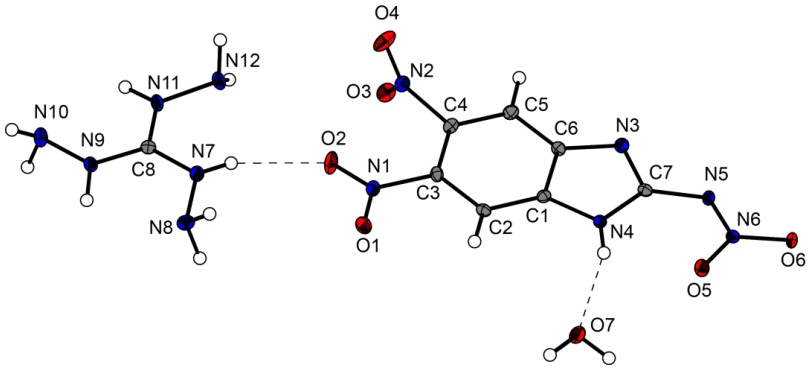


Fig. 4: Molecular unit of **1c**. Thermal ellipsoids are drawn at the 50% probability level.

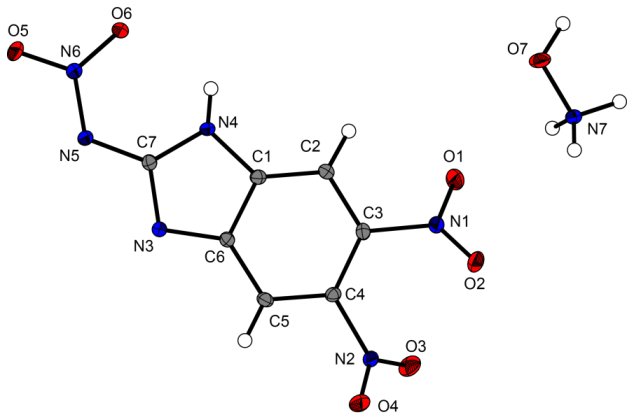


Fig. 5: Molecular unit of **1d**. Thermal ellipsoids are drawn at the 50% probability level.

2-Nitrobenzimidazole (**2**) crystallizes in the orthorhombic space group *Fdd*2 with 16 molecules in the unit cell. Interestingly its density of 1.593 g cm^{-3} (at 173 K) is significantly lower than that of **1** (1.85 g cm^{-3}) but still significantly higher than that of 2-aminobenzimidazole (1.347 g cm^{-3}) described in literature.[9] The nitro group is slightly twisted out from the benzimidazole plane (torsion angle: N1–C7–N3–O1 = −7.9(3)°). It forms a wave-like layer structure which is shown in Figure 6.

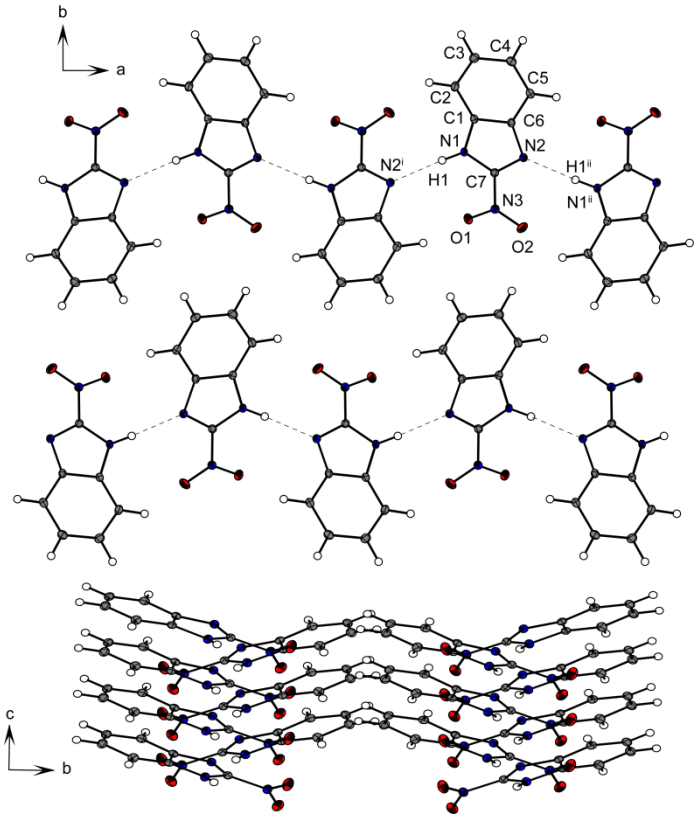


Fig. 6: View on the packing of **2**. Top: View along the *c*-axis and drawn H-bond interactions. Below: View along the *a* axis. Thermal ellipsoids are drawn at the 50% probability level.

The 2-nitrobenzimdazole molecules are linked by the hydrogen bond N1–H1···N2^{i} 89(3) ppm, 207(3) 294.1(2) 169(3)°; (i) −0.25+x, 0.25−y, −0.25+z.

4,5,6,7-Tetranitro-benzimidazol-2-one · 4/3 hydrate (**3**) crystallizes in the triclinic space group *P*–1 and a density of 1.825 g cm^{-3} (at 173 K). In addition to hexanitrobenzene[10] and pentanitroaminobenzene[11] it is the third example in the Cambridge crystallographic database (CCDC) which carries four vicinal nitro groups on one benzene ring. They all are twisted out of the ring plane due to sterical reasons. The structure can be compared best with that published for 5-nitro-benzimidazol-2-one monohydrate.[12] The asymmetric unit consists of three 4,5,6,7-tetranitro-benzimidazole and four crystal water molecules. Figure 7 shows a selected hydrogen bond connection of one 4,5,6,7-tetranitro-benzimidazol-2-one and one crystal water. The complex 3-dimensional packing of **3** · 4/3 H_2O is dominated by many hydrogen bond interactions involving all water molecules.

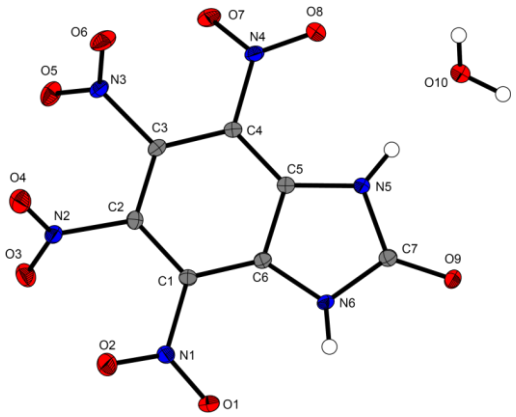


Fig. 7: Molecular unit of **3** ·4/3 H_2O. Thermal ellipsoids are drawn at the 50% probability level. For clarity two tetranitrobenzimidazoles and three crystal waters have been neglected.

7.4 Energetic and thermical properties

7.4.1 Thermal stabilities and sensitivity data

Compounds **1**-**3** were tested for their sensitivities towards impact (IS), friction (FS) and electrostatical discharge (ESD). Furthermore the decomposition temperatures ($T_{Dec.}$) of all here presented compounds (**1**-**3**) were determined using differential scanning calorimetry (DSC) with a heating rate of 5 °C min^{-1}. The corresponding DSC-curves oc compounds 1-1d are shown in Figure 8. As can be seen all these compounds have sharp decomposition points. The sensitivity data of compound **1**-**3** and their thermo stability are shown in Table 1.

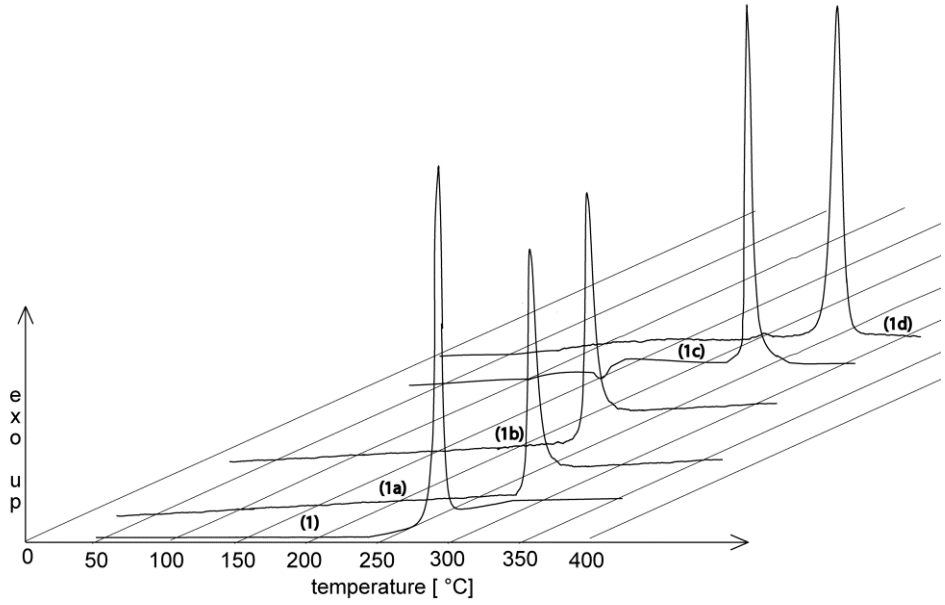


Figure 8: DSC plots of compounds **1**–**1d** measured with a heating rate of 5 °C min^{-1} (exo-up)

Table 1: Sensitivity data and thermal stability of compound **1**, **1a**–**1d, 2**, and **3**.

	IS **[J]** [a]	***FS*** **[N]** [b]	***ESD*** **[J]** [c]	**Grain Size [µm]**	$T_{Dec.}$ **[°C]** [d]
1	> 3	> 324	> 0.1	< 100	250
1a	> 20	> 360	> 0.3	< 100	275
1b	> 5	> 360	> 0.2	< 100	232
1c	> 5	> 360	> 0.4	100-500	218
1d	> 5	> 360	> 0.2	< 100	242
2	> 40	> 360	> 1.0	< 100	180
3	> 5	> 360	> 0.2	< 100	255
RDX[16]	> 7.5	> 120	> 0.1	< 100	210

[a] impact sensitivity (BAM drophammer, 1 of 6); [b] friction sensitivity (BAM friction tester 1 of 6); [c] electrostatic discharge device.

Regarding compounds **1**-**1d** one can observe that the guanidinium salt (**1a**) is the thermally most stable. An increasing number of N-N single bonds in the corresponding cation is followed by lower thermostability.

7.4.2 Detonation parameters

The detonation parameters were calculated with the EXPLO5.05 computer code[15] using calculated heats of formation (see SupInfo). Compound **1d** has the same density like **1** at 298 K but shows better detonation parameters due to its higher heat of formation ($\Delta_f H_m°$ = 80 kJ mol^{-1}(**1**), 126 kJ mol^{-1} (**1d**)). Although **1b** has a slightly higher heat of formation its density with 1.657 g cm^{-3} is quite low. The advantage of these compounds (**1** and its salts **1a**-**1d**) is the very simple one-step nitration reaction which yields secondary explosives with better performance than TNT and varying sensitivities: very high sensitive (**1**), moderate sensitive (**1b**, **c**, **d**) and low sensitive (**1d**) towards impact. Except for **1**, which showed slightly charcoal formation at 324 N, all of the investigated compounds are insensitive towards friction. The energetic characteristics for the solvent-free compounds **1**, **1a**, **1b** and **1d** are gathered in Table 2.

Table 2: Energetic properties of compounds **1**, **1a**, **1b** and **1d** in comparison to RDX.

	1	**1a**	**1b**	**1d**	**RDX**
Formula	$C_7H_3N_6O_6$	$C_8H_9N_9O_6$	$C_8H_{10}N_{10}O_6$	$C_7H_7N_7O_7$	$C_3H_6N_6O_6$
FW / g mol^{-1}	268.14	327.21	342.23	301.17	222.12
N / % [a]	31.34	38.53	40.93	32.55	37.84
Ω_{CO2} / % [b]	–59.7	–70.9	–70.1	–55.8	–21.61
ρ / g cm^{-3} [c]	1.850 (100K)	1.743 (100K),	1.706 (100K),	1.835 (173K),	1.858 (90K)[13]
	1.80 (298K)	1.69 (298K)	1.657 (298K)	1.80 (298K)	1.806 (298K)[14]
$\Delta_f H_m°$ / kJ mol^{-1} [d]	80.0	27.4	134.6	125.7	86
$\Delta_f U°$ / kJ kg^{-1} [e]	372.2	174.6	487.4	503.8	489
EXPLO5.05 values[j]:					
$\Delta_{Ex} U°$ / kJ kg^{-1} [f]	4911	4301	4497	5395	6190
$T_{Det.}$ / K [g]	3675	3117	3212	3767	4232
P_{CJ} / GPa [h]	26.2	22.1	22.1	29.4	38.0
$V_{Det.}$ / m s^{-1} [i]	7760	7526	7565	8177	8983
V_o / L kg^{-1} [i]	584	670	690	643	734

[a] Nitrogen content; [b] Oxygen balance; [c] From X-ray diffraction; [d] Calculated (CBS-4M) heat of formation; [e] Energy of formation; [f] Energy of explosion; [g] Explosion temperature; [h] Detonation pressure; [i] Detonation velocity; [j] Assuming only gaseous products.

7.5 Experimental section

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

2-Nitrimino-5,6-dinitro-benzimidazole (**1**):

2-Aminobenzimidazole (5.00 g, 37.58 mmol) was added to an ice cooled (0 °C) solution of red fuming nitric acid (100%, 20ml, 480 mmol) and concentrated sulfuric acid (96%, 35ml, 630 mmol) while stirring. Afterwards the mixture was stirred for 48 h at 25 °C before it was poured on crushed ice. The precipitate was filtered and washed with nitric acid (20%) and then with little water. 4.4 g (15.38 mmol; 41%) of **1** was obtained as a pale yellow solid. **DSC** (5 C min^{-1}, °C): $T_{Dec.}$ = 250°C; **EA** ($C_7H_4N_6O_6$ 268.02 g mol^{-1}) found (calc): C 31.11 (31.35), H 1.50 (1.50), N 30.77 (31.34); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ= 4.98 (s, br, 2H, NH), 8.08 (s, 2H, CH); **^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ= 109.7 (2C, CH), 132.4, 139.3, 155.7; **^{14}N NMR** ([D_6]DMSO, 25 °C, ppm): δ= –12 (3N, NO_2) ; **Raman** [cm^{-1}]: $\tilde{\nu}$ = 3084 (7), 1638 (26), 1582 (100), 1548 (9), 1478 (53), 1340 (69), 1264 (7), 1248 (26), 1226 (9), 1117 (6), 1080 (5), 1033 (5), 993 (78), 857 (20), 831 (5), 809 (11), 768 (17), 756 (6), 638 (4); **Sensitivities: IS:** > 3J; **FS:** > 324N; **ESD**: < 0.1J

Syntheses of compounds 1a-d (please see Sup Info)

2-Nitro-benzimidazole (**2**):

2-Aminobenzimidazole (5.00 g, 37.55 mmol) was dissolved in THF (200ml) at 25 °C. Potassium superoxide (18.00 g, 380 mmol) was added and the suspension was stirred for 72 h and filtered from the inorganic compound which was washed several times with THF. The filtrate was discarded and the precipitate was solved in water. The solution was adjusted to pH-value 1 with sulfuric acid. The orange precipitate was filtered and washed with cold water yielding 3.0 g (18.40 mmol, 49%) 2-nitrobenzimidazole as an orange solid. **DSC** (5 °C min^{-1}) $T_{Dec.}$ = 180°C): **EA** ($C_7H_5N_3O_2$ 163.04 g mol^{-1}) found (calc): C 51.83 (51.54), H 3.19 (3.09), N 25.41 (25.76); **^{1}H NMR** ([D_6]DMSO, 25°C, ppm): δ= 4.98 (s, br, 2H, NH), (AA'BB'-spectra, δ_A= 7.71 2H, CH, N = $|J_{AB} + J_{AB'}|$ = 9.45 Hz), AA'BB'-spectra, δ_B= 7.43 2H, CH, N = $|J_{AB} + J_{AB'}|$ = 9.45 Hz) **^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ= 109.0, 118.0, 126.3, 149.6; **^{14}N NMR** ([D_6]DMSO, 25 °C, ppm): δ= –19 (NO_2); **Raman** [cm^{-1}]: $\tilde{\nu}$ = 3089 (7), 3075 (3),

1585 (10), 1542 (5), 1503 (21), 1472 (11), 1407 (66), 1377 (3), 1331 (17), 1306 (9), 1267 (100), 1227 (38), 1209 (20), 1153 (25), 1141 (8), 1128 (13), 1018 (21), 995 (2), 784 (19), 615 (3); **IR** (ATR) [cm^{-1}]: $\tilde{\nu}$ = 3029 (vw), 2958 (vw), 2859 (vw); 2763 (vw), 2594 (vw), 1584 (vw), 1549 (s); 1503 (vs), 1472 (s), 1408 (m), 1375 (vw), 1337 (s), 1306 (m), 1265 (m), 1227 (w), 1202 (vw), 1140 (m), 1018 (vw), 994 (vw), 943 (vw), 904 (vw), 850 (m), 774 (w), 750 (m), 738 (vs); **Mass spec**.: (DEI (+) m/z): 163.1 (100) [M^+]. **Sensitivities: IS:** > 40J; **FS:** > 360N; **ESD**: 1.0J.

4,5,6,7-Tetranitro-benzimidazol-2-one (**3**):

2-Nitrobenzimidazole (2.80 g, 17.2 mmol) was added to an ice cooled solution (0 °C) of concentrated sulfuric acid (96%, 20ml, 0.48 mol) and red fuming nitric acid (100%, 5.0ml, 0.12 mol). The mixture was stirred for 16 h at 100 °C and poured on ice. The yellow suspension was extracted five times with 50 ml of ethyl acetate and afterwards with water and brine. A yellow-orange precipitate of crude 4,5,6,7-tetranitro-benzimidazole-2-one (**3**) (3.14 g 58%) was obtained. Single crystals obtained, contained 4/3 crystal water, whereas the crude compound does not. Proper NMR data could be obtained by recrystallizing the crude compound out of toluene/EtOH. During this process **3** precipitates as an adduct with one molecule of toluene. This was confirmed *via* CHN elemental analysis and ^{1}H and ^{13}C NMR spectroscopy using 4096 scans, a pulse delay of 2s and a pulse width of 30°. This adduct was dissolved in 20 mL THF and reprecipitated with an excess of ice-water. This results in the solvent-free compound **3**. **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 255 °C: **EA** (single crystals) (3 $C_7H_4N_6O_9 \cdot 4\ H_2O$ 337.94 g mol^{-1}) found (calc): C 25.35 (25.31), H 1.45 (1.21), N 24.62 (25.30); **EA** (waterfree compound **3**) ($C_7H_4N_6O_9$ 314.13 g mol^{-1}) found (calc): C 27.05 (26.76), H 0.92 (0.64), N 26.52 (26.75); **Mass spec**.: (DEI (+) m/z): 222.1 (8), 253.0 (2), 269.1 (6), 314.1 (100) [M^+]; **IR** (waterfree compound) (ATR) [cm^{-1}]: $\tilde{\nu}$ = 3388 (s), 3277 (s), 1763 (s), 1735 (s), 1618 (m), 1553 (vs), 1400 (m), 1332 (vs), 1312 (vs), 1197 (m), 1050 (m), 974 (m), 931 (m), 910 (s), 862 (m), 761 (m); **Sensitivities**: **IS**: > 5J; **FS:** > 360N; **ESD**: 0.2J. **EA** (toluene adduct) ($C_7H_2N_6O_9 \cdot C_7H_8$ 406.26 g mol^{-1}) found (calc): C 41.00 (41.39), H 2.75 (2.48), N 20.79 (20.69); **^{1}H NMR** ([D_6]acetone, 25 °C, ppm) toluene in adduct: 7.16 (m,5H,toluene), 2.30 (s, 3H, toluene); signals from 3 δ= 12.14 (s,br,2H,NH),**^{13}C NMR** ([D_6]acetone, 25 °C, ppm) toluene in adduct: δ= 21.4 (1C,CH_3,toluene), 126.1 (2C, toluene), 129.0 (2C, toluene), 129.8 (2C, toluene), 138.5 (1C, toluene); Signals from 3: δ= 123.7 (2C, C_q), 132.8 (2C, C-NO_2), 133.8 (2C, C-NO_2), 154.6 (1C, C=O); **^{14}N NMR** ([D_6]acetone, 25 °C, ppm): δ= −22;

7.6 Conclusion

From this experimental study the following conclusions can be drawn:
It has been shown that 2-aminobenzimidazole is a valuable and cheap starting material for the synthesis of energetic materials. Its nitration at ambient temperature yield the 2-nitrimino-5,6-dinitrobenzimidazole (**1**) in good yields. Nitrogen-rich salts of **1** could be synthesized in good yield by facile acid/base reaction. Furthermore we managed the oxidation of 2-aminobenzimidazole to its corresponding 2-nitro-derivative using potassium hyperoxide. All attempts to synthesize a pentanitrobenzimidazole yielded 4,5,6,7-tetranitro-benzimidazol-2-one (**3**), which was characterized by X-ray diffraction. Purification of **3** was achieved by recrystallizing **3** as toluene adduct. Afterwards the toluene could be removed by resolving the material in THF and precipitation of **3** with an excess of ice-water. All here synthesized compounds were characterized by low temperature X-ray diffraction. For compounds **1**, **1a**, **1b** and **1c**, which can be synthesized very easily, moderate detonation parameters were calculated.

7.7 References

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7.8 Supporting information

7.8.1 X-ray diffraction

Table S1: XRD data and parameters.

	NDNBI (1)	GNDNBI (1a)	AGNDNBI (1b)	TAGNDNBI · H_2O (1c)	HXNDNBI (1d)	NBI (2)	TNBIO ·1.33 H_2O (3)
Formula	$C_7H_4N_6O_6$	$C_8H_9N_9O_6$	$C_8H_{10}N_{10}O_6$	$C_8H_{14}N_{12}O_7$	$C_7H_7N_7O_7$	$C_7H_5N_3O_2$	$3(C_7H_4N_6O_{10}) \cdot 4H_2O$
FW [$gmol^{-1}$]	268.16	327.24	342.26	390.31	301.20	163.14	1014.50
Color, habit	yellow block	yellow rod	yellow needle	yellow rod	orange rod	orange, platelet	yellow block
Size [mm]	0.31x0.22x0.10	0.52x0.22x0.19	0.39x0.12x0.06	0.16x0.06x0.02	0.19x0.06x0.06	0.17×0.14×0.02	0.33x0.22x0.13
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P-1$	$P2_1/c$	$Fdd2$	$P-1$
a [nm]	0.8882(9)	0.7686(4)	0.6835(1)	0.6723(1)	0.7063(1)	1.9471(1)	1.1394(1)
b [nm]	0.8371(9)	1.0032(3)	1.2425(1)	0.7535(1)	1.1128(1)	3.7640(1)	1.3330(1)
c [nm]	1.2991(1)	1.6334(1)	1.5902(2)	1.5048(1)	1.4239(1)	0.3713(1)	1.3657(1)
α [°]	90	90	90	92.551(3)	90	90	63.043(2)

β [°]	94.556(11)	98.263(4)	99.340(13)	100.519(3)	103.083(2)	90	87.065(2)
γ [°]	90	90	90	93.541(3)	90	90	89.0110(10)
V [nm^3]	0.9628(2)	1.2468(2)	1.3326(1)	0.7469(1)	1.0901(1)	2.7212(1)	1.8462(1)
Z	4	4	4	2	4	16	2
ρ_{calc} [g cm^{-3}]	1.850	1.743	1.706	1.735	1.835	1.593	1.825
μ [mm^{-1}]	0.164	0.150	0.147	0.151	0.165	0.122	0.174
Irridiation [nm]	MoK_α 0.071073	MoK_α 0.071073	MoK_α 0.071073	MoK_α 0.071073	MoK_α 0.071073	MoK_α 0.071073	MoK_α 0.071073
F(000)	544	672	704	404	616	1344	1028
Θ-Bereich [°]	4.47-26.04	4.25-25.99	4.18-26.00	2.97-26.33	2.94-26.38	2.16–26.42	2.39-27.50
T [K]	100(2)	100	100	123	173(2)	173	173
Dataset h	– 10 ≤ h ≤ 10	–9 ≤ h ≤ 9	–4 ≤ h ≤ 8	–7 ≤ h ≤ 8	–8 ≤ h ≤ 8	-24 ≤ h ≤ 22	–14 ≤ h ≤ 13
Dataset k	–10 ≤ k ≤ 9	–12 ≤ k ≤ 12	–8 ≤ k ≤ 15	–9 ≤ k ≤ 9	–13 ≤ k ≤ 13	-46 ≤ k ≤ 46	–17 ≤ k ≤ 17
Dataset l	–7 ≤ l ≤ 16	–20 ≤ l ≤ 20	–18 ≤ l ≤ 19	–18 ≤ l ≤ 18	–17 ≤ l ≤ 17	-4 ≤ l ≤ 4	–17 ≤ l ≤ 17
Reflecions coll.	4881	17788	5309	14591	16299	10024	38190
Independent refl.	1882	2448	2607	3021	2215	1405	8428
Observed refl.	1421	2188	1725	2240	1857	1336	7051
Parameters	188	244	257	300	218	129	688
R (int)	0.0445	0.0280	0.0442	0.0539	0.0315	0.0299	0.0322
GOOF	1.009	1.040	1.042	1.024	1.073	1.243	1.027
R_1, wR_2 ($I>\sigma I_0$)	0.0382, 0.0801	0.0292, 0.0738	0.505, 0.0950	0.0363, 0.0788	0.0323, 0.0795	0.0315, 0.0855	0.0407, 0.0983
R_1, wR_2 (all data)	0.0583, 0.0902	0.0337, 0.0770	0.0889, 0.1154	0.0619, 0.0882	0.0427, 0.0846	0.0380, 0.1033	0.0512, 0.1055
Weighting scheme	0.0341, 0.0000	0.0389, 0.5402	0.0371, 0.0000	0.0406, 0.2628	0.0409, 0.4863	0.0663, 0.7020	0.0500, 1.3119
Remaining density [e /10^{-3} nm^3]	–0.229, 0.229	–0.246, 0.287	–0.299, 0.255	–0.227, 0.278	–0.176, 0.339	-0.434, 0.452	–0.406, 0.709
Device type	Oxford XCalibur3	Oxford XCalibur3	Oxford XCalibur3	Oxford XCalibur3	Oxford XCalibur3	Oxford XCalibur 3	Oxford XCalibur3
Adsorption corr.	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi scan	multi-scan

CCDC	986185	986187	986186	986189	986190	986191	986188

7.8.2 Syntheses

Syntheses of compounds 1a-d:

All salts were prepared by dissolving **1** (0.25 g, 0.93 mmol) in water (10 ml) and addition of the corresponding bases (amounts are listed Table 2). The suspensions were stirred for 30 min, filtered and washed with water. After recrystallization from a water-ethanol mixture the corresponding single-crystals could be obtained.

Table S1: Bases used for syntheses of compounds **1a**–**d**.

Product	Base	Amount	Yield [%]
1a	$G_2{\cdot}H_2CO_3$(s)	0.56 mmol, 0.10 g	94
1b	$AGHCO_3$(s)	1.1 mmol, 0.15 g	90
1c	TAGCl(s)	1.1 mmol, 0.15 g	82
1d	w50% NH_2OH in H_2O	16 mmol ,1.0 mL	79

Guanidinium 2-nitrimino-5,6-dinitro-benzimidazole (**1a**):

DSC (5 C min^{-1}): $T_{Dec.}$ = 275 °C; **EA** ($C_8H_9N_9O_6$ 327.07 g mol^{-1}) found (calc): C 29.32 (29.36), H 2.66 (2.77), N 37.91 (38.53); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 6.88 (6H, NH_2), 7.88 (1H, CH), 8.02 (1H, CH), 12.79 (1H, NH); **^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ= 108.4 (1C, CH), 112.5 (1C, CH), 134.2, 140.0, 146.2, 158.4, 161.9; **Raman** [cm^{-1}]**:** $\tilde{\nu}$ = 3087 (3), 1619 (14), 1524 (12), 1497 (81), 1474 (13), 1445 (25), 1425 (8), 1391 (12), 1368 (11), 1342 (57), 1294 (53), 1237 (6), 1228 (100), 1193 (32), 1121 (2), 1072 (8), 1026 (4), 1012 (11), 987 (33), 877 (7), 856 (8), 833 (3), 811 (16), 772 (3), 748 (8), 662 (2), 387 (4); **IR** (ATR) [cm^{-1}]: $\tilde{\nu}$ = 3443 (m), 3339 (m), 3179 (w), 1678 (w), 1641 (m), 1537 (m), 1525 (m), 1503 (s), 1474 (m), 1441 (w), 1421 (m), 1390 (m), 1344 (s), 1302 (vs), 1236 (s), 1224 (vs), 1189 (s), 1114 (m), 1070 (s), 1024 (s), 1009 (m), 985 (m), 887 (vs), 853 (s), 833 (m), 807 (m), 765 (vs), 757 (m), 741 (s), 699 (w), 667 (s); **Sensitivities**: **IS:** > 20 J; **FS:** > 360 N; **ESD**: 0.3 J

Aminoguanidinium 2-nitrimine-5,6-dinitro-benzimidazole (**1b**):

DSC (5 C min^{-1}): $T_{Dec.}$ = 232 °C; **EA** ($C_8H_{10}N_{10}O_6$ 342.06 g mol^{-1}) found (calc): C 28.08 (28.08), H 2.88 (2.95), N 40.43 (40.93); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ= 4.68 (2H, N-

NH_2), 6.71 (4H, NH_2), 7.92 (1H, CH), 8.04 (1H, CH), 8.56 (1H, C-NH), 12.82 (1H, NH); **Raman** [cm^{-1}]: $\tilde{\nu}$ = 3107 (2), 3090 (5), 1617 (19), 1528 (9), 1502 (100), 1475 (10), 1442 (25), 1421 (8), 1390 (5), 1354 (48), 1336 (21), 1295 (67), 1237 (13), 1229 (77), 1189 (35), 1114 (7) 1072 (9), 1023 (7), 988 (46), 899 (4), 859 (14), 835 (4), 812 (16), 767 (2), 753 (7), 733 (2), 663 (2), 608 (3), 501 (3), 399 (2), 372 (2); **IR** (ATR) [cm^{-1}]: $\tilde{\nu}$ = 3342 (w), 3092 (w), 1668 (m), 1618 (vw), 1525 (m), 1503 (s), 1471 (w), 1440 (w), 1420 (m), 1388 (w), 1326 (vs), 1307 (vs), 1235 (s), 1226 (s), 1185 (m), 1111 (m), 1068 (m), 1021 (m), 998 (m), 985 (m), 962 (m), 897 (s), 854 (s), 833 (m), 810 (m), 766 (vs), 759 (m), 740 (s), 699 (m), 664 (s); **Sensitivities**: **IS**: > 5 J; **FS**: > 360 N; **ESD**: 0.2 J

Triaminoguanidinium 2-nitrimino-5,6-dinitro-benzimidazole monohydrate (**1c**):

DSC (5 C min^{-1}): $T_{Dec.}$ = 218 °C; **EA** ($C_8H_{14}N_{12}O_7$ 390.27 g mol^{-1}) found (calc): C 24.67 (24.62), H 3.51 (3.62), N 42.46 (43.07); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): **δ=** 4.49 (6H, NH_2), 7.91 (1H, CH), 8.05 (1H, CH), 8.59 (3H, NH), 12.81 (1H, NH); **Raman** [cm^{-1}]: $\tilde{\nu}$ = 1624 (6), 1504 (67), 1477 (29), 1438 (18), 1396 (3), 1375 (3), 1318 (100), 1282 (24), 1230 (94), 1131 (3), 1114 (5), 1074 (3), 1031 (8), 984 (29), 900 (3), 855 (6), 836 (7), 809 (6), 768 (10), 643 (5), 373 (3), 227 (3); **IR** (ATR) [cm^{-1}]: $\tilde{\nu}$ = 3517 (vw), 3349 (vw), 3330 (vw), 3246 (w), 1674 (w), 1622 (vw), 1573 (vw), 1534 (w), 1515 (m), 1498 (m), 1472 (w), 1434 (w), 1418 (w), 1397 (vw), 1375 (vw), 1328 (w), 1273 (m), 1207 (m), 1188 (m), 1129 (m), 1110 (m), 1068 (m), 1017 (s), 936 (m), 880 (vs), 866 (s), 852 (m), 833 (s), 792 (s), 775 (s), 768 (s), 743 (vs), 728 (s), 695 (s), 672 (s), 660 (s); **Sensitivities**: **IS**: > 5 J; **FS**: > 360 N; **ESD**: 0.4 J.

Hydroxylammonium 2-nitrimino-5,6-dinitro-benzimidazole (**1d**):

DSC (5 C min^{-1}): $T_{Dec.}$ = 242 °C; **EA** ($C_7H_7N_7O_7$ 301.04 g mol^{-1}) found (calc): C 28.10 (27.92), H 2.31 (2.34), N 32.40 (32.55); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): **δ=** 7.94 (1H, CH), 8.02 (s, 1H, CH), 10.25 (s, br, 1H, N-OH), 12.85 (1H, NH); **^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): **δ=** 110.5 (2C, CH), 137.6, 139.1, 161.1; **Raman** [cm^{-1}]: $\tilde{\nu}$ = 3090 (9), 1621 (18), 1584 (4), 1505 (53), 1476 (15), 1441 (19), 1393 (4), 1372 (14), 1335 (100), 1308 (7), 1281 (12), 1238 (6), 1226 (51), 1184 (46), 1119 (4), 1078 (10), 1030 (11), 1004 (8), 995 (42), 880 (2), 861 (24), 838 (12), 815 (13), 763 (15), 662 (4), 440 (2), 390 (5); **IR** (ATR) [cm^{-1}]: $\tilde{\nu}$ = 3369 (w), 3221 (vw), 2720 (vw), 1621 (vw), 1505 (s), 1474 (m), 1438 (s), 1377 (m), 1344 (m), 1292 (vs), 1237 (m), 1220 (vs), 1173 (vs), 1116 (m), 1077 (m), 1028 (m), 1001 (m), 990 (m), 890 (s), 858 (m), 839 (m), 812 (m), 774 (s), 767 (m), 757 (m), 741 (s), 735 (m), 701 (m), 660 (m); **Sensitivities**: **IS**: > 5 J; **FS**: > 360 N; **ESD**: 0.2 J

7.8.3 Heat of formation calculations

Heats of formation of compounds **1**-**3** were calculated using the atomization method (equation S1) using room temperature CBS-4M enthalpies summarized in Table S2.[S8,S9]

$$\Delta_f H^\circ_{(g, M, 298)} = H_{(Molecule, 298)} - \sum H^\circ_{(Atoms, 298)} + \sum \Delta_f H^\circ_{(Atoms, 298)} \quad (S1)$$

Table S2:CBS-4M electronic enthalpies for atoms C, H, N and O and their literature values for atomic $\Delta H^\circ_f{}^{298}$ / kJ mol^{-1}

	$-H^{298}$ / a.u.	NIST [S10]
H	0.500991	218.2
C	37.786156	717.2
N	54.522462	473.1
O	74.991202	249.5

Quantum chemical calculations were carried out using the Gaussian G09 program package.[S11] The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method of Petersson and coworkers in order to obtain very accurate energies. The CBS models use the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated CBS limit. CBS-4 begins with an HF/3-21G(d) structure optimization; the zero point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy, and an MP2/6- 31+G calculation with a CBS extrapolation to correct the energy through second order. An MP4(SDQ)/6-31+ (d,p) calculation is used to approximate higher order contributions. In this study, we applied the modified CBS.

For neutral **1** the sublimation enthalpy, which is needed to convert the gas phase enthalpy of formation to the solid state one, was calculated by the *Trouton* rule.[S12] In the case of the ionic compounds, the lattice energy (U_L) and lattice enthalpy (ΔH_L) were calculated from the corresponding X-ray molecular volumes according to the equations provided by *Jenkins* and *Glasser.*[S13] With the calculated lattice enthalpy the gas-phase enthalpy of formation was converted into the solid state (standard conditions) enthalpy of formation. These molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid state energies of formation (ΔU_m) according to equation S2.

$$\Delta U_m = \Delta H_m - \Delta n\, RT \quad (S2)$$

(Δn being the change of moles of gaseous components)

Table S3: Calculation results.

M	–*H*298 [a] / a.u.	Δf*H*°(g,M) / kJ mol^{-1} [b]	VM / nm^3 [c]	Δ*UL*, Δ*HL* (**1a**,**1b**,**1d**);[d] Δ*Hsub* [e] (**1**) / kJ mol^{-1}	Δf*H*°(s) [f] / kJ mol^{-1}	Δ*n* [g]	Δf*U*(s) [f] / kJ kg^{-1}
1	1047.414497	178.3		98.3	80.0	8	372.2
1 anion	1046.934351	−94.6					
G$^+$	205.453192	571.9					
AG$^+$	260.701802	671.6					
NH_4O^+							
1a		477.3	0.321	446.4, 449.9	27.4	12	174.6
1b		577.0	0.343	438.9, 442.4	134.6	13	487.4
1c		592.6	0.278	464.4, 466.9	125.7	10.5	503.8

[a] CBS-4M electronic enthalpy; [b] gas phase enthalpy of formation; [c] molecular volumes taken from X-ray structures and corrected to room temperature; [d] lattice energy and enthalpy (calculated using Jenkins and Glasser equations); [e] enthalpy of sublimation (calculated by Trouton rule); [f] standard solid state enthalpy of formation; [g] solid state energy of formation.

7.8.4 References

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8. PUBLICATION F

Synthesis and Initiation Capabilities of Energetic Diazodinitrophenols

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8.1 Abstract

The two new diazophenols 3-amino-6-diazo-2,4-dinitrophenol (**4**) and 3-chloro-6-diazo-2,5-dinitrophenol (**8**) were synthesized and comprehensively characterized. The regio-selectivity of nitration reactions with *N,N'*-(1,4-phenylene)dimethanesulfonamide (**1**) and *N,N'*-(1,4-phenylene)diacetamide (**6**) was thus investigated in detail. The purity of the products was confirmed *via* low temperature X-ray diffraction, multinuclear NMR spectroscopy and elemental analysis. Moreover, the capability of **4** and **8** to initiate RDX (1,3,5-trinitro-1,3,5-triazinane) was tested, together with the two other recently presented diazophenols 4-diazo-2,6-dinitrophenol (***iso*-DDNP**) and 3-hydroxy-DDNP (**HODDNP**). The tests revealed superior properties of **HODDNP** compared to DDNP and the other tested diazophenols regarding its ability to initiate RDX.

8.2 Introduction

The current and the future scope of research in the field of energetic materials is the performance improvement of primary and secondary explosives in general.[1,2] In addition it is a common task to use heavy metal free compounds which are mostly more environmentally benign.[3,4]

The main difference between primary and secondary explosives is the unique ability of the former class to undergo the so called deflagration-to-detonation transition (DDT), meaning the acceleration of a subsonic heat based energy transfer of the decomposition reaction into a supersonic shockwave, even in an unconfined state. High performance primary explosives like lead azide (LA) detonate virtually immediately when exposed to heat even in the smallest quantities. Unfortunately, lead azide is a highly toxic compound and liberates hydrazoic acid in moist air due to the reaction with carbon dioxide. This lead to the development of more environmentally benign primary explosives like copper(I) 5-nitrotetrazolate (DBX-1),[5] or

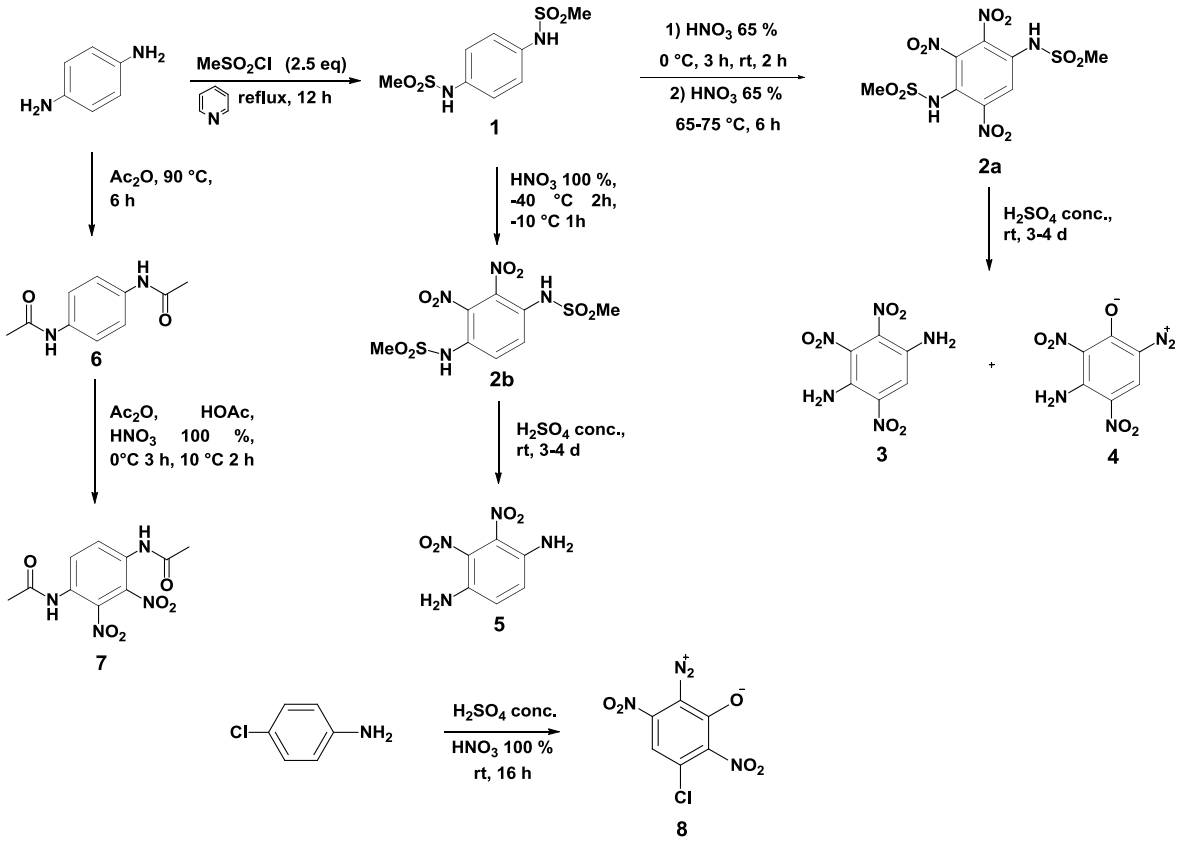
dipotassium 1,1'-dinitramino-5,5'-bitetrazolate.[6] Another option are metal-free primary explosives like 1-(5-tetrazolyl)-3-guanyltetrazene hydrate (tetrazene), 2-diazo-4,6-dinitrophenol (DDNP), or 2,4,6-triazido-1,3,5-triazine (TAT), but practically most of them only undergo a DDT when confined and even then rather large amounts (several hundred milligrams) are necessary for the reliable initiation of a secondary explosive, rendering them unserviceable for small initiation devices. As a result of this and their high sensitivities toward mechanical stimuli they are usually utilized either in (environmentally benign) percussion caps,[7] or as sensitizers in detonators. For example, the addition of 2 % tetrazene to LA lowers the stab initiation energy from 1000 mJ to 3 mJ.[8] However, TAT is currently under investigation as LA replacement in the NOL-130 stab mix employed in the M55 stab detonator,[9] owing to its better initiation capability than LA.[10] Unfortunately, it suffers from the major drawback of a high volatility due to the non-ionic structure with only weak intermolecular interactions. The recently presented,[11] and herein further investigated, 6-diazo-3-hydroxy-2,4-dinitrophenol (**HODDNP**) and 4-diazo-2,6-dinitrophenol (***iso*-DDNP**) offer the zwitterionic nature of DDNP coupled with a higher density. **HODDNP** with its additional hydroxy group in comparison to DDNP is a non-volatile metal-free primary explosive with superior initiation capability than DDNP itself.

Furthermore two new diazophenols, namely 6-diazo-3-amino-2,4-dinitrophenol (**4**) and 3-chloro-6-diazo-2,5-dinitrophenol (**8**) were synthesized. During the synthesis of **4** the regio-selectivity of the nitrations using *N*,*N'*-(1,4-phenylene)dimethanesulfonamide (**1**) and *N,N'*-(1,4-phenylene)diacetamide (**6**) as starting materials was investigated and confirmed by single crystal X-ray diffraction and NMR spectroscopy. The nitration of *N*,*N'*-(1,4-phenylene)dibenzenesulfonamide resulting in the formation of three regio-isomers was already described by K. -Y. Chu and J. Griffiths.[12] The use of the methanesulfonyl protection group resulted in two advantages described herein. Additionally, the initiation capability of these two compounds (**4** and **8**) was also tested in combination with RDX.

8.3 Results and discussion

8.3.1 Synthesis

A synthesis protocol is displayed in scheme 1.



Scheme 1: Syntheses of diazophenols **4** and **8**.

The first step was the protection of the free amines resulting either in the formation of *N*,*N'*-(1,4-phenylene)dimethanesulfonamide (**1**) or *N*,*N'*-(1,4-phenylene)diacetamide (**6**). After that the regio-selectivity toward the nitration of **1** and **6** was intensively studied. **2a** was synthesized *via* a two-step nitration. In the first step an isomeric mixture of twice nitrated species was obtained. This was confirmed via *CHN* analysis. When the nitration is heated up to 65–75 °C the corresponding trinitro-derivative (**2a**) was obtained. **2a** could only be obtained when methansulfonyl chloride was used as protection group. When, for example the benzenesulfonyl or the *p*-toluenylsulfonyl protection groups were used only the twice nitrated species were formed. Too harsh nitration conditions resulted in the cleavage of those protection groups or their nitration. *N*,*N'*-(2,3-dinitro-1,4-phenylene)dimethanesulfonamide (**2b**) or *N*,*N'*-(2,3-dinitro-1,4-phenylene)diacetamide (**7**) could also be synthesized selectively. Compound **2b** was synthesized using 100 % nitric acid at low temperatures and **7** by using acetylnitrate as nitrating reagent. The regio-selectivity was confirmed by crystallization of the

protected (for compound **7**) and the deprotected product (for compound **5**). It was also confirmed that **2b** can be used as a more efficient starting material for **2a** achieving higher yields. In this case **2a** was synthesized by using 82.5 % nitric acid at a reaction temperature of 45 °C resulting in an enhanced yield of **2a** (70 %). The deprotection of **2a** resulted in the formation of two different compounds. As expected 1,4-diamino-2,3,5-trinitrobenzene (**3**) is formed. Additionally the highly sensitive primary explosive 3-amino-6-diazo-2,4-dinitrophenol (**4**) is formed. This even happens in all attempts to synthesize 1,4-diamino-2,3,5,6-tetranitrobenzene with **3** as starting material. The same behavior was observed when using 4-amino-2,3,6-trinitrophenol, resulting in the formation of **HODDNP**.[11] The mechanism how **3** is converted into **4** could not be determined certainly. After isolation of pure **3** and **4** DSC curves were recorded to determine their decomposition temperatures (displayed in Figure 1). Additionally, compounds **5** and **7** were crystallized from DMSO.

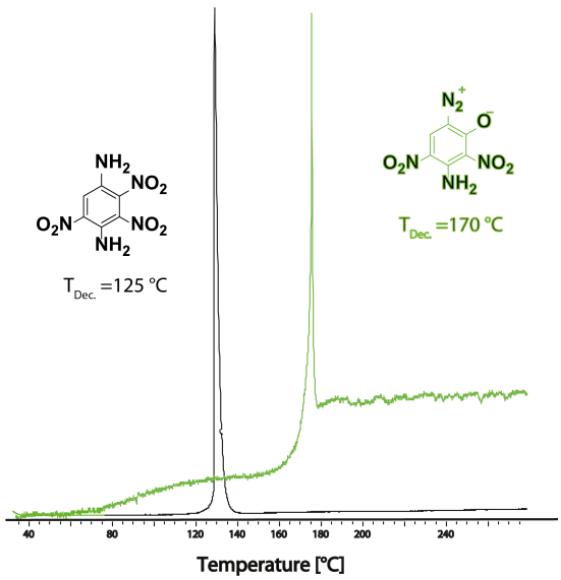


Figure 1: DSC curves of **3** and **4** (heating rate β = 5 °C min^{-1}).

These two products differ dramatically in their thermal stability. Interesting to mention is the unexpected low thermal stability of **3** (125 °C). The literature known constitution isomer 1,3-diamino-2,4,6-trinitrobenzene for example is stable up to 286 °C.[13] Compound **4** however shows the typical thermal stability of 170 °C. The purity of **3** could only be confirmed by *CHN* elemental analysis, high resolution mass spectrometry and additionally by IR spectroscopy due to the conversion of **3** into **4** in organic polar solvents. The diazo vibration at 2195 cm^{-1} and the carbonyl vibration at 1593 cm^{-1} only appear in the IR spectrum of **4**. The N–H vibrations of the amino groups appear at 3365 cm^{-1} and 3474 cm^{-1} whereas for **4** they are located at 3282 cm^{-1} and 3390 cm^{-1}. Finally, the nitration of 4-chloroaniline resulted in the formation of 3-Chloro-6-diazo-2,5-dinitrophenol (**8**).

8.3.2 Crystal structures

Suitable single crystal of compounds **2a**, **4**, **5**, **7** and **8** were picked from the crystallization mixtures and mounted in Kel-F oil, transferred to the N_2 stream of an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collection and data reduction was performed using the CRYSALISPRO software.[14] The solution and refinement of all structures were performed using the programs SIR-92[15], SHELXS-97[16] and SHELXL-97[17] implemented in the WINGX software package[18] and finally checked with the PLATON software.[19] The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined when possible. The absorptions were corrected with the SCALE3 ABSPACK multi-scan method.[20] Selected data of the measurements and the refinements are given in Table 1.

Table 1: Crystallographic data and refinement parameters of compound **2a**, **4**, **5**, **7** and **8**.

	2a	**4**	**5**	**7**	**8**
Formula	$C_{12}H_{21}N_5O_{12}S_4$	$C_6H_3N_5O_5$	$C_6H_6N_4O_4$	$C_{10}H_{10}N_4O_6$	$C_6HClN_4O_5$
FW [g mol^{-1}]	555.58	225.13	198.15	282.22	244.56
Crystal system	Triclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space Group	*P*−1 (No. 2)	*Pnma* (No. 62)	*C*2/*c* (No. 15)	*P*−1 (No. 2)	*Pc* (No. 7)
Color / Habit	Colorless plate	Orange block	Yellow block	Yellow needle	Yellow rod
Size [mm]	0.03 x 0.15 x 0.20	0.15 x 0.19 x 0.20	0.19 x 0.21 x 0.49	0.06 x 0.14 x 0.23	0.08 x 0.11 x 0.23
a [Å]	10.1892(11)	16.2313(6)	12.2042(6)	7.7535(16)	6.5289(4)
b [Å]	10.5895(9)	10.6548(4)	10.8478(4)	8.0847(11)	6.9889(4)
c [Å]	11.6355(15)	4.5210(2)	7.2959(4)	10.7662(19)	9.7159(6)
α [°]	97.918(9)	90	90	84.878(13)	90
□ [°]	104.484(10)	90	124.954(4)	70.272(17)	97.723(6)
γ [°]	103.643(8)	90	90	75.493(15)	90
V [Å^3]	1155.1(2)	781.87(5)	791.66(8)	615.0(2)	439.31(5)
Z	2	4	4	2	2
□$_{calc.}$ [g cm^{-3}]	1.597	1.913	1.663	1.524	1.849
□ [mm^{-1}]	0.479	0.170	0.142	0.128	0.450
F(000)	576	456	408	292	244
$\lambda_{MoK\alpha}$[Å]	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	298	173
ϑ min-max [°]	4.2, 26.0	4.6, 27.0	5.1, 26.5	4.3, 26.0	4.2, 26.0
Dataset h; k;	-12:12; -13:13; -14:14	-17:20; -13:13; -5:5	-15:15; -13:13; -9: 9	-9:9; -9:9; -11:13	-8:8; -8:8; -11:11

I					
Reflect. coll.	8374	5595	5627	4029	5976
Independ. refl.	4506	891	823	2385	1704
R_{int}	0.047	0.023	0.023	0.037	0.025
Reflection obs.	3236	822	742	1352	1662
No. parameters	316	88	76	221	149
R_1 (obs)	0.0868	0.0380	0.0303	0.0637	0.0212
wR_2 (all data)	0.1990	0.0947	0.0891	0.1770	0.0525
S	1.08	1.20	1.05	1.01	1.07
Resd. Dens.[e Å^{-3}]	-0.49, 1.63	-0.22, 0.27	-0.25, 0.19	0.22, 0.23	-0.13, 0.15
Device type	Oxford XCalibur3	Oxford XCalibur3	Oxford XCalibur3	Oxford XCalibur3	Oxford XCalibur3
Solution	SIR-92	SIR-92	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorpt. corr.	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
CCDC No.	1425273	1425274	1425276	1425275	1425272

N,*N*′-(2,3,5-trinitro-1,4-phenylene)dimethanesulfonamide (**2a**) could only obtained crystalline with inclusion of DMSO. The molecular unit consisting of one *N*,*N*′-(2,3,5-trinitro-1,4-phenylene)dimethanesulfonamide and two dimethylsulfoxide molecules is shown in Figure 2. The compound crystallizes in the triclinic space group *P*−1 with a density of 1.597 g cm^{-3} at −100 °C. As expected all nitro groups are twisted out of the ring plane.

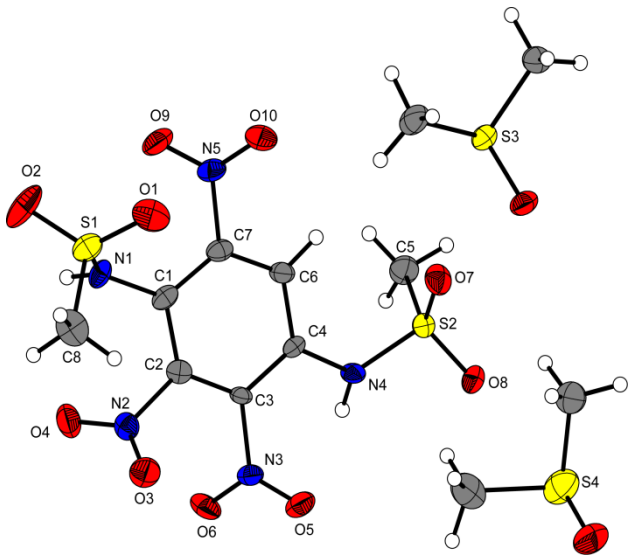


Figure. **2**: Molecular unit of **2a**. Ellipsoids of non-hydrogen atoms in all structures are drawn at the 50 % probability level. **Selected bond lengths** [Å]: C7–N5 1.479 (7), C2–N2 1.471 (8), 1.471 (8), C1–N1 1.411 (9), C4–N4 1.381 (9), S1–N1 1.628 (6), S2–N4 1.645 (6), S1–O1 1.434 (7), S1–O2 1.428 (8), S2–S8 1.426 (5), S1–C8 = S2–C5 1.745 (8); **Selected bond angles**

[°]: C2–C3–N3 117.87 (6), C3–C2–N2 119.22 (6), C6–C7–N5 115.64 (6), C4–N4–S2 125.93 (5), C1–N1–S1 124.31 (5), O1–S1–N1 107.67 (3), O2–S1–N1 105.19 (4), C8–S1–N1 105.68, O2–S1–O1 121.04 (4), O7–S2–O8 120.02 (3), C5–S2–N4 107.09 (3), O8–S2–N4 104.27 (3), O7–S2–N4 107.66 (3); **Selected torsion angles** [°]: C3–C2–N2–O3 57.3 (1), C2–C3–N3–O6 55.9 (1), C6–C7–N5–O10 46.9 (1), C2–C1–N1–S1 75.9 (1), C6–C4–N4–S2 9.4 (1).

The molecular unit of 3-amino-6-diazo-2,4-dinitrophenol (**4**) is depicted in Figure 3. The compound crystallizes in the orthorhombic space group *Pnma* with four molecules in the unit cell. Its density of 1.913 g cm^{-3} at −100 °C is significantly higher than that of the recently published **HODDNP** (1.837 g cm^{-3}).[11] The bond length N1–N2 of 1.098(3) Å clearly indicates a N≡N triple bond whereas the C1–N1 (1.367(3) Å) and C2–O1 (1.324(4) Å) bonds are also significantly shorter than typical C–N (1.47 Å) and C–O (1.43 Å) single bonds.

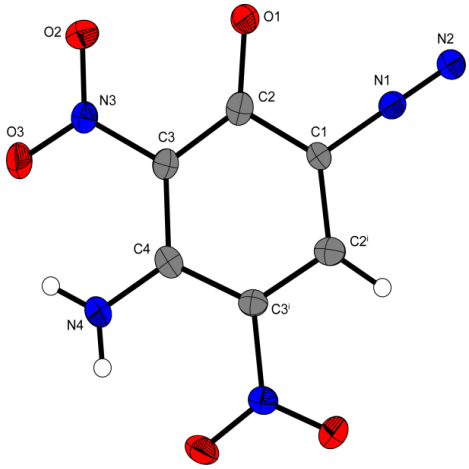


Figure 3: Molecular unit of **4**. Ellipsoids of non-hydrogen atoms in all structures are drawn at the 50 % probability level. **Selected bond lengths** [Å]: C1–N1 1.367 (3), N1–N2 1.098 (3), C2–O1 1.324 (4), C3–N3 1.441 (2), N3–O3 1.235 (2), C4–N4 1.321 (3), O3–N4 2.59 (1); **Selected bond angles** [°]: C1–N1–N2 177.7 (3), N3–O3–O2 121.3, O3–N3–O2 121.3; **Selected torsion angles** [°]: C2–C3–N3–O2 11.8 (2), C3–C4–N4–H 2.9 (2.9).

1,4-Diamino-2,3-dinitrobenzene (**5**), depicted in Figure 4, crystallizes in the monoclinic space group *C*2/*c* with four molecules in the unit cell. Its density at −100 °C is 1.663 g cm^{-3} which is slightly lower than that of 1,3-diamino-2,4-dinitrobenzene (1.74 g cm^{-3} at 298 K)[21] and 1,2-diamino-4,5-dinitrobenzene (1.725 g cm^{-3} at −100 °C).[22] The molecular unit is shown in Figure 4.

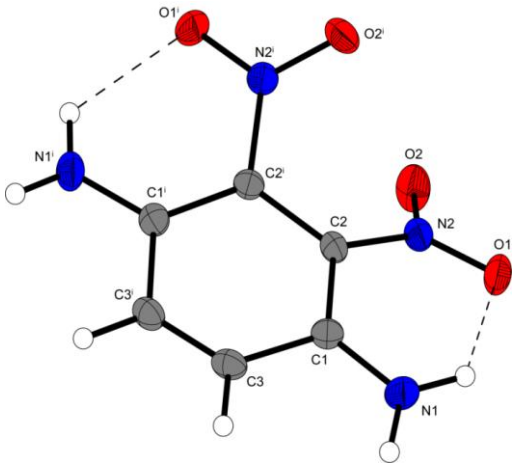


Figure. **4**: Molecular unit of **5**. Ellipsoids of non-hydrogen atoms in all structures are drawn at the 50 % probability level. **Selected bond lengths** [Å]: C1–N1 1.332 (2), C2–N2 1.411 (2), N2–O1 1.254 (2), N2–O2 1.239 (2); **Selected bond angles** [°]: O1–N2–O2 120.8 (2); **Selected torsion angles** [°]: C2–C2i–N2–O2 15.1 (2), C2–C1–N1–H1B 6.8 (2);

The twice N-protected *N,N'*-(2,3-dinitrophenyl)1,4-diacetamide (**7**) crystallizes in the triclinic pace group *P*−1 with two molecular units (Figure 5) in the unit cell. Its density (1.524 g cm^{-3}) is significantly lower than that of **5**.

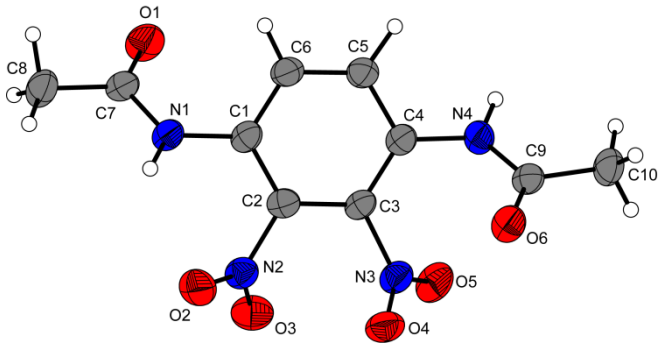


Figure 5: Molecular unit of **7**. **Selected bond lengths [Å]**: C1–N1 1.423 (4), C2–N2 1.464 (4), C3–N3 1.475 (4), C4–N4 1.411 (4), N2–O2 1.217 (3), N2–O3 1.222 (3), N3–O4 1.215 (3), N3–O5 1.221 (3), C7–O1 1.219 (4), C9–O6 1.223 (4), **Selected bond angles [°]**: N1–C1–O1 122.3 (3), O2–N2–O3 123.8 (3), O4–N3–O5 125.5 (3), N4–C9–O6 122.4 (3); **Selected torsion angles [°]**: C3–C4–N4–C9 50.2 (5), C6–C1–N1–C7 42.9 (5), C4–C3–N3–O5 51.5 (5), C3–C2–N2 O3 48.5 (4).

3-Chloro-6-diazo-2,5-dinitrophenol (**8**), depicted in Figure 6, crystallizes in the monoclinic space group *Pc* with two molecules in the unit cell. Its density at −100 °C is 1.849 g cm^{-3} which interestingly is lower than that of **4 (**1.913 g $cm^{-3)}$. The diazo bond N2–N9 (1.111(2) Å) is again in the range of a N≡N triple bond whereas the C4–N5 bond length is significantly shorter (1.234(2) Å) than the C–O bond observed in structure of **4**.

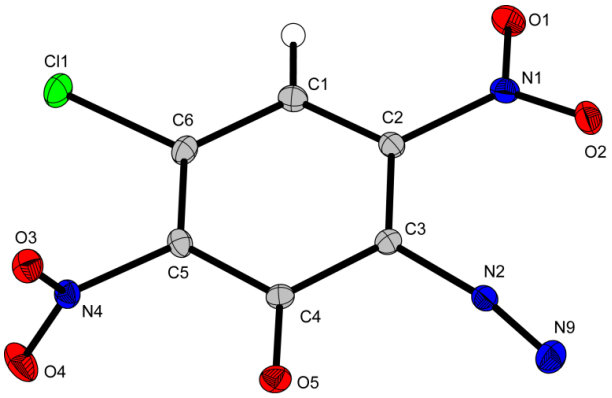


Figure 6. Molecular unit of **8**. Ellipsoids of non-hydrogen atoms in all structures are drawn at the 50% probability level. **Selected bond lengths [Å]:** C3–N2 1.354 (2), N2–N9 1.111 (2), C4–O5 1.234 (2), C5–N4 1.465 (2), N4–O3 1.221 (2), N4–O4 1.220 (2), C6–Cl1 1.714 (2), C2–N1 1.470 (2), N1–O1 1.228 (2), N1–O2 1.219 (2); **Selected bond angles [°]:** C3–N2–N9 168.3 (2), O2–N1–O1 125.0 (2), O3–N4–O4 125.1 (2); **Selected torsion angles [°]:** C4–C3–N2–N9 0.7 (1), C4–C5–N4–O3 77.4 (2), C3–C2–N1–O2 12.8 (2).

8.3.3 Initiation capability testing and energetic properties

The capability of the compounds to undergo a DDT was tested with some basic heating methods. First, a small amount (approx. 5 mg) of **HODDNP**, ***iso*-DDNP**, **4** or **8** was heated on a spatula using a lighter, without direct flame contact. Typical for metal-free primary explosives the compounds only deflagrated upon reaching their corresponding ignition temperatures due to the missing confinement, similar to tetrazene and DDNP. Rapid heating by touching a small amount of the compounds with a hot needle or a hot spatula thus also only resulted in a deflagration. To investigate the capability of the compounds to nevertheless initiate a secondary explosive the commonly used RDX (200 mg) was loaded into an aluminum tube (58.0 mm × 7.2 mm, inner diameter 6.5 mm) glued to the center of a copper witness plate (50 mm × 50 mm × 1 mm) and slightly pressed manually. Varying amounts of those diazophenols were loaded onto the RDX and also slightly pressed manually. For the ignition a commercial type A electrical igniter was used on top, with a direct contact of the fusehead to the primary explosive. The isolator casing of the igniter was clamped with the metal tube (see Figure 7 for a schematic). The whole setup was placed in a wooden box and covered with slightly wet sand. While ***iso*-DDNP**, **4** and **8** (50 mg of each) were not able to initiate RDX, similar to DDNP itself (also 50 mg), **HODDNP** on the other hand was able to initiate RDX. Figure 8 shows the test results of **HODDNP** together with the witness plate of a lead azide (50 mg) test sample. The plates clearly reveal that not only did 25 mg of **HODDNP** result in a full detonation of RDX but even a small amount of only 10 mg were able to detonate the secondary explosive. DDNP itself, ***iso*-DDNP**, **4** and **8** only resulted in a (partial) deflagration of the output charge, with merely a small dent in the copper plate, or no damage at all. In the case of a detonation the aluminum tube is completely

shattered into very small pieces, while in the case of a deflagration it is usually only torn open. Typically, in the case of the latter about half of the RDX load can still remain in the bottom of the tube with no visible changes to it.

Furthermore the thermal stability of **HODDNP** was tested by isoperibolic long term measurement in an open glass vessel using a Systag Flexy TSC equipped with a Radex V5 measuring cell, revealing that the compound is stable for at least 60 hours at 75 °C. Moreover, storage of this compound in an oven at 100 °C for 60 hours does not result in any mass lost or change in the chemical composition. This was proven *via CHN* elemental analysis and ^{1}H NMR spectroscopy. In addition, **HODDNP** is stable when stored under water, which is important for shipping security reasons. After suspending it in 30 ml of water the suspension was allowed to stand for a few days at ambient temperature until the water evaporated. The chemical composition was subsequently again confirmed via *CHN* elemental analysis and ^{1}H NMR spectroscopy as unchanged and pure.

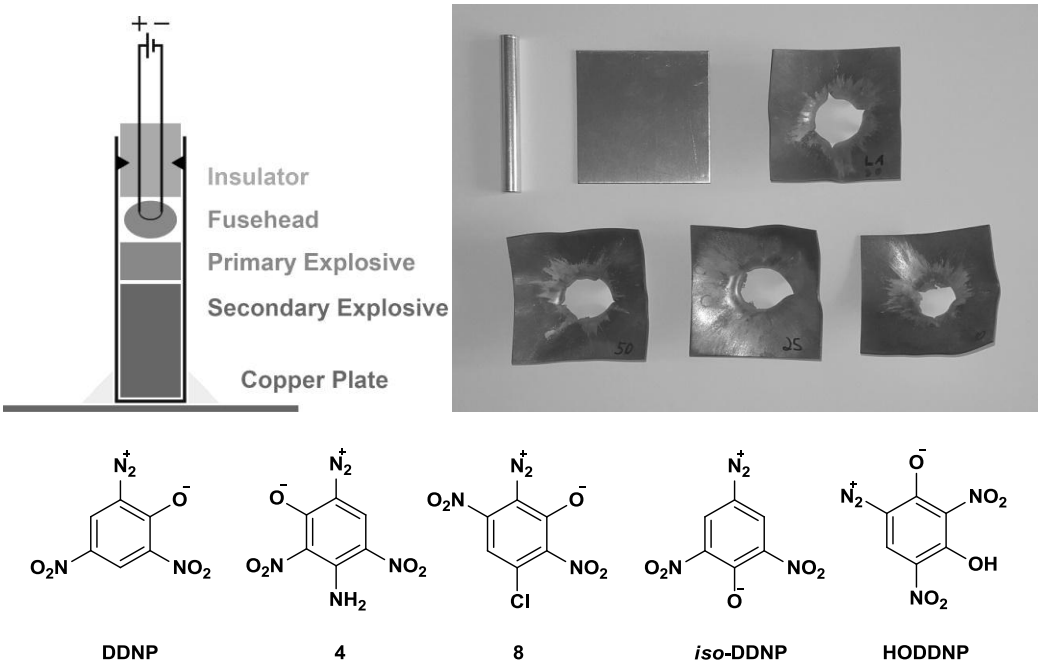


Fig. 7: Schematic test setup (top left), tested primary explosives (row below) and results of the initiation capability test of **HODDNP** (top right): Upper row: aluminum tube, copper plate, copper plate of the lead azide (50 mg) benchmark; lower row: copper plates of the tests with **HODDNP** (50, 25, 10 mg); each test performed with 200 mg RDX as secondary explosive.

8.4 Conclusions

The regio-selective nitration of double protected *p*-phenylene-1,4-diamine was investigated.The methanesulfonyl protection group seems to be superior in comparison to the acetyl group because it allows the phenyl ring to be nitrated three times and the cleavage of that group works straight forward. The yields for *N*,*N'*-(2,3,5-trinitro-1,4-

phenylene)dimethanesulfonamide (**2a**) could be improved by two steps by first nitrating *N*,*N'*-(1,4-phenylene)dimethanesulfonamide twice in C2 and C3 position and then in C5 position with 82.5 % HNO_3 at 45 °C.The capability of the synthesized diazophenols (**4**, **8**, **HODDNP** and ***iso*-DDNP**) to initiate RDX was tested and compared to DDNP. **HODDNP** shows superior properties as RDX initiator in comparison to DDNP. It is thermally stable for a prolonged time (100 °C for 60 hours), stable in water and obtainable *via* a low cost straight forward synthesis.

8.5 Experimental section

NMR spectra were recorded using the spectrometers JEOL Eclipse 270, Eclipse 400, JEOL ECX 400 and Bruker Avance III 400. The measurements were conducted in regular glass NMR tubes (Ø 5 mm) and, if not stated otherwise, at 25 °C. Tetramethylsilane (^{1}H, ^{13}C) and nitromethane (^{15}N) were used as external standards. As an additional internal standard the reference values of the partially deuterated solvent impurity (^{1}H) and the fully deuterated solvent (^{13}C) were used.[23] Infrared (IR) spectra were recorded on a PerkinElmer BX FT IR spectrometer equipped with a Smiths DuraSamplIR II diamond ATR unit using pure samples. Transmittance values are qualitatively described as “strong” (s), “medium” (m) and “weak” (w). The determination of the carbon, hydrogen and nitrogen contents (EA analysis) was carried out by combustion analysis using an Elementar Vario EL. Differential scanning calorimetry was conducted with a Linseis DSC-PT10 in closed aluminum pans, equipped with a hole (Ø 0.1 mm) for gas release, and at a heating rate of 5 °C min^{-1}. Melting points were checked with a Büchi Melting Point B-540 apparatus in open glass capillaries. The sensitivities to impact (IS) and friction (FS) were determined according to BAM[24] standards using a BAM drop hammer (100 cm maximum drop height; 1, 5 and 10 kg weights; compound contained between two steel cylinders held together by a steel ring) and a BAM friction apparatus (5 to 360 N range).[25] The compounds were sieved to determine the grain size (< 100 µm, 100 to 500 µm, > 500 µm).

N,*N'*-(1,4-phenylene)dimethanesulfonamide (**1**):

P-Phenylene-diamine (36.2 g, 335 mmol) was dissolved in pyridine (350 mL). The solution was cooled down to 0 °C and methanesulfonylchloride (57.0 ml, 781 mmol) was added slowly. After 1 h the cooling was removed and the suspension was stirred at ambient temperature for about 3 h. Subsequently, the suspension was refluxed for at least 16 h. After that the solution was poured onto crushed ice (1 kg) and filtered. The precipitate was washed with large amounts of 2 M hydrochloric acid and water. **2** was obtained as a cocoa-colored powder (84.8 g, 96 %). *N*,*N'*-(1,4-phenylene)dimethanesulfonamide ($C_8H_{12}N_2O_4S_2$

264.32 g mol^{-1}) (**1**): **EA** found (calc): C 36.49 (36.35), H 4.75 (4.58), N 10.89 (10.60), S 24.40 (24.26); **^{1}H NMR** ([D$_6$]DMSO, 25 °C): δ [ppm] = 2.91 (s, 6H, CH$_3$), 7.15 (s, 4H, CH$_{arom.}$), 9.58 (s, br, 2H, NH); **^{13}C{^{1}H} NMR** ([D$_6$]DMSO, 25 °C): δ [ppm] = 39.6 (2C, CH$_3$), 122.2 (4C, CH), 135.1 (2C, C-N);

N,*N*′-(2,3,5-trinitro-1,4-phenylene)dimethanesulfonamide (**2a**):

Nitric acid (65 %, 200 ml) was cooled to 0 °C. **1** (25 g, 95 mmol) was added portion wise so that the temperature did not exceed 5 °C. The solution was stirred at 0 °C for 6 h. After that the solution was further stirred at ambient temperature for about 12 h. The formed yellow precipitate is a mixture of isomeric *N*,*N*′-(dinitro-1,4-phenylene)dimethanesulfonamide and **2a**. The suspension was poured onto crushed ice (1 kg) and filtered. After washing with large amounts of water the crude solid was dried in an oven at 60 °C for about 12 h. Then, nitric acid (65 %, 250 ml) was heated up to 65–70 °C. The crude material isolated before was added slowly, resulting in the release of huge amounts of nitrous fumes. The suspension was stirred until no such fumes occurred anymore (typically four to five hours). After that the suspension was poured onto crushed ice (500 g). The bright yellow solid was filtered off and washed only with small amounts of ice water to remove the acid. The obtained **2a** was dried in an oven at 60 °C for 12 h. After that, **2a** was further purified. The yellow solid was refluxed in glacial acetic acid overnight. Subsequently the suspension was filtered directly after cooling down to ambient temperature and pure **2a** was obtained (12 g, 32 %). *N*,*N*′-(2,3,5-trinitro-1,4-phenylene)dimethanesulfonamide ($C_8H_9N_5O_{10}S_2$ 399.31 g mol^{-1}) (**2a**) **DSC** (5 °C min^{-1}): $T_{dec.}$ = 230 °C, **EA** found (calc): C 24.18 (24.06), H 2.35 (2.27), N 17.79 (17.54), S 16.30 (16.06); **^{1}H NMR** ([D$_6$]DMSO, 25 °C): δ [ppm] = 3.05 (s, 3H, CH$_3$), 3.23 (s, 3H, CH$_3$), 8.37 (s, 1H, CH$_{arom.}$); Note: The N-H protons could not be observed; **^{13}C{^{1}H} NMR** ([D$_6$]DMSO, 25 °C): δ [ppm] = 41.6 (1C, CH$_3$), 42.5 (1C, CH$_3$), 118.8 (1C, C-H), 124.0, 133.1, 138.2, 143.8, 149.5; **^{15}N NMR** ([D$_6$]DMSO, 75 °C, 25 °C): δ [ppm] = –18.5 (d,$^{3}J_{N-H}$ = 2.8 Hz, 1N, NO$_2$), –23.7 (s, 1N, NO$_2$), –24.1 (d, $^{4}J_{N-H}$ = 2.8 Hz, 1N, NO$_2$), –262.3 (d, $^{3}J_{N-H}$ = 0.8 Hz, 1N, NH-SO$_2$Me), –281.6 (s, 1N, NH-SO$_2$Me);

Alternative synthesis of **2a** using **2b** as starting material: Nitric acid (65 %, 20 ml) was mixed with nitric acid (100 %, 20 ml) under cooling. After that **2b** (4.5 g, 13 mmol) was added slowly. After 1 h the suspension was heated to 45 °C and the temperature was held for 16 h. The suspension was filtered through a borosilicate glass filter (pore size 3) after cooling down to ambient temperature. The precipitate was washed first with water, then with ethanol and diethyl ether. **2a** was thus obtained as a pale yellow powder (3.6 g, 70 %). Analytics for **2a** see above.

N,*N'*-(2,3-Dinitro-1,4-phenylene)dimethanesulfonamide (**2b**):

Nitric acid (100 %, 150 ml) was cooled down to −40 °C. After that **1** (20.0 g, 75.7 mmol) was added slowly so that the temperature did not exceed −30 °C. After that the dark solution was stirred at −40 °C for 2 h. Then, the solution was warmed up to −10 °C and further stirred for 1 h. Afterwards it was poured onto crushed ice and **2b** precipitated as a brownish powder. **2b** was filtered and washed with ice water to get rid of nitric acid. (14.9 g, 56 %) *N*,*N'*-(2,3,-dinitro-1,4-phenylene)dimethanesulfonamide ($C_8H_{10}N_4O_8S_2$ 354.32 g mol^{-1}) (**2b**) **EA** found (calc): C 27.20 (27.12), H 2.55 (2.84), N 15.74 (15.81), S 18.22 (18.10); **^{1}H NMR** ([D_6]DMSO, 25 °C): δ [ppm] = 3.17 (s, 3H, CH_3), 7.88 (s, 2H, C-$H_{arom.}$), 10.30 (s, br, 2H, N-H); **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C): δ [ppm] = 41.3 (2C, CH_3), 128.6 (2C, C-H), 131.3 (2C, C-$NH_{sulfonamide}$), 139.2 (2C, C-NO2);

1,4-Diamino-2,3,5-trinitrobenzene (**3**):

2a (10 g, 25 mmol) was suspended in concentrated sulfuric acid (250 ml) at 0 °C and water (10 ml) was added very slowly so that the temperature did not exceed 15 °C. The suspension was stirred until a dark red solution was obtained (typically 24–48 hours!!). After that the solution was filtered using a very fine borosilica consisting suction strainer (pore size 4) to get rid of traces of **2a**. The clear filtrate was slowly poured onto large amounts of crushed ice (about 1 kg) so that the temperature did not rise significantly. **3** was obtained as a dark purple powder (1.8 g 30 %). 1,4-Diamino-2,3,5-trinitrobenzene ($C_6H_5N_5O_6$ 243.13 g mol^{-1}) (**3**) **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 125 °C; **EA** found (calc): C 29.77 (29.64), H 2.07 (2.07), N 28.91 (28.80); **HRMS** (% (err-mmu)): 243.0231 (-0.9);MS (DEI+,(%)): 243.1 (100), 197.1 (M-HNO_2 (2)), 151.1 (197.1-NO_2(58)), 105.1 (151.1-NO_2(23); **IR** (ATR cm^{-1}) ν = 3474 (m), 3365 (s), 3090 (w), 1549 (s), 1528 (s), 1427 (m), 1390 (w), 1348 (m), 1253 (vs), 885 (s), 809 (s), 766 (m), 743 (m); Good NMR data could not be obtained so far. It is proposed that **3** decomposes to **4** in any organic solvent.

When the mother liquor of **3** is stored in the fridge at 4 °C for at least 24 hours compound **4** slowly started to precipitate. This also happens when the solution during the deprotection exceeds 30 °C. 3-Amino-6-diazo-2,4-dinitrophenol ($C_6H_3N_5O_5$ 225.13 g mol^{-1}) (**4**) : **DSC** (5 °C min^{-1}): $T_{dec.}$ = 170 °C; **EA** found (calc): C 31.94 (32.01), H 1.40 (1.34), N 30.87 (31.11); **^{1}H NMR** ([D_6]DMSO, 75 °C, 25 °C): δ [ppm] = 8.69 (s, br, 2H, NH_2), 9.32 (s, 1H, CH_{arom}), **^{13}C{^{1}H} NMR** (*D*[D_6]DMSO, 25 °C): δ [ppm] = 87.3 (1C, C-N_2), 123.7, 125.1, 137.2, 147.0, 163.9 (1C, C-O); **^{15}N NMR** ([D_6]DMSO, 25 °C): δ [ppm] = –15.0 (s, 1N, NO_2), –16.4 (d $^3J_{N\text{-}H}$ = 2.8 Hz, 1N, NO_2), –37.5 (s, 1N, N_2, N_β), –137.1 (d, $^3J_{N\text{-}H}$ = 3.2 Hz, 1N, N_2, N_α), –288.7 (s, 1N, NH_2); **IR** (ATR cm^{-1}) ν = 3390 (m), 3282 (m), 3076 (w), 2195 (s), 1593 (vs), 1557 (s), 1520

(m), 1477 (m), 1368 (m), 1311 (m), 1277 (s), 1242 (s), 1162 (m), 1128 (m), 1033 (m), 929 (m), 887 (m), 781 (m), 755 (m), 570 (s); **Sensitivities** (grain size < 100 µm): IS 1 J, FS 28 N.

1,4-Diamino-2,3-dinitrobenzene (**5**):

2b (10.0 g, 28.2 mmol) was dissolved in concentrated sulfuric acid (150 ml) and water (5 ml) was added slowly. The dark solution was stirred at ambient temperature for at least three days. Afterwards the solution was poured onto crushed ice (1 kg). **5** precipitated as a dark reddish powder (3.8 g, 68 %). 1,4-diamino-2,3-dinitrobenzene ($C_6H_6N_4O_4$ 198.14 g mol^{-1}) (**5**): **^{1}H NMR** ([D_6]DMSO, 25 °C): δ [ppm] = 7.13 (s, 2H, C-$H_{arom.}$), 7.19 (s, br, 2H, NH_2); **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C): δ [ppm] = 123.1 (2C, C-NH_2), 128.2 (2C, C-$H_{arom.}$) 139.8 (2C, C-NO_2);

N,*N*′-(1,4-Phenylene)diacetamide (**6**):

P-phenylenediamine (10 g, 93 mmol) was dissolved in acetic anhydride (100 ml) at ambient temperature. The slurry was boiled at 90 °C for 6 h. Afterwards the mixture was poured onto ice water (500 g) and stirred until the acetic anhydride was completely hydrolyzed. After filtration the solid was washed with large amounts of water and 2 M HCl to remove the acetic acid. After drying at 60 °C for 12 h, **6** was obtained as a colorless powder. (12.5 g 70 %). *N*,*N*′-(1,4-phenylene)-diacetamide ($C_{10}H_{12}N_2O_2$ 192.21 g mol^{-1}) (**3**): **EA** found (calc.): C 62.68 (62.49), H 6.50 (6.29), N 14.74 (14.57); **^{1}H NMR** ([D_6]DMSO, 25 °C): δ [ppm] = 2.02 (s, 6H, CH_3), 7.49 (s, 4H, C-$H_{arom.}$), 9.85 (s, br, 2H, N-$H_{acetamide}$); **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C): δ [ppm] = 24.3 (s, 2C, CH_3), 119.9 (s, 4C, C-$H_{arom.}$), 135.1 (s, 2C, C-N-$H_{acetamide}$), 168.4 (s, 2C, C=O);

N,*N*′-(2,3-Dinitro-1,4-phenylene)diacetamide (**7**):

In a two necked 250 ml flask equipped with a thermometer nitric acid (99.5 %, 10 ml) was dropwise added to Ac_2O (100 ml, 1.06 mol) at 0 °C. The temperature should not rise above 10 °C. After that glacial acetic acid (10.0 ml, 175 mmol) was added. The solution was stirred at 0 °C for at least 1 h. In the next step **6** (8.0 g 42 mmol) was added slowly so that the temperature did not exceed 10 °C, resulting in a solution after several minutes. After one hour the temperature was risen to ambient temperature using a water bath. The formed suspension was further stirred at ambient temperature for 4 h. Then the suspension was poured onto crushed ice (600 g). After stirring for 1 h the precipitate was filtered off, washed with large amounts of cold water to remove traces of acid and then dried in an oven at 60 °C for 12 h. **7** was obtained as a white-yellow powder (10.5 g, 89 %). *N*,*N*′-(2,3-Dinitro-1,4-phenylene)diacetamide ($C_{10}H_{10}N_4O_6$ 282.22 g mol^{-1}) (**7**): **EA** found (calc): C 42.58 (42.56), H

3.42 (3.57), N 19.74 (19.85); **^{1}H NMR** ([D_6]DMSO, 25 °C): *δ* [ppm] = 2.06 (s, 6H, CH_3), 7.78 (s, 2H, C-$H_{arom.}$), 10.38 (s, br, 2H, N-$H_{acetamide}$); **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C): *δ* [ppm] = 23.4 (s, 2C, CH_3), 128.7 (s, 2C, C-$H_{arom.}$), 130.8 (s, 2C, C-N-$H_{acetamide}$), 138.3 (s, 2C, C-NO_2), 169.7 (s, 2C, C=O);**^{15}N NMR** ([D_6]DMSO, 25 °C): *δ* [ppm] = –17.8 (t, N = $I^4J_{N,H}$ + $^5J_{N,H}I$ = 0.6 Hz, 2N, NO_2), –257.1 (d, $^1J_{N-H}$ = 92.0 Hz, 2N, N-$H_{acetamide}$); **^{15}N{^{1}H} NMR** ([D_6]DMSO, 25 °C): *δ* [ppm] = –17.8 (s, 2N, NO_2), –257.1 (s, 2N, N-$H_{acetamide}$).

3-chloro-6-diazo-2,5-dinitrophenol (**8**):

4-Chloroaniline (3.0 g, 24 mmol) was dissolved in concentrated sulfuric acid (30 ml) at ambient temperature. After that nitric acid (100 %, 3.5 ml) was added slowly so that the temperature did not exceed 40 °C. The formed suspension was further stirred at ambient temperature for 12–16 h and then poured onto crushed ice (250 g). A powder was formed which was filtered off and washed with small amounts of ice-water to remove traces of acid. After drying at ambient temperature **8** was obtained as a brilliant yellow powder (3.1 g 53 %). 3-chloro-6-diazo-2,5-dinitrophenol ($C_6HClN_4O_5$ 244.55 g mol^{-1}) (8): **DSC** (5 °C min^{-1}): $T_{dec.}$ = 165 °C; **EA** found (calc): C 29.51 (29.47), H 0.58 (0.41), N 22.76 (22.91); **^{1}H NMR** ([D_6]acetone, 25 °C): *δ* [ppm] = 7.50 (s, 1H, C-$H_{arom.}$); **^{13}C{^{1}H} NMR** ([D_6]acetone, 25 °C): *δ* [ppm] = 86.0 (s, 1C, C-N_2), 113.1 (s, 1C, C-$H_{arom.}$), 134.9 (s, 1C, C-Cl), 143.1 (s, 1C, C-NO_2), 148.0 (s, 1C, C-NO_2), 164.9 (s, 1C, C-O); **Sensitivities** (grain size < 100 µm): IS 1 J, FS 12 N.

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9. Unpublished results

The second part of this doctoral thesis consists of three main topics. The first chapter of this part comprises the work that aimed to achieve the synthesis of 1,4 disubstituted polynitrobenzenes. This kind of 1,4 disubstituted polynitrobenzenes has only been scarcely described in literature so far.[1] Only 1,4-dimethoxy-2,3,5,6-tetranitrobenzene has been mentioned as yet as a potential melt-castable explosive.[2,3] Most benzene-based explosives show high decomposition points and mostly have amino groups neighboring nitro groups, which has two great advantages. Hydrogen-bonding between those groups enhances the thermal-stability and in addition the density rises significantly.[4,5] Such amino-nitro-benzenes also show low sensitivity towards external stimuli making them safer for handling. Therefore, amino and hydroxy groups are favoured as substituents in new benzene based explosives. The attempted synthesis of 1,4-diamino-2,3,5,6-tetranitrobenzene (**1**) was one of the main focuses in this chapter. This compound is one of the last not yet described benzene-based potential secondary explosives. In the first part of this chapter different synthetical approaches made so far are described. The second chapter comprises the syntheses of several energetic compounds already known in literature. These compounds were synthesized to calculate their detonation parameters and to confirm or refine their sensitivity data towards external stimuli like impact, friction and electrostatic discharge and thermal properties with our standardized BAM certified methods. The last chapter describes, among other topics, undesired side reactions that took place in the syntheses presented in the cumulative publication part of this doctoral thesis. In addition, it is mentioned that some results in this chapter concerning the syntheses of dinitrodiazophenols are already described in publication F (chapter 8).

9.1 Results for new 1,4-disubstituted polynitro-benzene-based chemistry

9.1.1 Calculation of the energetic properties of 1,4-diamino-2,3,5,6-tetranitrobenzene (1)

This chapter is meant to describe the synthetical approaches for 1,4-diamino-2,3,5,6-tetranitro-benzene (1,4-diamino-2,3,5,6-tetranitro-benzene) (**1**). First a CBS-4M calculation was performed using the GAUSSIAN software to determine the potential of this compound regarding its energetic performance. In order to obtain realistic detonation parameters using the EXPLO5 6.01 computer code, thermal stability ($T_{Dec.}$ = 250 °C) and density (ρ = 1.90-1.95 g cm^{-3}) had to be estimated. Compound **1** was calculated using the CBS-4M Gaussian computer code to obtain its energy of formation ($\Delta_f U°$ / kJ kg^{-1}). The estimation of its density and thermal stability is based on literature known compounds. A density of 1.90-1.95 g cm^{-3}

and a thermal stability of 250 °C seem to be realistic. Its theoretical detonation parameters in comparison to RDX, calculated with EXPLO5 6.01, are displayed in table 1.

Table 1: Theoretical detonation parameters of compound **1** in comparison to RDX with ρ = 1.90 g cm^{-3}and 1.95 g cm^{-3}

	1	**1**	**RDX**
$\Delta_f H_m°$ / kJ mol^{-1} [a]	207	207	70
$\Delta_f U°$ / kJ kg^{-1} [b]	795	795	417
ρ / g cm^{-3} [c]	1.90	1.95	1.80
Ω / % [d]	–33.3	–33.3	–21.6
EXPLO 5 6.01 values:			
$-\Delta_{Ex}U°$ / kJ kg^{-1} [e]	5926	5960	5732
$T_{Det.}$ / K [f]	4068	4024	3804
P_{CJ} / kbar [g]	359	378	349
$V_{Det.}$ / m s^{-1} [h]	8846	9024	8795
V_o / L kg^{-1} [i]	677	667	794

[a] Heat of formation; [b] Energy of formation; [c] Estimated density at 298 K, [d] Oxygen balance [e] Energy of explosion; [f] Explosion temperature; [g] Detonation pressure; [h] Detonation velocity; [i] Volume of gaseous detonation products.

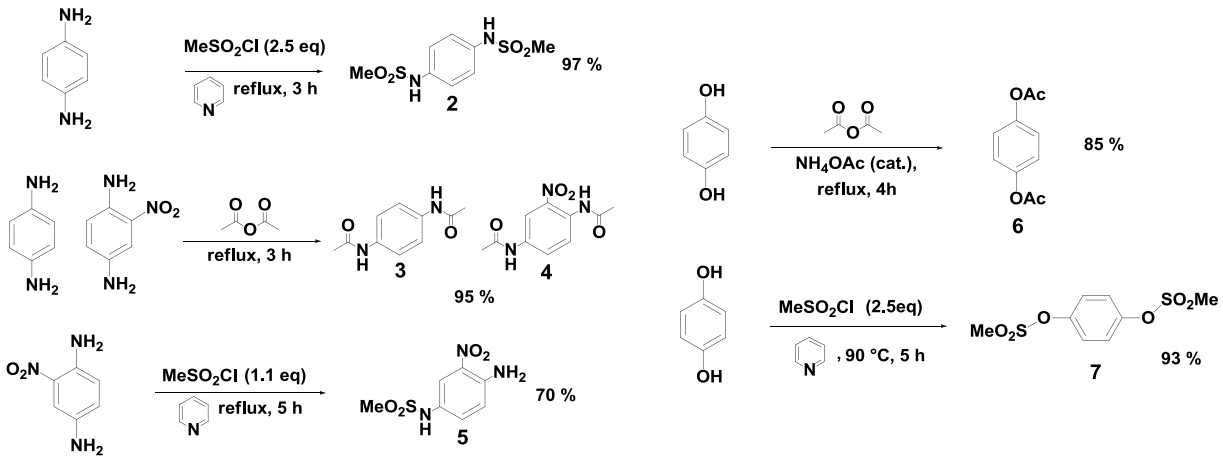
Regarding the EXPLO 5 values for **1**, the detonation parameters are at least equal, if not better than those of RDX. In addition, polynitro-aromatics have the advantage that they are more insensitive towards friction and usually display high densities due to amino-nitro interactions, which lead to high values regarding the theoretical detonation pressure.

9.1.2 Possible synthetical approaches for the synthesis of 1

9.1.2.1 Protection group chemistry

In literature there has only been one description of the attempt to synthesize **1** so far, although it was not possible to deprotect *N*-(4-amino-2,3,5,6-tetranitrophenylene)-trifluoroacetamide.[1] Considering the difficulty of the synthesis of **1**, many new approaches using inexpensive and commercially available starting materials had to be taken. Direct nitration reactions of 1,4-diaminobenzene (*p*-phenylene-1,4-diamine), 1,4-diamino-2-nitrobenzene (2-nitro-*p*-phenylene-1,4-diamine), 3,5-dinitroaniline or 1,4-dihydroxybenzene (1,4-dihydro-*p*-quinone), 4-chloro-aniline and 1,4-dimethoxybenzene were tested. Most 1,4 disubstituted starting materials, without protected amino or hydroxy groups, are not compatible with HNO_3 at deep temperatures because it seems to be too oxidative, even when used in concentrations as low as 65 %. In this case, two different approaches can be pursued. On the one hand, concentrated sulfuric acid paired with a stochiometric amount of nitric acid can be used for this purpose, while, on the other hand, a path applying protection groups can be chosen. Therefore nitration reactions of those amines and phenols were carried out, after protecting the amines and hydroxy functionalities with suitable protection

groups. Typical protection groups like the acetyl, methanesulfonyl, benzenesulfonyl and *p*-toluenylsulfonyl-groups were used.[6,7] A syntheses protocol of this protection group chemistry is displayed in scheme 1. When using methanesulfonylchloride as a protection agent the reaction is typically carried out in pyridine. Hydrochloric acid, which is eliminated during the reaction, is directly removed, thus forming pyridinium-chloride. The esterification of 1,4-dihydro-*p*-quinone and the formation of *N,N'*(*p*-phenylene)-1,4-diacetamide can be achieved directly in acetic anhydride under reflux conditions for several hours. The use of catalytical amounts of NH_4OAc in such acetylation reactions turned out to be very effective in order to optimize the yields. If only one protection group is required like in compound **5**, the reaction can be controlled by reducing the amount of protection reagent added. An overall syntheses protocol is displayed in scheme 1. The purity of all protected precursor molecules (**2**-**7**) was confirmed by ^{1}H,^{13}C {^{1}H} NMR spectroscopy and *CHN* elemental analysis.



Scheme 1: Protection group chemistry of 1,4 Disubstituted benzenes

Whereas the purity of compounds **2**,**3**,**4**,**6** and **7** was confirmed by these analytic methods described above, the regio-selectivity of the protection reaction yielding **5** was validated by low temperature X-ray diffraction. As expected the methanesulfonyl group is attached at the C_4 bonded amine, which is much more nucleophilic than the amine neighbouring the nitro group. Single crystals of compound **5** were grown out of acetone. **5** crystallizes in the monoclinic space group *C2/c* with 8 molecular units per unit cell. The dimensions are a = 20.0686(14) Å, b = 7.183(5) Å, c = 14.0897(12) Å and β = 90.12(2)°. At 173 K the unit cell volume amounts 1984.5(3) Å^3 with a density of 1.548 g cm^{-3}. Figure 1 shows the molecular unit of 5.

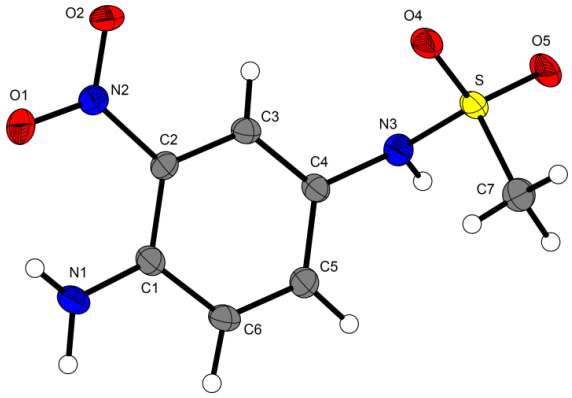
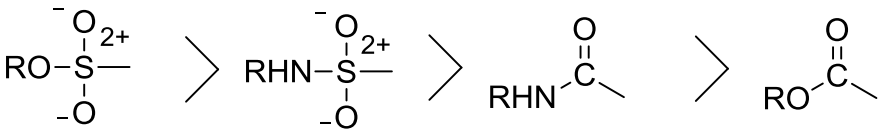


Fig. 1: Molecular unit of compound **5**. The non-hydrogen atoms are represented by displacement ellipsoids at a 50% probability level; **Selected bond lengths** [Å]: C2–N2 1.439 (4), N2–O2 1.234 (3), N2–O1 1.230 (3), C1–N1 1.349 (4), C4–N3 1.436 (4), N3–S1 1.630 (3), S1–O4 1.425 (4), S1–O5 1.430 (2), S1–C7 1.739 (4); **Selected bond angles** [°]: O1–N2–O2 121.6 (3), N1–C1–C2 125.1 (3), C4–N3–S1 119.1 (2), O4–S1–O5 119.0 (2), O5–S1–C7 107.9 (2), N3–S1–C7 106.9 (2); **Selected torsion angles** [°]: C3–C2–N2–O2 3.1 (4), C2–C1–N1–H11 7.7 (4), C3–C4–N3–S1 79.2 (3).

The bond lengths in **5** are within the expected range. The N2–O1 and N2–O1 distance of the nitro group is between a N–O single and a N=O double bond. The amine and the nitro group are nearly planar whereas the methanesulfonyl group is twisted out of the benzene-N3 plane within 79.2(3)°. The bond angle O4–S1–O5 in the protection group is 119.0(2)° indicating a distorted tetrahedral coordination sphere of the sulphur atom. This could be explained by the repulsion of the free electron pairs of the oxygen atoms. Usually S–O single bonds are in the range of 1.70 Å. The S–O bond length in **5** is much shorter than a normal single bond indicating a strong character of ionic interaction.

9.1.2.2 Nitration of 1,4-diprotected benzenes

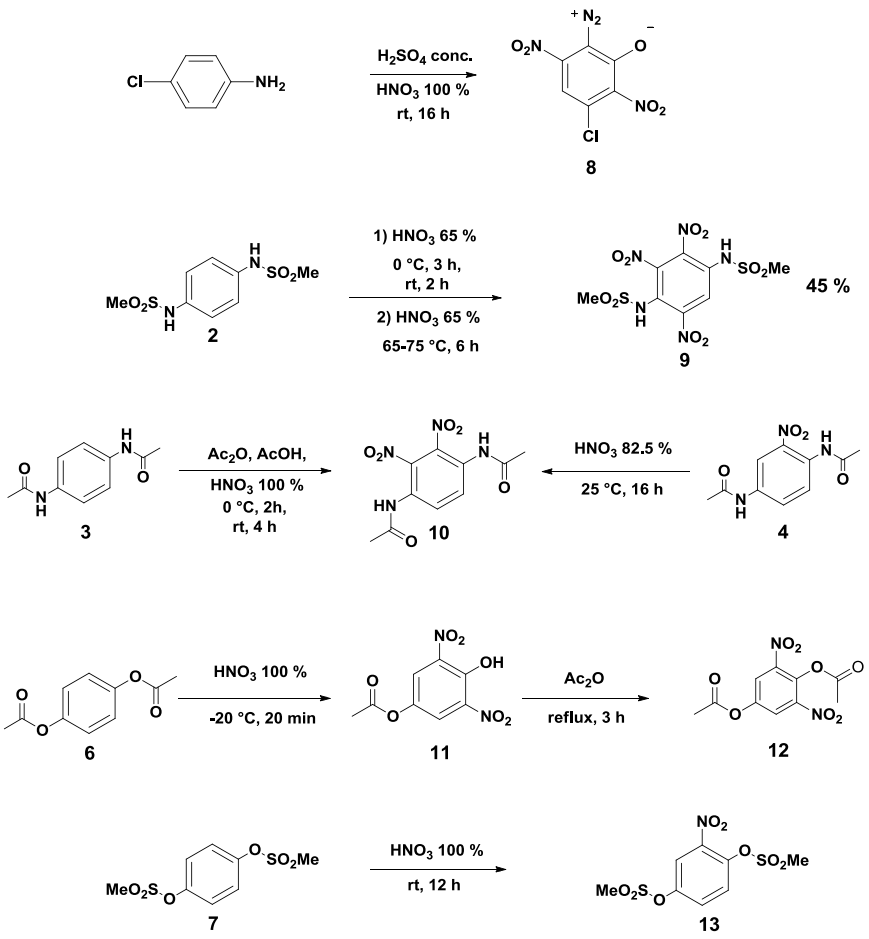
After the protection step the best nitration conditions had to be ascertained, concluding that these protected precursors were only nitrated twice in most cases.[8] It turned out to be an ambitious task to find out the optimal nitration conditions for all those starting materials. The stability and solubility of the different protection groups used differ dramatically in the presence of concentrated oxidizing acids. The stability trend of those protection groups in nitric acid is shown in scheme 2.



Scheme 2: Stability of protection groups in the presence of nitric acid (65-99.5 %) in 1,4-di-protected molecules **2**,**3**,**4**,**6** and **7**.

It was confirmed that the methanesulfonyl protection group is very stable in nitration reactions where only 65 % nitric acid is used. The acetyl protected 1,4-diamines (**3** and **4**),

however, are much more sensitive towards hydrolysis and are barely soluble in nitric acid until a concentration of at least 82.5 % is reached. Although **3** and **4** showed a higher selectivity towards nitration in 82.5 % nitric acid at ambient temperature, the yields are under 45 %. Heating such nitrations when acetamide-groups are involved is not possible and leads to decomposition and sometimes to explosions. Therefore **3** and **4** can only be nitrated twice. An additional effect destabilizing the protection groups could be observed when mono-protected precursors (compound **5**) are used in nitration reactions. Hydrolysis seems to be the first step taking place in nitrating media regardless of the reaction temperature, especially if a free amino group is located in *para* position to a sulfonamide or an acetamide. This intensifies the basicity of the oxygen in the protection group. Using methanesulfonylchloride as a protection reagent for 1,4-dihydro-*p*-quinone yielded **6**. Any attempts to nitrate this compound resulted in the formation of **12** and no dinitro-derivative could be obtained. In contrast to this result the stability of acetyl protected alcohols is drastically lower. This was confirmed in the nitration of compound **7**, which yielded **10**. Here it seems that in the first step one of the ester groups was hydrolyzed even at –20 °C and then the nitration took place in C2 and C6 position. The second acetoxy group in **10** turned out be less alkaline and was therefore not cleaved, at least at 0 °C. Concentrated sulfuric acid or 6 M hydrochloric acid were always used for deprotection reactions. The deprotection of the nitrated products always depends on the basicity of the oxygen which is protonated in the first step of the ester or amide cleavage. Since a bis-sulfonamide is much more acidic than a diacetamide it is harder to protonate and needs much more time. Therefore sulfuric acid free nitration conditions were carried out mainly. In this case 65 % nitric acid is the most commonly used concentration. Concentrations of 82.5 % (equal volumes of 65 % (ρ = 1.40 g cm^{-3}), 90 % (volumes of 65 % and 99.5 % nitric acid = 1:2) and 99.5 % nitric acid (ρ = 1.51 g cm^{-3}) were also applied. An overview of these nitration reactions carried out is displayed in scheme 3.



Scheme 3: Nitration of 4-chloroaniline and protected precursor molecules

First, the nitration product of 4-chloroaniline was analyzed in detail. The expected products were 4-chloro-2,6-dinitroaniline or a 2,3,5-trinitro-derivative. However, after the nitration reaction 3-chloro-6-diazo-2,5-dinitrophenol (**8**) was obtained. This is a very sensitive compound towards external stimuli like impact and friction and must be handled with extreme care. A preliminary test to distinguish between diazophenols and polynitroanilines was achieved by burning the substances over an open flame. While diazophenols usually display a very strong deflagration behavior, polynitroanilines don't. To get a confirmation of the structure of **8** some single crystals were isolated out of dichloromethane for low temperature X-ray diffraction. **8** crystallizes in the monoclinic space group *Pc* with 2 molecular units per unit cell. At 173 K it has a cell volume of 439.31(5) $Å^3$ and a density of 1.849 g cm^{-3}. The cell parameters are a = 6.5289(4) Å, b = 6.9889(4) Å, c = 9.7159(6) Å and β = 97.723(6)°. The molecular unit of **8** is displayed in figure 2.

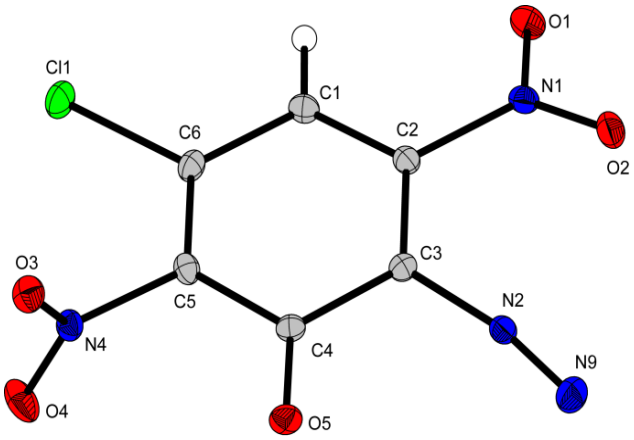


Fig 2: Molecular unit of compound **8**. The non-hydrogen atoms are represented by displacement ellipsoids at a 50% probability level; **Selected bond lengths** [Å]: C3–N2 1.354 (2), N2–N9 1.111 (2), C4–O5 1.234 (2), C5–N4 1.465 (2), N4–O3 1.221 (2), N4–O4 1.220 (2), C6–Cl1 1.714 (2), C2–N1 1.470 (2), N1–O1 1.228 (2), N1–O2 1.219 (2); **Selected bond angles** [°]: C3–N2–N9 168.3 (2), O2–N1–O1 125.0 (2), O3–N4–O4 125.1 (2); **Selected torsion angles** [°]: C4–C3–N2–N9 0.7 (1), C4–C5–N4–O3 77.4 (2), C3–C2–N1–O2 12.8 (2).

The diazo group in **8** shows a typical N2–N9 bond length of 1.111(2) Å, which is in the range of a N–N triple bond. The C3–N2 bond 1.354(2) Å is between a single C–N and a C–N double bond. The C–N bonds of the benzene and the nitro groups are single bonds whereas the N–O bonds within the nitro groups are typically in the range of N–O double bonds. The nitro group in C2 position is twisted out of the benzene plane within 12.8(2)° whereas the other nitro group in C5 position is nearly perpendicular to the benzene plane. The purity of **8** was confirmed via ^{1}H, ^{13}C{^{1}H} and ^{15}N NMR spectroscopy. In the ^{1}H NMR spectrum there is only one signal, a sharp singlet at 7.50 ppm. A further identification of diazophenols in general could be easily achieved by recording a ^{13}C NMR spectrum. The phenolic-carbon always appeared between 163.0 and 167.5 ppm in combination with the diazo-carbon which is located between 80.0 and 92.5 ppm. Regarding a proton coupled ^{15}N NMR spectrum four different signals could be observed. The N1-nitro group at –25.3 ppm shows a doublet with a $^{3}J_{N\text{-}H}$ = 2.8 Hz whereas the N4-nitro group at –20.1 ppm shows only a very small doublet with a $^{4}J_{N\text{-}H}$ coupling constant of 0.8 Hz. The diazo group shows two different signals. The N_{α}, which is directly bond at the phenyl ring, appears at –138.6 ppm with a small $^{4}J_{N\text{-}H}$ coupling constant of 1.2 Hz. N_{β} appears as a singlet at –25.3 ppm in the middle of the doublet of the N2-nitro group.

The next step was the nitration of the protected precursor molecules **2**-**7**. The most interesting results were the following: Compound **2** could be nitrated three times yielding **9** in a two-step nitration. The structure of **9** was determined *via* low temperature X-ray diffraction and a proton coupled ^{15}N NMR spectrum. Single crystals of compound **9** were grown out of DMSO. **9** · 2 DMSO crystallizes in the triclinic space group *P*–1 with 2 molecular units per unit cell. The dimensions are *a* = 10.1892(11) Å, *b* = 10.5895(9) Å and *c* = 11.6355(15) Å. At

173 K the unit cell volume amounts 1155.1(2) Å^3 with a density of 1.597 g cm^{-3}. Figure 3 shows the molecular unit of **9**.

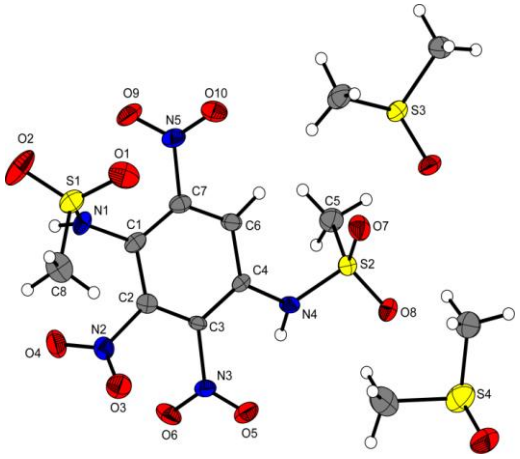


Fig 3: Molecular unit of compound **9**. The non-hydrogen atoms are represented by displacement ellipsoids at a 50% probability level; **Selected bond lengths** [Å]: C7–N5 1.479 (7), C2–N2 1.471 (8), 1.471 (8), C1–N1 1.411 (9), C4–N4 1.381 (9), S1–N1 1.628 (6), S2–N4 1.645 (6), S1–O1 1.434 (7), S1–O2 1.428 (8), S2–O7 = S2–S8 1.426 (5), S1–C8 = S2–C5 1.745 (8); **Selected bond angles** [°]: C2–C3–N3 117.87 (6), C3–C2–N2 119.22 (6), C6–C7–N5 115.64 (6), C4–N4–S2 125.93 (5), C1–N1–S1 124.31 (5), O1–S1–N1 107.67 (3), O2–S1–N1 105.19 (4), C8–S1–N1 105.68, O2–S1–O1 121.04 (4), O7–S2–O8 120.02 (3), C5–S2–N4 107.09 (3), O8–S2–N4 104.27 (3), O7–S2–N4 107.66 (3); **Selected torsion angles** [°]: C3–C2–N2–O3 57.3 (1), C2–C3–N3–O6 55.9 (1), C6–C7–N5–O10 46.9 (1), C2–C1–N1–S1 75.9 (1), C6–C4–N4–S2 9.4 (1).

The sulfur atoms S1 and S2 show a typical slightly distorted tetrahedral coordination sphere. Due to the electrostatic attraction of the sulfur and the oxygen, the S–O bond length is larger than in a typical double bond, but shorter than in a single bond. The O–S–O bond angles are larger than in a typical tetrahedron. This probably comes from the electronic repulsion of the free electron pairs located at both oxygen atoms. The N–O bond length of the nitro groups are in the typical range between 1.22-1.23 Å. The nitro group with N3 is twisted out of the benzene–N3 plane with 55.9(1)°and the nitro group with N2 within 57.3(1)°. The nitro group with N5 is twisted out of the benzene–N5 plane within 46.9(1)°. The methanesulfonyl groups have highly different torsion angles towards the phenyl moiety. Whereas the methanesulfonyl group in C1-position is twisted out of plane within 75.9(1)°, the other protection group at C4 position is only twisted out slightly within 9.4(1)°.

Before compound **9** could be identified *via* low temperature X-ray diffraction it was analyzed by NMR spectroscopy. A proton coupled ^{15}N NMR spectrum was recorded and all five nitrogen atoms could be assigned. An excerpt of the spectrum between –18 and –24 ppm is shown in figure 4. Here three different nitro signals were observed. Those nitro-nitrogens were distinguished due to their different coupling constants with the remaining phenyl-proton. N_α shows a $^3J_{N\text{-}H}$ coupling constant of 2.8 Hz. However N_γ only shows a small coupling

constant $^4J_{N-H}$ of 1.2 Hz. The remaining N_β appears as a singlet because a theoretical $^5J_{N-H}$ is too small to be detected.

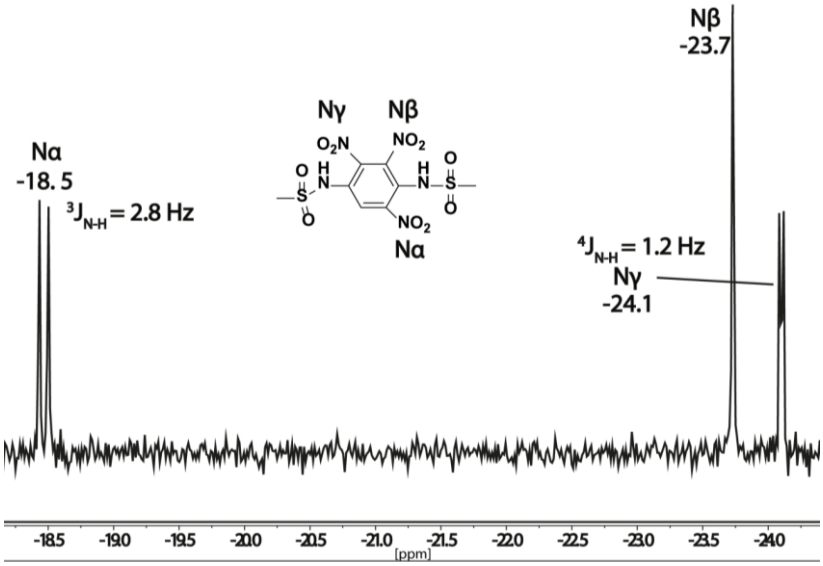
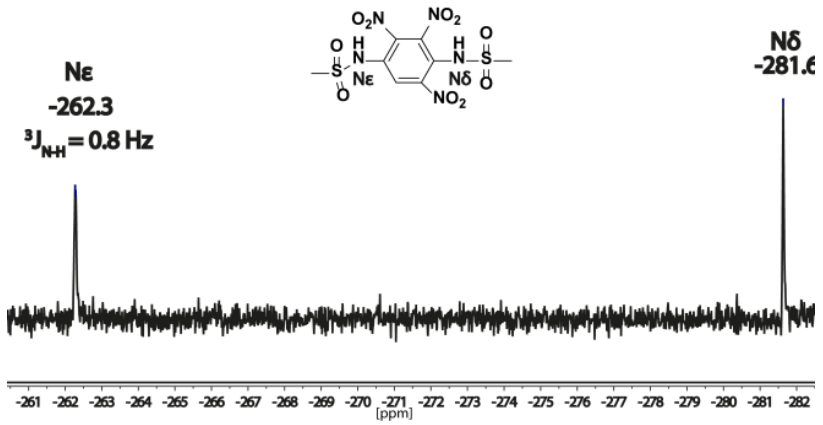


Fig. 4: ^{15}N NMR spectrum of compound **9** between –18 and –24 ppm.

The second range within this spectrum that was analyzed was the one between –261 and –282 ppm. As expected, two signals were detected. A non-magnified view of the NMR spectrum revealed two singlets. When the left signal (N_ε) at –262.3 Hz was regarded at high magnification, a small doublet with a coupling constant of $^3J_{N-H}$ = 0.8 Hz was observed. N_δ only appeared as singlet at –281.6 Hz. The signals related to the sulfonamides in compound **9** and the magnification of N_ε are shown in figure 5a and 5b.



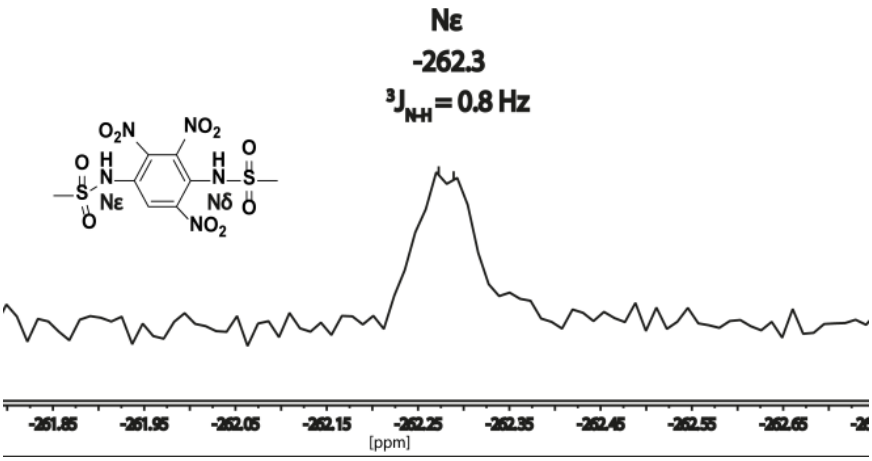


Fig 5a and **5b**: "^{15}N NMR spectrum of compound **9** between –261 and –282 ppm (top) and magnified area showing a small doublet of $N_ε$ (below)

The next nitration product that was synthesized was *N*,*N'*-(2,3-dinitrophenyl)1,4-diacetamide (**10**). There were two different methods established to synthesize this compound. 82.5 % nitric acid, as well as the combination of Ac_2O, HOAc and 100 % nitric acid, was applied in order to nitrate **4**. However, the instability of the acetamide protection group towards 82.5 %nitric acid, resulting in low yields of **10**, could be confirmed. The second method mentioned above is much more effective and delivered high yields of **10**. This is due to the pH, which deriving from acetic acid during the nitration minimizes the hydrolysis of the acetamide. The next interesting fact about the synthesis of **10** is the regio-selectivity. The acetamide group has a negative inductive effect (– I) but a positive mesomeric effect (+ M). In the first nitration step all aromatic carbons are identical and this doesn't matter. The new nitro group which has a – I and a – M effect normally controls the next nitration to the *meta* position. That means that the formation of the 2,6-dinitroisomer was expected. Regarding the sterical-hindrace of the acetamide group the formation of the 2,5-dinitro-isomer would have also been possible. The 2,6 dinitro-isomer is the only one which would show two different methyl groups, two carbonyl groups and four different aromatic carbon signals instead of three. Since only one methyl signal was observed in the ^{13}C NMR spectrum, the presence of the 2,6 dinitro-isomer was ruled out. Since the nitro group only shows a singlet at –17.8 ppm, the 2,5-dinitro-isomer was also ruled out because a theoretical $^3J_{N-H}$ coupling would have been observed. However, a strong ($^1J_{N-H}$ = 94.1 Hz) coupling of the acetamide nitrogen was observed in the proton coupled ^{15}N NMR spectrum. To verify this strong N-H coupling constant a proton decoupled ^{15}N NMR spectrum was also recorded, in which the acetamide nitrogen showed only one singlet at –257.1 ppm. The ^{13}C and proton coupled ^{15}N NMR spectra of compound **10** are displayed in figure 6a and 6b.

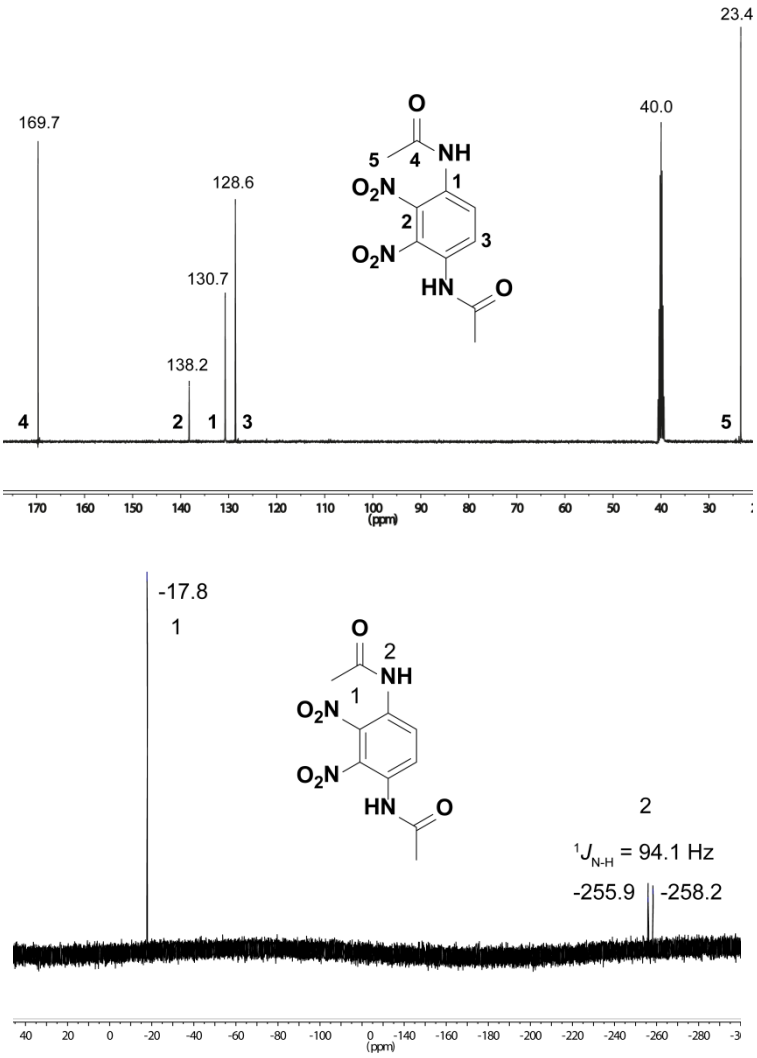


Fig. 6a and **6b**: ^{13}C (top) and proton coupled ^{15}N NMR spectra (below) of compound **10**.

Finally it was confirmed by the combination of NMR spectroscopy and low temperature X-ray diffraction that only the 2,3-dinitroisomer (**10**) was formed. Single crystals of **10** were grown out of DMSO. **10** crystallizes in the triclinic space group *P*–1 with 2 formula units per cell. At 298 K **10** has a cell volume of 615.00(2) $Å^3$ and a density of 1.524 g cm^{-3}. The unit cell parameters are *a* = 7.754(2) Å, *b* = 8.085(2) Å, *c* = 10.766(2) Å with α = 84.88(2)°, *β* = 70.27(1)° and γ = 75.49(2)°. Figure 7 shows the molecular unit of **10**. The measurement was done at ambient temperature resulting in larger thermal ellipsoids.

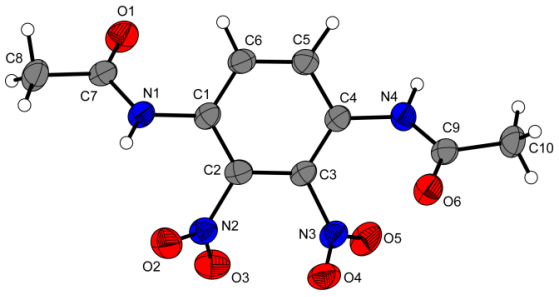


Fig 7: Molecular unit of compound **10**. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level; **Selected bond lengths** [Å]: C1–N1 1.423 (4), C2–N2 1.464 (4), C3–N3 1.475 (4), C4–N4 1.411 (4), N2–O2

1.217 (3), N2–O3 1.222 (3), N3–O4 1.215 (3), N3–O5 1.221 (3), C7–O1 1.219 (4), C9–O6 1.223 (4), **Selected bond angles** [°]: N1–C1–O1 122.3 (3), O2–N2–O3 123.8 (3), O4–N3–O5 125.5 (3), N4–C9–O6 122.4 (3); **Selected torsion angles** [°]: C3–C4–N4–C9 50.2 (5), C6–C1–N1–C7 42.9 (5), C4–C3–N3–O5 51.5 (5), C3–C2–N2 O3 48.5 (4).

The nitration product of compound **7** was the 4-acetoxy-2,6-dinitrophenol (**11**). In this reaction one ester group is hydrolyzed at the beginning of the reaction resulting in the high regio-selectivity in this nitration. To clarify the position of the nitro groups the crystal structure of **11** was also determined. This regio-selectivity resulting in the formation of the 2,6-dinitroisomer was also confirmed by ^{13}C NMR spectroscopy. Since four different aromatic signals were observed, the 2,3 dinitro and the 2,5 dinitro-isomer could be ruled out. Afterwards **11** could be acetylated again what resulted in the formation of **12**. The molecular units of **11** and **12** are displayed in figures 8a and 8b.

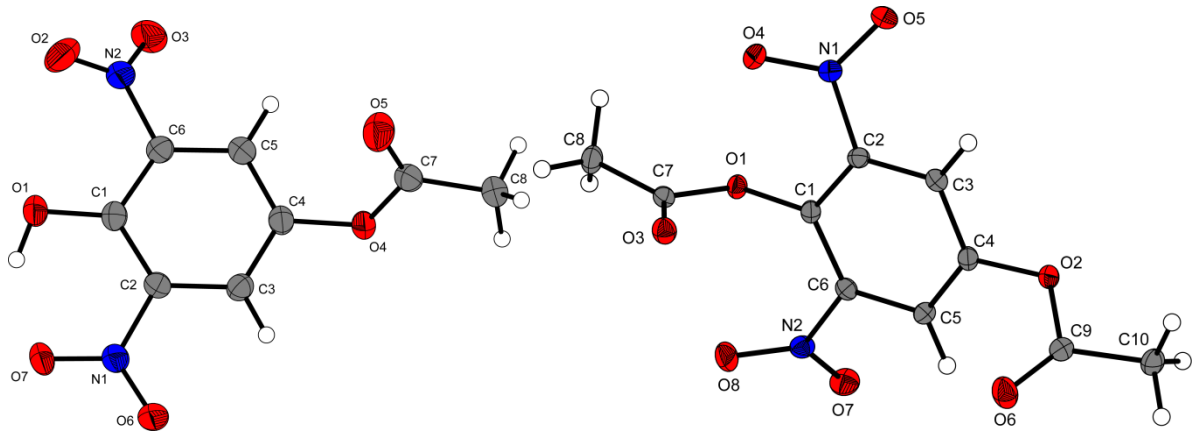
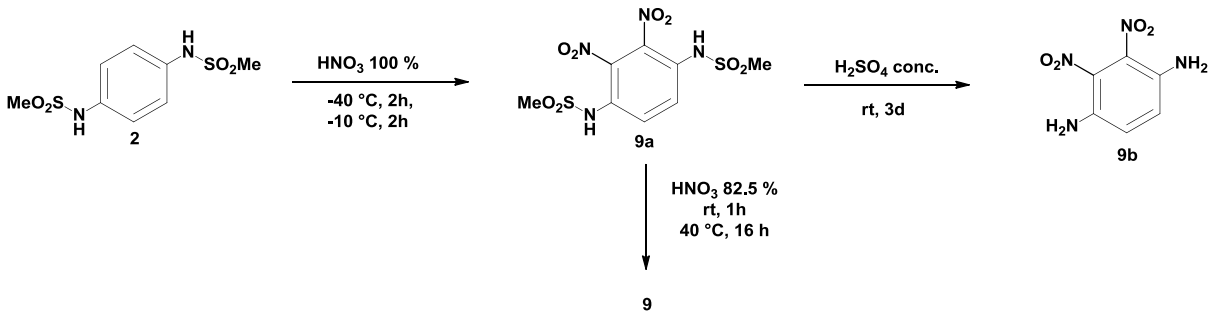


Fig 8a and **8b**: Molecular unit of compound **11** (left). The non-hydrogen atoms are represented by displacement ellipsoids at a 50% probability level; **Selected bond lengths** [Å]: C1–O1 1.330 (2), O1–H 0.89 (2), O7···H 1.76 (2), O1–O7 2.554 (2), C2–N1 1.451 (2), N1–O6 1.216 (2), N1–O7 1.236 (2), C6–N2 1.459 (2), N2–O3 1.221 (2), N2–O2 1.220 (2), C4–O4 1.393 (2), O4–C7 1.379 (2), C7–O5 1.190 (2); **Selected bond angles** [°]: O7–N1–O6 122.0 (1), O2–N2–O3 124.7 (2), C1–O1–H 107.0 (2), C4–O4–C7 117.4 (2), O4–C7–O5 121.7 (2), O7–H–O1 145.0 (2); **Selected torsion angles** [°]: C5–C6–N2–O3 37.7 (2), C3–C2–N1–O6 4.6 (2), C5–C4–O4–C7 66.3 (2). Molecular unit of compound **12** (right). The non-hydrogen atoms are represented by displacement ellipsoids at a 50% probability level. **Selected bond lengths** [Å]: C2–N1 1.473 (2), C6–N2 1.471 (2), N1–O5 1.221 (2), N1–O4 1.226 (2), N2–O7 1.221 (2), N2–O8 1.224 (2), C1–O1 1.376 (2), C7–O1 1.392 (2), C7–O3 1.191 (2), C4–O2 1.388 (2), O2–C9 1.373 (2), C9–O6 1.192 (2); **Selected bond angles** [°]: O4–N1–O5 124.2 (1), O8–N2–O7 125.2 (1), O1–C7–O3 121.6 (1), O2–C9–O6 122.1 (1); **Selected torsion angles** [°]: C3–C2–N1–O5 27.3 (2), C5–C6–N2–O7 40.4 (2), C2–C1–O1–C7 89.2 (2), C3–C4–O2–C9 52.8 (1).

The bond lengths in **11** are in the typical range as expected for nitro groups, carbonyl groups and alcohols. The N2-nitro group is twisted out of the benzene-N2 plane within 37.7(2)°, whereas the N1-nitro group, which is nearly completely planar, participating in a O···H–O hydrogen bond (donor acceptor distance of 2.55(2) Å and O7···H–O1 145.0 (2)) with the hydroxy group in C1 position. **11** can be reacetylated in boiling Ac_2O resulting in **12**. Further nitration reactions were attempted with **12** but only **11** could be isolated again. Single crystals of **12** were grown out of acetone. **12** crystallizes in the triclinic space group *P*−1 with 2

formula units per cell. At 173 K **12** has a cell volume of 583.29(9) Å^3 and a density of 1.618 g cm^{-3}. The unit cell parameters are *a* = 8.5133(7) Å, *b* = 8.6062(8) Å, *c* = 8.7948(7) Å with α = 69.73(1)°, *β* = 79.69(1)° and γ = 76.00(1)°. Figure 10b shows the molecular unit of the double acetylated derivative **12.** Due to the absence of possible hydrogen bonds both nitro groups are twisted out of the corresponding benzene-N plane with 27.3(2)° and 40.4(2)°. The acetoxy groups are also twisted out of the benzene plane, especially the acetoxy group in C1 position is orientated almost perpendicular to the benzene plane.

Another interesting case where a regio-selective nitration was performed was the reaction of **2** with 99.5 % nitric acid at a very low temperature. As displayed in scheme 4 only the 2,3-dinitro derivative (**9a**) was isolated. After that **9a** was easily deprotected, yielding the free diamine **9b**. In an alternative reaction, a third nitro group was attached resulting in the formation of **9**, leading to a yield of about 79 %.



Scheme 4: Regio-selective synthesis of **9a** and its deprotection

The regio-selectivity was confirmed through ^{1}H NMR spectroscopy. For compound **9a** only one aromatic signal could be observed, indicating that only one of the three possible dinitro isomers was synthesized. In the ^{13}C NMR spectrum only three aromatic ^{13}C signals were observed, thus ruling out the 2,6-dinitroisomer. To determine whether the 2,3-dinitro or the 2,5-dinitro isomer were synthesized, the methanesulfonyl protection groups of **9a** were cleaved, resulting in the formation of **9b**. Single crystals of **9b** were grown out of acetone. **9b** crystallizes in the monoclinic space group *C*2/*c* with four molecules in the unit cell. Its density at −100 °C is 1.663 g cm^{-3}. The molecular unit of **9b** is displayed in figure 9.

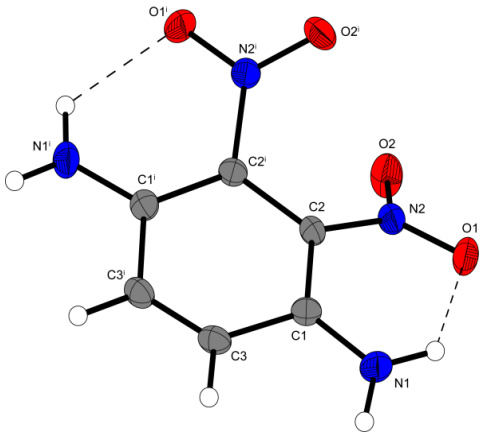
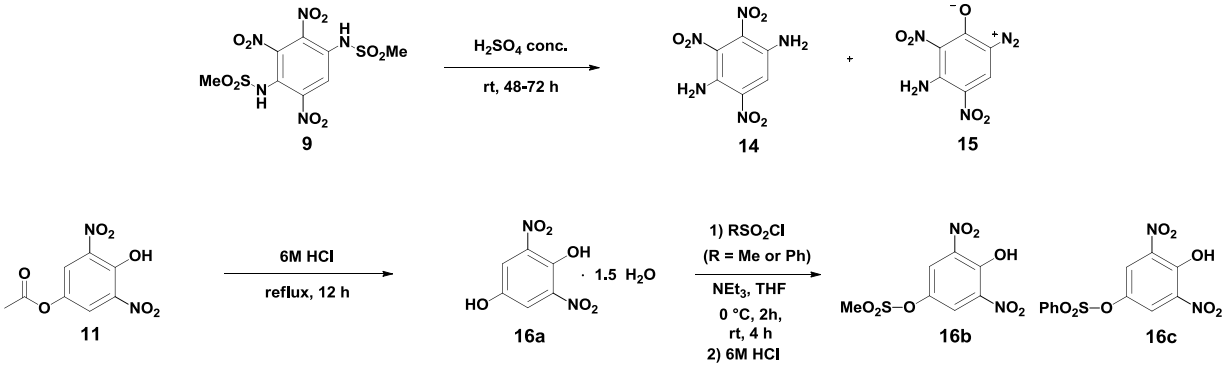


Fig. 9: Molecular unit of **9b**. Ellipsoids of non-hydrogen atoms in all structures are drawn at a 50 % probability level. **Selected bond lengths** [Å]: C1–N1 1.367 (3), N1–N2 1.098 (3), C2–O1 1.324 (4), C3–N3 1.441 (2), N3–O3 1.235 (2), C4–N4 1.321 (3), O3–N4 2.59 (1); **Selected bond angles** [°]: C1–N1–N2 177.7 (3), N3–O3–O2 121.3, O3–N3–O2 121.3; **Selected torsion angles** [°]: C2–C3–N3–O2 11.8 (2), C3–C4–N4–H 2.9 (2).

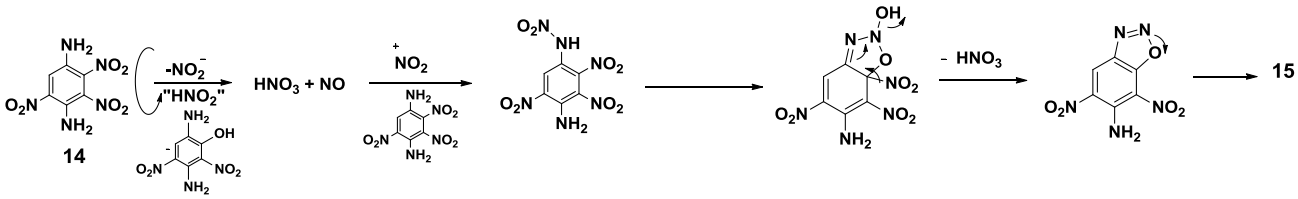
9.1.2.3 Deprotection of compounds **9**, **10** and **11**

In the next step **9** and **11** were succesfully deprotected. All attempts to cleave the amides in compound **10** to obtain the free diamine (**9b**) failed. This kind of deprotection can be performed either in concentrated sulfuric acid at ambient temperature or in 15 % hydrochloric acid under reflux. The choice of the acid depends on the alkalinity of the leaving group. In the case of alkysulfonic protection groups it is necessary to use concentrated sulfuric acid. The low alkalinity of the sulfonamide inhibits its protonation by hydrochloric acid. The cleavage of the esters could be easily achieved by using 15 % hydrochloric acid. The performed deprotection reactions are displayed in scheme 5. Alkaline deprotection methods are not suitable for polynitro-benzenes and mostly resulted in a substitution of a nitro group by OH^-. In addition, the hydroxy group of **16a** in C4 position was protected again in order to perform further nitration attempts.



Scheme 5: Deprotection reactions of nitrated precursor molecules and protection reactions of **16a**.

The deprotection of **9** results in the formation of two different compounds. As expected, **14** is formed. Additionally the highly sensitive primary explosive 3-amino-6-diazo-2,4-dinitrophenol (**15**) is obtained. The mechanism describing the conversion of **14** into **15** is not fully understood so far. Therefore a possible mechanism resulting in the formation of **15** was proposed. This is shown in scheme 6.



Scheme 6: Proposed mechanism of the conversion of compound **14** into **15** in concentrated sulfuric acid.

In the first step the nitro group in C_2-position seems to be hydrolyzed, resulting in the formation of the phenol derivative. The leaving nitrite disproportionates into nitric acid and NO. Finally a new nitronium cation is formed and nitrates the amine in C_1-position of another molecule of **14**. This newly formed nitramine neighbouring a nitro group in *ortho* position undergoes a typical cyclic transition state. This results in the formation of **15** after nitric acid was released in a two step elimination including a 1,2 proton-shift. This rearrangement was also proposed by Atkins et al.[10] After isolating clean samples of **14** and **15**, DSC curves were recorded in order to determine their decomposition temperatures. The DSC curves of **14** and **15** are displayed in figure 10.

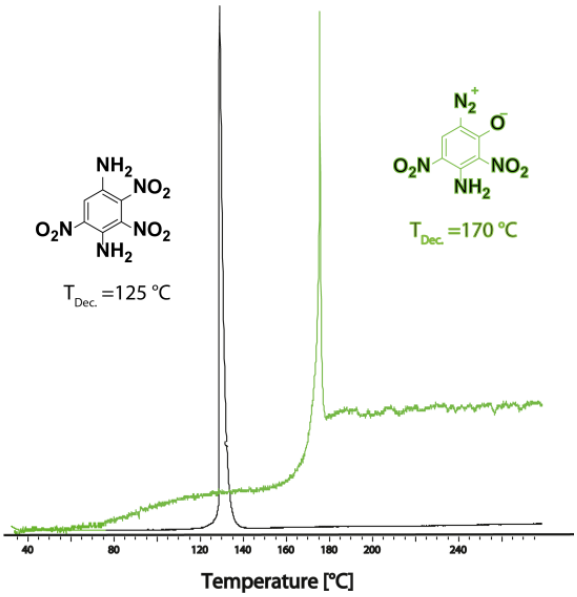


Fig 10: DSC curves of **14** (black) and **15** (green) (heating rate β = 5 °C min^{-1})

These two products differ dramatically in regard to their thermal stability. It is interesting to mention that the thermal stability of **14** (125 °C) was unexpectedly low. Its constitution isomer 1,3-diamino-2,4,6-trinitrobenzene, for example, is stable up to 288 °C.[11] The diazophenol

(**15**), however, shows the typical thermal stability for diazophenols (170 °C). The purity of **14** could only be confirmed by *CHN* elemental analysis, high resolution mass spectrometry (DEI+ method) and additionally by infra-red spectroscopy. When **14** was dissolved in organic solvents it slowly decomposed and in addition, only the NMR signals of compound **15** were detected. The diazo-vibration at 2195 cm^{-1} and the carbonyl vibration at 1593 cm^{-1} only appeared in the infra-red spectrum of **15**. The N-H vibrations of the amino groups appear at 3365 cm^{-1} and 3474 cm^{-1}, whereas in the case of **15** they are located at 3282 cm^{-1} and 3390 cm^{-1}.

Single crystals of compound **15** were grown out of water. **15** crystallizes in the orthorhombic space group *Pnma* with 4 molecular units per unit cell. The dimensions are *a* = 16.2313(6) Å, *b* = 10.6548(4) Å and *c* = 4.5210(2) Å. At 173 K the unit cell volume amounts 781.87(5) $Å^3$ with a high density of 1.913 g cm^{-3}. Figure 11 shows the molecular unit of **15**.

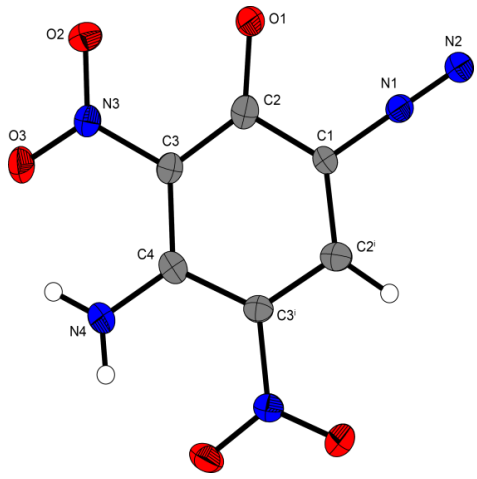


Fig 11: Molecular unit of compound **15**. The non-hydrogen atoms are represented by displacement ellipsoids at a 50% probability level; **Selected bond lengths** [Å]: C1–N1 1.367 (3), N1–N2 1.098 (3), C2–O1 1.324 (4), C3–N3 1.441 (2), N3–O3 1.235 (2), C4–N4 1.321 (3), O3–N4 2.59 (1); **Selected bond angles** [°]: C1–N1–N2 177.7 (3), N3–O3–O2 121.3, O3–N3–O2 121.3; **Selected torsion angles** [°]: C2–C3–N3–O2 11.8 (2), C3–C4–N4–H 2.9 (2.9).

With a bond length of 1.098(3) Å the N–N bond is in the typical range of a triple bond, whereas the C–O bond of the carbonyl function is between a single and a double bond. The nitro group is only twisted out of plane within a small angle of 11.8(2)° and forms a strong hydrogen bond with the amine in *ortho* position (donor-acceptor distance N–H···O3 = 2.59 Å, N–H···O1 131.6(2)°). In addition, a proton coupled ^{15}N NMR spectrum was recorded. An excerpt of this can be seen in figure 12.

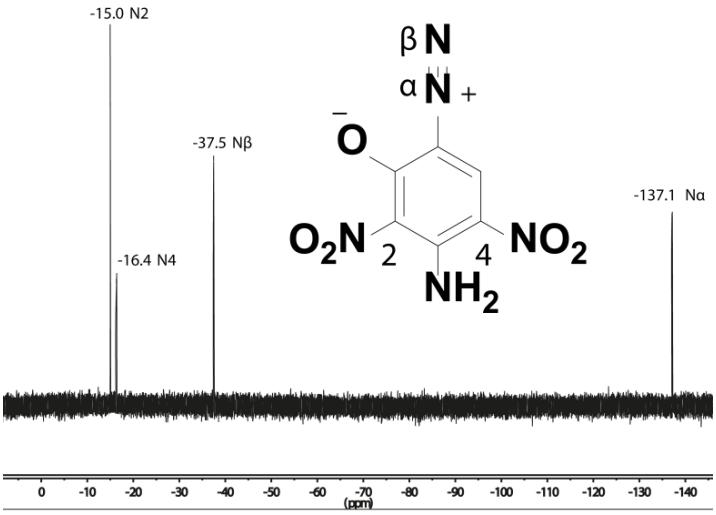


Fig. 12: ^{15}N NMR spectrum of **15**. The amine peak is not shown.

As expected, five signals could be observed (NH_2 signal not shown in figure 14). Two different nitro groups show the typical ^{15}N NMR shifts at –15.0 and –16.4 ppm. The diazo-group signals appear at –37.5 and –137.1 ppm. The amine peak at –288.7 ppm is very weak. To assign the signals properly a magnification of each area is necessary. This is shown in figure 13a for N_2, N_4 and N_β. N_4 appears as a doublet with a $^3J_{N\text{-}H}$ = 2.8 Hz whereas N_2 shows a singlet. N_β appears as singlet as well. In figure 13b the N_α is shown as a doublet with a $^3J_{N\text{-}H}$ = 3.2 Hz.

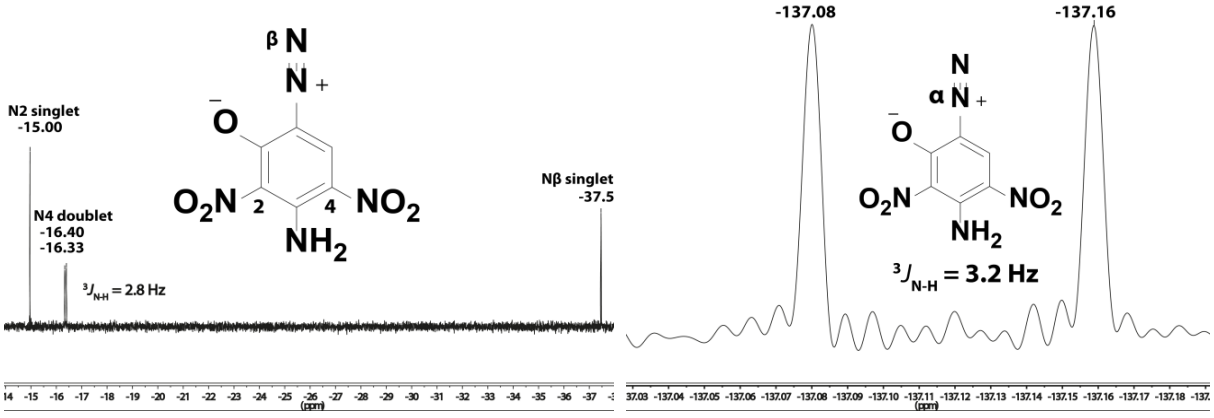


Fig 13a and **13b** Magnified areas of the ^{15}N NMR spectrum of compound **15**.

With the crystal density of **8** and **15** at 173 K it was possible to calculate it at 298 K. Additionally the heat of formation was calculated using the CBS4M method and the detonation parameters were determined using the EXPLO5 V 6.01 computer code. These parameters were compared with those of DDNP (2-diazo-4,6-dinitrophenol). The energetic properties of **8**, **15** and DDNP are given in table 2. Compound **15** has many advantages compared DDNP. On the one hand it has a higher density resulting in a higher detonation pressure and velocity, on the other hand **15** is more thermally stable than DDNP by 12 °C.

The only disadvantage is the low yield in the deprotection step that the synthesis delivers. Compound **8**, however, does not provide any reasonable advantages, but it can be synthesized in moderate yield in one step using the cheap 4-chloroaniline as starting material.

Table 2: Energetic properties of compounds **8** and **15** in comparison to DDNP

Compound	**8**	**15**	**DDNP*****
Formula	$C_6HClN_4O_5$	$C_6H_3N_5O_5$	$C_6H_2N_4O_5$
FW / g mol^{-1}	244.55	225.12	210.10
IS / J [a]	1	1	1
FS / N [b]	12	28	5
N / % [c]	22.91	31.11	26.67
$T_{Dec.}$ /°C [d]	165	170	158
ρ / g cm^{-3} (298 K) [e] **	1.815	1.880	1.727
$\Delta_f H_m°$ / kJ mol^{-1} [f]	109.2	116.8	142.4
$\Delta_f U°$ / kJ kg^{-1} [g]	502.3	590.0	742.6
EXPLO 5 6.01 values: *			
$\Delta_{Ex}U°$ / kJ kg^{-1} [h]	4263	4830	5009
$T_{Det.}$ / K [i]	3722	3426	3737
P_{CJ} / kbar [j]	232	294	241
$V_{Det.}$ / m s^{-1} [k]	7482	8257	7685
V_o / L kg^{-1} [l]	635	624	632

[a] impact sensitivity (BAM drophammer, 1 of 6); [b] friction sensitivity (BAM friction tester 1 of 6); [c] nitrogen content; [d] decomposition temperature from DSC (β = 5 °C); [e] from X-ray diffraction; [f] calculated (CBS-4M) heat of formation; [g] energy of formation; [h] energy of explosion; [i] explosion temperature; [j] detonation pressure; [k] detonation velocity; [l] assuming only gaseous products; *Values have been calculated by using room temperature densities, ** density at 298 K was calculated using the formula $\rho_{298K} = \rho_T/1+\alpha_v(298-T_0)$ with $\alpha = 1.50 \cdot 10^{-4}$ K^{-1} and $T_0 = 173$ K[8]; ***a DDNP sample of high purity was provided by another group member.

As already mentioned above, for potential primary explosives, the behavior of the tested compounds towards a open flame is very important. **8** and **15** do not detonate in the flame but rather show a very strong deflagration. A hot plate test was also performed for both compounds. In this test set up, small amounts of a substance are deposited on a copper plate, while the plate is slowly heated up with a Bunsen burner from below. Also in this test, decompositions can be characterized as strong deflagration.

After the deprotection of **11** yielding **16a** further nitrations were tried to obtain a tri or tetranitro-*p*-quinone.[9] All those attempts failed and therefore more acid resistant protection groups, namely the methanesulfonyl or the benzenesulfonyl group were introduced resulting in the formation of **16b** and **16c**. The regio-selectivity of this protection group was confirmed via low temperature X-ray diffraction. Single crystals of **16b** were grown out of acetone. The potassium salt of **16c** crystallized out of water. The molecular unit are displayed in figure 14.

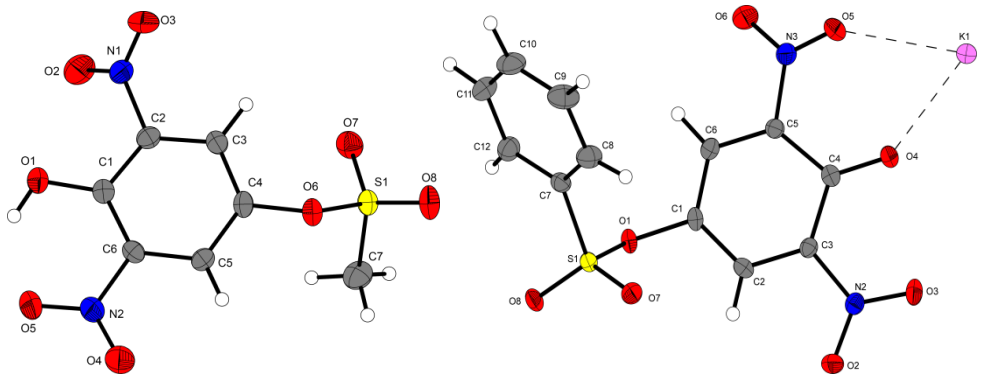


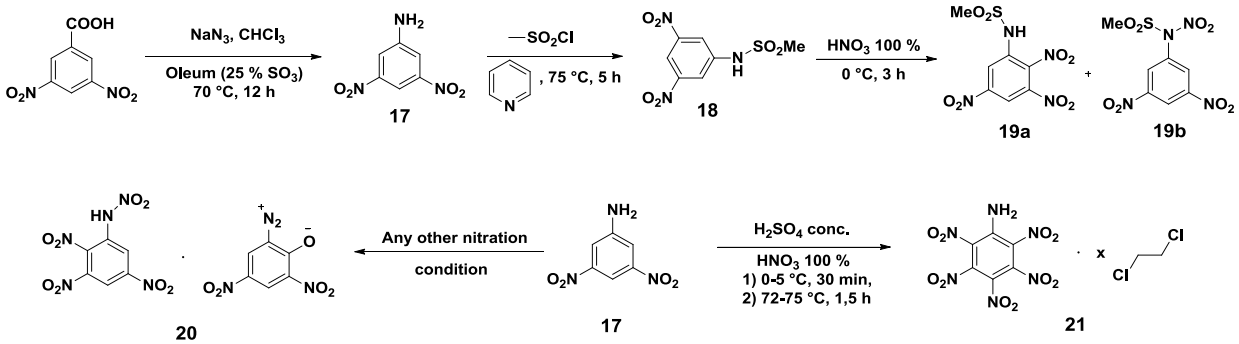
Fig. 14: Molecular units of compound **16b** and the potassium salt of **16c**. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. **Selected bond lengths** [Å] (16b):C1–O1 1.331 (3), N2–O6 1.458 (3), N2–O4 1.222 (3), N2–O5 1.234 (3), C2–N1 1.469 (3), N1–O2 1.221 (3), N1–O3 1.227 (3), C4–O6 1.406 (3), O6–S1 1.609 (2), S1–O7 1.430 (2), S1–O8 1.420 (2), S1–C7 1.749 (3); **Selected bond angles** [°] (16b): O5–N2–O4 123.1 (2), O2–N1–O3 124.5 (2), C4–O6–S1 120.6 (2), O7–S1–O8 119.4 (1), O6–S1–C7 103.0 (1); **Selected torsion angles** [°] (16b): C1–C6–N2–O5 5.1 (3), C1–C2–N1–O2 47.2 (3). **Selected bond lengths** [Å] (potassium salt of **16c**): C4–O4 1.246 (3), N3–O5 1.226 (3), C1–O7 1.415 (3), C5–N3 1.450 (3), C3–N2 1.437 (3); **Selected torsion angles** [°] (potassium salt of **16c**): C4–C3–N2–O3 0.78 (3), C4–C5–N3–O5 28.2 (3). **Atom distances** [Å] (potassium salt of **16c**): K1–O4 2.70 (1), K1–O5 2.77 (1).

16b crystallizes in the orthorhombic space group *Pca*2_1 with 4 molecular units per unit cell. The cell dimensions are *a* = 14.6639 (7) Å, *b* = 5.7308 (2) Å and *c* = 12.3700 (5) Å. At 173 K it has a density of 1.778 g cm^{-3} and a cell volume of *V* = 1039.52 (7) Å^3. The potassium salt of **16c**, however, crystallizes in the orthorhombic space group *Pbca* with 8 molecular units per unit cell. The cell dimensions are *a* = 10.4168 (4) Å, *b* = 9.4354 (3) Å and *c* = 28.7467 (11) Å. At 173 K it has a density of 1.779 g cm^{-3} and a cell volume of *V* = 2825.42 (18) Å^3. In **16b** the nitro group, participating in the hydrogen bond with the hydroxy group, is only slightly twisted out of the benzene plane. The C1–O1 bond length is longer the corresponding bond (C4–O4) in the potassium salt of **16c**. The potassium ion is coordinated by the phenolic oxygen and one of the neighboring nitro groups per anion. The atom distances between the potassium ion and the oxygens of the anion are rather short (K1–O4 2.70(1) Å, K1–O5 2.77 1) Å), which indicates a strong electrostatical interaction.

9.1.2.4 Functionalisation of 3,5-dinitro benzoic acid

The next approach in the attempted synthesis of **1** was the functionalisation of 3,5-dinitrobenzoic acid. In the first step a so called "Schmidt reaction" was carried out in order to convert the carboxyl group into an amine using *in situ* generated HN_3 as a nucleophile. First HN_3 attacks the acylium carbon formed after the elimination of water followed by nitrogen elimination (Curtius rearrangement). The oleum (35 % SO_3 by weight) used in this reaction has a double function. On the one hand it is necessary to dissolve the 3,5-dinitrobenzoic acid and to form the acylium cation, while on the other hand it is required to eliminate water in

several *in situ* formed intermediates. After that a rearrangement occurs, finally resulting in the formation of a isocyanate. After the suspension was poured on crushed ice, this isocyanate was hydrolyzed to the corresponding carbamic acid, which is not stable and eliminates CO_2 resulting in the formation of the free amine (**17**) after re-protonation. Then several attempts to synthesize a 2,3,5-trinitro or 2,3,5,6-tetranitroaniline derivative directly or after the protection of the amine were attempted. When using **18** in nitration reactions two constitution isomers were formed (**19a** and **19b**). This was proven by the ^{1}H shifts. In d_6-acetone **18** shows a doublet at 8.58 ppm with a $^{3}J_{H\text{-}H}$ = 1.93 Hz and a triplet at 8.64 ppm with the same coupling constant. After nitration one triplet and three doublets were observed. The triplet can only occur when the coupling to two magnetic identical protons is given. The only case in which this is possible is the formation of a nitrosulfonamide (**19b**). The triplet occurs at 9.19 ppm and a doublet at 9.04 ppm with $^{4}J_{H\text{-}H}$ = 2.0 Hz. Compound **19a**, however, shows two doublets at 8.85 and 9.00 ppm with $^{4}J_{H\text{-}H}$ = 2.4 Hz. Using ^{1}H integrals one can consider that the ratio **19a**:**19b** = 1:3. A further separation of those two isomers or a selective cleavage of the methanesulfonamide was not possible so far. Therefore it was decided to study the direct nitration of **17** extensively. The original goal was to control the nitration in such a way, that either 2,3,5-trinitroaniline or 2,3,5,6 tetranitroaniline would be obtained. It would have been possible to introduce an additional amino group in C_4 position using the “vicarious radical amination” if the synthesis mentioned above had worked. However, either pentanitroaniline (**21**) was formed using H_2SO_4/HNO_3 and heating conditions, or 6-diazo-2,4-dinitrophenol (DDNP) was obtained using cold conditions and only nitric acid. The formation of pentanitroaniline (**21**) is the main product which is formed when thermodynamic conditions (elevated temperatures) are used for a short time. In the work up process **21** may not be poured on crushed ice after the nitration because **21** is very prone to hydrolysis. Since **21** precipitates out of the sulfuric acid during the nitration procedure, the suspension is directly filtrated using a glass frit. After that the yellow solid is re-dissolved in 1,2-dichloroethane. Then the solution is transferred into a separating funnel. Here the last traces of sulfuric acid can be separated. Subsequently cooling for 48 h at –20 °C leads to the crystallisation of **21** · x 1,2-dichloroethane. When pentanitroaniline was used as electrophile in further reactions it turned out that recrystallisation of **21** out of benzene yields a clean pentanitroaniline · benzene adduct with a stoichiometric composition of 1:1. Using any other nitration condition for compound **17** resulted in the formation of DDNP or an adduct of DDNP · *N*,2,3,5-tetranitroaniline (**20**). An overview of these synthetic steps is displayed in scheme 7. To prove the purity single crystals of compounds **18**, **20** and **21** · benzene, these were isolated to confirm their structure by low temperature X-ray diffraction.



Scheme 7: Functionalisation of 3,5-dinitrobenzoic acid.

Single crystals of **18** were grown through recrystallisation of **18** out of water/ethanol for further purification. **18** crystallizes in the orthorhombic space group $P2_12_12_1$ with 4 molecular units per unit cell. The dimensions are a = 5.2956(3) Å, b = 12.6113(7) Å, c = 15.1910(7) Å. At 173 K the unit cell volume amounts 1015.5(2) Å^3 with a density of 1.710 g cm^{-3}. Figure 15 shows the molecular unit of **18**.

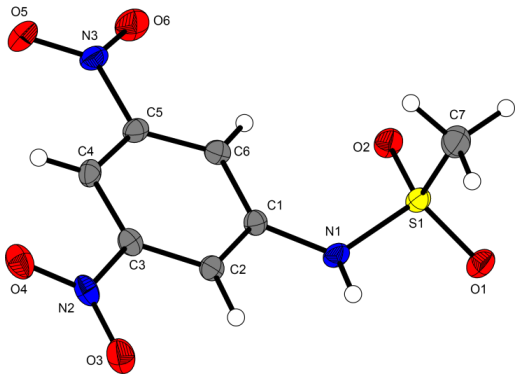


Fig. 15: Molecular unit of compound **18**. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level; **Selected bond lengths** [Å]: C1–N1 1.415 (3), C3–N2 1.470 (3), N2–O3 1.228 (3), N2–O4 1.219 (3), C5–N3 1.482 (3), N3–O5 1.224 (2), N3–O6 1.219 (3), 1.219 (3), N1–S1 1.633 (2), S1–O1 1.436 (2), S1–O2 1.422 (2), S1–C7 1.750 (3); **Selected bond angles** [°]: O5–N3–N6 124.4 (3), O3–N2–O4 123.9 (2), C1–N1–S1 126.8 (2), O2–S1–O1 118.7 (2); **Selected torsion angles** [°]: C6–C5–N3–O6 3.8 (3), C2–C3–N2–O4 7.2 (3), C6–C1–N1–S1 34.6 (3), C1–N1–S1–C7 69.6 (2);

20 crystallizes in the monoclinic space group $P2_1/c$ with 4 molecular units per unit cell, a cell volume of 1789.2(2) Å^3 and a density of 1.794 g cm^{-3} at 173 K. The unit cell parameters are a = 9.1208(6) Å, b = 15.4370(8) Å, c = 12.7076(7) Å and β = 90.23(1)°. Figure 16 shows the molecular unit of **20**.

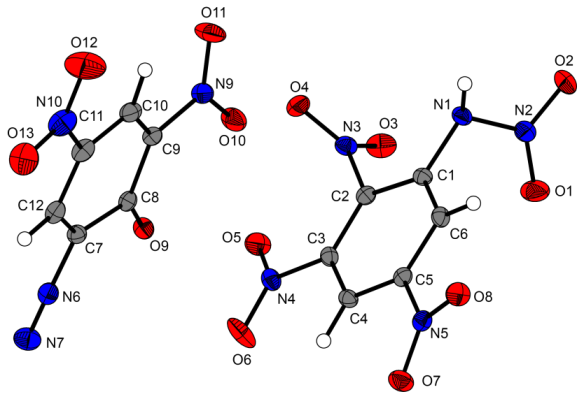


Fig. 16: Molecular unit of compound **20**. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. **Selected bond lengths** [Å]: C1–N1 1.431 (3), N1–N2 1.385 (3), N2–O2 1.224 (2), N2–O1 1.220 (2), C2–N3 1.474 (3), N3–O3 1.221 (2), N3–O4 1.220 (2), C3–N4 1.475 (3), N4–O5 1.220 (2), N4–O6 1.209 (2), C5–N5 1.472 (3), N5–O7 1.217 (2), N5–O8 1.227 (2), C7–N6 1.379 (3), N6–N7 1.100 (2), C8–O9 1.246 (3), C9–N9 1.458 (3), N9–O10 1.223 (3), N9–O11 1.220 (2), C11–N10 1.462 (3), N10–O12 1.222 (3), N10–O13 1.232 (3); **Selected bond angles** [°]: C1–N1–N2 113.5 (2), O1–N2–O2 125.7 (2), O7–N5–O8 125.0 (2), O6–N4–O5 125.2 (2), O4–N3–O3 126.1 (2), C7–N6–N7 174.0 (2), O12–N10–O10 123.3 (2), **Selected torsion angles** [°]: C6–C1–N1–N2 75.3 (2), C6–C5–N5–O8 18.5 (3), C4–C3–N4–O6 3.2 (3), C3–C2–N3–O4 79.9 (2), C8–C9–N9–O10 15.1 (3), C10–C11–N10–O12 3.5 (3).

21 crystallizes in the monoclinic space group $P2_1/c$ with 8 formula units per cell. At 173 K **21** has a cell volume of 3199.6(2) Å^3 and a density of 1.645 g cm^{-3}. The unit cell parameters are a = 9.0537(2) Å, b = 20.2030(5) Å, c = 17.7542(4) Å with β = 99.85(1)°. Figure 17 shows the molecular unit of **21** · benzene.

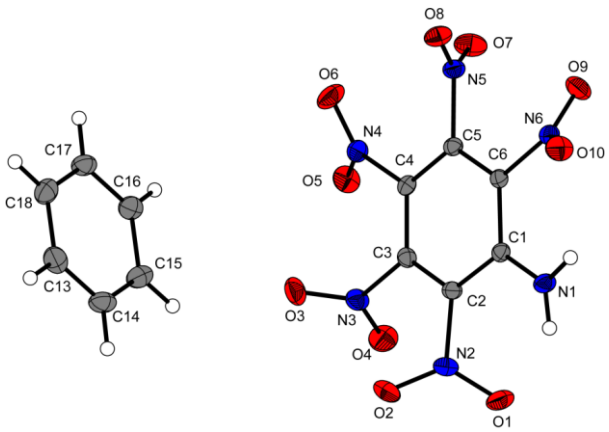


Fig. 17: Molecular unit of compound **21** · benzene. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. **Selected bond lengths** [Å]: C1–N1 1.326 (2), C2–N2 1.471 (2), C3–N3 1.478 (2), C4–N4 1.464 (2), C5–N5 1.482 (2), C6–N6 1.464 (2), N2–O1 1.223 (2), N2–O2 1.218 (2), N3–O4 1.220 (2), N3–O3 1.213 (2), N4–O5 1.216 (2), N4–O6 1.221 (2), N5–O7 1.210 (2), N5–O8 1.217, N6–O9 1.222 (2), N6–O10 1.224 (2); **Selected bond angles** [°]: O1–N2–O2 125.4 (2), O4–N3–O3 126.9 (2), O5–N4–O6 125.6 (2), O7–N5–O8 126.7 (2), O9–N6–O10 125.5 (2); **Selected torsion angles** [°]: C1–C2–N2–O1 41.9 (2), C2–C3–N3–O4 66.4 (2), C3–C4–N4–O5 40.1 (2), C4–C5–N5–O7 63.7 (2), C5–C6–N6–O9 42.5 (2).

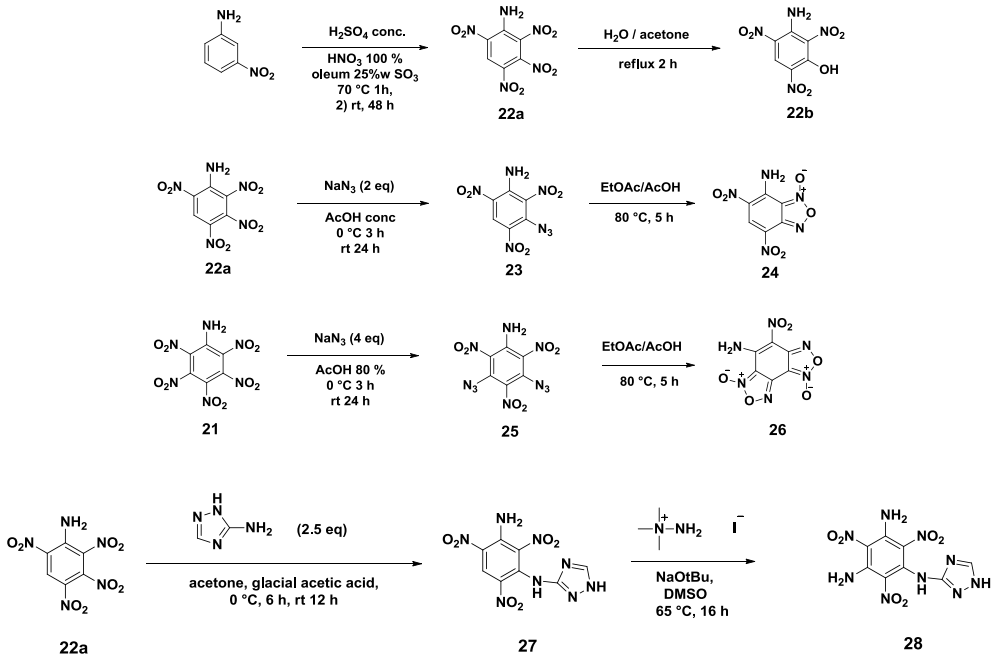
The length of the benzene-amino bond (C_1–N_1) in **21** is between a single and a double bond, whereas all C–NO_2 bonds seem to be single bonds. Interesting to mention here are the torsion angles of the nitro group towards the benzene plane. All nitro groups are twisted out

of plane, but in the case of the two nitro groups in C_3 and C_5 position the torsion angles are much more prominent. Both nitro groups are twisted out of plane within 63.7 (2)° and 66.4 (2)°. The next chapter discusses the regio-selective substitution of two nitro groups in C_3 and C_5 position, which was achieved using azide as nucleophile. This is an important hint as to why this regio-selectivity towards nucleophilic substitution takes place. Assuming that there is no free rotation of the nitro groups in solution, as it is in the crystal, this would explain why the C_3 and the C_5 position are the desired positions for nucleophilic substitution. In addition, the amine of **21** transfers electrons into the *ortho* and the *para*, but not into *meta* position. All attempts to obtain solvent free pentanitroaniline were not successful and nitrous gases were observed.

9.2 Nucleophilic substitutions of nitro groups in 2,3,4,6-tetranitroaniline and 2,3,4,5,6-pentanitroaniline

9.2.1 Syntheses and crystal structures

This chapter is meant to describe the synthesis of 2,3,4,6-tetranitroaniline (**22a**) in laboratory scale (10 g) and some substitution products, namely the 7-amino-4,6-dinitrobenzofuroxan (**24**) and the N^3-(3-amino-2,4,6-trinitrophenyl)-amino-1,2,4-triazole (**27**), as well as its aminated derivative (**28**). Furthermore 8-amino-7-nitro-benzodifuroxane (**26**) was synthesized using pentanitroaniline as starting material. An overview of those syntheses is displayed in scheme 8.



Scheme 8: Syntheses of compounds **22a**-**28**.

The synthesis of **22a** was intensively studied by Vanderah et al.[12] This reaction is very exothermic and must be handled with great care. First the 3-nitroaniline must be dissolved in concentrated sulfuric acid. After heating the solution to 65 °C, a specific mixture of 100 % nitric acid in oleum (20 % weight SO_3) was added. The temperature of the solution must always be kept between 65-75 °C during the addition and should never rise above 80 °C, as this can result in heavy explosions. Afterwards the suspension must be stirred for two days at ambient temperature to obtain **22a** in good yields. It is believed that first the *N*,3,4,6-tetranitroaniline is formed and then slowly rearranges to thermodynamically more stable 22a. The purity of **22a** was confirmed via ^{1}H NMR spectroscopy and *CHN* elemental analysis. In the proton spectrum, recorded in [D_6]-acetone, only two different signals were observed. One broadened signal at 8.83 ppm representing the amine and a sharp singlet at 9.27 ppm for the remaining phenyl proton. ^{13}C or ^{15}N spectra could not be recorded because of the bad solubility in acetone or chlorofom. **22a** is incompatible to DMSO because of its alkalinity, which results in the hydrolysis of the nitro group in C_3 position. This was proven after several recrystallization attempts out of acetone/water. The formation of this phenol-derivative (3-amino-2,4,6-trinitrophenol, **22b**) was proven singles crystal grown out of acetone/water. Therefore it was an important step to optimize the synthesis of **22a**, so that a clean product could be obtained without any further purification steps. The crystal structure of **22a** was already described by C. Dickinson in 1966, measured at 298 K.[13] 22a was crystallized and measured at 173 K in order to compare the densities at different temperatures. **22a** crystallizes in the monoclinic space group $P2_1/c$ with 4 molecular units per unit cell. At 173 K it has a unit cell volume of 954.6(1) Å^3 and a density of 1.900 g cm^{-3}. The cell dimensions are a = 7.2411(4) Å, b = 11.0410(7) Å, c = 12.0522(7) Å and β = 97.79(2)°. **22b**, also known in literature as 3-amino-picric acid[14] crystallizes in the monoclinic space group $P2_1/n$ with 4 molecular units per unit cell. At 173 K it has a cell volume of 866.4(1) Å^3 and a density of 1.872 g cm^{-3}. The unit cell parameters are a = 6.6383(4) Å, b = 8.5899(5) Å, c = 15.5133(13) Å with β = 101.64(1)°. Figure 18 shows the molecular units of **22a** and **22b**. The analysis of the crystal structure of **22a** revealed that the N_3-nitro group is rotated out of the benzene plane within 65.2(2)°. If the free rotation of those nitro groups is hindered in solution as well, this could explain the regio-selectivity of further nucleophilic substitution reactions. In addition, the amino always seems to stabilize the nitro groups in ortho and para position. The electron deficiency is therefore more pronounced at the C_3 carbon. This was also observed in pentanitroaniline (**21**) at the C_3 and C_5 position. An interesting fact is that **22a** is slightly more thermally stable than **22b**. **22a** decomposes after melting at 228 °C, whereas **22b** already decomposes at 218 °C.

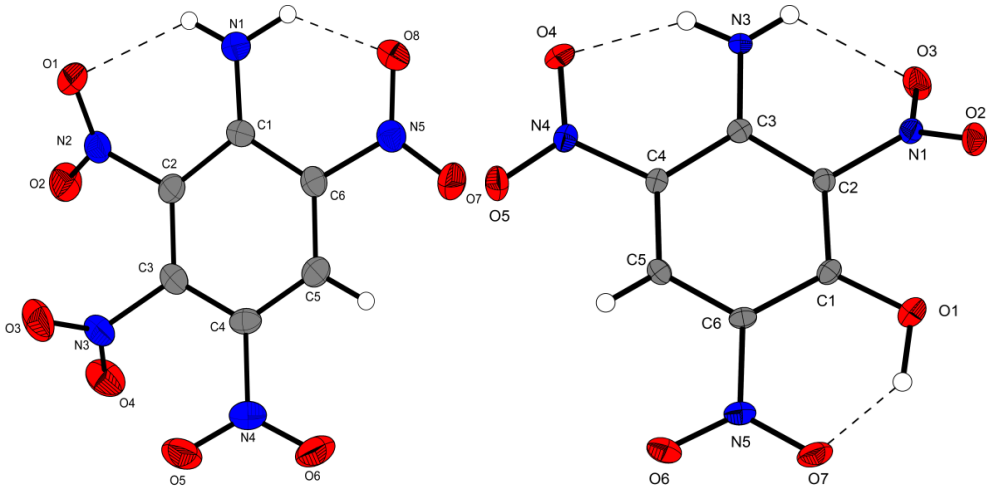


Fig. **18**: Molecular structures of **22a** (left) and **22 b** (right). The non-hydrogen atoms are represented by displacement ellipsoids at a 50% probability level. **Selected bond lengths** [Å] (**22a**): C1–N1 1.317 (2), C2–N2 1.462 (2), C3–N3 1.486 (2), C4–N4 1.453 (2), C6–N5 1.462 (2), N1–O8 2.625 (2), N1–O1 2.713 (2); **Selected bond angles** [°] (**22a**): N1-H···O8 131.1 (2), N1-H···O1 127.7 (2); **Selected torsion angles** [°] (**22a**): C1–C2–N2–O1 44.4 (2), C2–C3–N3–O3 65.2 (2), C3–C4–N4–O5 16.2 (2), C5–C6–N5–O7 1.3 (2); **Selected bond lengths** [Å] (**22b**): C1–O1 1.327 (2), O1–O7 2.582 (2), C2–N1 1.457 (2), C3–N3 1.320 (3), C4–N4 1.447 (2), C6–N5 1.444 (3); **Selected bond angles** [°] (**22b**): O1–H···O7 139.0 (2), N3–H···O4 139.9 (2), N3–H···O3 121.8 (2); **Selected torsion angles** [°] (**22b**): C1–C6–N5–O7 1.6 (2), C1–C2–N1–O2 44.0 (2), C3–C4–N4–O4 1.4 (2);

As described above, the nitro group in C_3 position of **22a** can be easily substituted by several nucleophiles. This also applies to the C_3 and C_5 nitro groups in **21**. Compounds **22a**, **24** and **26**, which have already been described in literature, were synthesized and tested by measuring the thermal stabilities by DSC (heating rate of 5 °C min^{-1}) and by determining the densities *via* crystal structures measured at 173 K. Those were compared to known ambient-temperature densities to justify the use of "$\alpha_v = 1.5 \cdot 10^{-4}\ K^{-1}$", the semi-empiric volume coefficient of thermal expansion in the formula by C. Xu et al.[15] This formula can be used to convert densities measured at 173 K into densities at other temperatures. Furthermore, the sensitivities towards impact and friction were determined by BAM certified testing machines. Additionally, SSRTs of compounds **22a**, **24** and **26** were carried out in order to confirm their ability to be initiated.

A further nucleophile used for the substitution of the C3-nitro group of compound **22a** is 3-amino-1,2,4-triazole. The reaction was carried out in a solvent mixture containing acetone and glacial acetic acid, in which the aminotriazole was protonated. This leads to a highly regio-selective reaction where the primary amine in the C3 position reacted with **22a**. Here the nitro group in C_3 position was substitued and **27** was obtained in very good yields. After that, **27** was aminated using the “vicarious-amination” reaction, which is based on a radical mechanism. This is an alternative synthesis of **28** without using the expensive 1,3,5-trifluorobenzene, as known in literature.[16]

9.2.2 Detonation parameters

The detonation parameters were also calculated and are displayed in table 3.

Table 3: Energetic properties of compounds **22**, **24**, **26**, **27** and **28** in comparison to RDX and HNS

	22a	**24**	**26**	**27**	**28**	**RDX**	**HNS**
Formula	$C_6H_3N_5O_8$	$C_6H_3N_5O_6$	$C_6H_2N_6O_6$	$C_8H_6N_8O_6$	$C_8H_7N_9O_6$	$C_3H_6N_6O_6$	$C_{14}H_6N_6O_{12}$
FW / g mol^{-1}	273.12	241.12	254.12	310.18	325.20	222.12	450.23
Grain Size / µm	<100	<100	<100	<100	<100	<100	<100
IS / J [a]	>10	>7	>9	35	40	>7.5	5
FS / N [b]	>360	>360	>360	>360	>360	120	240
N / % [d]	25.64	29.05	33.07	36.12	38.76	37.84	18.67
Ω / % [e]	–32.2	–49.8	–44.1	–67.1	–66.4	–21.6	–67.5
$T_{Dec.}$ / °C [f]	228	268	183	287	300	205	318
ρ / g cm^{-3} [g]	1.865**	1.91**	1.92**	1.79 (pyc.)	1.86 (pyc.)	1.80	1.74
$\Delta_f H_m°$ / kJ mol^{-1} [h]	–16.7	181.5	435.4	131.2	220.6	70.3	174.0
$\Delta_f U°$ / kJ kg^{-1} [i]	11.5	824.7	1781.7	502.5	762.2	417.0	240.1
EXPLO6.01 values:							
$-\Delta_{Ex}U°$ / kJ kg^{-1} [j]	5398	5468	6017	4408	4581	5732	5476
T_{Det} / K [k]	3894	3798	4240	3145	3154	3804	3960
P_{CJ} / kbar [l]	322	335	360	252	290	349	242
$V_{Det.}$ / m s^{-1} [m]	8502	8608	8950	7912	8357	8795	7436
V_o / L kg^{-1} [n]	666	633	657	673	688	794	530

[a] Impact sensitivity (BAM drophammer, 1 of 6); [b] Friction sensitivity (BAM friction tester 1 of 6); [c] Nitrogen content; [d] Decomposition temperature from DSC (β = 5 °C); [e] From X-ray diffraction; [f] Calculated (CBS-4M) heat of formation; [g] Energy of formation; [h] Energy of explosion; [i] Explosion temperature; [j] Detonation pressure; [k] Detonation velocity; [l] Assuming only gaseous products; *Values have been calculated by using room temperature densities, ** Density at 298 K was calculated using the formula $\rho_{298K} = \rho_T/1+\alpha_v(298-T_0)$ with $\alpha = 1.50 \cdot 10^{-4}$ K^{-1} and $T_0 = 173$ K[8];

The crystal densities of **22a**, **24** and **26** at 298 K, which are necessary to calculate the detonation parameters of these compounds, are already known from recently published literature and were confirmed by low temperature X-ray measurements at 173 K[13,14,17,18]. Those values were used to calculate the density at 298 K using the following formula:

$$\rho_{298K} = \rho_{T(0)} / [1+\alpha_v(298-T_0)] \quad (3)$$

(with $\alpha_v = 1.50 \cdot 10^{-4}$ K^{-1} and $T_0 = 173$ K)

These theoretical densities were compared to the densities of already published crystal structures (298 K) in order to confirm the correctness of the value α_v.

Table 4: Calculated densities of **22a**,**24** and **26** in comparison to x-ray data.

Compound	ρ (x-ray 173 K)	ρ (x-ray 298 K)	ρ (calc.with formula (1))
22a	1.900	1.870[13]	1.865
22b	1.872	1.823[14]	1.838
24	1.944	1.910[17]	1.911
26	1.956	1.930[18]	1.920

The deviation using $1.50 \cdot 10^{-4}$ K^{-1} for α_v is between 0.005 and 0.01 g cm^{-3} for the calculated densities compared to the X-ray densities at 298 K. Such small deviations barely influence the detonation parameters, which are calculated with the EXPLO5 computer code. To confirm these parameters, each explosive must be initiated several times in a large setup with at least 25 g. In addition, the initiability of such explosives, as well as their critical diameter, have to be experimentally determined. The initiability, however, can be analyzed with the so called "Smal Scale Shock Reactivity Test" (SSRT), which is described in chapter 9.4.1.

Note:

The crystal structures of **24** and **26** were already determined by H. L. Ammon in 1982[17] and 1986 at a temperature range from 283-303 K.[18] The molecular units of **24** and **26** are shown in figure 19. **24** crystallizes in the monoclinice space group $P2_1/c$ with 4 formula units in the elemental cell. The cell dimensions are a = 7.1442(3) Å, b = 9.8515(5) Å, and c = 11.8198(5) Å and β = 97.989(4)°. At 173 K it has a cell volume of V = 823.84(6) $Å^3$ and a density of 1.944 g cm^{-3}. In contrast to that, **26** crystallizes in the orthorhombic space group $P2_12_12_1$ with 4 molecular unit per unit cell. At 173 K it has a unit cell volume of 863.10(9) $Å^3$ and a density of 1.956 g cm^{-3}. The cell dimensions are a = 6.5565(4) Å, b = 9.3660(6) Å, and c = 14.0552(8) Å.

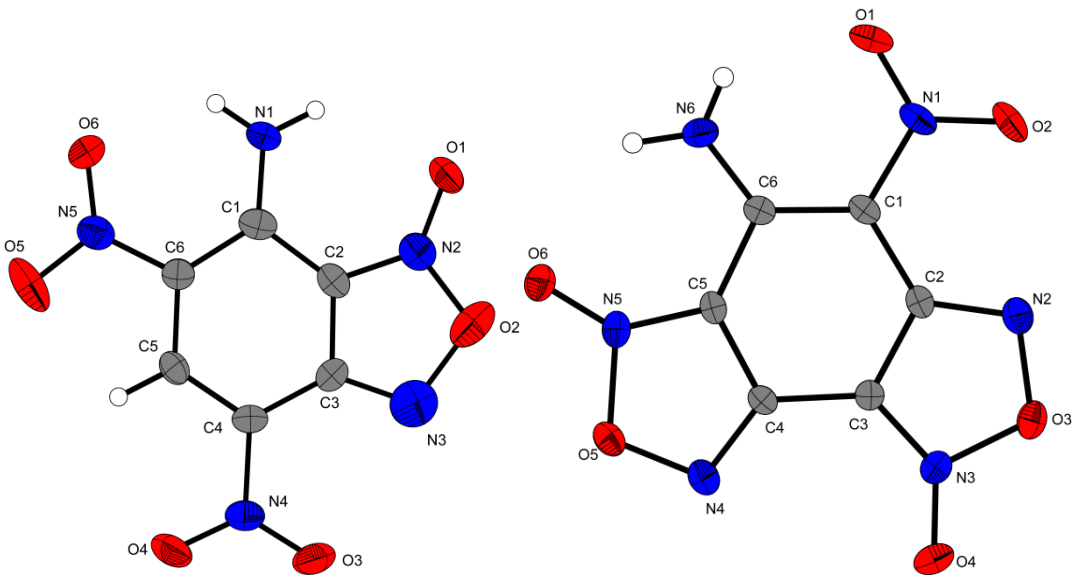


Fig. 19: Molecular units of compounds **24** and **26**. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. **Selected bond lengths** [Å] (24): C1–N1 1.315 (5), C2–N2 1.350 (6), N2–O1 1.223 (4), N2–O2 1.368 (5), O2–N3 1.482 (7), C6–N5 1.401 (6), N5–O6 1.223 (5), N5–O5 1.276 (5), C4–N4 1.442 (5), N4–O4 1.232 (5), N4–O3 1.234 (5), N1–O1 2.850 (5), N1–O6 2.719 (5); **Selected bond angles** [°] **(**24**):** O6–N5–O5 120.6 (4), O4–N4–O3 123.5 (4), O1–N2–O2 121.3 (4), N2–O2–N3 105.4; **Selected torsion angles** [°] (24): C1–C6–N5–O6 6.0 (6), C5–C4–N4–O4 0.4 (6), C1–C2–N2–O1 2.6 (7). **Selected bond lengths** [Å] (26): C6–N6 1.307 (4), C1–N1 1.410 (4), N1–O1 1.243 (4), N1–O2 1.231 (4), C2–N2 1.324 (4), N2–O3 1.411 (4), O3–N3 1.429 (4), N3–O4 1.227 (4), C4–N4 1.301 (4), N4–O5 1.367 (4), O5–N5 1.476 (4), N5–O6 1.202 (4); **Selected bond angles** [°] **(**26**): O1**–N1–O2 122.3 (3), N2–O3–N3 108.6 (2), O3–N3–O4 117.8 (3), N4–O5–N5 108.6 (2), O5–N5–O6 118.0; **Selected torsion angles** [°] (26): C6–C1–N1–O1 1.8 (5).

9.2.3 Crystal structure of compound **27** and thermical properties of compound **28**

The crystallization of **27** revealed the regio-selectivity of the triazole-benzene connectivity. It was proven that 3-amino-1,2,4-triazole attacks the C_3 carbon of **22a** with the free primary amine and not with the ring itself. Single crystals of compound **27** were grown out of DMSO. **6** crystallizes in the triclinic space group *P*–1 with 2 molecular units per unit cell. The dimensions are *a* = 8.7125(8) Å, *b* = 9.5625(8) Å and *c* = 10.5487(9) Å. At 173 K the unit cell volume amounts 753.63(13) $Å^3$ with a density of 1.711 g cm^{-3}. Figure 20 shows the molecular unit of **27**.

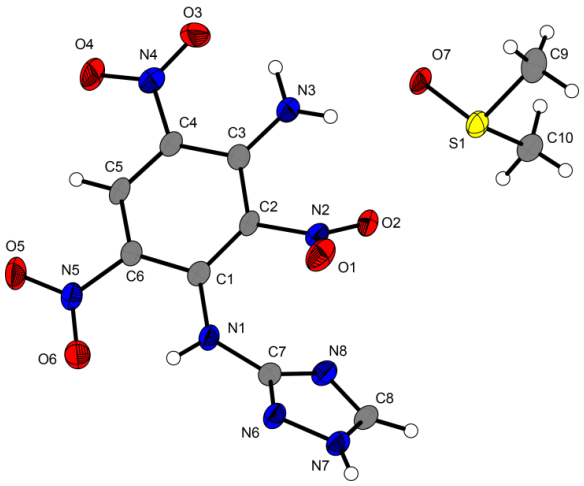


Fig 20: Molecular unit of compound **27**. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level; **Selected bond lengths** [Å] (27): C3–N3 1.335 (3), C4–N4 1.448 (2), N4–O3 1.237 (2), N4–O4 1.227 (2), C5–N5 1.443 (2), N5–O5 1.230 (2), N5–O6 1.235 (2), C2–N2 1.459 (3), N2–O2 1.231 (2), N2–O1 1.224 (3), C1–N1 1.335 (2), N1–C7 1.399 (2), N6–N7 1.364 (2); **Selected bond angles** [°] **(**24**):** O2–N2–O1 123.6 (2), O3–N4–O4 122.7 (2), O5–N5–O6 121.6 (2), C1–N1–C7 130.5 (2); **Selected torsion angles** [°] (27): C3–C2–N2–O2 52.6 (3), C3–C4–N4–O3 0.4 (3), C5–C6–N5–O5 2.7 (3), C1–N1–C7–N8 39.0 (4).

In addition, some DSC measurements were performed on compounds **27** and **28**. The increase in thermal stability by aminating **27** was not very high. The density, however, rose from 1.79 g cm^{-3} (**27**) to 1.86 g cm^{-3} (**28**). Both compounds show sharp decomposition points, displayed in figure 21. Regarding their sensitivity towards impact and friction, **27** and **28** can be classified as less sensitive.

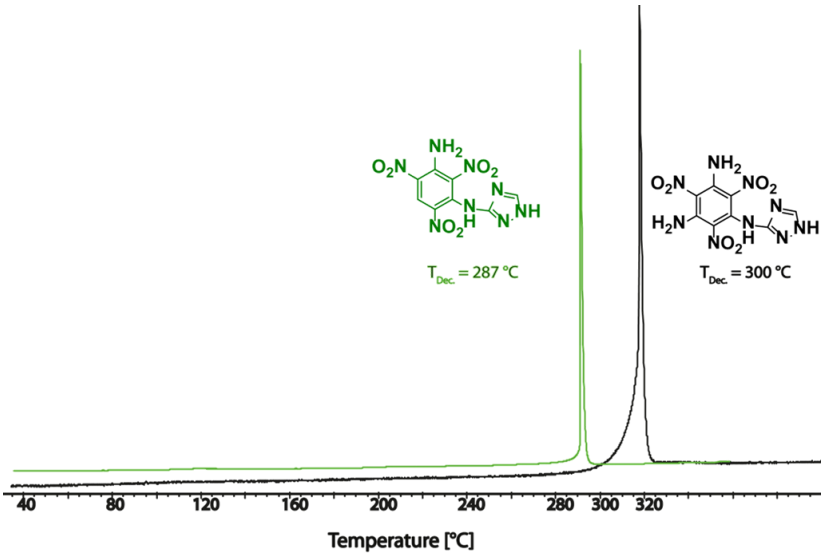


Fig. 21: DSC curves of **27** (green) and **28** (black) (heating rate β = 5 °C min^{-1})

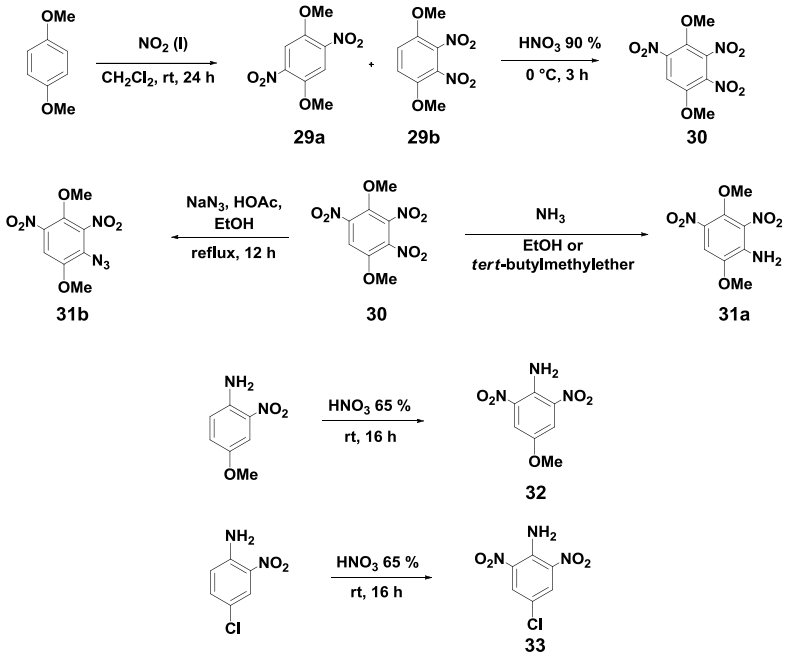
9.3 Nitration of 1,4-dimethoxybenzene and the syntheses of 4-methoxy-2,6-dinitroaniline and 4-chloro-2,6-dinitroaniline

9.3.1 Syntheses

The first part of this chapter adresses the nitration of 1,4-dimethoxybenzene.[2,3] The idea behind using this compound was to analyze how many nitro groups can be introduced and to research the substitutions of one or more methoxy groups by ammonia. It turned out that this starting material can be easily nitrated twice using NO_2(l) in dichloromethane. This is a radical nitration yielding nearly 100 % of an isomeric mixture of **29a** and **29b** in the ratio 2.5 : 1. This was proven by ^{1}H NMR integrals and crystallizing **29a**. Alternatively 65 % nitric acid was used as well, but resulted in lower yields. When recrystallizing the isomeric mixture, pure **29a** was obtained. This was the only nitration reaction of 1,4-disubstituted starting materials where mainly the 2,5-dinitroisomer was formed. In the next nitration step, a third NO_2 group was introduced. This reaction requires at least 90 % nitric acid. Higher yields of **30** can be achieved by using 99.5 % nitric acid and a temperature range between –20 and 0 °C. After that, two nucleophilic substitutions using ammonia or azide in different protic and aprotic solvents were performed. The synthesis of TATB by methoxy/amine exchange using 1,3,5-trimethoxy-2,4,6-trinitrobenzene is well known.[19] Therefore the formation of 4-methoxy-2,3,5-trinitroaniline or **14** was expected. In contrast to that, this 1,4-disubstituted polynitrobenzene shows a completely different behavior. Unfortunately, no methoxy group, but instead only one specific nitro group, could be substituted. This resulted in the formation of 3,6-dimethoxy-2,4-dinitroaniline (**31a**) or the corresponding azide (**31b**) when sodium azide was used as nucleophile in ethanol/glacial acetic acid. In the case of **31b** no ring

closure resulting in the formation of a furoxane was observed. An overview of the performed reactions is displayed in scheme 9.

A second approach in this chapter was the synthesis of 4-methoxy-2,6-dinitroaniline[20] (**32**) and its chloro-derivative (**33**).[21] These compounds can be easily synthesized by stirring their corresponding starting materials in 65 % nitric acid overnight at ambient temperature. Any further attempts to obtain a tri- or tetranitro-derivative of **32** and **33** failed and only decomposition was observed when the nitrating conditions were too harsh. Therefore, these attempted approaches to synthesize **1** or **14** were discarded. Those five compounds (**29a**, **30**, **31a**, **31b** and **32**) were crystallized to determine their crystal structure by low temperature X-ray diffraction. All crystalline samples were grown out of acetone.



Scheme 9: Nitration of further 1,4-disubstituted nitro aromatics

9.3.2 Crystal structures

29a crystallizes in the monoclinic space group *P*–1 with 2 molecular units per unit cell. At a temperature of 100 K it has a cell volume of 462.94(7) Å^3 and a density of 1.637 g cm^{-3}. The cell parameters are a = 7.7332(7) Å, b = 7.9323(6) Å, c = 8.4258(8) Å and α = 87.831(7)°, β = 82.831(8)°, γ = 64.540(8)°. **30**, however, crystallizes in the monoclinic space group $P2_1/c$ with 4 molecules per unit cell. At 293 K it has a unit cell volume of 1121.0(2) Å^3 and a density of 1.619 g cm^{-3}. The cell dimensions are a = 9.429(1) Å, b = 12.453(1) Å, c = 9.990(1) Å and β = 107.123(12)°. The molecular unit of **30** is shown in figure 22.

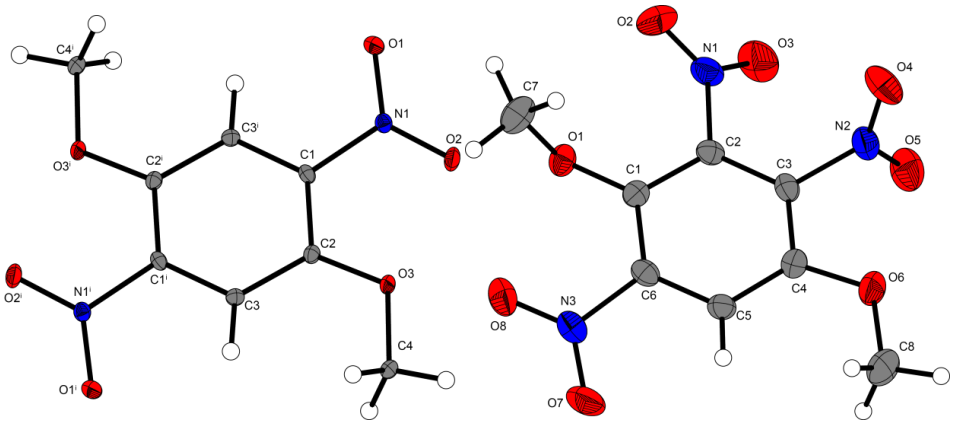


Fig 22. Molecular unit of compound **29a** (left) and **30** (right). The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level; **Selected bond lengths** [Å] (**29a**): C2–O3 1.348 (2), O3–C4 1.441 (2), C1–N1 (1.470), N1–O1 1.234 (1), N1–O2 1.222 (1); **Selected bond angles** [°] **(29a):** N1–O1–O2 123.7 (1), C2–O3–C4 117.3 (1); **Selected torsion angles** [°] (**29a**): C3–C1–N1–O1 23.5 (2), C3–C2–O3–C4 5.7 (2); **Selected bond lengths** [Å] (**30**): C4–O6 1.347 (3), O6–C8 1.432 (3), C1–O1 1.348 (3), O1–C7 1.453 (3), C3–N2 1.477, C2–N2 1.477, C2–N1 1.471 (3), C6–N3 1.480 (3); **Selected bond angles** [°] **(30)**: C4–O6–C8 118.4 (2), O5–N2–O4 125.6 (2), O3–N1–O2 124.9 (3), C1–O1–C7 115.4 (2), O8–N3–O7 123.9 (2); **Selected torsion angles** [°] (**30**): C5–C4–O6–C8 1.8 (3), C4–C3–N2–O5 75.2 (3), C3–C2–N1–O3 39.1 (3), C2–C1–O1–C7 87.7 (2), C1–C6–N3–O8 15.7 (3).

Regarding the torsion angles of the nitro and methoxy groups in **29a** and **30**, it can be observed that in the case of compound **30**, the N2-nitro group is strongly twisted out of the benzene plane (75.2°). In addition, the methoxy group between the two nitro groups stand almost perpendicular (87.7°) towards the benzene plane, wheras in **29a** they are nearly planar (5.7°). This can be explained due to sterical hindrance. The methyl groups are oriented in the opposite direction of the nitro group. Assuming that there is no free rotation anymore even in solution, possible nucleophilic substitutions were applied. Crystallization of **31a** and **31b** revealed that only the N2-nitro group is substituted.

31a crystallizes in the triclinic space group *P*–1 with 2 molecules per unit cell. At 173 K it has a unit cell volume of 495.59(8) Å^3 and a density of 1.630 g cm^{-3}. The cell dimensions are a = 3.9794(4) Å, b = 9.1778(9) Å, c = 14.3134(13) Å and α = 72.80(1)°, β = 88.37(1) and γ = 82.80(1)°. The molecular units of **31a** and **31b** are shown in figure 23. In contrast to that, **31b** crystallizes in the monoclinic space group $P2_1/n$ with 8 molecules per unit cell. At 173 K it has a unit cell volume of 2213.9(3) Å^3 and a density of 1.615 g cm^{-3}. The cell dimensions are a = 15.8783(15) Å, b = 7.9215(4) Å, c = 19.1044(18) Å and β = 112.88(2).

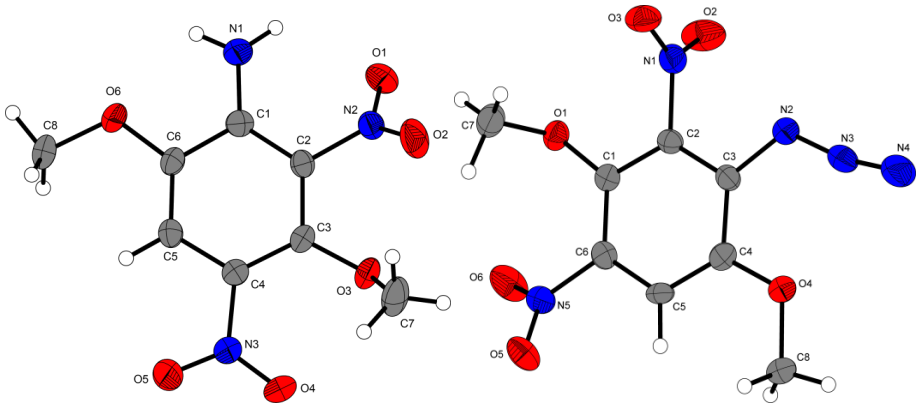


Fig 23. Molecular units of compounds **31a** and **31b**. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level; **Selected bond lengths** [Å] (**31a**): C1–N1 1.346 (3), C2–N2 1.454 (2), C3–O3 1.357 (2), C4–N3 1.455 (3), C6–O6 1.364 (2), O3–C7 1.438 (3), O6–C8 1.435 (2); **Selected bond angles** [°] (**31a**): O1–N2–O2 123.0 (2), C3–O3–C7 117.8 (2), O5–N3–O4 120.9 (2), C6–O6–C8 117.5 (2); **Selected torsion angles** [°] (**31a**): C1–C2–N2–O1 41.8 (2), C2–C3–O3–C7 71.9 (2), C3–C4–N3–O4 4.6 (3), C1–C6–O6–C8 6.2 (3). **Selected bond lengths** [Å] (**31b**): C1–O1 1.363 (4), C4–O4 1.340 (4), C6–N5 1.470 (6), C2–N1 1.473 (5), C3–N2 1.390 (6), N2–N3 1.251 (5), N3–N4 1.124 (6); **Selected bond angles** [°] (**31b**): N2–N3–N4 167.9 (4);); **Selected torsion angles** [°] (**31b**): C5–C4–O4–C8 1.6 (6), C6–C1–O1–C7 73.5 (5), C1–C6–N5–O6 34.4 (5), C1–C2–N1–O3 82.9 (4).

32 crystallizes in the triclinic space group *P*–1 with 4 molecular units per unit cell. The dimensions are a = 9.0377(8) Å, b = 9.6823(6) Å, c = 10.7174(8) Å and α = 71.258(6)°, β = 70.417(7)°, γ = 82.606(6)°. At a temperature of 100 K it has a cell volume of 836.50(11) Å^3 and a density of 1.693 g cm^{-3}. The molecular unit of **32** is shown in figure 24.

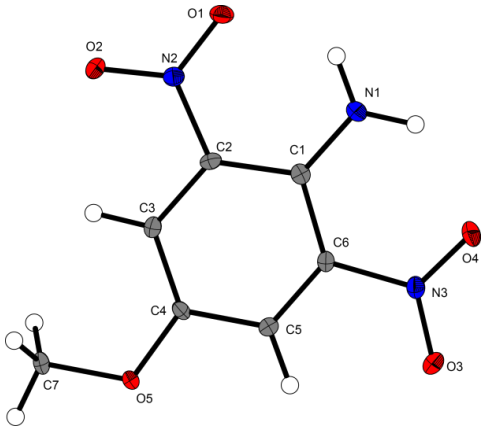


Fig 24. Molecular unit of compound 32. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level; **Selected bond lengths** [Å] (**32**): C1–N1 1.341 (2), C2–N2 1.448 (2), C4–O5 1.363 (2), C6–N3 1.462 (2), O5–C7 1.438 (2); **Selected bond angles** [°] (**32**): C4–O5–C7 116.1 (1); **Selected torsion angles** [°] (**32**): C1–C2–N2–O1 2.9 (2), C1–C6–N3–O4 3.3 (2), C3–C4–O5–C7 4.5 (2).

Regarding the torsion angles in **32**, the nitro groups and the amine, as well as the methoxy group, are nearly coplanar.

9.4 RDX initiation capability tests by selected diazophenols and Small Scale Shock Reactivity Tests of secondary explosives (SSRT)

9.4.1 Small Scale Shock Reactivity Tests (SSRT) of selected secondary explosives

In this chapter, Small Scale Shock Reactivity Tests were performed on the most promising secondary explosives. These SSRT results were compared to those of RDX, TNT and HNS. In this test setup a defined volume of 0.287 ml was pressed into a perforated steel block (Figure 25 left). This was topped with a commercially available detonator (Orica, DYNADET-C2-0ms). Initiation of the tested explosive resulted in denting a separate aluminium block, which was placed right underneath the steel block. The volume of the dent was then filled with sand to compare the performance of the tested sample with RDX, TNT and HNS. The choice of tested compounds depended mainly on their thermal stability and their calculated performance, especially the detonation pressure and velocity. Whereas **22**, **24**, **26, BHTTNBI** and **BHT(NT)$_2$** were potential candidates for RDX replacements, **28**, **BDATT**, **K$_2$TNBI** and **G$_2$TNBI** were compared to HNS and TNT. A depiction of this setup and the tested compounds is displayed in figure 25.

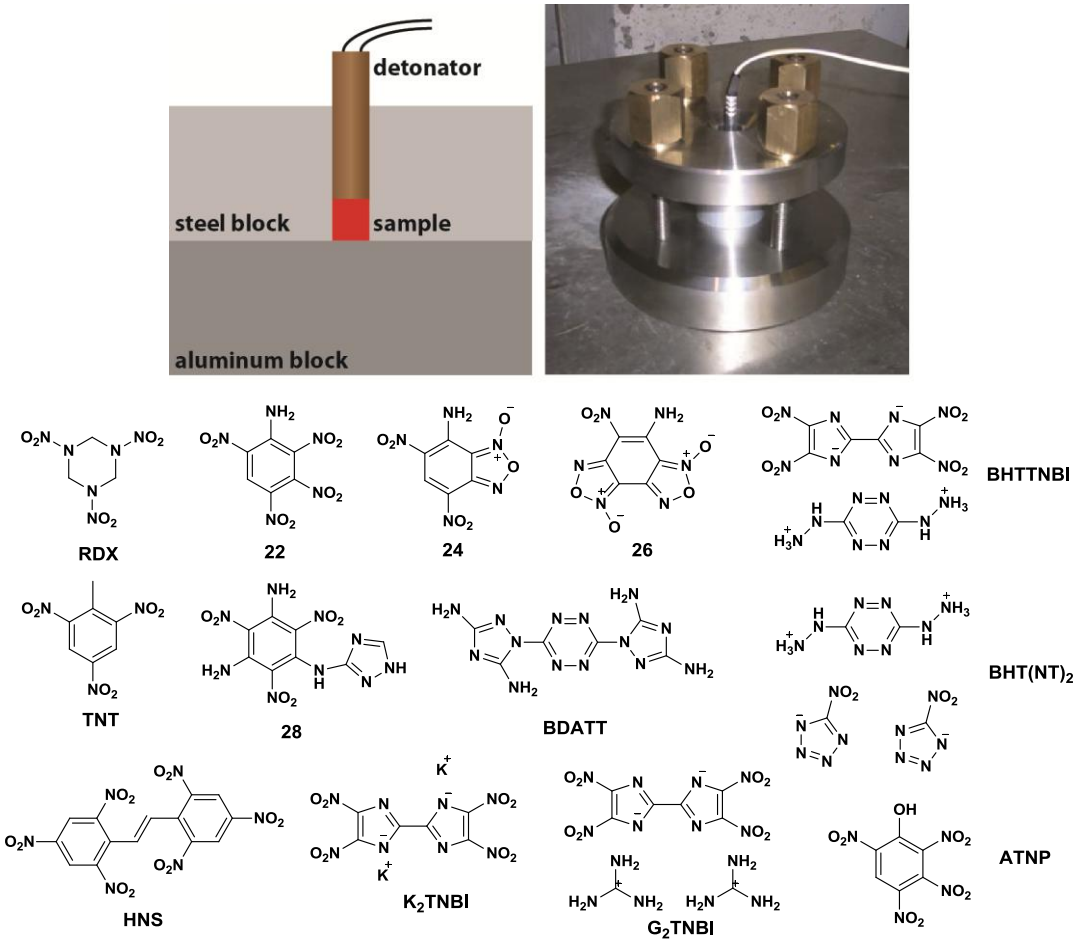


Fig 25: SSRT setup for testing the initiation of secondary explosives (top) and tested compounds (below).

The detonation parameters of all tested compounds, calculated with EXPLO 5 V 6.01 are shown in table 5.

Table 5 Energetic Properties of SSRT tested compounds

	22a	**24**	**26**	**28**	**K_2TNBI**	**G_2TNBI**	**BHTTNBI**	**BHT(NT)$_2$**
Formula	$C_6H_3N_5O_8$	$C_6H_3N_5O_6$	$C_6H_2N_6O_6$	$C_8H_7N_9O_6$	$K_2C_6N_8O_8$	$C_8H_{12}N_{14}O_8$	$C_8H_8N_{16}O_8$	$C_4H_8N_{18}O_4$
FW / g mol^{-1}	273.12	241.12	254.12	325.20	390.31	432.27	456.25	372.22
Grain Size / µm	<100	<100	<100	<100	<100	<100	<100	<100
IS / J [a]	>10	>7	>9	>40	>40	>40	>8	2
FS / N [b]	>360	>360	>360	>360	>288	>360	252	24
N / % [c]	25.64	29.05	33.07	38.76	28.71	45.36	49.12	67.73
Ω / % [d]	–32.2	–49.8	–44.1	–66.4	–20.5	–51.8	–42.4	–34.4
$T_{Dec.}$ / °C [e]	228	268	183	300	312	332	217	176
ρ / g cm^{-3} [f]	1.865**	1.91**	1.92**	1.86(pyc.)	2.08	1.80(pyc.)	1.84	1.75
$\Delta_f H_m°$ / kJ mol^{-1} [g]	–16.7	181.5	435.4	220.6	–356.7	–114.5	495.1	762.4
$\Delta_f U°$ / kJ kg^{-1} [h]	11.5	824.7	1781.7	762.2	–863.0	–167.4	1172.0	2148.0
EXPLO6.01 values:								
$-\Delta_{Ex}U°$ / kJ kg^{-1} [i]	5398	5468	6017	4581	4434	3904	4679	4593
T_{Det} / K [j]	3894	3798	4240	3154	3198	2808	3373	3331
P_{CJ} / kbar [k]	322	335	360	290	283	264	308	286
$V_{Det.}$ / m s^{-1} [l]	8502	8608	8950	8357	8184	8194	8553	8580
V_o / L kg^{-1} [m]	666	633	657	688	430	640	747	851
F / kJ kg^{-1} [n]	881	817	946	737	468	752	856	971

	ATNP	**BDATT**	**RDX**	**HNS**	**TNT**
Formula	$C_7H_5N_3O_6$	$C_6H_8N_{14}$	$C_3H_6N_6O_6$	$C_{14}H_6N_6O_{12}$	$C_7H_5N_3O_6$
FW / g mol^{-1}	244.12	276.24	222.12	450.23	227.13
Grain Size / µm	<100	<100	<100	<100	<100
IS / J [a]	>8	>40	>7.5	5	–
FS / N [b]	360	>360	120	240	–
N / % [c]	22.95	70.99	37.84	18.67	18.50
Ω / % [d]	–45.9	–92.7	–21.6	–67.5	–73.96
$T_{Dec.}$ / °C [e]	119	370	205	318	T_m = 80.1
ρ / g cm^{-3} [f]	1.80	1.75(pyc.)	1.80	1.74	1.65
$\Delta_f H_m°$ / kJ mol^{-1} [g]	–190.4	707.5	70.3	174.0	–59.3
$\Delta_f U°$ / kJ kg^{-1} [h]	–703.8	2659.4	417.0	240.1	–184.9
EXPLO6.01 values:					
$-\Delta_{Ex}U°$ / kJ kg^{-1} [i]	4755	3052	5732	5476	4917
T_{Det} / K [j]	3435	2237	3804	3960	3414
P_{CJ} / kbar [k]	275	225	349	242	213
$V_{Det.}$ / m s^{-1} [l]	7934	8035	8795	7436	7304
V_o / L kg^{-1} [m]	649	740	794	530	644
F / kJ kg^{-1} [n]	757	562	1026	753	747

[a] Impact sensitivity (BAM drophammer, 1 of 6); [b] Friction sensitivity (BAM friction tester 1 of 6); [c] Nitrogen content; [d] Oxygen balance, [e] Decomposition temperature from DSC (β = 5 °C); [f] From X-ray diffraction, ** Density at 298 K was calculated using the formula $\rho_{298K} = \rho_T/1+\alpha_v(298-T_0)$ with $\alpha = 1.50 \cdot 10^{-4}$ K^{-1} and $T_0 = 173$ K[8]; [g] Calculated (CBS-4M) heat of formation; [h] Energy of formation; [i] Energy of explosion; [j] Explosion temperature; [k] Detonation pressure; [l] Detonation velocity; [m] Assuming only gaseous products; [n] Free energy $F = T_{det} \cdot R \cdot n(gas)$ *Values have been calculated by using room temperature densities.

After the compounds were initiated in this setup, the dents formed by the detonation were refilled with SiO_2. The amount of sand and the mass used of each explosive (depending on its density at 298 K) is listed in table 6.

Table 6 Results of SSRT test

Compound	**22**	**24**	**26**	**28**	**BDATT**	**K_2TNBI**	**G_2TNBI**	**ATNP**	**BHTTNBI**	**BHT(NT)$_2$**
m used [mg]	535	520	523	534	477	573	485	491	502	467
ρ [g cm^{-3}]	1.87	1.91	1.92	1.86	1.75	2.08	1.80	1.80	1.83	1.72
m SiO_2 [mg]	781	747	794	538	n.i.	531	451	674	702	727
F / kJ kg$^{-1\ n}$	881	817	946	737	562	468	752	757	856	971

Compound	**RDX**	**HNS**	**TNT**
m used [mg]	504	474	450
ρ [g cm^{-3}]	1.80	1.74	1.65
m SiO_2 [mg]	858	703	761
F / kJ kg$^{-1\ n}$	1026	753	747

RDX shows the best performance within this test setup. Compounds **22a**, **24** and **26** are in the same range and are significantly better than HNS and TNT. Compounds **28**, **K_2TNBI** and **G_2TNBI** show only average performance and are even worse than HNS, whereas **BHTTNBI** and **BHT(NT)$_2$** show similar performance compared to HNS and TNT. **BDATT** could not be initiated. The deviation of the theoretical performance from the results of this test could be explained with the critical diameter. Since the diameter is restricted here to a fixed value, some compounds only detonate partially. Compounds with a small critical diameter always achieve complete detonation. Therefore this test setup only determines whether the initiation of an explosive is possible or not, but not a reliable quantification of its magnitude. For more realistic values all explosives must be initiated in big setups, where the critical diameter can be adapted. This would require kilogram scales of each compound.

9.4.2 RDX initiation by selected diazophenols

This test was carried out to confirm the possibility to initiate RDX by using some diazophenols synthesized in this thesis. The test setup is schematically displayed in figure 26.

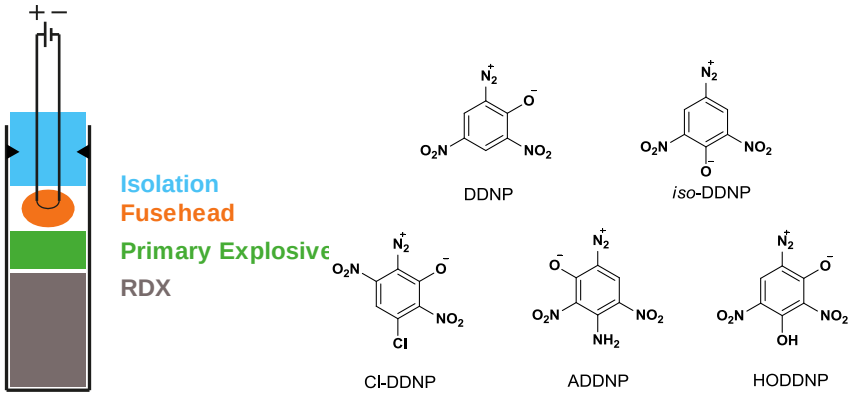


Fig 26: Initiation setup for RDX and tested diazophenols as primary explosives.

The capability of the compounds to undergo a DDT was tested with some basic heating methods. First, a small amount (approx. 5 mg) of **HODDNP**, ***iso*-DDNP**, **4** or **8** was heated on a spatula using a lighter, without direct flame contact. As it is expected in the case of metal-free primary explosives, the compounds only deflagrated upon reaching their corresponding ignition temperatures due to the missing confinement, similar to tetrazene and DDNP. Rapid heating by touching a small amount of the compounds with a hot needle or a hot spatula also resulted in a deflagration. To investigate the capability of the compounds to nevertheless initiate a secondary explosive, RDX (200 mg) was loaded into an aluminium tube (58.0 mm × 7.2 mm, inner diameter 6.5 mm) glued to the center of a copper plate (50 mm × 50 mm × 1 mm) and slightly pressed manually. Varying amounts of diazophenols were loaded on the RDX and also slightly pressed manually. For the ignition a commercial type A electrical igniter was used on top, with a direct contact of the fusehead to the primary explosive. The isolator casing of the igniter was clamped with the metal tube (see Figure 26 for a schematic). The whole setup was placed in a wooden box and covered with damp sand. While ***iso*-DDNP**, **8** and **15** (50 mg of each) were not able to initiate RDX, similar to DDNP itself (also 50 mg), **HODDNP**, on the other hand, was able to initiate RDX. Figure 27 shows the test results of **HODDNP** together with the plate belonging to a lead azide (50 mg) test sample.

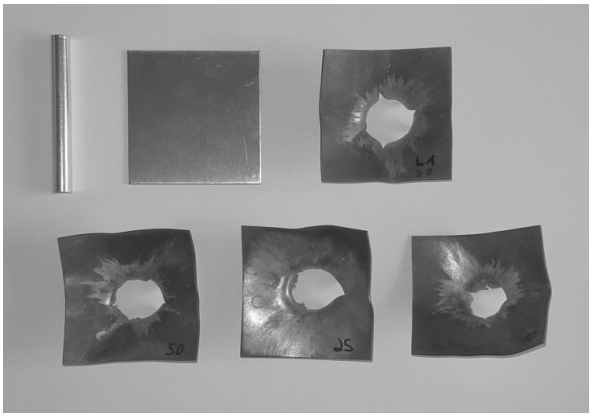


Fig 27: Copper plates after RDX initiation

The plates clearly reveal that not only did 25 mg of **HODDNP** result in a full detonation of RDX, but even a small amount of only 10 mg were able to detonate the secondary explosive. DDNP itself, ***iso*-DDNP**, **4** and **8** only resulted in a (partial) deflagration of the output charge, with merely a small dent in the copper plate, or no damage at all. In the case of a detonation the aluminum tube is completely shattered into very small pieces, while in the case of a deflagration it is usually only torn open. Typically, in the case of the latter about half of the RDX load can still remain in the bottom of the tube with no visible changes to it.

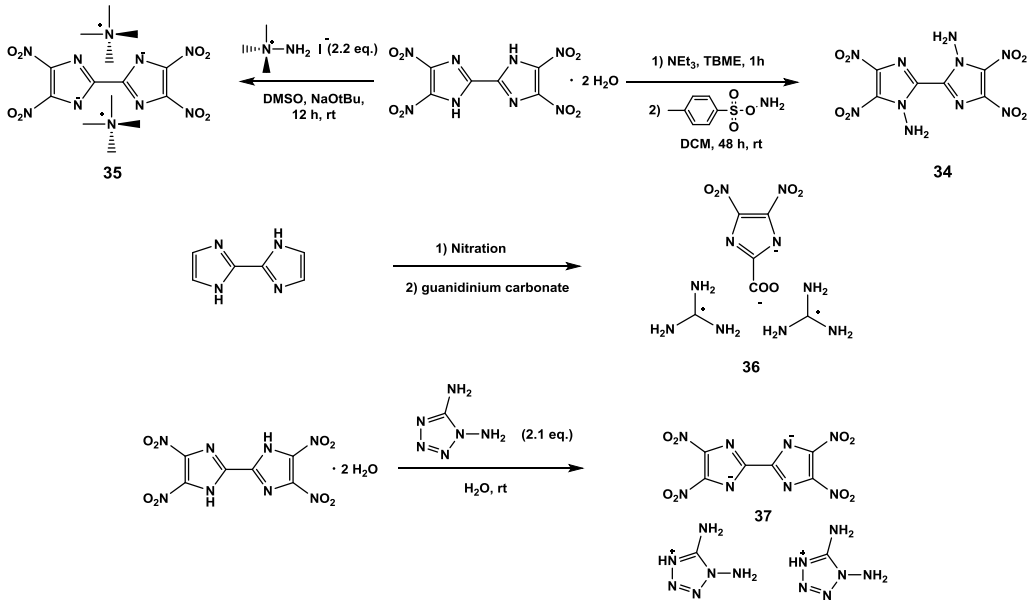
Furthermore, the thermal stability of **HODDNP** was tested by isoperibolic long term measurement in an open glass vessel using a Systag Flexy TSC equipped with a Radex V5 measuring cell, revealing that the compound is stable for at least 60 hours at 75 °C. Moreover, storage of this compound in an oven at 100 °C for 60 hours does not result in any mass loss or change in the chemical composition. This was proven *via CHN* elemental analysis and ^{1}H NMR spectroscopy. In addition, **HODDNP** is stable when stored under water, which is important for shipping security reasons. After suspending it in 30 mL of water, it was allowed to stand for a few days at ambient temperature until the water evaporated. The chemical composition was subsequently confirmed via *CHN* elemental analysis and ^{1}H NMR spectroscopy as unchanged and pure.

9.5. Interesting additional reactions

9.5.1 About the amination of 4,4',5,5'-tetranitro-2,2'-bisimidazole, its hydrolysis product and the bis-(1,5-diaminotetrazolium) salt of TNBI

Note: Background information regarding the synthesis and the energetic properties of 4,4',5,5'-tetranitro-2,2'-bisimidazole (TNBI) and its energetic nitrogen-rich containing salts was described in publication **A**.

Additional derivatives of TNBI were synthesized, its 1,1'-diamino derivative (**34**) being the primary target. Two different amination methods were applied, which resulted in two different products. **34** could only be obtained through an ionic amination similar to the method described by M. M. Breiner et al..[22] Using the radical vicarious amination lead to the formation of the bis-tetramethylammonium dihydrate salt of TNBI (**35**). During the synthesis of TNBI, small amounts of an hydrolysis product, namely the 2-carboxy-4,5-dinitroimidazole, were isolated as bis-guanidinium salt (**36**). An interesting fact is that **36** crystallizes in two different modifications. It can be obtained solvent free (**36a**) or as monohydrate (**36b**). Both species crystallized out of the same solution. The last step was the synthesis of the highly energetic bis-(1,5-diaminotetrazolium) TNBI salt (**37**). These reactions are displayed in scheme 10. In order to confirm the identity of these products as well as their purity, single crystals of each compound were measured and *CHN* elemental analysis was performed.



Scheme 10 Additional derivatives of 2,2'-bisimidazole

34 crystallizes in the monoclinic space group $P2_1/c$ with 4 formula units per unit cell. The unit cell has the dimension of a = 4.9048(13) Å, b = 6.9631(19) Å, c = 17.410(5) Å and β = 93.68(3)°. It crystallizes with a cell volume of 593.4(3) Å^3 and a density of 1.926 g cm^{-3} at 298 K. The molecular unit of 34 is displayed in figure 28.

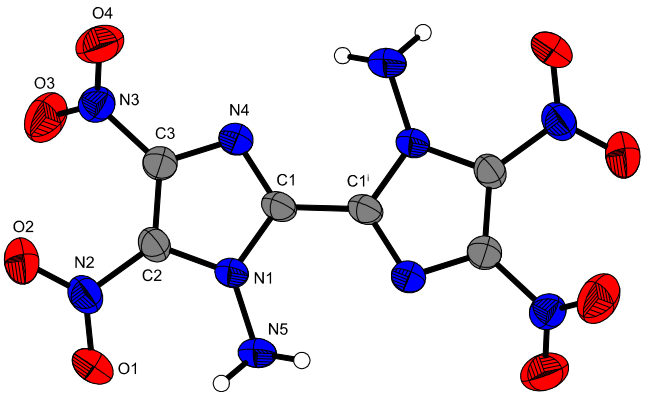


Fig. **28** Molecular unit of **34.** The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. **Selected bond lengths** [Å] (32): C1–C1^{i} 1.445 (4), C1–N1 1.364 (3), N1–C2 1.372 (3), C2–C3 1.366 (3), C4–N4 1.331 (3), N1–N5 1.404 (3), C2–N2 1.426 (3), N2–O1 1.219 (3), N2–O2 1.225 (3), C3–N3 1.454 (3), N3–O4 1.214 (3), N3–O3 1.211 (3); **Selected bond angles** [°] **(**32**):** O1–N2–O2 124.8 (2), O3–N3–O4 124.4 (2); **Selected torsion angles** [°] (32): N1–C2–N2–O1 15.1 (4), N4–C3–N3–O4 49.6 (3).

In order to confirm the formation of **35**, crystals were isolated and measured. Their poor quality lead to an improper diffraction and thus to an incomplete dataset, which was, however, sufficient to confirm the predicted structure. The molecular unit of **35** is displayed in figure 29. The formation of the tetramethylammonium cation has not been fully understood

so far. An explanation could be a methyl shift of the trimethylhydrazinium cation during the reaction.

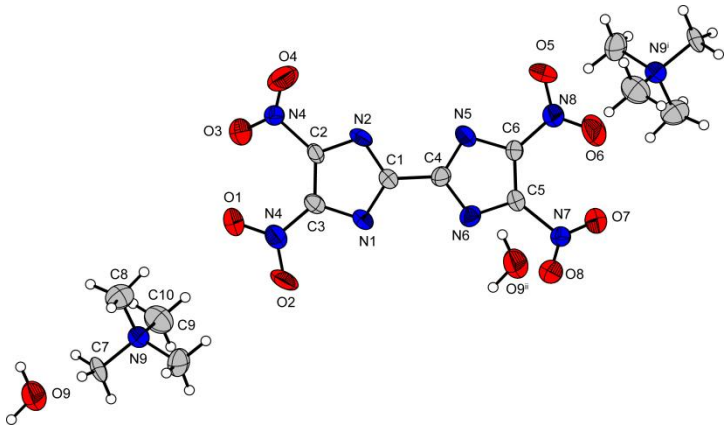


Fig 29: Molecular unit of **35** · 2 H_2O. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level.

36a crystallizes in the monoclinic space group $P2_1/n$ with 4 formula units in the unit cell. At 173 K it has a unit cell volume of 1257.9(1) Å^3 and a density of 1.691 g cm^{-3}. The cell dimensions are a = 7.089(3) Å, b = 19.910(10) Å, c = 9.566(4) Å and β = 111.31(5)°. The monohydrate (**36b**), however, crystallizes in the orthorhombic space group *Pbca* with 8 formula units per elemental cell. At 173 K it has a unit cell volume of 2752.4(4) Å^3 and a density of 1.633 g cm^{-3}. The cell dimensions are a = 11.2159(8) Å, b = 8.5821(10) Å, c = 28.595(2). The molecular units of **36a** and **36b** are shown in figure 30.

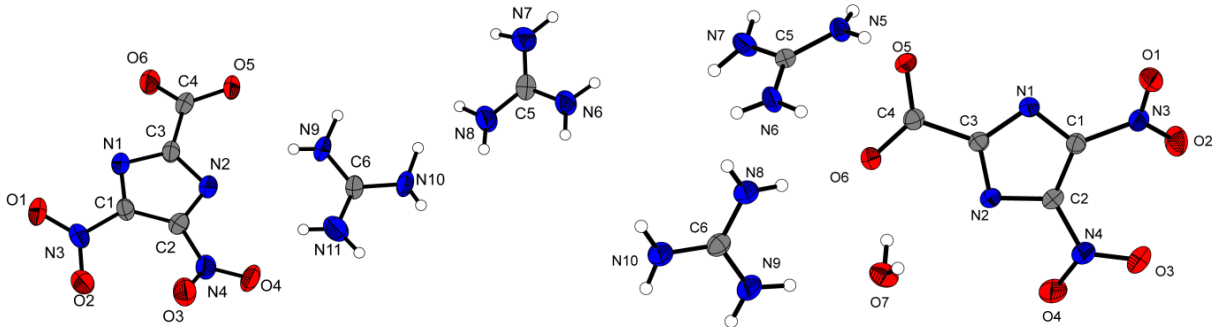


Fig. 30 Molecular units of **36 a** (left) and **36 b** (right). The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. **Selected bond lengths** [Å] (34a): N1–C3 1.353 (4), C3–N2 1.357 (4), N2–C2 1.337 (5), C2–C1 1.399 (5), C1–N1 1.340 (5), C3–C4 1.476 (5), C4–O6 1.248 (5), C4–O5 1.268 (5), C2–N4 1.423 (5), N4–O3 1.229 (4), N4–O4 1.235 (4), C1–N3 1.428 (5), N3–O2 1.225 (4), N3–O1 1.228 (4); **Selected torsion angle**s [°] (34a): N2–C2–N4–O4 23.5 (5), C2–C1–N3–O2 13.0(6), N1–C3–C4–O6 22.5 (5); **Selected bond lengths** [Å] (34b): N1–C3 1.349 (2), C3–N2 1.351 (2), N2–C2 1.344 (3), C2–C1 1.389 (3), C1–N1 1.335 (3), C3–C4 1.492 (3), C4–O6 1.264 (2), C4–O5 1.254 (2), C2–N4 1.429 (3), N4–O3 1.236 (2), N4–O4 1.226 (2), C1–N3 1.444 (3), N3–O2 1.231 (2), N3–O1 1.224 (2); **Selected torsion angle**s [°] (34a): N2–C2–N4–O4 19.0 (3), C2–C1–N3–O2 24.2 (2), N1–C3–C4–O6 14.1 (2);

A further TNBI salt that was synthesized was the bis-(1,5-diaminotetrazolium) TNBI (**37**). 1,5-diaminotetrazolium salts have a very high heat of formation but often tend to thermal

instability. Therefore the combination of such a highly energetic cation with a highly thermally stable anion was analyzed. It turned out that **37** is stable up to 165 °C. The impact sensitivity is 5 J and the friction sensitivity is 80 N. Solvent free single crystals were obtained out of water. **37** crystallizes in the monoclinic space group $P2_1/n$. At 173 K it has a unit cell volume of 921.2(2) Å^3 and a density of 1.854 g cm^{-3}. The cell dimensions are a = 5.1640(2) Å, b = 16.2136(7) Å, c = 11.0655(4) Å and β = 96.14(4)°. As depicted in figure 31, there is a strong hydrogen bonding network between the imidazole rings of TNBI and the diaminotetrazolium cation. The donor-acceptor distance is significantly lower than the sum of the N–N van der Waals radii (r(v.d.W) (N–N) = 3.10 Å). This leads to a high density and resulted in good theoretical detonation values (see 5.4).

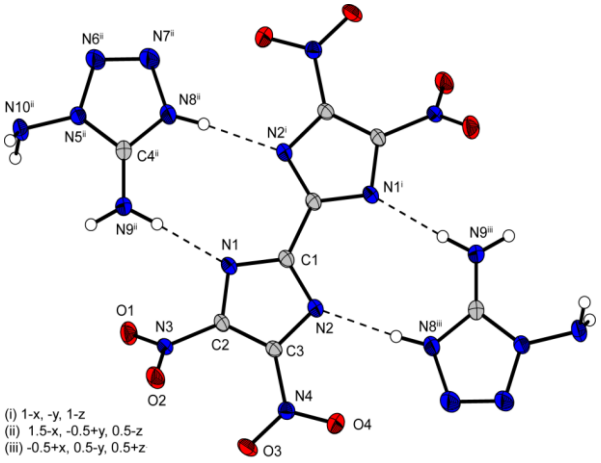
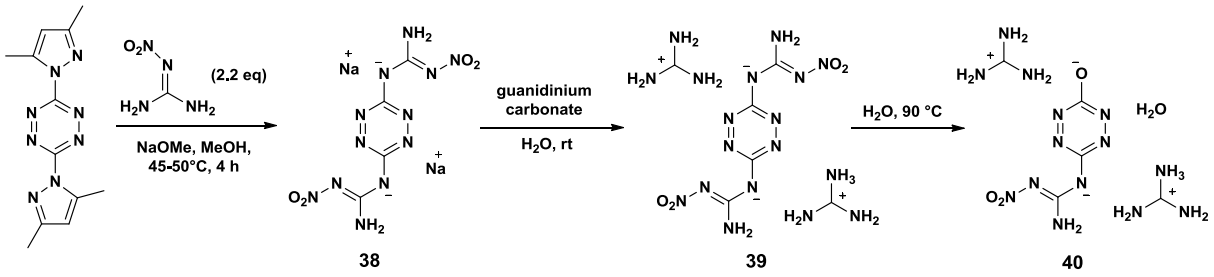


Fig.31 Molecular units of **37**. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. Selected bond lengths [Å] (**35**):**Selected hydrogen donor-acceptor atom distances** d(D···A) [Å]: (**35**):N9^{iii}–N1^{i} 2.896 (2), N8^{iii}–N2 2.923 (2); **Selected hydrogen donor-acceptor bond angels** <(D–H···A) [°]: (**35**): N9^{iii}–H–N1^{i} 177.0 (2), N8^{iii}–H–N2 173.6 (2);

9.5.2 Bis guanidinium 3,6-bis(nitroguanidyl)-1,2,4,5-tetrazinate and its hydrolysis product

Chavez et al. synthesized the 3,6-bis(nitroguanidyl)-1,2,4,5-tetrazine in 2005.[23] The neutral compound is thermally stable up to 220 °C. Therefore the guanidinium salt was analyzed to check if higher decomposition points are possible by salt formation. These syntheses are displayed in scheme 11.



Scheme 11: Synthesis of **39** and its hydrolysis product (**40**).

Since **39** already decomposes at 235 °C, it is not suitable for applications where explosives showing a high thermal stability ($T_{Dec.}$ > 300 °C) are required. The structure of **39** could not be confirmed by X-ray diffraction, but its hydrolysis product (**40**) was isolated while recrystallizing out of water. The molecular unit of **38** is displayed in figure 32. **38** is a novel compound.

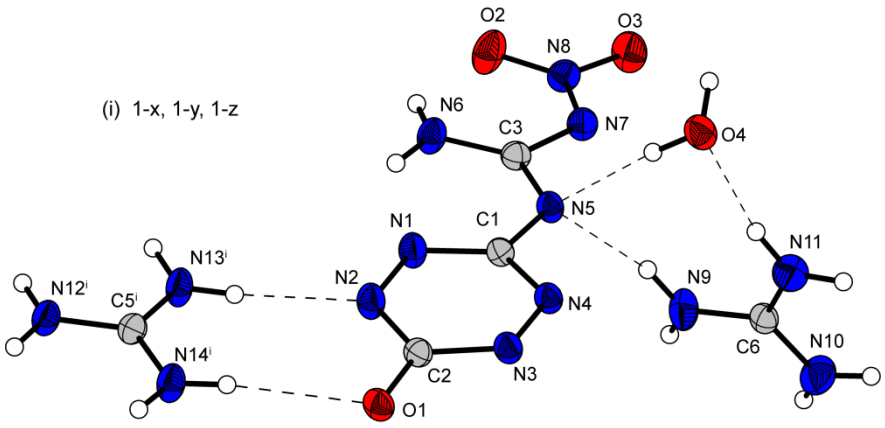


Fig. 32: Molecular unit of **40**. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. Selected bond lengths [Å] (**40**): **Selected bond lengths** [Å] (**40**): C2–O1 1.264 (2), N3–N4 1.309 (2), N1–N2 1.325 (2), C1–N5 1.371 (2), N7–C3 1.392; **Selected hydrogen donor-acceptor atom distances** d(D···A) [Å]: $N14^{i}$–O1 3.18 (2), $N13^{i}$–N2 2.92 (2), N5–O4 2.86 (2), O4–O11 163.2 (2), N5–N9 3.13 (2); **Selected hydrogen donor-acceptor bond angels** <(D–H···A) [°]: (**40**): N14i–H–O1 172.9 (2), N13i–H–N2 175.6 (2), N5–H–O4 174.1 (2), O4–H–N11 163.2 (2), N5–H–N9 162.4 (2).

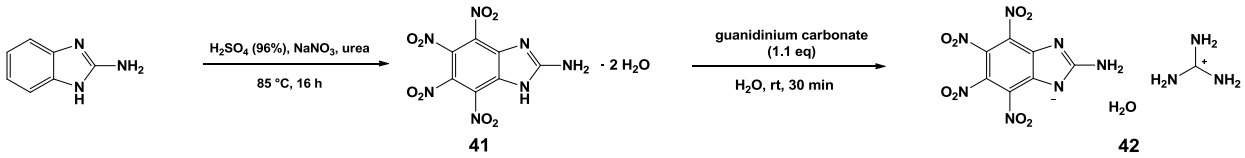
Compound **40** crystallizes in the monoclinic space group $P2_1/c$. At 173 K it has a unit cell volume of 1411.4(13) $Å^3$ and a density of 1.583 g cm^{-3}. The cell dimensions are a = 6.910(4) Å, b = 17.299(8) Å, c = 12.096(6) Å and β = 102.55(5)°. As depicted in figure 32, strong H-bonds between the guanidinium amines and the tetrazine moiety are observed on the left side. In addition, a water molecule is included in the structure. It forms further hydrogen bonds with the deprotonated nitrogen of the nitroguanidine and another guanidinium cation. Due to the low decomposition temperature of this compound (210 °C), any further research was interrupted. Any attempts to isolate the neutral compound by adding hydrochloric acid resulted in decomposition. The solution slowly started to lose its pink-reddish color, which is typical for 1,2,4,5-tetrazines, and gas formation was observed.

9.5.3 Synthesis of 2-amino-4,5,6,7-tetranitrobenzimidazole (41)

Note: Background information regarding the nitration reactions using 2-aminobenzimidazole was described in publication E.

This chapter is meant to describe a further product which can be obtained when 2-aminobenzimidazole (ABI) is nitrated with a different method than described in publication E. When 2-aminobenzimidazole is nitrated in a suspension of $NaNO_3$ in concentrated sulfuric

acid at 85 °C, **41** is obtained as dihydrate. Catalytic ammounts of urea enhance the yield up to 70 % in this reaction. The performed reactions are displayed in scheme 12.



41 42

Scheme 12 Synthesis of **41** and its corresponding guanidinium salt (**42**).

In order to increase the yields and the purity of the nitrated product, several different amounts of sodium nitrate and urea were added. It was confirmed that a huge excess of $NaNO_3$ decreases the yields of **41**. This could be explained by the decreasing concentration of the sulfuric acid when NO_2^+ is generated during the reaction. Experiment 4, as listed in table 7, seems to be the best reaction condition. A first indication of pure **41** · 2 H_2O was provided by elemental analysis (C 23.99 (24.08), H 1.90 (2.02), N 27.10 (28.08)), which merely shows low deviations. This result was confirmed by the measured mass spectrum. These results are also confirmed by the Raman spectrum, which shows the desired values for the symmetrical and asymmetrical NO_2 valence vibrations (1589 (15), 1387 (99), 1339 (51) cm^{-1}). Appropriate NMR data could not be obtained because **41** is not soluble enough in common deuterated solvents. Further attempts to synthesize an azo-coupled derivative of **41** were not sucessful.

Table 7: Different nitration conditions to obtain **41**.

	Experiment 1	**Experiment 2**	**Experiment 3**	**Experiment 4**
ABI [mg]	500	500	1000	1000
H_2SO_4 [mL]	20	40	20	20
$NaNO_3$ [g]	5	5	15	7
Urea [mg]	20	20	30	30
Temperature [°C]	80	80	85	85
Time [h]	16	16	16	16
EA	mononitration, but no pure EA	four times nitration, but no pure EA	four times nitration, but no pure EA	four times nitration and pure EA

In order to obtain a crystalline sample, many different organic solvents were used. A solvent free single crystal could not be isolated. The molecular units of the 2-amino-4,5,6,7-tetranitrobenzimidazole (**41a**) ethylacetate adduct and the 2-amino-4,5,6,7-tetranitrobenzimidazole (**41b**) acetone adduct are displayed in figure 33. **41a** crystallizes in the triclinic space group *P*–1 with 8 formula units per unit cell. The unit cell has the dimensions of a = 10.4670(10) Å, b = 12.9768(13) Å, c = 14.5338(14) Å, α = 110.51(1)°, β = 101.98(1)°, γ = 100.73(1)°. It crystallizes with a cell volume of 1734.9(3) $Å^3$ and a density

of 1.536 g cm^{-3} at a temperature of 298 K. The acetone adduct (**41b**) in contrast crystallizes in the monoclinic space group $P2_1/n$. The unit cell has the dimensions of a = 12.480(3) Å, b = 5.9837(15) Å, c = 20.339(6) Å and β = 100.15(3)°. It crystallizes with a cell volume of 1495.1(7) Å^3 and a density of 1.649 g cm^{-3} at a temperature of 100 K.

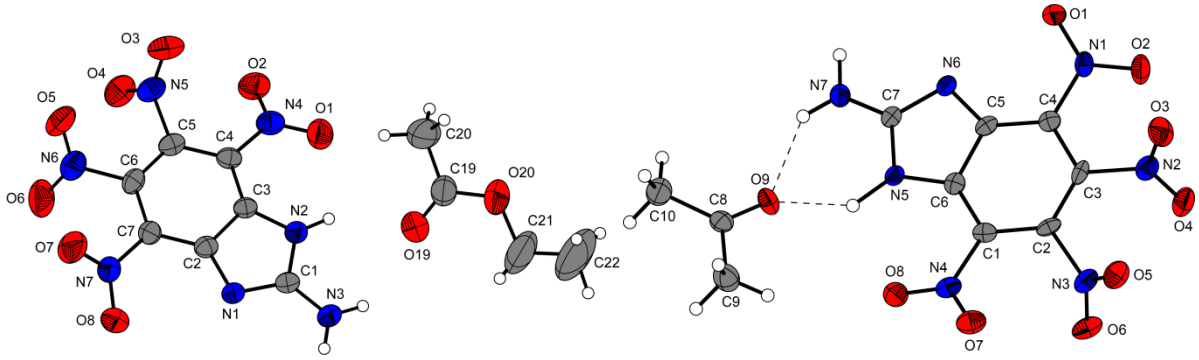


Fig 33: Molecular units of **41 a** (left) and **41 b** (right). The non-hydrogen atoms are represented by displacement ellipsoids at a 50% probability level. **Selected bond lengths** [Å] (**41a**): C1–N3 1.320 (4), C2–C3 1.434 (4), C4–N4 1.465 (4), C5–N5 1.485 (4), C6–N6 1.482 (4), C7–N7 1.469 (4); **Selected torsion angles** [°] (**41a**): C2–C7–N7–O8 41.1 (4), C7–C6–N6–O6 55.6 (4), C6–C5–N5–O4 66.4 (4), C5–C4–N4–O2 12.1 (4); **Selected hydrogen bonds** d(D···A) [Å]: (**41a**):N3–O19 3.09 (2), N2–O19 2.84 (2); **Selected hydrogen donor-acceptor bond angels** <(D–H···A) [°]: (**41a**):N3–H–O19 141.4 (3), N2–H–O19 145.4 (2)**Selected hydrogen bonds** d(D···A) [Å]: (**41b**): N5–O9 2.77 (1), N7–O9 2.86 (1); **Selected hydrogen donor-acceptor bond angels** <(D–H···A) [°]: (**41b**): N5–H–O9 140.5 (4), N7–H–O9 142.6 (4).

The torsion angles of the nitro groups regarding the benzene plane are interesting to mention in this case. Especially the two nitro groups in the middle (C5-NO_2, C6-NO_2 in **41a** and C2-NO_2 and C3-NO_2 in **41b**) are strongly twisted out of plane because of sterical hindrance. The primary and the secondary amine functions of the imidazole moeity form two strong hydrogen bonds with the carbonyl oxygen of the acetone or ethylacetate included in structures **41a** and **41b**.

Single crystals of the corresponding guanidinium salt (**42**) were obtained out of aqueous solution. It crystallizes as a monohydrate in the triclinic spacegroup P–1 with 2 formula units in the elemental cell which has the dimension of a = 7.6358(12) Å, b = 9.8548(13) Å, c = 10.4657(14) Å, α = 102.85(1) °, β = 95.18(1) ° and γ = 91.91(1) °. At 293 K it has a volume of 763.5 (3) Å^3 and a density of 1.697 cm^{-3}. The molecular unit of **42** is shown in figure 34.

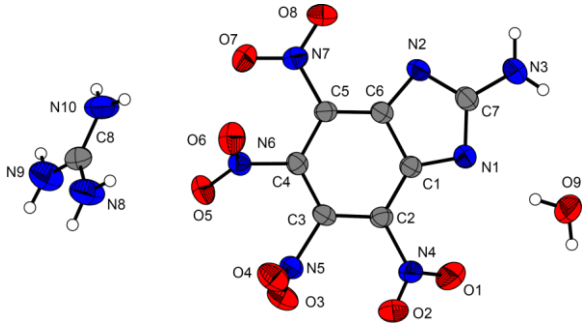


Fig. 34: Molecular units of **42**. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. **Selected bond lengths** [Å] (**42**): C2–N4 1.459 (2), C5–C3 1.473 (2), C4–N6 1.469 (2), C5–N7 1.450 (2), C7–N3 1.341 (2),;

Selected torsion angles [°] (**42**): C3–C2–N4–O2 26.1 (2), C2–C3–N5–O3 64.2 (2), C3–C4–N6–O5 58.0 (2), C4–C5–N7–O7 28.5 (2).

The deprotonation of **41** does not enhance the thermal stability of the molecule. The neutral compound decomposes at 205 °C while **42** is only stable up to 195 °C. **41** can be dried in an oven at 100 °C for 48 h to eliminate the crystal water. Afterwards the density was measured by pycnometric methods. A value of ρ = 1.78 g cm^{-3} was confirmed at 298 K.

9.5.4 Energetic Properties of compounds 34, 37 and 41

The detonation parameters of compounds **34**, **37** and **41** were calculated using EXPLO 5 V 6.01 and are displayed in table 8. Compound **34** shows theoretical detonation parameters that are slightly better than those of RDX. In addition, it is less sensitive regarding its friction sensitivity. Nevertheless, **34** is prone to hydrolysis. This was proven by stirring a suspension of **34** in water for two days, after which only 4,4',5,5'-tetranitro-2,2'-bisimidazole (TNBI) could be detected in a mass spectrum. **37**, however, is the best TNBI salt regarding its energetic properties but displays low thermal stability (165 °C) and is too sensitive towards friction (80 N). **41** shows the worst energetic properties. A moderate density in combination with a high carbon content prevents **41** from being a good explosive.

Table 8: Energetic Properties of compounds **34**, **37** and **41** in comparison to RDX

	34	**37**	**41**	**RDX**
Formula	$C_6H_4N_{10}O_8$	$C_8H_{10}N_{20}O_8$	$C_7H_3N_7O_8$	$C_3H_6N_6O_6$
FW / g mol^{-1}	344.16	514.10	313.12	222.12
Grain Size / µm	100-500µm	100-500µm	100-500µm	<100
IS / J [a]	> 8	> 5	> 5	> 7.5
FS / N [b]	> 360	80	80	120
N / % [c]	40.70	54.5	31.3	37.84
Ω / % [d]	–27.9	–40.4	–38.3	–21.6
$T_{Dec.}$ / °C [e]	190	165	205	205
ρ / g cm^{-3} [f]	1.926	1.820**	1.78***	1.80
$\Delta_f H_m°$ / kJ mol^{-1} [g]	423.0	846.4	70.0	70.3
$\Delta_f U°$ / kJ kg^{-1} [h]	1308.3	1737.3	294.8	417.0
EXPLO6.01 values:*				
$-\Delta_{Ex}U°$ / kJ kg^{-1} [i]	5614	4937	4942	5732
T_{Det} / K [j]	3969	3485	3742	3804
P_{CJ} / kbar [k]	376	313	277	349
$V_{Det.}$ / m s^{-1} [l]	9073	8697	8101	8795
V_o / L kg^{-1} [m]	712	783	681	794

[a] Impact sensitivity (BAM drophammer, 1 of 6); [b] Friction sensitivity (BAM friction tester 1 of 6); [c] Nitrogen content; [d] Oxygen balance, [e] Decomposition temperature from DSC (β = 5 °C); [f] From X-ray diffraction, [g] Calculated (CBS-4M) heat of formation; [h] Energy of formation; [i] Energy of explosion; [j] Explosion temperature; [k] Detonation pressure; [l] Detonation velocity; [m] Assuming only gaseous products; *Values have been calculated by using room temperature densities, ** Density at 298 K was calculated using the formula $\rho_{298K} = \rho_T/1+\alpha_v(298-T_0)$ with $\alpha = 1.50 \cdot 10^{-4}$ K^{-1} and T_0 = 173 K[8]; *** Density was determined by pycnometric methods at 298 K for waterfree compound **41**.

9.6 Experimental section

Raman spectra were recorded with a Bruker MultiRAM FT-Raman instrument fitted with a liquid-nitrogen-cooled germanium detector and a Nd:YAG laser (λ = 1064 nm), infrared spectra were measured with a Perkin–Elmer Spectrum BX-FTIR spectrometer equipped with a Smiths DuraSamplIR II ATR device. All spectra were recorded at ambient temperature; the samples were neat solids. NMR spectra were recorded with a JEOL Eclipse 400 ECX instrument or a BRUKER AVANCE III, all samples were measured at 25 °C. Mass spectrometric data was obtained with a JEOL MStation JMS 700 spectrometer (DEI^+ / $FAB^{+/-}$). *C/H/N* analysis was carried out by the department's internal micro analytical laboratory on a *Elementar Vario el* by pyrolysis of the sample and subsequent analysis of the formed gases. Differential Scanning Calorimetry (DSC) was performed on a *LINSEIS DSC PT10* with about 1 mg substance in a perforated aluminum vessel and a heating rate of 5 K min^{-1} and a nitrogen steam of 5 L h^{-1}. Melting points were determined in the same way. The sensitivities of the compounds were determined according to the BAM (German: Bundesanstalt für Materialforschung und Prüfung) standard for friction and impact. [S9] The impact sensitivities were tested according to STANAG 4489 modified instruction using a BAM drophammer. The friction sensitivities were tested according to STANAG 4487 modified instructions using a BAM friction tester. The tested compounds were classified from the results by the "UN Recommendations on the Transport of Dangerous Goods".

N,N'-(1,4-phenylene)dimethanesulfonamide (**2**)

P-phenylenediamine (36.2 g, 335.1 mmol) was dissolved in pyridine (350 ml). The solution was cooled down to 0 °C and methanesulfonylchloride (57.0 ml, 780.8 mmol) was added slowly. After 1 h the cooling was stopped and the suspension was stirred at ambient temperature for about 3 h. Subsequently the suspension was refluxed for at least 16 h. After that the solution was poured onto crushed ice (1 kg) and filtrated. The precipitate was washed with large amounts of 2M hydrochloric acid and water, ethanol and diethylether. **2** is obtained as a cocoa-colored powder (84.8 g, 96 %). ***N,N'*-(1,4-phenylene)dimethanesulfonamide** ($C_8H_{12}N_2O_4S_2$ 264.32 g mol^{-1}) (**2**): **EA** found (calc): C 36.49 (36.35), H 4.75 (4.58), N 10.89 (10.60), S 24.40 (24.26); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 2.91 (s, 6H, CH_3), 7.15 (s, 4H, $CH_{arom.}$), 9.58 (s, br, 2H, NH); **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C, ppm): δ = 39.6 (CH_3), 122.2 (C-$H_{arom.}$), 135.1 (C-$NH_{sulfonamide}$).

N,N'-(1,4-phenylene)diacetamide (**3**)

P-phenylenediamine (10 g, 92.5 mmol) was dissolved in acetic anhydride (100 ml) at ambient temperature. The slurry was boiled at 90 °C for 5 h. Afterwards the mixture was

poured onto ice water (500 g) and stirred until the acetic anhydride was completely hydrolized. After filtration the solid was washed with much water and 2M HCl to get rid of the acetic acid. ***N,N'*-(1,4-phenylene)diacetamide** ($C_{10}H_{12}N_2O_2$ 192.21 g mol^{-1}) (**3**): **EA** found (calc.): C 62.68 (62.49), H 6.50 (6.29), N 14.74 (14.57); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 2.02 (s, 6H, CH_3), 7.49 (s, 4H, C-$H_{arom.}$), 9.85 (s, br, 2H, $NH_{acetamide}$); **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C, ppm): δ = 24.3 (CH_3), 119.9 (C-$H_{arom.}$), 135.1 (C-$NH_{acetamide}$), 168.4 (C=O).

N,N'-(2-nitro-1,4-phenylene)diacetamide (**4**)

2-nitro-*p*-phenylenediamine (10 g, 92.5 mmol) was dissolved in acetic anhydride (100 ml) at ambient temperature. The slurry was boiled at 80 °C for 5 h. Afterwards the mixture was put onto ice water (500 g) and stirred until the acetic anhydride was completely hydrolized. After filtration the solid was washed with much water and 2M HCl to get rid of the acetic acid. ***N,N'*-(2-nitro-1,4-phenylene)diacetamide** ($C_{10}H_{11}N_3O_4$ 237.21 g mol^{-1}) (**3**): **EA** found (calc.): C 50.64 (50.63), H 4.50 (4.67), N 17.74 (17.51); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 2.05 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 7.54 (d, $^3J_{H\text{-}H}$ = 8.0 Hz), 7.74 (d, $^3J_{H\text{-}H}$ = 8.0 Hz), 8.32 (s, 1H, C-$H_{arom.}$), 10.13 (s, br, 1H, $NH_{acetamide}$), 10.31 (s, br, 1H, $NH_{acetamide}$); **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C, ppm): δ = 23.7 (CH_3), 24.4 (CH_3), 114.8 (C-$H_{arom.}$), 124.3 (C-$H_{arom.}$), 126.5 (C-$NH_{acetamide}$), 126.6 (C-$NH_{acetamide}$), 136.7 (C-$H_{arom.}$), 142.9 (C-NO_2), 168.9 (C=O), 169.3 (C=O).

N-(4-amino-3-nitrophenyl)methanesulfonamide (**5**)

2-nitro-*p*-phenylenediamine (10 g, 92.5 mmol) was dissolved in THF (100 ml) at 0 °C. Methanesulfonylchloride (6.94 ml, 95.0 mmol) was added slowly. Afterwards the suspension was stirred 3 h at 0 °C and further 16 h at ambient temperature. A red precipitate was formed. After filtration the solid was washed with much water and 2M HCl to get rid of the hydrochloric acid. After washing the red solid four times with cold THF (100 ml), **5** was dried in a 60 °C oven for 12 h. **5** was obtained as a bright-red powder. ***N*-(4-amino-3-nitrophenyl)methanesulfonamide** ($C_7H_9SN_3O_4$ 231.23 g mol^{-1}) (**5**): **EA** found (calc.): C 36.68 (36.36), H 4.20 (3.92), N 17.97 (18.17); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 2.92 (s, 3H, CH_3), 7.02 (d, $^3J_{H\text{-}H}$ = 10.8 Hz, 1H, C-$H_{arom.}$), 7.31 (dd, $^3J_{H\text{-}H}$ = 10.8 Hz, $^4J_{H\text{-}H}$ = 2.7 Hz, 1H, C-$H_{arom.}$), 7.40 (s, br, 2H, NH_2), 7.82 (d, $^4J_{H\text{-}H}$ = 2.7 Hz, 1H, C-$H_{arom.}$), 9.42 (s, br, 1H, NH-sulfonamide); **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C, ppm): δ = 39.1 (CH_3), 118.3 (C-$H_{arom.}$), 120.7 (C-$H_{arom.}$), 126.6 (C-$H_{arom.}$), 130.1 (C-NH_2), 132.3 (C-NO_2), 145.7 (C-$NH_{sulfonamide}$).

1,4-phenylenediacetate (**6**)

Dihydroquinone (25.0 g, 227.3 mmol) was dissolved in acetic anhydride (150 ml) at ambient temperature. After that ammonium acetate (5.0 g, 64.9 mmol) was added. The suspension was stirred 2 h at ambient temperature and then refluxed for 4 h. After cooling the suspension was poured onto crushed ice (1 kg) and stirred for further 2 h. The colorless

crystalline precipitate was filtrated and washed with much water to get rid of traces of acid. **1,4-phenylenediacetate** ($C_{10}H_{10}O_4$ 194.18 g mol^{-1}) (6): **EA** found (calc.): C 61.77 (61.85), H 5.78 (5.19); **^{1}H NMR** ([D_6]acetone, 25 °C, ppm): δ = 2.27 (s, 6H, CH_3), 7.17 (s, 4H, C-$H_{arom.}$); **^{13}C{^{1}H} NMR** ([D_6]acetone, 25 °C, ppm): δ = 20.0 (CH_3), 122.5 (C-$H_{arom.}$), 148.4 (C-OAc), 168.9 (C=O).

O,*O*'-(1,4-phenylene)dimethanesulfonate (**7**)

Dihydroquinone (25.0 g, 227.3 mmol) was dissolved in pyridine (250 ml). Afterwards the solution was cooled down to 0 °C and methanesulfonylchloride (43.9 ml, 43.9 mmol) was added dropwise under further cooling. After complete addition the solution was refluxed for 16 h. Then the mixture was cooled down to ambient temperature and poured onto crushed ice (1 kg). **7** precipitated as a colorless crystalline powder. ***O,O'*-(1,4-phenylene)dimethanesulfonate** ($C_8H_{10}S_2O_6$ 266.29 g mol^{-1}) (**7**): **EA** found (calc): C 36.37 (36.08), H 3.74 (3.79), S 23.88 (24.08).

3-Chloro-6-diazo-2,5-dinitrophenol (**8**)

4-Chloroaniline (3.0 g, 23.5 mmol) was dissolved in concentrated sulfuric acid (30 ml) at ambient temperature. After that nitric acid (3.5 ml, 99.5 %) was added slowly so that the temperature does not exceed 40 °C. The suspension formed was stirred for further 12-16 h at ambient temperature and then poured onto crushed ice (250 g). A brilliant yellow powder was obtained. The precipitate was filtrated and washed with small amounts of ice-cold water to get rid of acid. **3-Chloro-6-diazo-2,5-dinitrophenol** ($C_6HClN_4O_5$ 244.55 g mol^{-1}) (**8**): **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 165 °C; **EA** found (calc): C 29.51 (29.47), H 0.58 (0.41), N 22.76 (22.91); **^{1}H NMR** ([D_6]acetone, 25 °C, ppm): δ = 7.50 (s, 1H, C-$H_{arom.}$); **^{13}C{^{1}H} NMR** ([D_6]acetone, 25 °C, ppm): δ = 86.0 (C-N_2), 113.1 (C-$H_{arom.}$), 134.9 (C-Cl), 143.1 (C-NO_2), 148.0 (C-NO_2), 164.9 (C-O).

N,*N'*-(2,3,5-trinitro-1,4-phenylene)dimethanesulfonamide (**9**)

Nitric acid (200 ml, 65 %) was cooled to 0 °C. **2** (25 g, 94.6 mmol) was added portionwise so that the temperature does not exceed 5 °C. The solution was stirred at 0 °C for 6 h. After that the solution was further stirred at ambient temperature for about 12 h. The resulting yellow precipitate is a mixture of isomeric *N*,*N'*-(dinitro-1,4-phenylene)dimethanesulfonamide and **9**. The suspension was poured onto crushed ice (1 kg) and filtrated. After washing with much water the crude solid was dried in an 60 °C oven for about 12 h. Afterwards nitric acid (250 ml, 65 %) was heated up to 65-70 °C. The crude material isolated before was added slowly. One could observe huge amounts of nitrous fumes. The suspension was stirred until no such fumes occured anymore (typically 4-5 h). After that the suspension was poured onto

crushed ice (500 g). The bright yellow solid was filtered and washed with only small amounts of ice cold water to get rid of acid. **9** was dried in an 60 °C oven for 12 h. After that **9** was purified further. The yellow solid was refluxed in glacial acetic acid overnight. Subsequently the suspension was filtered directly after cooling down to ambient temperature and pure **9** was obtained after washing with ethanol (12 g, 32 %). ***N,N'*-(2,3,5-trinitro-1,4-phenylene)dimethanesulfonamide** ($C_8H_9N_5O_{10}S_2$ 399.31 g mol^{-1}) (**9**) **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 230 °C, **EA** found (calc): C 24.18 (24.06), H 2.35 (2.27), N 17.79 (17.54), S 16.30 (16.06); **^{1}H NMR** ([D$_6$]DMSO, 25 °C, ppm): δ = 3.05 (s, 3H, CH_3), 3.23 (s, 3H, CH_3), 8.37 (s, 1H, $CH_{arom.}$); Note: The N-H protons could not be observed; **^{13}C{^{1}H} NMR** ([D$_6$]DMSO, 25 °C, ppm): δ = 41.6 (CH_3), 42.5 (CH_3), 118.8 (C-$H_{arom.}$), 124.0 ($C_{arom.}$), 133.1 ($C_{arom.}$), 138.2 ($C_{arom.}$), 143.8 ($C_{arom.}$), 149.5 ($C_{arom.}$); **^{15}N NMR** ([D$_6$]DMSO, 75 °C, ppm): δ = –18.5 (d, $^3J_{N\text{-}H}$ = 2.8 Hz, 1N, NO_2), –23.7 (s, 1N, NO_2), –24.1 (d, $^4J_{N\text{-}H}$ = 2.8 Hz, 1N, NO_2), –262.3 (d, $^3J_{N\text{-}H}$ = 0.8 Hz, 1N, NH-SO_2Me), –281.6 (s, 1N, NH-SO_2Me).

N,N'-(2,3-Dinitro-1,4-phenylene)dimethanesulfonamide (**9a**)

Nitric acid (150 ml, 99.5 %) was cooled down to –40 °C. After that **2** (20.0 g, 75.7 mmol) was added slowly so that the temperature did not exceed –30 °C. After that the dark solution was stirred at –40 °C for 2 h. Then, the solution was warmed up to –10 °C and further stirred for 1 h. Afterwards, it was poured onto crushed ice (600 g) and **9a** precipitated as a brownish powder. **9a** was filtered and washed with ice cold water to get rid of nitric acid. (14.9 g, 56 %) ***N,N'*-(2,3,-dinitro-1,4-phenylene)dimethanesulfonamide** ($C_8H_{10}N_4O_8S_2$ 354.32 g mol^{-1}) (**9a**) **EA** found (calc): C 27.20 (27.12), H 2.55 (2.84), N 15.74 (15.81), S 18.22 (18.10); **^{1}H NMR** ([D$_6$]DMSO, 25 °C, ppm): δ = 3.17 (s, 3H, CH_3), 7.88 (s, 2H, C-$H_{arom.}$), 10.30 (s, br, 2H, N-H); **^{13}C{^{1}H} NMR** ([D$_6$]DMSO, 25 °C, ppm): δ = 41.3 (CH_3), 128.6 (C-$H_{arom.}$), 131.3 (C-$NH_{sulfonamide}$), 139.2 (C-NO_2).

1,4-Diamino-2,3-dinitrobenzene (**9b**)

9a (10.0 g, 28.2 mmol) was dissolved in concentrated sulfuric acid (150 ml) and water (5 ml) was added slowly. The dark solution was stirred at ambient temperature for at least three days. Afterwards the solution was poured onto crushed ice (1 kg). **9b** precipitated as a dark reddish powder (3.8 g, 68 %). 1,4-diamino-2,3-dinitrobenzene ($C_6H_6N_4O_4$ 198.14 g mol^{-1}) (**9b**): **^{1}H NMR** ([D$_6$]DMSO, 25 °C, ppm): δ = 7.13 (s, 2H, C-$H_{arom.}$), 7.19 (s, br, 2H, NH_2); **^{13}C{^{1}H} NMR** ([D$_6$]DMSO, 25 °C, ppm): δ = 123.1 (C-NH_2), 128.2 (C-$H_{arom.}$) 139.8 (C-NO_2).

N,N'-(2,3-dinitro-1,4-phenylene)diacetamide (**10**)

4 (2.67 g, 11.3 mmol) was slowly dissolved in nitric acid (24 ml, 82.5 %) at 0 °C. This is very exothermic and must be handled with care ! After that the solution was stirred 4 h at 0 °C and

further 12 h at ambient temperature. Afterwards the solution was poured onto crushed ice (200 g). The precipitate was filtrated and washed with small amounts of water to get rid of nitric acid. After drying in a oven at 60 °C for 12 h **10** was obtained as a white-yellow powder (1.42 g, 45 %). ***N,N'*-(2,3-dinitro-1,4-phenylene)diacetamide** ($C_{10}H_{10}N_4O_6$ 282.22 g mol^{-1}) (**10**): **EA** found (calc): C 42.58 (42.56), H 3.42 (3.57), N 19.74 (19.85); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 2.06 (s, 6H, CH_3), 7.78 (s, 2H, C-$H_{arom.}$), 10.38 (s, br, 2H, N-$H_{acetamide}$); **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C, ppm): δ = 23.4 (CH_3), 128.7 (C-$H_{arom.}$), 130.8 (C-N-$H_{acetamide}$), 138.3 (C-NO_2), 169.7 (C=O); **^{15}N NMR** ([D_6]DMSO, 25 °C, ppm): δ = –17.8 (t, N = I$^{4}J_{N,H}$ + $^{5}J_{N,H}$I = 0.6 Hz, 2N, NO_2), –257.1 (d, $^{1}J_{N-H}$ = 92.0 Hz, 2N, N-$H_{acetamide}$); **^{15}N{^{1}H} NMR** ([D_6]DMSO, 25 °C, ppm): δ = –17.8 (s, 2N, NO_2), –257.1 (s, 2N, N-$H_{acetamide}$).

Alternative high yield synthesis route for compound **10**:

In a two necked 250 ml flusk equipped with a thermometer nitric acid (10 ml, 99.5 %) was dropped to Ac_2O (100 ml, 1.06 mol) at 0 °C. The temperature should not rise above 10 °C. After that glacial acetic acid (10 ml, 175 mmol) was added. The solution was stirred at 0 °C for at least 1 h. In the next step **3** (8.0 g, 41.6 mmol) was added slowly so that the temperature does not exceed 10 °C. Then a solution is obtained after several minutes. After one hour the temperature was risen to ambient temperature using a water bath. The suspension formed was further stirred for 4 h at ambient temperature. Then the suspension was poured onto crushed ice (600 g). After stirring for 1 h the precipitate was filtered and washed with much cold water to get rid of acid. After drying in an oven at 60 °C for 12 h, **10** was obtained as a white-yellow powder (10.5 g, 89 %). For analytics, see above.

4-Acetoxy-2,6-dinitrophenol (**11**) and 1,4-diacetoxy-2,6-dinitrobenzol (**12**)

6 (5 g, 25.7 mmol) was dissolved slowly in HNO_3 (20 ml, 99.5 %) at –20 °C. The temperature may not exceed 0 °C during the addition. After adding **6**, the solution was stirred for 20 min at –20 °C and further 30 min at 0 °C. Then the red solution was poured onto of crushed ice (150 g). **11** was obtained as a pale yellow powder (3.9 g, 63 %). **4-Acetoxy-2,6-dinitrophenol** ($C_8H_6N_2O_7$ 242.14 g mol^{-1}) (**11**): **EA** found (calc): C 39.39 (39.68), H 2.70 (2.50), N 11.50 (11.57); **^{1}H NMR** ([D_6]acetone, 25 °C, ppm): δ = 2.34 (s, 3H, CH_3), 8.25 (s, 2H, C-$H_{arom.}$), 11.17 (s, br, 1H, OH); **^{13}C{^{1}H} NMR** ([D_6]acetone, 25 °C, ppm): δ = 19.8 (CH_3), 124.7 (C-$H_{arom.}$), 138.1 (C-NO_2), 141.2 (C-OAc), 146.0 (C-OH), 168.7 (C=O). Note: Reacetylation of **11**, yielding **12** can be easily performed by dissolving **11** in Ac_2O (50 ml) and refluxing for 6-12 h. **1**,**4-Diacetoxy-2,6-dinitrophenol** ($C_{10}H_8N_2O_8$ 284.18 g mol^{-1}) (**12**): **EA** found (calc): C 42.39 (42.26), H 2.74 (2.84), N 9.58 (9.86); **^{1}H NMR** ([D_6]acetone, 25 °C, ppm): δ = 2.38 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 8.37 (s, 2H, C-$H_{arom.}$); **^{13}C{^{1}H} NMR**

([D_6]acetone, 25 °C, ppm): δ = 19.5 (CH_3), 19.9 (CH_3), 124.3 (C-$H_{arom.}$), 135.4 (C-NO_2), 143.7 (C-OAc), 147.8 (C-OAc), 167.3 (C=O), 168.2 (C=O).

O,O'-(2-nitro-1,4-phenylene)dimethanesulfonate (**13**)

7 (10 g 37.6 mmol) was dissolved in nitric acid (25 ml, 99.5 %) at ambient temperature. The solution was stirred for 16 h. After that the solution was poured onto crushed ice (200 g). A white powder precipitated which was filtered and washed several time with water to obtain **13** (11.5 g, 98 %). **O,O'-(2-nitro-1,4-phenylene)-dimethanesulfonate** ($C_8H_9S_2NO_8$ 311.29 g mol^{-1}) (**13**): **EA** found (calc): C 30.69 (30.87), H 2.70 (2.91), S 20.48 (20.60).

1,4-Diamino-2,3,5-trinitrobenzene (**14**)

9 (10 g, 25 mmol) was suspended in concentrated sulfuric acid (250 ml) at 0 °C and water (10 ml) was added very slowly so that the temperature does not exceed 15 °C. The suspension was stirred until a dark red solution is obtained (typically 24-48 h !!). After that the solution was filtered using a very fine borosilica consisting suction strainer (pore size: at least 4) to get rid of traces of **9**. Then the solution was slowly poured onto large amounts of crushed ice (~1 kg) so that the temperature does not rise significantly. **14** was obtained as a dark purple powder (1.8 g, 30 %). **1,4-Diamino-2,3,5-trinitrobenzene** ($C_6H_5N_5O_6$ 243.13 g mol^{-1}) (14) **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 125 °C; **EA** found (calc): C 29.77 (29.64), H 2.07 (2.07), N 28.91 (28.80); **HRMS** (% (err-mmu)): 243.0231 (-0.9);MS (DEI+,(%)): 243.1 (100), 197.1 (M-HNO_2 (2)), 151.1 (197.1-NO_2(58)), 105.1 (151.1-NO_2(23); **IR** (ATR cm^{-1}) $\tilde{\nu}$ = 3474 (m), 3365 (s), 3090 (w), 1549 (s), 1528 (s), 1427 (m), 1390 (w), 1348 (m), 1253 (vs), 885 (s), 809 (s), 766 (m), 743 (m). Good NMR data could not be obtained so far.

When the mother liquor of **14** is stored in the fridge at 4 °C for at least 24 h compound **15** slowly started to precipitate. This also happens when the solution during the deprotection exceeds 30 °C.

3-Amino-6-diazo-2,4-dinitrophenol ($C_6H_3N_5O_5$ 225.13 g mol^{-1}) (**15**): **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 170 °C; **EA** found (calc): C 31.94 (32.01), H 1.40 (1.34), N 30.87 (31.11); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 8.69 (s, br, 2H, NH_2), 9.32 (s, 1H, CH_{arom}); **^{13}C{^{1}H} NMR** ([D_6]DMSO, 75 °C, ppm): δ = 87.3 (C-N_2), 123.7 ($C_{arom.}$), 125.1 ($C_{arom.}$), 137.2 ($C_{arom.}$), 147.0($C_{arom.}$), 163.9 (C-O); **^{15}N NMR** ([D_6]DMSO, 25 °C, ppm): δ = –15.0 (s, 1N, NO_2), –16.4 (d $^3J_{N\text{-}H}$ = 2.8 Hz, 1N, NO_2), –37.5 (s, 1N, N_2, N_β), –137.1 (d, $^3J_{N\text{-}H}$ = 3.2 Hz, 1N, N_2, N_α), –288.7 (s, 1N, NH_2); **IR** (ATR cm^{-1}) $\tilde{\nu}$ = 3390 (m), 3282 (m), 3076 (w), 2195 (s), 1593 (vs), 1557 (s), 1520 (m), 1477 (m), 1368 (m), 1311 (m), 1277 (s), 1242 (s), 1162 (m), 1128 (m), 1033 (m), 929 (m), 887 (m), 781 (m), 755 (m), 570 (s).

2,6-Dinitro-hydroquinone · 1.5 H_2O (**16a**)

11 (15 g, 61.9 mmol) was suspended in 6M HCl (150 ml). The suspension was refluxed until a solution was obtained (typically 2-3 h). After cooling in an ice-water bath **16a** started to crystallize slowly in long yellow-orange needles. The crystallization was extended for 16 h in a fridge at 4 °C. Afterwards **16a** was filtrated and washed with small amounts of ice-water. After drying at ambient temperature **16** was obtained as yellow needles (10 g, 71 %). **2,6-Dinitro-hydroquinone · 1.5 H_2O** ($C_6H_7N_2O_{7.5}$ 227.15 g mol^{-1}) (**16a**): **EA** found (calc): C 31.59 (31.73), H 2.95 (3.11), N 12.50 (12.33); **^{1}H NMR** ([D_6]acetone, 25 °C, ppm): δ = 4.00 (s, br, 1H, OH), 7.73 (s, 2H, C-$H_{arom.}$); Note: The phenolic proton between the nitro groups could not be observed. **^{13}C{^{1}H} NMR** ([D_6]acetone, 25 °C, ppm): δ = 117.4 (C-$H_{arom.}$), 138.3 (C-NO_2), 141.4 (C-OH), 148.9 (C-OH).

<u>*O*-(4-hydroxy-3,6-dinitrophenyl)methanesulfonate (**16b**)</u>

16a (5 g, 22.0 mmol) was dissolved in THF (100 ml) at 0 °C. Afterwards NEt_3 (6.9 ml, 50 mmol) was added slowly. A red precipitate was formed. Methanesulfonylchloride (1.93 ml, 25.0 mmol) was added. During the addition a solution is obtained. The reaction was allowed to stir for 16 h at ambient temperature. After the addition of water (20 ml) THF was evaporated *in vacuo*. The residue was acidified with 6M hydrochloric acid and boiled for 2 h at 80 °C. **16b** precipitated as a pale-yellow powder. *O*-(4-hydroxy-3,6-dinitrophenyl)methanesulfonate ($C_7H_6SN_2O_8$ 277.98 g mol^{-1}) (**16b**): **EA** found (calc): C 30.10 (30.22), H 2.35 (2.17), N 10.14 (10.07), S 11.70 (11.53); **^{1}H NMR** ([D_6]acetone, 25 °C, ppm): δ = 3.49 (s, 3H, CH_3), 8.43 (s, 2H, $CH_{arom.}$), 10.72 (s, br, 1O, OH); **^{13}C{^{1}H} NMR** ([D_6]acetone, 25 °C, ppm): δ = 37.0 (CH_3), 125.2 (C-$H_{arom.}$), 138.4 ($C_{arom.}$), 139.4 ($C_{arom.}$), 147.1 ($C_{arom.}$).

<u>Potassium salt of *O*-(4-hydroxy-3,5-dinitrophenyl)benzenesulfonate (**16c**)</u>

16a (5 g, 22.0 mmol) was dissolved in THF (100 ml) at 0 °C. Afterwards NEt_3 (13.8 ml, 100 mmol) was added slowly. A red precipitate was formed. Benzenesulfonylchloride (3.20 ml, 25.0 mmol) was added. During the addition a solution is obtained. The reaction was allowed to stir for 16 h at ambient temperature. After the addition of water (20 ml) THF was evaporated *in vacuo*. The residue was acidified with 6M hydrochloric acid and boiled for 2 h at 80 °C. A pale-yellow precipitate was formed and filtered off. The crude material was re-dissolved in ethanol (30 ml, 80 %) and 0.5 M KOH solution in 80 % ethanol (75 ml) was added. A red precipitate was formed, filtered off and washed several times with cold ethanol. Potassium-*O*-(4-hydroxy-3,6-dinitrophenyl)benzenesulfonate ($KC_{12}H_7SN_2O_8$ 277.98 g mol^{-1}) (**16c**): **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 7.43 (s, 2H, C-Harom.), 7.70 (m, $CH_{arom.}$), 7.84 (m, $CH_{arom.}$), 7.89 (m, $CH_{arom.}$); **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C, ppm): δ = 125.2 ($C_{arom.}$), 126.7 ($C_{arom.}$), 128.9 ($C_{arom.}$), 130.3 ($C_{arom.}$), 134.4 ($C_{arom.}$), 135.6 ($C_{arom.}$), 142.1 ($C_{arom.}$), 158.7 ($C_{arom.}$).

3,5-Dinitroaniline (**17**)

3,5-dinitrobenzoic acid (10.0 g, 47.1 mmol) was dissolved in a mixture of oleum (22 ml, 65 % SO_3 by weight) and concentrated sulfuric acid (13 ml) at ambient temperature. After that $CHCl_3$ (40 ml) was added to the solution. Afterwards the mixture was heated to 30-35 °C and sodium azide (5.7 g, 87.7 mmol) was added slowly. The solution was refluxed for 12 h. Subsequently the mixture was cooled and poured onto crushed ice (200 g). The precipitate was filtered and washed acid free with much ice cold water. **17** was obtained as a yellow-brown solid (6.5 g, 75 %). **3,5-Dinitroaniline** ($C_6H_5N_3O_4$ 183.12 g mol^{-1}) (**17**): **EA** found (calc): C 39.58 (39.35), H 2.50 (2.75), N 22.74 (22.95); **^{1}H NMR** ([D$_6$]acetone, 25 °C, ppm): δ = 8.04 (t, $^4J_{H\text{-}H}$ = 1.98 Hz, 1H, C-H$_{arom.}$), 7.83 (d, $^4J_{H\text{-}H}$ = 1.98 Hz, 2H, C-H$_{arom.}$), 4.08 (s, br, 2H, NH_2); **^{13}C{^{1}H} NMR** ([D$_6$]acetone, 25 °C, ppm): δ = 151.0 (C-NO_2), 149.4 (C-NH_2), 112.7 (C-H$_{arom.}$), 104.7 (C-H$_{arom.}$);

N-(3,5-dinitrophenyl)methanesulfonamide (**18**)

17 (4 g, 21.8 mmol) was dissolved in pyridine (25 ml) and cooled to 0 °C. Afterwards methanesulfonylchloride (1.93 ml, 25 mmol) was slowly added. The mixture was stirred for 1 h and then boiled for 5 h at 70 °C. Afterwards the solution was poured onto crushed ice (150 g). After filtration the solid was washed with much ice-cold water and 2M HCl. **18** was obtained as a almost colorless powder (5.0 g, 88 %). ***N*-(3,5-dinitrophenyl)methanesulfonamide** ($C_7H_7SN_3O_6$ 261.21 g mol^{-1}) (**18**): **EA** found (calc): C 32.48 (32.19), H 2.89 (2.70), N 15.78 (16.09); **^{1}H NMR** ([D$_6$]acetone, 25 °C, ppm): δ = 9.71 (s, br 1H, NH), 8.64 (t, 1H, C-H$_{arom.}$, $^4J_{H\text{-}H}$ = 1.93 Hz), 8.58 (d, 2H, C-H$_{arom.}$, $^4J_{H\text{-}H}$ = 1.93 Hz), 3.25 (s, 3H, CH_3); **^{13}C NMR** ([D$_6$]acetone, 25 °C, ppm): δ = 39.7 (CH_3), 112.9 (C-H$_{arom.}$), 118.7 (C$_{arom.}$), 141.4 (C$_{arom.}$), 149.3 (C$_{arom.}$).

N'-(2,3,5-trinitrophenyl)methanesulfonamide (**19a**) and *N*-(3,5-dinitrophenyl)-*N*-nitromethanesulfonamide (**19b**)

18 (1.00 g, 3.83 mmol) was dissolved in nitric acid (15 ml, 99.5 %) at 0 °C. After 1 h the solution was allowed to warm up to ambient temperature. After 30 minutes the solution was poured onto crushed ice (75 g). The white precipitate was filtered and washed with ice-cold water (3 x 50 ml). (0.75 g, 2.45 mmol) was obtained. Impurities, for example starting material, were still in the mixture, therefore no yield is mentioned. ***N*-(2,3,5-trinitrophenyl)methanesulfonamide** ($C_7H_6SN_4O_8$ 261.21 g mol^{-1}) (**19a**): **^{1}H NMR** ([D$_6$]acetone, 25 °C, ppm): δ = 3.35 (s, 3H, CH_3), 8.85 (d, $^4J_{H\text{-}H}$ = 2.4 Hz, 1H, C-H$_{arom.}$), 9.00 (d, $^4J_{H\text{-}H}$ = 2.4 Hz, 1H, C-H$_{arom.}$), 10.18 (s, br, 1H, N-H$_{sulfonamide}$). ***N*-(3,5-dinitrophenyl)-*N*-nitromethanesulfonamide** ($C_7H_6SN_4O_8$ 261.21 g mol^{-1}) (**19b**): **^{1}H NMR** ([D$_6$]acetone, 25 °C,

ppm): δ = 4.00 (s, 3H, CH_3), 9.04 (d, $^4J_{H\text{-}H}$ = 2.0 Hz, 2H, C-$H_{arom.}$), 9.19 (t, $^4J_{H\text{-}H}$ = 2.0 Hz, 1H, C-$H_{arom.}$).

6-Diazo-2,4-dinitrophenol · *N*,2,3,5-tetranitroaniline adduct (**20**)

17 (1.00 g, 5.46 mmol) was dissolved in nitric acid (12 ml, 100 %) at 0 °C. The solution was stirred for 2 hours. Afterwards it was poured onto crushed ice. A pale yellow precipitate was formed which was filtered and washed one time with ice-cold water (10 ml). Some single crystals of **20** were obtained out of the mother liquor. In organic solvents only the typical NMR shifts for DDNP were detected. **6-Diazo-2,4-dinitrophenol** ($C_6H_2N_4O_5$ 210.00 g mol^{-1}): **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 8.87 (d, $^4J_{H\text{-}H}$ = 3.2 Hz, 1H, C-$H_{arom.}$), 9.34 (d, $^4J_{H\text{-}H}$ = 3.2 Hz, 1H, C-$H_{arom.}$); **^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ = 99.5 (C-N_2), 129.2 (C-$H_{arom.}$), 130.6 (C-$H_{arom.}$), 134.7 (C-NO_2), 140.7 (C-NO_2), 164.4 (C-O).

2,3,4,5,6-Pentanitroaniline · benzene adduct (**21**)

17 (3.5 g, 19.1 mmol) was dissolved in concentrated sulfuric acid (60 ml). Afterwards oleum (25 % SO_3 by weight) (35 ml) was added. The solution was cooled to 0-5 °C. Afterwards HNO_3 (6.5 ml, 99.5 %) was added slowly so that the temperature does not exceed 5 °C. After that the mixture was stirred at 72-75 °C for 90 min. During this time a yellow precipitate was slowly formed. The mixture was cooled to 0 °C again for 1 h. After filtration the yellow residue was re-dissolved in 1,2-dichloroethane (120 ml). This solution was decanted, separating the solution of sulfuric acid. In the next step, the solvent was evaporated at 30 °C until 30 ml remained. Afterwards it was put into a –20 °C freezer for overnight. A bright-yellow crystalline product was obtained, filtered and recrystallized out of benzene. Huge blocks of **21** were obtained (2.3 g, 31 %). ($C_6H_2N_6O_{10} \cdot C_6H_6$ · 396.23 g mol^{-1}) (**21**): **EA** found (calc): C 36.49 (36.38), H 2.29 (2.01), N 21.06 (21.21).

2,3,4,6-Tetranitroaniline (**22a**)

3-nitroaniline (4 g, 29.0 mmol) was dissolved in concentrated sulfuric acid (40 ml). Afterwards the solution was heated to up 60-65 °C. Then a mixture of nitric acid (4.5 ml, 99.5 %) in oleum (25 % SO_3 by weight) (13 ml) was added slowly so that the temperature does not exceed 75 °C ! While adding this mixture, **22a** slowly started to precipitate. The suspension is stirred for 36-48 h at ambient temperature to complete the N-nitro-C-nitro rearrangement. After that the suspension was poured onto crushed ice (200 g). After filtration and washing with ice-cold water **22a** (4.90 g, 62 %) was obtained as a yellow powder. **2,3,4,6-Tetranitroaniline** ($C_6H_3N_5O_8$ 273.12 g mol^{-1}) (17): **DSC** (5° C min^{-1}): $T_{Dec.}$ = T_m = 228 °C; **EA** found (calc): C 26.29 (26.39), H 0.97 (1.11), N 25.50 (25.64); **^{1}H NMR** ([D_6]acetone, 25 °C, ppm): δ = 9.27 (s, 1H, CH), 8.83 (s, br, 2H, NH_2); Note: **22b** was easily synthesized by

hydrolysis of **22a** in acetone/water while refluxing for 6 h. Identification was only confirmed by low-temperature X-ray diffraction of single crystals.

3-Azido-2,4,6-trinitroaniline (**23**)

22a (2.5 g, 9.15 mmol) was added to a stirring solution of sodium azide (1 g, 15.4 mmol) in acetic acid (15 ml, 75 %) at 0 °C. The suspension was stirred 2 h and further 3 h at ambient temperature. Afterwards the suspension was poured onto crushed ice (100 g). After melting the orange solid was filtered and washed with much ice-cold water. After drying at ambient temperature (1.8 g, 73 %) of **23** was obtained. **3-Azido-2,4,6-trinitroaniline** ($C_6H_3N_7O_6$ 269.13 g mol^{-1}) (**23**): **EA** found (calc.): C 26.96 (26.78), H 1.15 (1.12), N 36.40 (36.43); **^{1}H NMR** ([D$_6$]DMSO, 25 °C, ppm): δ = 8.44 (br, s, 2H, NH_2), 8.93 (s, 1H, C-$H_{arom.}$); **^{13}C NMR {^{1}H}** ([D$_6$]DMSO, 25 °C, ppm): δ = 127.3($C_{arom.}$), 128.3 ($C_{arom.}$), 129.8 ($C_{arom.}$), 133.3 ($C_{arom.}$), 134.9 ($C_{arom.}$), 141.3 ($C_{arom.}$).

7-Amino-4,6-dinitrobenzofuroxane (**24**)

23 (1.25 g, 4.65 mmol) was dissolved in ethylacetate (20 ml) and was refluxed for 6 h. During this time **24** slowly started to precipitate and nitrogen gas was released. After cooling down the suspension to ambient temperature the dark orange solid was filtered and washed three times with ethylacetate (20 ml). 1.05 g of **24** was obtained (94 %). **7-Amino-4,6-dinitrobenzofuroxane** ($C_6H_3N_5O_6$ 241.12 g mol^{-1}) (**24**): **EA** found (calc.): C 29.91 (29.89), H 1.19 (1.25), N 29.30 (29.05); **^{1}H NMR** ([D$_6$]acetone: [D$_6$]DMSO = 2.5:1, 25 °C, ppm): δ = 9.13 (s, 1H, C-$H_{arom.}$) 9.33 (br, s, 1H, NH_2), 10.03 (s, 1H, NH_2); **^{13}C{^{1}H} NMR** ([D$_6$]acetone : [D$_6$]DMSO = 2.5 : 1, 25 °C, ppm): δ = 111.1 ($C_{arom.}$), 120.9 ($C_{arom.}$), 122.7 ($C_{arom.}$), 132.4 ($C_{arom.}$), 143.1 ($C_{arom.}$), 146.6 ($C_{arom.}$).

3,5-Diazido-2,4,6-trinitroaniline (**25**)

21 · benzene adduct (2.5 g, 6.31 mmol) was added slowly to a stirring solution of sodium azide (1.5 g, 23.1 mmol) in acetic acid (30 ml, 80 %) at 5-10 °C. The suspension was stirred at this temperature for further 2 h and 3 h at ambient temperature. Afterwards the suspension was filtered and washed with much ice-cold water to get rid of acid. **25** is obtained as a bright yellow powder (1.65 g, 84 %). **3,5-Diazido-2,4,6-trinitroaniline** ($C_6H_2N_{10}O_6$ 310.14 g mol^{-1}) (**25**): **EA** found (calc.): C 22.99 (23.24), H 1.00 (0.65), N 44.90 (45.16); **^{1}H NMR** ([D$_6$]DMSO, 25 °C, ppm): δ = 7.77 (br, s, 2H, NH_2); **^{13}C{^{1}H} NMR** ([D$_6$]DMSO, 25 °C, ppm): δ = 127.5 ($C_{arom.}$), 128.4 ($C_{arom.}$), 132.5 ($C_{arom.}$), 139.0 ($C_{arom.}$).

7-Amino-8-nitro-benzodifuroxane (**26**)

25 (2 g, 6.45 mmol) was dissolved in ethylacetate (30 ml) at ambient temperature. Afterwards the suspension was refluxed for 5-6 h. In the meantime a yellow precipitate is formed. After cooling the suspension was stored at –20 °C in a freezer for 12 h. Then the suspension was filtered and washed with Et_2O (50 ml). **26** was obtained as a yellow powder (1.4 g, 85 %). **7-Amino-8-nitro-benzodifuroxane** ($C_6H_2N_6O_6$ 254.12 g mol^{-1}) (**26**): **EA** found (calc.): C 28.29 (28.36), H 1.03 (0.79), N 33.20 (33.07); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 9.22 (br, s, 1H, NH_2), 10.23 (br, s, 1H, NH_2); **^{13}C{^{1}H} NMR** ([D_6]DMSO, 25 °C, ppm): δ = 102.2 ($C_{arom.}$), 108.2 ($C_{arom.}$), 111.3 ($C_{arom.}$), 141.2 ($C_{arom.}$), 143.1 ($C_{arom.}$), 148.7 ($C_{arom.}$).

3-Aminotriazolyl-2,4,6-trinitroaniline (**27**)

3-amino-1,2,4-triazole (1.34 g, 16 mmol) was suspended in acetone (20 ml). The suspension was cooled down to 0 °C. Then glacial acetic acid (typically 3-4 ml) was added, so that a solution is obtained. After that **22a** (1 g, 3.66 mmol) was added slowly so that the temperature did not exceed at 0 °C. The suspension was stirred for 6 h at 0 °C and furthermore at ambient temperature for 12 h. After that the suspension was filtered and washed with acetone (5 x 100 ml). **27** is obtained as a yellow-beige powder (888 mg, 78 %). **3-Aminotriazolyl-2,4,6-trinitroaniline** ($C_8H_6N_8O_6$ 310.10 g mol^{-1}) (**27**): **DSC** (5 °C min^{-1}: $T_{Dec.}$ = 287 °C); **EA** found (calc): C 31.22 (30.98), H 2.15 (1.95), N 36.24 (36.12); **^{1}H NMR** ([D_6]DMSO, 75 °C, ppm): δ = 8.21 (s, 2H, C-H), 8.92 (br, s, NH_2), 10.40 (br, s, N-H), 13.62 (br, s N-H).

3-Aminotriazolyl-5-amino-2,4,6-trinitroaniline (**28**)

27 (2.0 g, 6.4 mmol) was dissolved in of DMSO (20 ml) at ambient temperature. After that *N*,*N*,*N*-trimethylhydrazinium iodide (2.0 g, 9.9 mmol) was added. After a solution was obtained the mixture was heated up to 60-65 °C and sodium *tert*-butoxide (2.9 g, 30 mmol) was added at once. The suspension was stirred further for 12-16 h. Then the suspension was cooled down to ambient temperature and poured onto crushed ice (150 g). Adding 2M hydrochloric acid (50 ml) resulted in the formation of a brownish precipitate. The crude material of **28** was filtered and washed with large amounts of water. After drying in an oven (60 °C) for 12 h **28** was boiled in DMF (100 ml) for 1 h and filtrated hot. To get rid of the DMF the solid was further washed with large amounts of water and then ethanol. Pure **28** is obtained as a yellow powder (1.6 g, 77 %). **3-Aminotriazolyl-5-amino-2,4,6-trinitroaniline** ($C_8H_7N_9O_6$ 325.20 g mol^{-1}) (7): **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 300 °C; **EA** found (calc): C 29.29 (29.55), H 2.25 (2.17), N 38.64 (38.76); **^{1}H NMR** ([D_6]DMSO, 80 °C, ppm): δ = 8.19 (s, 1H, C-H (triazole)), 9.00 (s, br, 4H, NH_2), 10.90 (1H,NH). Note: The ring proton of the triazole was not detected.

Isomeric 1,4-dimethoxy-dinitro-benzene (**29**)

A solution of $NO_{2(l)}$ (25 ml) in dichloromethane (40 ml) was cooled to –40 °C. 1,4-dimethoxybenzene (5.00 g, 36.21 mmol) was added and stirred for 12 h at ambient temperature. Afterwards all solvents were evaporated under reduced pressure, yielding the isomeric mixture of 1,4-dimethoxy-dinitrobenzene as a bright yellow solid (88.25 g, 99%). **Isomeric mixture of 1,4-dimethoxy-dinitrobenzene** ($C_8H_8N_2O_6$ 228.04 g mol^{-1}) (29): **EA** found (calc): C 42.11 (42.20), H 3.59 (3.53), N 12.17 (12.28); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm) **1,4-Dimethoxy-2,5-dinitrobenzene** (**29a**): δ = 7.69 (s, 2H, CH), 3.93 (s, 6H, OMe); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm) **1,4-Dimethoxy-2,3-dinitrobenzene** (**29b**): δ = 7.93 (s, 2H, C-$H_{arom.}$), 3.95 (s, 6H, OMe), **^{13}C{^{1}H} NMR** (**29a** and **29b**) ([D_6]DMSO, 25 °C, ppm): δ = 145.4 ($C_{arom.}$), 142.0 ($C_{arom.}$), 133.3 ($C_{arom.}$), 119.5 ($C_{arom.}$), 115.2 ($C_{arom.}$), 111.5 ($C_{arom.}$), 58.3 (2C, OMe), 58.1 (2C, OMe); **^{14}N NMR** ([D_6]DMSO, 25 °C, ppm): δ = –14 (s, br, 2N, C-NO_2); **Raman** [cm^{-1}]: $\tilde{\nu}$ = 3102 (13), 3036 (32), 2984 (6), 2948 (23), 2850 (21), 1643 (6), 1575 (24), 1551 (17), 1532 (14), 1495 (3), 1449 (17), 1432 (5), 1369 (25), 1353 (82), 1306 (100), 1287 (11); 1274 (6), 1195 (45), 1059 (4), 936 (21), 820 (4), 812 (78), 793 (6), 771 (6), 658 (3); **IR** (ATR) [cm^{-1}]: $\tilde{\nu}$ = 3099 (vw), 2848 (vw), 1537 (vs), 1492 (s), 1456 (w), 1438 (m), 1399 (vw), 1353 (m), 1276 (vs), 1232 (m), 1188 (m), 1156 (w), 1108 (vw), 1055 (m), 1018 (m), 934 (w); 884 (w), 870 (w), 810 (m), 793 (w), 778 (w), 763 (w), 750 (w), 726 (w); **Mass spec**.: 228.0 (100) [M^+].

1,4-Dimethoxy-2,3,5-trinitro-benzene (**30**)

Nitric acid (10.0 ml, 99.5 %) was cooled down to –25 °C. Afterwards **29** (1.00 g, 4.38 mmol) was added in small portions. The red-brown solution was stirred for 2 h at –20 °C and 1 h at 0 °C. The mixture was poured onto crushed ice (100 g) and a solid precipitated. It was filtered off and subsequently washed with ice-cold water and dried at 60 °C. A pale-yellow powder of 1,4-dimethoxy-2,3,5-trinitro-benzene (650 mg, 56 %) was obtained. **1,4-Dimethoxy-2,3,5-trinitro-benzene** ($C_8H_7N_3O_8$ 273.16 g mol^{-1}) (**30**) **EA** found (calc): C 35.38 (35.18), H 2.60 (2.58), N 15.08 (15.38); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 4.04 (s, 3H, C-OMe), 4.18 (s, 3H, C-OMe), 8.26 (s, 1H, C-$H_{arom.}$); **^{13}C NMR {^{1}H}** ([D_6]DMSO, 25 °C, ppm): δ = 58.3(1C, OMe), 65.3(1C, OMe), 114.2 (C-$H_{arom.}$), 135.4 ($C_{arom.}$), 139.4 ($C_{arom.}$), 140.0 ($C_{arom.}$), 146.4 ($C_{arom.}$), 148.1 ($C_{arom.}$); **^{14}N NMR** ([D_6]DMSO, 25 °C, ppm): δ = –19 (2N, NO_2), –13 (1N, NO_2);

3,6-Dimethoxy-2,4-dinitroaniline (**31a**)

Ammonia was bubbled through ethanol (100 ml) for 20 minutes at 0 °C. Afterwards **30** (2 g, 7.32 mmol) was added at once. The solution was stirred for 4 h at 0 °C. A orange precipitate was formed. After filtration, **31** was washed with small amounts of ice-cold water and

subsequently with cold ethanol. **31** was obtained as a yellow-orange powder (1.7 g, 96 %). **3,6-Dimethoxy-2,4-dinitroaniline** ($C_8H_9N_3O_6$ 243.17 g mol^{-1}) (**31**): **EA** found (calc.): C 39.48 (39.51), H 3.60 (3.73), N 17.04 (17.28); **^{1}H NMR** ([D_6]acetone, 25 °C, ppm): δ = 3.92 (s, 3H, OMe), 4.00 (s, 3H, OMe), 6.49 (s, br, 2H, NH_2), 7.57 (s, 1H, C-$H_{arom.}$).

(3,6-Dimethoxy-2,4-dinitrophenyl)azid (**31b**)

Sodium azide (1.0 g, 15.4 mmol) was dissolved in glacial acetic acid (10 ml) and ethanol (10 ml) at ambient temperature. Afterwards, 30 (1.5 g 5.5 mmol) was added at once. The suspension was stirred at ambient temperature for 3 h and then heated to reflux for 16 h. The resulting solution was poured on crushed ice (100 g). The yellow precipitate was filtered and washed with ice-cold water to get **31b** (680 mg, 46 %). **(3,6-Dimethoxy-2,4-dinitrophenyl)azid** ($C_8H_7N_5O_6$ 269.17 g mol^{-1}) (**31b**): **^{1}H NMR** ([D_6]acetone, 25 °C, ppm): δ = 3.79 (s, 3H, OMe), 4.02 (s, 3H, OMe), 7.73 (s, 1H, C-$H_{arom.}$); **^{13}C{^{1}H} NMR** ([D_6]acetone, 25 °C, ppm): δ = 57.5 (OMe), 64.3 (OMe), 109.7 (C-$H_{arom.}$), 110.0 ($C_{arom.}$), 127.3 ($C_{arom.}$), 138.6 ($C_{arom.}$), 138.7 ($C_{arom.}$), 149.7 ($C_{arom.}$); **^{14}N NMR** ([D_6]acetone, 25 °C, ppm): δ = –18 (NO_2), –19 (NO_2), –147 (N_3, N_β), –175 (N_3, N_γ), –314 (N_3, N_α).

4-Methoxy-2,6-dinitroaniline (**32**)

4-Methoxy-2-nitroaniline (15.00 g, 89.26 mmol) was added to an ice cooled (0 °C) solution of concentrated nitric acid (65 ml, 65 %) and stirred for 16 h at 25 °C. The dark red solution was filtered and first washed with half-concentrated nitric acid (30 %) and second with cold water. After drying at ambient temperature a red powder was obtained (9.8 g, 52 %). If necessary the product can be recrystallized out of ethanol. **4-Methoxy-2,6-dinitroaniline** ($C_7H_7N_3O_5$ 213.04 g mol^{-1}) (32): **EA** found (calc): C 39.24 (39.44), H 3.38 (3.31), N 19.44 (19.71); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 3.78 (3H, OMe), 8.01 (s, br, 4H, CH+NH_2); **^{13}C NMR{^{1}H}** ([D_6]DMSO, 25 °C, ppm): δ = 56.9 (1C, OMe), 120.3 (2C, C-H), 135.3 ($C_{arom.}$), 136.7 ($C_{arom.}$), 146.9 ($C_{arom.}$); **^{14}N NMR** ([D_6]DMSO, 25 °C, ppm): δ = –8 (2N, C-NO_2); **IR** (ATR) [cm^{-1}]: $\tilde{\nu}$ = 3472 (w), 3354 (m), 3082 (vw), 2977 (vw), 2938 (vw), 1650 (w), 1526 (vs), 1462 (w), 1438 (m), 1408 (s), 1367 (w), 1342 (w), 1258 (s), 1215 (vs), 1188 (vs), 1089 (w), 1047 (vs), 944 (w), 926 (vw), 900 (m), 886 (vs), 819 (vw), 788 (m), 769 (m), 736 (w), 682 (vw); **Mass spec**.: (DEI (+) m/z): 122.2 (47), 168.2 (100), 213.2 (96) [M^+].

4-Chloro-2,6-dinitroaniline (**33**)

Nitric acid (70 ml, 65 %) was cooled in an ice bath (0 °C) before adding 4-chloro-2-nitroaniline (10.0 g, 58.0 mmol). The solution was stirred for 16 h at 25 °C and directly filtered off. The yellow-orange precipitate was filtered and washed with water. The solid was dried at

60 °C (6.55 g, 52 %). **4-Chloro-2,6-dinitroaniline** ($C_6H_4ClN_3O_4$ 216.99 g mol^{-1}): **EA** found (calc): C 33.13 (33.12), H 1.85 (1.85), N 19.28 (19.31); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 8.31 (2H, C-NH_2), 8.38 (2H, CH); **^{13}C NMR {^{1}H}** ([D_6]DMSO, 25 °C, ppm): δ = 117.3 ($C_{arom.}$), 133.6 ($C_{arom.}$), 135.9 ($C_{arom.}$), 140.1 ($C_{arom.}$); **^{14}N NMR** ([D_6]DMSO, 25 °C, ppm): δ = –8 (2N, C-NO_2); **Raman** [cm^{-1}]: $\tilde{\nu}$ = 3351 (10), 3092 (8), 1640 (8), 1586 (9), 1529 (24), 1517 (8), 1342 (100), 1298 (64), 1169 (18), 1155 (66), 1111 (7), 900 (12), 821 (94), 742 (28); **IR** (ATR) [cm^{-1}]: $\tilde{\nu}$ = 3460 (w), 3348 (m), 3083 (w), 1637 (m), 1584 (w), 1512 (vs), 1437 (w), 1396 (m), 1355 (m), 1230 (vs), 1037 (w), 942 (vw), 908 (w), 893 (vs), 820 (vw), 769 (w), 728 (m); **Mass spec**. (DEI (+) m/z): 90.1 (17), 125.1 (21), 217.1 (100) [M^+].

1,1'-Diamino-4,4',5,5'-tetranitro-2,2'-bisimidazole (**34**)

To a stirring solution of TNBI · 2 H_2O (1.00 g, 2.86 mmol) in tetrahydrofuran (30 ml) triethylamine (1.00 ml, 7.21 mmol) was added. The suspension was stirred for 1 h. Then the solvents were evaporated at 60 °C. The bis-triethylammonium salt can be isolated as a yellow/orange powder (1.40 g, 2.71 mmol).

Afterwards the amination reagent was synthesized. An ice-cold solution of ethyl acetohydroximate (4.50 g, 43.6 mmol) and triethylamine (6.18 ml, 44.5 mmol) in dimethylformamide (30.0 ml) was treated over 10 minutes with toluene-*p*-sulphonyl chloride (8.30 g, 43.5 mmol). The solution was stirred for 2 h at ambient temperature. Then the triethylamine hydrochloride was filtered off and washed with ether. After evaporation the residual solution was added to ice-cold water (300 ml) which gave the ethyl-*O*-*p*-toluenyl-sulphonyl-acetohydroximate.

Ethyl-*O*-*p*-toluenyl-sulphonyl-acetohydroximate (3.50 g, 13.6 mmol) was dissolved in perchloric acid (30 ml, 60 %). The mixture was stirred for 2 h at ambient temperature. Then the suspension was poured onto crushed ice. After extraction with dichloromethane (5 x 30 ml) the organic layer was added to the prepared bis-triethylammonium TNBI and stirred at ambient temperature for 48 h. The solution was filtered and water (50 ml) was added. Afterwards dichloromethane was evaporated and 1,1'-diamino-4,4',5,5'-tetranitro-2,2'-bisimidazole precipitated, which was filtered. The product was washed with water (5 x 50.0 ml) and solution of water and ethanol (5 x 50.0 ml, in a ratio of 1 : 1). After recrystallization out of chloroform / acetonitrile (0.64 g, 65 %) yellow-orange needles of **34** were obtained. **1,1'-diamino-4,4',5,5'-tetranitro-2,2'-bisimidazole** ($C_6H_4N_{10}O_8$ 344.16 g mol^{-1}) (**34**): **DSC** (5 °C min^{-1}): $T_{Melt.}$ = $T_{Dec.}$ = 190 °C; **EA** found (calc): C 21.28 (20.28), H 1.27 (1.17), N 40.21 (40.70); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 6.92 (s, br, 4H, N-NH_2); **^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ =131.8 ($C_{arom.}$), 134.4 (C-NO_2), 135.8 (C-NO_2); **Raman** [cm^{-1}]: $\tilde{\nu}$ = 3260 (4), 1594 (100), 1560 (46), 1537 (19), 1499 (16), 1469 (2), 1389 (22), 1362 (21), 1348 (3), 1331 (71), 1255 (12), 1210 (31), 1068 (10), 861 (11), 786 (2), 723 (2), 463 (3), 375

(4), 318 (2), 280 (2); **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 3359 (s), 3259 (s), 1595 (m), 1557 (m), 1530 (vs), 1499 (br, vs), 1388 (s), 1362 (s), 1305 (br, vs), 1260 vs), 1218 (s), 1144 (s), 1093 (br, s), 1044 (br, s), 1019 (br, s), 849 (vs), 811 (vs), 758 (vs), 746 (vs), 706 (vs), 607 (vs); **Mass spec**. (DEI (+) m/z): 185.0 (3), 200.1 (100), 329.0 (3), 344.0 (44) [M^+].

Bisguanidinium-2-carboxyl-4,5-dinitroimidazolate (**36**)

During the synthesis of TNBI (according publication A) sometimes a solution instead of a suspension is obtained. After cooling to 0 °C the solution was neutralized with guandinium carbonate until a pH = 10 is reached. **36** started to crystallize after a few minutes. **Bisguanidinium-2-carboxyl-4,5-dinitroimidazolate** ($C_6H_{14}N_{10}O_7$ 338.24 g mol^{-1}) (**36**): **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 268 °C; **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 7.53 (s, br, 6H, NH_2); **^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ = 139.9 (C-NO_2), 146.3 (C-COO^-), 159.0 ($C_{guanidine}$), 166.4 (COO^-).

Bis-1,5-diaminotetrazolium 4,4',5,5'-tetranitro-2,2'-bisimidazolate (**37**):

To a stirring solution of TNBI · 2 H_2O (0.25 g, 0.71 mmol) was added 1,5-diaminotetrazole (0.152 g, 1.5 mmol). The solution was stirred for 2 h at ambient temperature. Long needles started to crystallize. Afterwards the needles were filtered off and dried at ambient temperature . Bis-1,5-diaminotetrazolium 4,4',5,5'-tetranitro-2,2'-bisimidazolate ($C_8H_{10}N_{20}O_8$ 514.29 g mol^{-1}) (**37**): **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 165 °C; **EA** found (calc): C 18.79 (18.68), H 2.04 (1.96), N 54.00 (54.47).

Bissodium-3,6-bis(nitroguanidyl)-1,2,4,5-tetrazinate (**38**)

Sodium methoxide (2.1 g, 30 mmol) was dissolved in MeOH (50 ml). Afterwards dry nitroguandine (1.44 g, 13.8 mmol) was added. The suspension was heated up to 55 °C until a solution was obtained. Then 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (1.8 g, 6.7 mmol) was added portion-wise. After 10-15 minutes a dark-red precipitate was formed. The suspension was further stirred at 55 °C for 3 h. After cooling to ambient temperature the suspension was filtered off and washed with cold MeOH (3 x 30 ml). **38** was obtained as a red-metallic powder. **Bissodium-3,6-bis(nitroguanidyl)-1,2,4,5-tetrazinate** ($Na_2C_4H_4N_{12}O_4$ 330.15 g mol^{-1})(**38**): **EA** found (calc): C 14.76 (14.55), H 1.39 (1.22), N 50.57 (50.91); **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 9.20 (s, br, 4H, NH_2); **^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ = 157.8, 165.3.

Bisguanidinium-3,6-bis(nitroguanidyl)-1,2,4,5-tetrazinate (**39**)

38 (1 g, 3.03 mmol) was suspended in water (20 ml). Guanidinium carbonate (0.72 g, 4.0 mmol) was added. The solution was stirred until a precipitae was formed. It was filtered

off and washed with ice-cold water (3 x 20 ml). **39** was obtained as a orange-reddish powder (0.9 g, 74 %). **Bisguanidinium-3,6-bis(nitroguanidyl)-1,2,4,5-tetrazinate** ($C_6H_{16}N_{18}O_4$ 404.31 g mol^{-1}) (**39**): **DSC** (5 °C · min^{-1}): $T_{Dec.}$ = 235 °C; **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 7.53 (s, br, 6H, NH_2), 9.20 (s, br, 4H, NH_2); **^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ = 157.8, 159.0 ($C_{guanidine}$), 165.3.

Bisguanidinium-(3-hydroxy-6-nitroguanidyl-1,2,4,5-tetrazinate) · H_2O (**40**)

39 (1.0 g, 2.5 mmol) was suspended in water (25 ml) and refluxed for 3 h. After cooling to 0 °C, **40** started to crystallize in long red needles. The needles were filtered off and dried at ambient temperature (0.6 g, 68 %). **Bisguanidinium-(3-nitroguanidyl-6-hydroxy-1,2,4,5-tetrazinate) · H_2O** ($C_5H_{16}N_{14}O_4$ 336.32 g mol^{-1}) (**40**): **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 210 °C; **^{1}H NMR** ([D_6]DMSO, 25 °C, ppm): δ = 7.62 (s, br, 12H, NH_2), 8.95 (s, br, 2H, NH_2); **^{13}C NMR** ([D_6]DMSO, 25 °C, ppm): δ = 158.7, 158.9 ($C_{guanidine}$), 161.6, 165.4.

2-Amino-4,5,6,7-tetranitro-*1H*-1,3-benzimidazole dihydrate (**41**)

To a stirring suspension of sodium nitrate (7.00 g, 82.4 mmol) and urea (0.03 g, 0.50 mmol) in concentrated sulfuric acid (20.0 ml, 374 mmol) on an ice bath (0 °C), 2-aminobenzimidazole (1.00 g, 7.51 mmol) was added. The mixture was brought to ambient temperature and heated to 85 °C for 16 h. The solution was poured onto crushed ice (150 g) and stirred for 20 minutes. The yellow precipitate was filtered off and the residue washed with ice-cold water, yielding 1.10 g (3.51 mmol, 47 %) of yellow **41**. Afterwards **41** was dried at 120 °C in a high-temperature furnace for 16 h to gain the dehydrated species. **2-Amino-4,5,6,7-tetranitro-*1H*-1,3-benzimidazole · 2 H_2O** ($C_7H_7N_7O_{10}$ 349.17 g mol^{-1}) (**41**): **DSC** (5 °C min^{-1}): T_{Dec} = 205 °C; **EA** found (calc): C 23.99 (24.08), H 1.90 (2.02), N 27.90 (28.08); **Raman** [cm^{-1}]: $\tilde{\nu}$ = 1589 (15), 1539 (7), 1478 (61), 1441 (12), 1387 (99), 1339 (51), 1270 (31), 1012 (20), 873 (7), 826 (22), 762 (11), 723 (8), 589 (8), 480 (7), 349 (31), 301 (10); **Mass spec**.: (DEI (+) m/z): 101.1 (14), 177.1 (8), 209.1 (10), 314.1 (6) [$C_7H_4N_7O_8^+$], 313.2 (14) [$C_7H_3N_7O_8$]. **2-Amino-4,5,6,7-tetranitro-*1H*-1,3-benzimidazole** ($C_7H_3N_7O_8$ 313.14 g mol^{-1}): **EA** found (calc): C 26.91 (26.85), H 1.20 (0.97), N 30.94 (31.31).

Guanidinium-2-amino-4,5,6,7-tetranitro-*1H*-1,3-benzimidazolate · H_2O (**42**)

To a solution of guanidinium carbonate (500 mg, 1.28 mmol) in water (10.0 ml) **41** (0.447 mg, 1.28 mmol) was added. The suspension was stirred until a solution was obtained. Afterwards it was stored in a fridge for 48 h at 4 °C. The crystalline material then was filtered off and dried at ambient temperature, yielding 1.10 g (1.11 mmol, 87 %) of **42** as yellow-orange needles. **Guanidinium 2-amino-4,5,6,7-tetranitro-*1H*-1,3-benzimidazolate · H_2O**

($C_8H_{10}N_{10}O_9$ 390.23 g mol^{-1}) (**42**): **DSC** (5 °C min^{-1}): $T_{Dec.}$ = 195 °C; **EA** found (calc): C 24.78 (24.62), H 2.50 (2.58), N 35.67 (35.89).

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10. Summary and Conclusion

4,4',5,5'-Tetranitro-2,2'-bisimidazole (TNBI) was synthesized by nitration of 2,2'-bisimidazole and recrystallized from acetone to form a crystalline acetone adduct. Its ammonium salt was obtained by the reaction with gaseous ammonia. In order to explore new explosives or propellants, several energetic nitrogen-rich 2:1 salts such as the hydroxylammonium, guanidinium, aminoguanidinium, diaminoguanidinium and triaminoguanidinium 4,4',5,5'-tetranitro-2,2'-bisimidazolate were prepared by metathesis reactions. It was confirmed that the choice of the cation influences the thermal stability of the corresponding salt. With an increasing number of N–N bonds within the used cation, the thermal stability decreases dramatically. Whereas the bis-guanidinium salt is stable up to 328 °C, the bis-aminoguanidinium salt already decomposes at 209 °C. In addition, methylated 1,1'-dimethyl-4,4',5,5'-tetranitro-2,2'-bisimidazole (Me_2TNBI) was synthesized by the reaction of the bis-potassium salt and dimethyl sulfate. This compound has a melting point of 236 °C and decomposes at 258 °C. This gap between melting and decomposition is unfortunately too small for applications where melt-castable explosives are required. Metal salts of TNBI can also be easily synthesized by using the corresponding metal bases. This was proven by the synthesis of pyrotechnically relevant dipotassium 4,4',5,5'-tetranitro-2,2'-bisimidazolate, which is a highly efficient burning component, *e.g.* in near-infrared flares, and does not decompose at temperatures lower than 312 °C. All compounds were characterized by single crystal X-ray diffraction, NMR and vibrational spectroscopy, elemental analysis and DSC. The sensitivities were determined by BAM methods (drophammer and friction tester). The heats of formation were calculated using CBS-4M electronic enthalpies and the atomization method. With these values and mostly the X-ray densities, different detonation parameters were computed with the EXPLO5 V5.05 computer code. Due to the great thermal stabilities, low sensitivities towards external stimuli and good detonation parameters of the bis-potassium-TNBI (312 °C) and the corresponding bis-guanidinium salt (328 °C), these two compounds could serve as HNS replacements. Therefore the initiation of these two compounds was successfully tested within the SSRT setup. Due to the restriction of the non-adaptable critical diameter within this test setup, a bigger setup lacking this restriction would be required. A bigger setup could provide more accurate experimental conditions, which might, in turn, deliver results more similar to the theoretical values. Long term stability tests at 260 °C of those compounds must be carried out in the future.

A further approach to synthesize new explosives comprised the study of the nitration reaction towards 2-aminobenzimidazole. It provided the insight that different nitration conditions resulted in the formation of two distinct products, namely 2-nitrimino-5,6-dinitrobenzimidazole and 2-amino-4,5,6,7-tetranitrobenzimidazole. In both cases, highly energetic nitrogen rich

salts were prepared. In this case, the same trend of decreasing thermal stability with increasing number of N–N single bonds within the used cation could be observed. Additionally, these compounds showed lower theoretical detonation parameters compared to the corresponding TNBI salts. The thermally most stable salt of 2-nitrimino-5,6-dinitrobenzimidazole was the guanidinium salt. Considering it already decomposes at 264 °C, the anion doesn't seem suitable for applications where explosives like HNS are required. In the case of 2-amino-4,5,6,7-tetranitrobenzimidazole, the thermal properties of its corresponding salts behave *vice versa*. Whereas the neutral compound decomposes at 205 °C, the corresponding guanidinium salt is only stable up to 195 °C. 2-Aminobenzimidazole can also be converted into the corresponding 2-nitrobenzimidazole by oxidation using KO_2 in THF. The nitration of this compound finally resulted in the formation of 4,5,6,7-tetranitrobenzimidazol-2-one. This compound should be further analyzed in regard to its nitrogen rich salts.

A third approach to synthesize thermally high stable secondary explosives was the synthesis of new 1,2,4,5-tetrazines. This heterocycle was chosen because of its high heat of formation. By nucleophilic substitution of the chloro atoms in 3,6-dichloro-1,2,4,5-tetrazine and 3-amino-6-chloro-1,2,4,5-tetrazine using 3,5-diamino-1,2,4-triazole as a nucleophile, two new 1,2,4,5-tetrazines could be synthesized. Especially the disubstituted product, namely the 3,6-bis(3,5-diamino-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine, which is the thermally most stable tetrazine compound known in literature so far, does not decompose below 370 °C. It has a nitrogen content of almost 71 %, a high heat of formation ($\Delta_f H_m° = 707.5$ kJ mol^{-1}) and is insensitive towards external stimuli. The detonation parameters of this compound are comparable to those of HNS regarding the detonation velocity. The initiation of this compound in the SSRT test was attempted as well, albeit unsuccessfully. This could be explained by a lack of oxygen within this compound and a high critical diameter. The further testing of this substance as a gas-generating compound should be carried out. A further approach was the synthesis of nitrogen-rich salts of 3,6-bishydrazino-1,2,4,5-tetrazine (BHT). Due to the high heat of formation ($\Delta_f H_m° = 577.0$ kJ mol^{-1}) of BHT, the synthesis of highly energetic salts was intensively studied. Since BHT already decomposes at 140 °C, the impact salt formation has on thermal stability proved to be an interesting subject. Several salts including energetic heterocyclic anions were prepared. Most of them contain crystal water or suffer from low thermal stability. The most promising compounds were 3,6-bishydrazino-1,2,4,5-tetrazinium-bis-5-nitrotetrazolate ($BHT(NT)_2$) and BHTTNBI. Both compounds were successfully initiated in the SSRT test. BHTTNBI has a high density ($\rho = 1.84$ g cm^{-3}) and is stable up to 217 °C. In comparison to RDX their performance is only moderate. Although $BHT(NT)_2$ has a higher heat of formation ($\Delta_f H_m° = 762.3$ kJ mol^{-1}) than BHTTNBI ($\Delta_f H_m° = 353.0$ kJ mol^{-1}), both compounds show a similar performance within the SSRT test setup. In addition, $BHT(NT)_2$ is

highly sensitive towards impact (2 J) and already decomposes at 176 °C. Moreover, some interesting compounds already described in literature were synthesized, as well as characterized towards their energetic properties and tested with the SSRT setup. 2,3,4,6-tetranitroaniline (TNA), 7-amino-4,6-dinitrobenzofuroxane (ADNBF) and 7-amino-8-nitrobenzodifuroxane (ANBDF) were crystallized and their structure was determined at 173 K. These crystal structures were already determined by several researchers at 298 K. The densities were compared to justify the use of use of "$\alpha_v = 1.5 \cdot 10^{-4}\ K^{-1}$", the semi-empiric volume coefficient of thermal expansion in the formula by Xu et al. This formula can be used to convert densities measured at a specific temperature into densities at other temperatures. The synthesis of TNA was optimized for a 10 g laboratory scale starting with the inexpensive commercially available 3-nitroaniline. No further purification of TNA was required. ADNBF was synthesized by an azide/nitro exchange of TNA, followed by a ring closure reaction. ANBDF could be synthesized in four steps. First, 3,5-dinitrobenzoic acid was converted into the corresponding amine. 3,5-dinitroaniline was nitrated three times, yielding 2,3,4,5,6-pentanitroaniline (PNA) as a benzene adduct after recrystallizing. Afterwards, a double azide/nitro exchange, followed by a ring closure reaction, was performed. 3-Amino-1,2,4-triazole (3-AT) was also tested as a nucleophile when TNA acted as an electrophile. The nitro group in C3 position of TNA was selectively substituted by 3-AT. In addition, the link between the phenyl moiety and the triazole was determined to be a bond between the primary amine of the triazole and the phenyl ring. This was confirmed by X-ray diffraction. The thermal stability of the product, namely 3-amino-1,2,4-triazolyl-2,4,6-trinitroaniline ($T_{Dec.}$ = 287 °C), as well as its density (ρ = 1.79 g cm^{-3} (measured with pycnometric methods at 298 K)), were determined. By using the “vicarious amination” reaction, a second amino group could be introduced into the benzene ring yielding 3-amino-1,2,4-triazolyl-5-amino-2,4,6-trinitroaniline. The thermal stability gain was only 13 °C, but the density increased to 1.86 g cm^{-3}. These compounds were also tested within the SSRT setup. All of them could be initiated. TNA, ADNBF and ANBDF delivered similar results and are only slightly less efficient than RDX in this setup. Their impact sensitivities are comparable to those of RDX, but they are less sensitive towards friction. Since TNA can be synthesized in one step using the inexpensive 3-nitroaniline and its decomposition temperature is 228 °C, it can be safely stated that, while displaying a slightly worse performance than RDX, this compound could be a viable replacement. ADNBF shows additional advantages in regard to thermal stability and performance compared to TNA. Its high density (ρ = 1.91 g cm^{-3} at 298 K) and thermal stability ($T_{Dec.}$ = 268 °C) contribute to a performance similar to that of RDX in regard to the EXPLO5 values. ANBDF shows a remarkable increase of theoretical performance but suffers from low thermal stability (183 °C). The nitration of 1,4-disubstituted benzenes was another project in this doctoral thesis. The original goal of these reactions was

the synthesis of new polynitro-aromatics like 1,4-diamino-2,3,5,6-tetranitrobenzene or 4-amino-2,3,5,6-tetranitrophenol. After the nitration of 4-chloroaniline, which resulted in the formation of 5-chloro-2-diazo-3,6-dinitrophenol (ClDDNP), it was confirmed that in most cases (when 1,4-diaminobenzene, 4-aminophenol and 1,4-dihydroparaquinone serve as starting materials), the use of protection groups is absolutely necessary. Therefore mainly alkysulfonyl and acetyl protection groups were used. The methanesulfonyl protection group seems to be more resistant to oxidizing and nitrating media. When using only nitric acid the benzene moeity was nitrated a maximum of three times. Ester functions, which are generated by boiling the corresponding phenol in acetic anhydride, are often hydrolyzed in nitric acid. In the case of double acetylated 4-aminophenol, this resulted in the formation of *N*-(4-hydroxy,2,3,5-trinitrophenyl)acetamide, which was successfully deprotected in concentrated sulfuric acid yielding the free amine (4-amino-2,3,6-trinitrophenol) in high yields. Attempts to synthesize the corresponding tetranitro-derivative always resulted in the formation of 6-diazo-3-hydroxy-2,4-dinitrophenol (HODDNP). In the case of 1,4-diaminobenzene, the regio-selectivity of those nitrations could be successfully determined by X-ray diffraction and NMR spectroscopy. At low temperature conditions, the nitration of *N,N'*-(1,4-phenylene)dimethanesulfonamide resulted in the formation of 1,4-diamino-2,3-dinitrobenzene after the protection group was cleaved. Harsher nitration conditions lead to *N,N'*-(2,3,5-trinitro-1,4-phenylene)dimethanesulfonamide. The deprotection reaction mainly resulted in the formation of the free diamine, but 3-amino-6-diazo-2,4-dinitrophenol (ADDNP) was obtained as well. In order to synthesize 1,4-diamino-2,6-dinitrobenzene selectively, another route had to be chosen. First, the 4-fluoro-3,5-dinitroaniline was synthesized. Afterwards, an amino/fluorine exchange could be performed. Further nitration reactions always resulted in the formation of 4-diazo-2,6-dinitrophenol (*iso*-DDNP). Additionally, nitration reactions using 1,4-dimethoxybenzene were researched. It turned out that three nitro groups can be attached to the benzene ring. Afterwards, an amino/methoxy exchange was tested. It is commonly known that TATB can be synthesized by such substitutions using 1,3,5-trimethoxy-2,4,6-trinitrobenzene as the starting material. In the case of 1,4-dimethoxy-2,3,5-trinitrobenzene, it is *vice versa*. Here a specific nitro group is substituted resulting in the formation of 3,6-dimethoxy-2,4-dinitroaniline. Due to the fact that neither 1,4-diamino-2,3,5,6 tetranitrobenzene nor 4-amino-2,3,5,6-tetranitrophenol could be synthesized, the energetic properties of those new diazophenols were intensively investigated. All those diazophenols (displayed in figure 35) revealed to be primary explosives.

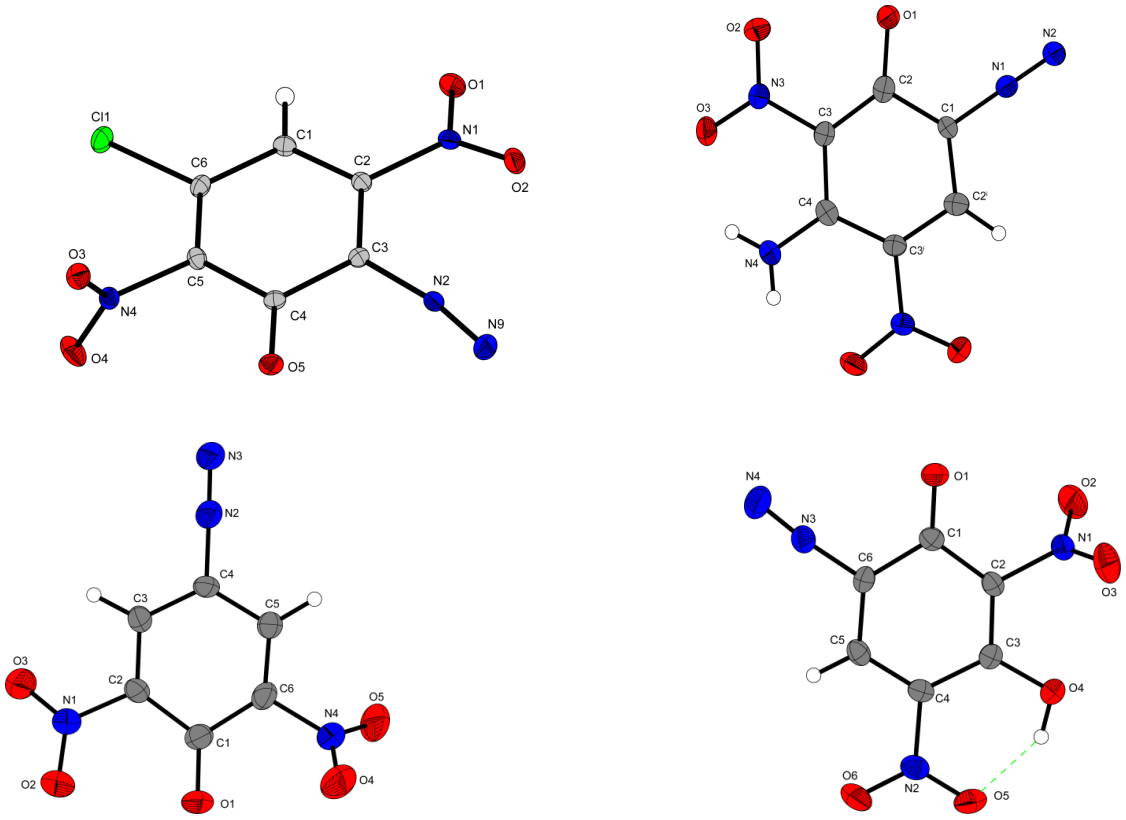

Fig. 35 Molecular units of newly synthesized Diazophenols:3-Chloro-6-diazo-2,5-dinitrophenol (Cl-DDNP)(left top), 3-Amino-6-diazo-2,4-dinitrophenol (ADDNP)(right top), 4-Diazo-2,6-dinitrophenol (*iso*-DDNP)(left bottom), 3-Hydroxy-6-diazo-2,4-dinitrophenol (HODDNP)(right bottom).

They are thermally stable between 165-170 °C and show sensitivities of 1 J and 12-28 N Their initiation capability towards RDX was tested. HODDNP is particularly remarkable in view of the fact that it is thermally more stable than DDNP by 12 °C, as well as far more insensitive towards friction (FS (DDNP) = 5 N; FS (HODDNP) = 16 N). Even small amounts of HODDNP were able to initiate RDX without confinement. Considering the inexpensiveness of the starting materials (4-aminophenol) and reagents involved in the synthesis (Ac_2O, HNO_3 65 % and concentrated H_2SO_4), HODDNP is a really good replacement for compounds like 2,4,6-triazidotriazine, DDNP or tetrazene, which are commonly used as metal free primary explosives. Furthermore, the thermal stability of HODDNP was tested by an isoperibolic long term measurement, revealing that the compound is stable for at least 60 hours at 75 °C. Moreover, storage of this compound in an oven at 100 °C for 60 hours does not result in any mass loss or change in the chemical composition. This was proven *via CHN* elemental analysis and ^{1}H NMR spectroscopy. In addition, HODDNP is stable when stored under water, which is important for shipping security reasons. After suspending it in 30 mL of water, it was allowed to stand for a few days at ambient temperature until the water evaporated. The chemical composition was subsequently confirmed via *CHN* elemental analysis and ^{1}H NMR spectroscopy as unchanged and pure.

11. X-ray diffraction data

Table XRD Data

	5	**8**	**9**	**9b**	**10**	**11**
Formula	$C_7H_9SN_3O_4$	$C_6HClN_4O_5$	$C_{12}H_{21}S_4N_5O_{12}$	$C_6H_6N_4O_4$	$C_{10}H_{10}N_4O_6$	$C_8H_6N_2O_7$
FW [g mol^{-1}]	231.23	244.56	555.58	198.15	282.22	242.15
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space Group	*C*2/*c*	*Pc*	*P–1*	*C*2/*c* (No. 15)	*P–1*	$P2_1/c$
Color / Habit	Orange needle	Yellow rod	Colorless plate	Yellow block	Yellow needle	Yellow block
Size [mm]	0.3 x 0.1 x 0.03	0.23 x 0.11 x 0.08	0.20 x 0.15 x 0.03	0.19 x 0.21 x 0.49	0.23 x 0.14 x 0.06	0.58 x 0.33 x 0.26
a [Å]	20.0686(14)	6.4289(4)	10.1892(11)	12.2042(6)	7.7535(16)	7.5999(3)
b [Å]	7.0183(5)	6.9889(4)	10.5895(9)	10.8478(4)	8.0847(11)	12.0515(5)
c [Å]	14.0897(12)	9.7159(6)	11.6355(15)	7.2959(4)	10.7662(19)	21.1395(9)
α [°]	90	90	97.918(9)	90	84.878(13)	90
β [°]	90.119(7)	97.723(6)	104.484(10)	124.954(4)	70.272(17)	94.330(4)
γ [°]	90	90	103.643(8)	90	75.493(15)	90
V [Å^3]	1984.5(3)	439.3(1)	1155.1(2)	791.66(8)	615.0(2)	1930.64(14)
Z	8	2	2	4	2	8
$\rho_{calc.}$ [g cm^{-3}]	1.548	1.849	1.597	1.663	1.524	1.666
μ [mm^{-1}]	0.325	0.450	0.479	0.142	0.128	0.150
F(000)	960	244	576	408	292	992
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	173	298	173
θ Min–Max [°]	4.21, 24.99	4.6, 31.7	4.3, 27.0	5.1, 26.5	4.8, 24.2	4.5, 30.3
Dataset	–22:23; –8:7; –16:16	–8:8 ; –8:8 ; –11:11	–12:12; –13:13; –14:14	-15:15; -13:13; -9: 9	–9:9; –9:9; –11:13	–9:8; –15:15; –14:26
Reflections collected	5939	5976	8374	5627	4029	7894
Independent refl.	1744	1704	4506	823	2385	3989
R_{int}	0.046	0.025	0.047	0.023	0.037	0.021
Observed reflections	1238	1662	3236	742	1352	3192
Parameters	172	149	316	76	221	333
R_1 (obs)	0.048	0.021	0.087	0.0303	0.064	0.0389
wR_2 (all data)	0.1189	0.0525	0.199	0.0891	0.177	0.101
S^c	1.035	1.070	1.083	1.05	1.013	1.050
Resd. Dens. [e Å^{-3}]	–0.27, 0.25	–0.13, 0.15	–0.49, 1.63	-0.25, 0.19	–0.22, 0.23	–0.29, 0.25
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford XCalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD

Solution	SIR-92	SIR-92	SIR-92	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Measurment	jx101	ix119	kx220	kx320	kx271	kx111

	12	**15**	**16b**	**16c**	**18**	**20**
Formula	$C_{10}H_8N_2O_8$	$C_6H_3N_5O_5$	$C_7H_6SN_2O_8$	$KC_{12}H_{17}SN_2O_8$	$C_6H_7SN_3O_6$	$C_{12}H_5N_9O_{13}$
FW [g mol^{-1}]	284.18	225.13	278.20	378.36	261.22	483.25
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space Group	*P–1*	*Pnma*	*Pca*2$_1$	*Pbca*	*P*2$_1$2$_1$2$_1$	*P*2$_1$/*c*
Color / Habit	Colorless block	Orange block	Yellow block	Orange plate	Yellow block	Orange block
Size [mm]	0.40 x 0.40 x 0.36	0.20 x 0.19 x 0.15	0.38 x 0.32 x 0.21	0.02 x 0.14 x 0.16	0.40 x 0.25 x 0.24	0.25 x 0.2 x 0.1
a [Å]	8.5133(7)	16.2313(6)	14.6639(7)	10.4168(4)	5.2956(3)	9.1208(6)
b [Å]	8.6062(8)	10.6548(4)	5.7308(2)	9.4354(3)	12.6113(7)	15.4370(8)
c [Å]	8.7948(7)	4.5210(2)	12.3700(5)	28.7467(11)	15.1910(7)	12.7076(7)
α [°]	69.730(8)	90	90	90	90	90
β [°]	79.693(7)	90	90	90	90	90.233(5)
γ [°]	75.997(7)	90	90	90	90	90
V [Å^3]	583.29(9)	781.87(5)	1039.52(7)	2825.42(18)	1014.52(9)	1789.19(18)
Z	2	4	4	8	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.618	1.913	1.778	1.779	1.710	1.794
μ [mm^{-1}]	0.144	0.170	0.352	0.573	0.343	0.165
F(000)	292	456	568	1536	536	976
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	173	173	173
θ Min–Max [°]	4.7, 31.9	4.9, 31.8	4.3, 31.9	4.2, 26.0	5.0, 31.6	4.7, 29.1
Dataset	–10:10; –10:5; –10:10	–17:20; –13:13; –5:5	–18:18; –7:7; –15:15	–11:12; –11:11; –21:35	–5:6; –15:11; –19:16	–11:11; –19:17; –15:15
Reflections collected	4333	5595	8007	18322	3046	13988
Independent refl.	2287	891	1189	2773	2025	3491
R_{int}	0.017	0.023	0.031	0.059	0.026	0.050
Observed reflections	1959	822	1127	2126	1898	2510
Parameters	213	88	176	245	171	327
R_1 (obs)	0.0335	0.038	0.028	0.037	0.031	0.041
wR_2 (all data)	0.0869	0.0947	0.073	0.090	0.0729	0.098

S^c	1.033	1.196	1.050	1.05	1.061	1.057
Resd. Dens. [e Å^{-3}]	–0.23, 0.25	–0.22, 0.27	–0.22, 0.27	–0.31, 0.33	–0.32, 0.17	–0.21, 0.21
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SIR-92	SIR-92	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Measurement	jx133	kx249	Kx105	kx390	jx099	jx056

	21	**22a**	**22b**	**24**	**26**	**27**
Formula	$C_{12}H_8N_6O_{10}$	$C_6H_3N_5O_8$	$C_6H_4N_4O_7$	$C_6H_3N_5O_6$	$C_6H_2N_6O_6$	$C_{10}H_{12}SN_8O_7$
FW [g mol^{-1}]	396.24	273.13	244.13	241.13	254.14	388.34
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_12_12_1$	P–1
Color / Habit	Yellow block	Yellow plate	Yellow plate	Yellow block	Yellow block	Orange block
Size [mm]	0.36 x 0.29 x 0.25	0.35 x 0.15 x 0.04	0.35 x 0.3 x 0.05	0.28 x 0.24 x 0.14	0.40 x 0.12 x 0.04	0.23 x 0.18 x 0.09
a [Å]	9.0537(2)	7.2411(4)	6.6383(4)	7.1442(3)	6.5565(4)	8.7125(8)
b [Å]	20.2030(5)	11.0410(7)	8.5899(5)	9.8515(5)	9.3660(6)	9.5625(8)
c [Å]	17.7542(4)	12.0522(7)	15.5133(13)	11.8198(5)	14.0552(8)	10.5487(9)
α [°]	90	90	90	90	90	80.757(7)
β [°]	99.845(2)	97.792(6)	101.644(7)	97.989(4)	90	73.944(8)
γ [°]	90	90	90	90	90	63.269(9)
V [Å^3]	3199.63(13)	954.66(10)	866.40(10)	823.84(6)	863.10(9)	753.63(13)
Z	8	4	4	4	4	2
$\rho_{calc.}$ [g cm^{-3}]	1.645	1.900	1.872	1.944	1.956	1.711
μ [mm^{-1}]	0.146	0.180	0.174	0.177	0.177	0.276
F(000)	1616	552	496	488	512	400
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	173	173	173
θ Min–Max [°]	4.6, 32.0	4.7, 28.0	4.8, 31.8	4.5, 31.2	5.4, 31.9	4.3, 28.1
Dataset	–11:7; –25:15; –21:22	–8:9; –11:13; –15:14	–8:8; –10:10; –19:12	–8:8; –12:12; –14:12	–8:7; –7:11; –17:12	–10:10; –11:12; –13:13
Reflections collected	13831	7132	6342	6229	2663	5162
Independent refl.	6606	1965	1691	1598	1057	3111
R_{int}	0.020	0.033	0.029	0.021	0.036	0.025

Observed reflections	5198	1561	1378	1422	944	2424
Parameters	569	184	170	154	171	283
R_1 (obs)	0.037	0.037	0.035	0.094	0.041	0.040
wR_2 (all data)	0.091	0.096	0.091	0.241	0.112	0.094
S^c	1.031	1.035	1.057	1.085	1.050	1.074
Resd. Dens. [e Å^{-3}]	–0.24, 0.25	–0.22, 0.29	–0.21, 0.20	–0.51, 2.47	–0.22, 0.54	–0.38, 0.24
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SIR-92	SIR-92	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Measurement	jx246	jx248	jx082	kx283	jx318	kx175

	29a	**30**	**31a**	**31b**	**32**	**34**
Formula	$C_8H_8N_2O_6$	$C_8H_7N_3O_8$	$C_8H_9N_3O_6$	$C_8H_7N_5O_6$	$C_7H_7N_3O_5$	$C_6H_4N_{10}O_8$
FW [g mol^{-1}]	228.16	273.11	243.18	269.19	213.16	344.20
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space Group	*P*–1	$P2_1/c$	*P*–1	$P2_1/n$	*P*–1	$P2_1/c$
Color / Habit	Yellow plate	Colorless block	Colorless rod	Colorless rod	Red block	Orange block
Size [mm]	0.35 x 0.34 x 0.05	0.40 x 0.21 x 0.12	0.50 x 0.12 x 0.10	0.18 x 0.12 x 0.04	0.43 x 0.26 x 0.16	0.15 x 0.10 x 0.05
a [Å]	7.7332(7)	9.4290(14)	3.9794(4)	15.8783(15)	9.0377(8)	4.9048(13)
b [Å]	7.9323(6)	12.4530(11)	9.1778(9)	7.9215(4)	9.6823(6)	6.9631(19)
c [Å]	8.4258(8)	9.9900(11)	14.3184(13)	19.1044(18)	10.7174(8)	17.410(5)
α [°]	87.831(7)	90	72.803(9)	90	71.258(6)	90
β [°]	82.831(8)	107.123(12)	88.372(8)	112.880(12)	70.417(7)	93.68(3)
γ [°]	64.540(8)	90	82.795(8)	90	82.606(6)	90
V [Å^3]	462.94(7)	1121.0(2)	781.87(5)	2213.9(4)	836.50(11)	593.4(3)
Z	2	4	2	8	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.637	1.619	1.630	1.615	1.693	1.926
μ [mm^{-1}]	0.143	0.148	0.142	0.141	0.146	0.178
F(000)	236	560	252	1104	440	348
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	100	292	173	173	100	298
θ Min–Max [°]	5.2, 31.3	4.4, 32.2	4.9, 31.8	4.2, 26.0	4.3, 32.1	4.2, 28.7
Dataset	–9:9; –9:9; –10:10	–11:11; –11:15; –12:12	–4:4; –11:11; –17:16	–19:19; –9:9; –23:19	–11:10; –12:12; –13:13	–6:5; –8:7; –11:21

Reflections collected	4612	5394	3676	15252	6551	2152
Independent refl.	1808	2188	2026	4328	3455	1186
R_{int}	0.022	0.066	0.017	0.080	0.025	0.033
Observed reflections	1465	1496	1614	2065	2272	867
Parameters	177	179	190	399	327	117
R_1 (obs)	0.034	0.052	0.046	0.063	0.037	0.049
wR_2 (all data)	0.102	0.179	0.122	0.122	0.100	0.147
S^c	1.054	1.053	1.043	0.990	1.044	1.068
Resd. Dens. [e Å^{-3}]	–0.27, 0.28	–0.28, 0.33	–0.29, 0.30	–0.25,0.25	–0.24, 0.34	–0.26, 0.28
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SIR-92	SIR-92	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Measurement	ix394	ix414	kx160	kx403	ix367	hx410

	36a	**36b**	**37**	**40**
Formula	$C_6H_{12}N_{10}O_6$	$C_6H_{14}N_{10}O_7$	$C_8H_{10}N_{20}O_8$	$C_5H_{16}N_{14}O_4$
FW [g mol^{-1}]	320.26	338.27	514.36	336.32
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space Group	*P*2$_1$/*n*	*Pbca*	*P*2$_1$/*n*	*P*2$_1$/*c*
Color / Habit	Colorless rod	Colorless block	Yellow plate	Red needle
Size [mm]	0.17 x 0.12 x 0.09	0.25 x 0.21 x 0.20	0.22 x 0.14 x 0.08	0.18 x 0.12 x 0.04
a [Å]	7.089(3)	11.2159(8)	5.1640(2)	6.910(4)
b [Å]	19.910(10)	8.5821(10)	16.2136(7)	17.299(8)
c [Å]	9.566(4)	28.595(2)	11.0655(4)	12.096(6)
α [°]	90	90	90	90
β [°]	111.31(5)	90	96.140(4)	102.55(5)
γ [°]	90	90	90	90
V [Å^3]	1257.9(10)	2752.4(4)	921.17(6)	1411.4(13)
Z	4	8	2	4
$\rho_{calc.}$ [g cm^{-3}]	1.691	1.633	1.854	1.583
μ [mm^{-1}]	0.149	0.146	0.163	0.134
F(000)	664	1408	524	704
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073

T [K]	173	173	173	173
θ Min–Max [°]	4.4, 26.5	4.1, 26.0	4.3, 26.5	4.2, 26.0
Dataset	–18:7; –24:24; –10:12	–13:13; –10:9; –35:29	–6:6; –20:20; –13:13	–8:8; –21:21; –14:14
Reflections collected	6601	13249	9545	14043
Independent refl.	2580	2700	1903	2763
R_{int}	0.081	0.075	0.032	0.028
Observed reflections	1256	1916	1620	2341
Parameters	247	264	183	272
R_1 (obs)	0.052	0.040	0.031	0.031
wR_2 (all data)	0.132	0.091	0.081	0.079
S^c	0.975	1.011	1.027	1.041
Resd. Dens. [e Å^{-3}]	–0.27, 0.23	–0.22, 0.22	–0.25, 0.33	–0.20, 0.15
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
Measurement	gx473	gx479	hx310	gx666

	41a	**41b**	**42**
Formula	$C_{11}H_{11}N_7O_{10}$	$C_{10}H_9N_7O_9$	$C_8H_8N_{10}O_9$
FW [g mol^{-1}]	401.27.20	371.24	390.26
Crystal system	Triclinic	Monoclinic	Triclinic
Space Group	*P*–1	$P2_1/n$	*P*–1
Color / Habit	Yellow rod	Yellow needle	Yellow block
Size [mm]	0.20 x 0.14 x 0.14	0.32 x 0.06 x 0.03	0.05 x 0.15 x 0.30
a [Å]	10.4670(10)	12.480(3)	7.6358(12)
b [Å]	12.9768(13)	5.9837(15)	9.8548(13)
c [Å]	14.5338(14)	20.339(6)	10.4657(14)
α [°]	110.511(9)	90	102.845(11)
β [°]	101.983(8)	100.15(3)	95.184(12)
γ [°]	100.734(8)	90	91.911(12)
V [Å^3]	1734.9(3)	1495.1(7)	763.53(19)
Z	4	4	2
$\rho_{calc.}$ [g cm^{-3}]	1.536	1.649	1.697

μ [mm^{-1}]	0.137	0.147	0.154
F(000)	824	760	400
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	298	100	293
θ Min–Max [°]	4.1, 32.2	4.6, 22.2	4.3, 26.0
Dataset	–12:12; –15:15; –17:17	–15:15; –7:7; –25:23	–9:9; –12:12; –12:12
Reflections collected	17541	7371	7689
Independent refl.	6770	2921	2987
R_{int}	0.055	0.098	0.023
Observed reflections	3612	1508	2347
Parameters	535	249	284
R_1 (obs)	0.053	0.062	0.034
wR_2 (all data)	0.130	0.108	0.091
S^c	0.977	0.933	1.030
Resd. Dens. [e Å^{-3}]	–0.21, 0.24	–0.38, 0.27	–0.18, 0.19
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan	multi-scan
Measurement	hx470	ix099	hx423

12.) List of publications

1) Energetic Derivatives of 4,4‘,5,5‘-Tetranitro-2,2‘-bisimidazole, T. M. Klapötke, A. Preimesser, J. Stierstorfer, *Z. Allg. Anorg. Chem.* **2012**, *638*, 1278–1286.

2) Syntheses and Energetic Properties of 4-Diazo-2,6-dinitrophenol and 6-Diazo-3-hydroxy-2,4-dinitrophenol, T. M. Klapötke, A. Preimesser, J. Stierstorfer, *Eur. J. Org. Chem.* **2015**, 4311–4315.

3) Highly Energetic Salts of 3,6-Bishydrazino-1,2,4,5-tetrazine, T. M. Klapötke, A. Preimesser, S. Schedlbauer and J. Stierstorfer, *Cent. Eur. J. Energ. Mat*. **2013**, *10*, 151–170.

4) Thermally Stable 3,6-Disubstituted 1,2,4,5-Tetrazines, T. M. Klapötke, A. Preimesser and J. Stierstorfer, *Z. Naturforsch.* **2013**, *68B*, 1310–1320.

5) Energetic Derivatives of 2-Nitrimino-5,6-dinitro-benzimidazole, T. M. Klapötke, A. Preimesser, J. Stierstorfer, *Propellants Explos. Pyrotech.* **2014**, *40*, 60–66.

6) Syntheses and Inititation Capabilities of Energetic Diazodinitrophenols, D. Izsák, T. M. Klapötke, A. Preimesser, J. Stierstorfer, Article submitted and accepted in *Z. Allg. Anorg. Chem.* **2015**.